Nanostructured Polymers for Photonics

or

Polymer Materials with Periodic Structures

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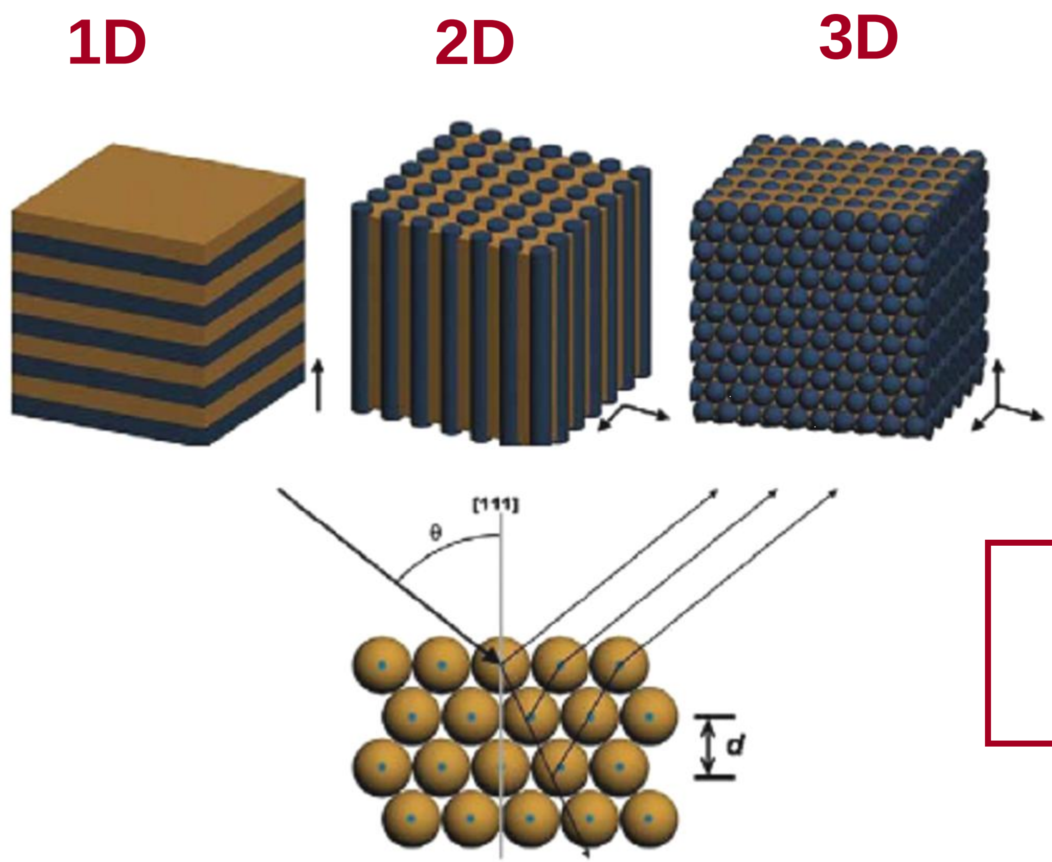
WHAT IS PHOTONICS?

- **Photonics** is an interdisciplinary field of science and technology with a focus on the transport and manipulation of light.

- **In particular, interaction of light with materials possessing a periodic modulation in their structure leads to a range of interesting effects.**

- **Applications: Bragg mirrors, switches, filters, superprisms, waveguides, and optical resonators.**



The arrows show the direction in which a periodic modulation in the refractive index exists

$$k\lambda_{sb} \approx 2d\,(n_{eff}^2 - \sin^2\theta)^{1/2}$$

- Incident light with a wavelength predicted by a modified Bragg equation undergoes diffraction when propagating through a photonic crystal. The wavelength of light that is coherently scattered (λ_{sb}), is determined by the angle of incidence, θ, the effective refractive index of the PPC, n_{eff}, and the periodicity of the structure, d.

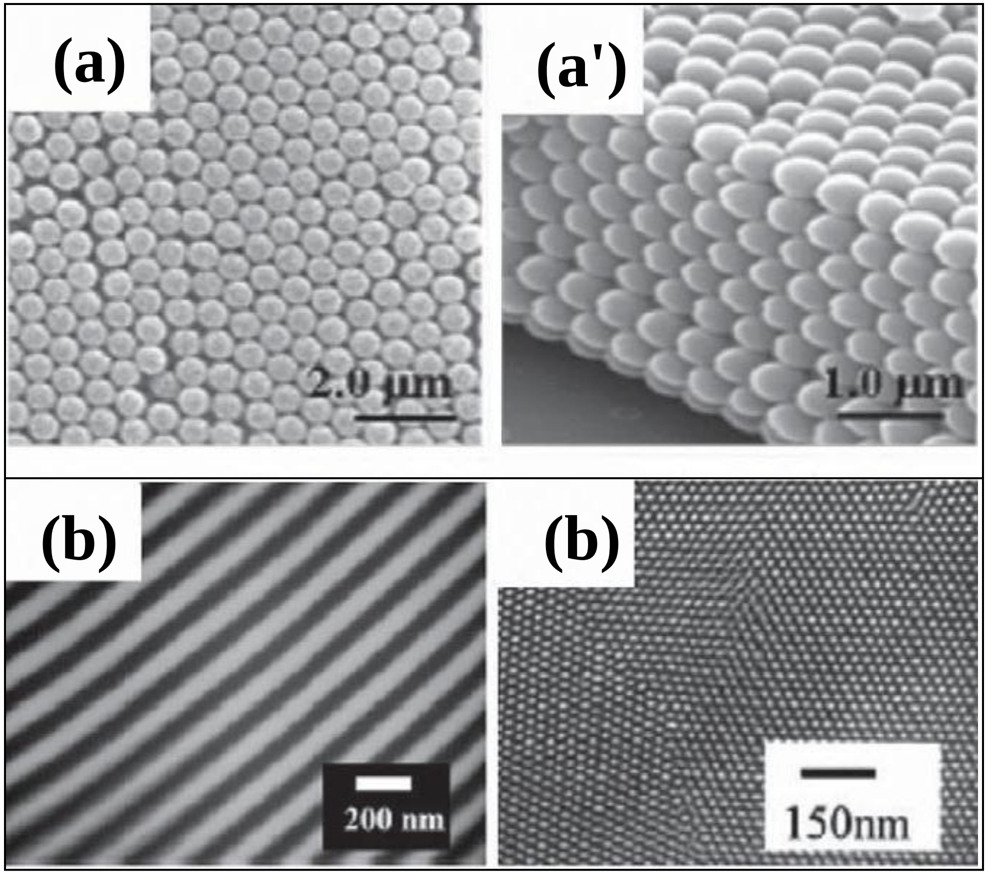
WHY POLYMERS?

Polymers are inexpensive, can be readily functionalized to achieve required optical, electronic, or mechanical properties and are compatible with various patterning methods

Polymers can be used as materials for photonics in several ways

- **Polymers in themselves can possess useful optical properties, e. g., electroluminescence, photoluminescence, or nonlinear optical properties**
- **Polymers can act as matrices for optically active species, e.g. for dyes, liquid crystals, semiconductor quantum dots, or metal nanoparticles**
- **Polymers possessing topographic and/or compositional patterns can coherently scatter light**
- **Polymer templates are routinely used for producing photonic materials**

Fabrication of polymer photonic crystals: self-assembly

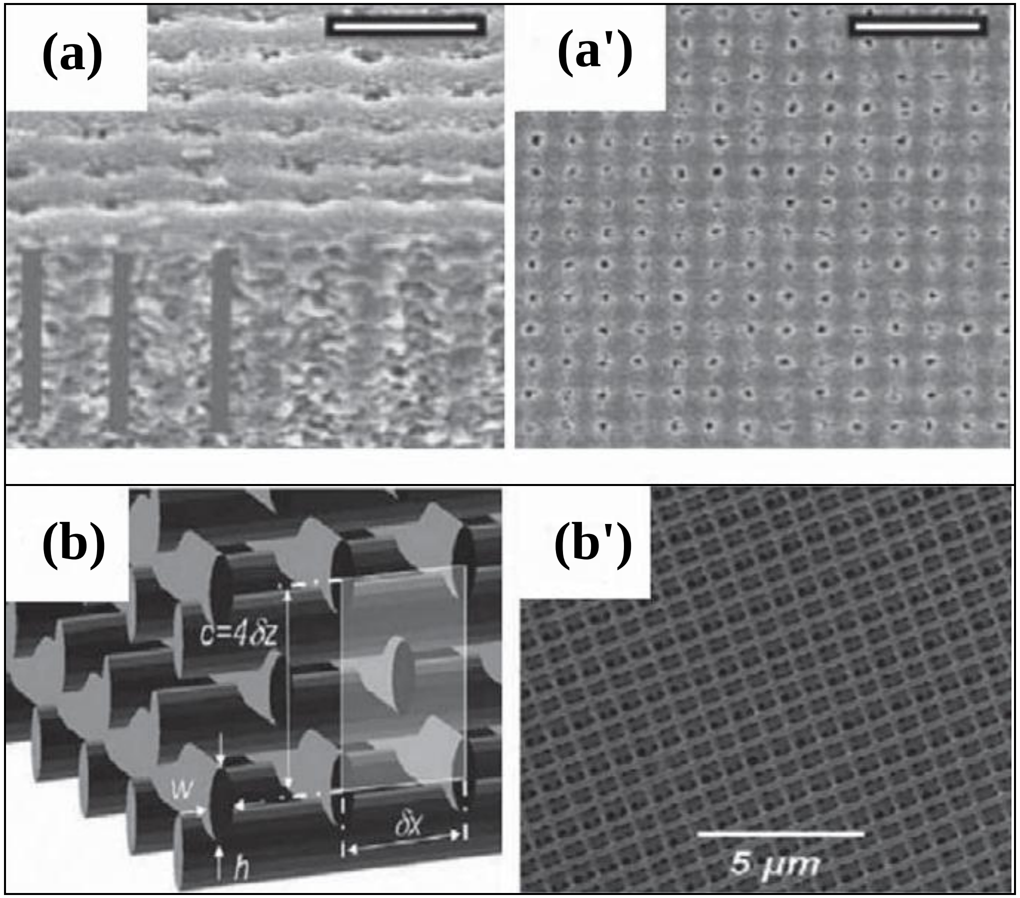


a, a': SEM mages of a colloid crystal self-assembled from polystyrene particles

b, b': TEM images of self-assembled PS-b-PI BCP films

Paquet, C., Kumacheva, E., *Adv. Funct. Mater.* (2006) 16, 1892, Yoon, J., *et al., Nano Lett. (2006) 6, 2211*; Honeker, C. C., and Thomas, E. L., *Chem. Mater.* (1996) 8, 1702

Fabrication of polymer photonic crystals: microfabrication

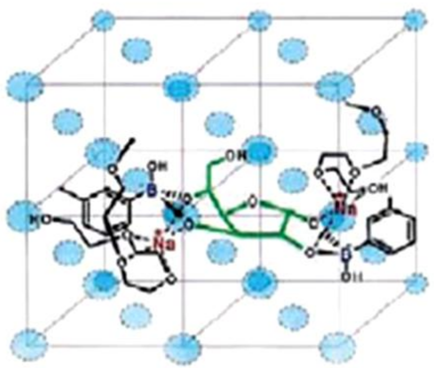


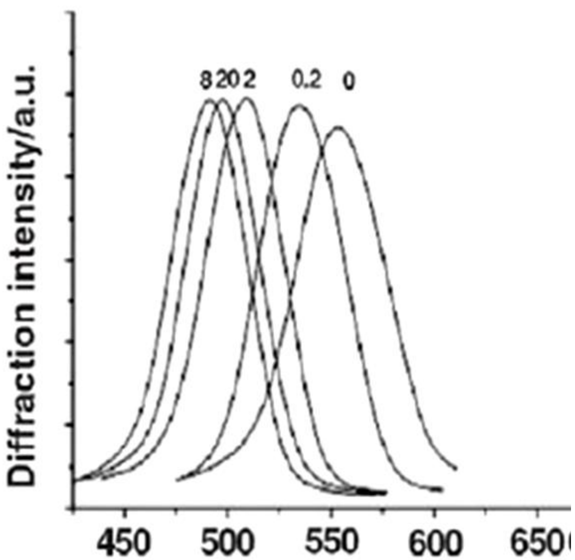
(a, a'): SEM images of a LC-polymer material obtained by holographic patterning of a LC-monomer mixture. The dark areas are void regions in which the LC droplets resided prior to SEM imaging.

(b, b'): Fabrication of materials by two-photon polymerization:
(b) computer-generated sketch of a woodpile structure, and (d) SEM image of a woodpile structure fabricated in a polymer resin

Wu, S., *et al., J. Photochem. Photobiol. A: Chem. (2006) 181, 1;* Jakubiak, R., *et al., Adv. Mater. (2005) 17, 2807*

Applications of polymer photonic crystals: chemical sensors





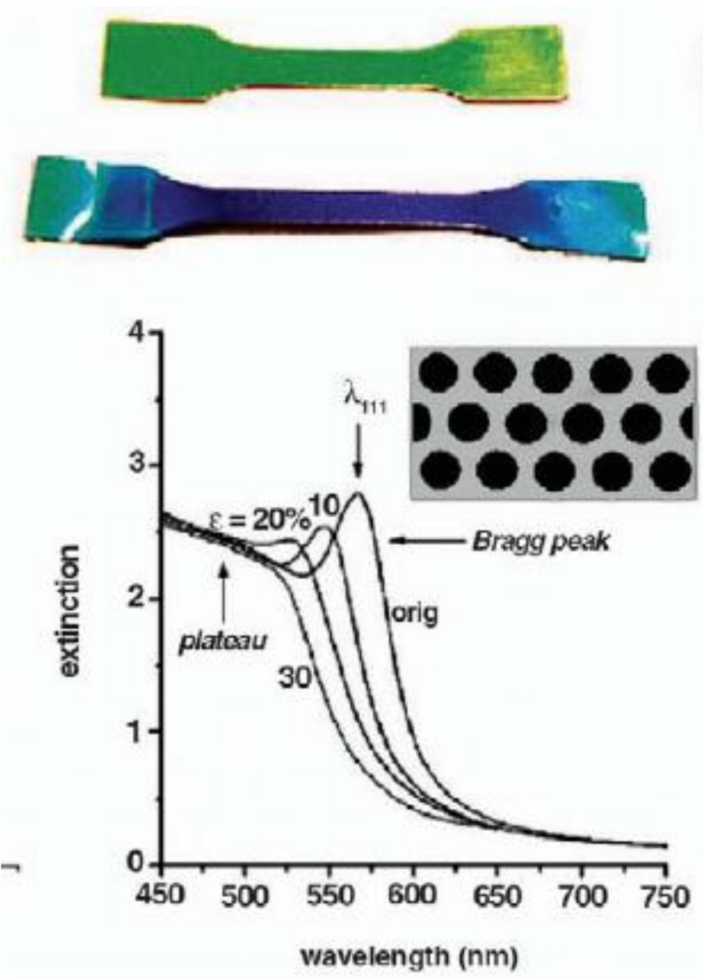
Sensor derived from a colloid crystal embedded in a polyacrylamide-poly(ethylene glycol) hydrogel with pendant phenylboronic acid groups.

Complexation of glucose with the phenylboronic acid and poly(ethylene glycol) → reduction in the hydrogel volume

Dependence of the diffraction spectrum of the sensor on the concentration of glucose in an aqueous solution containing
2 mM tris-HCl (pH 8.5) and 150 mM NaCl

Alexeev, V., *et al., Anal. Chem. (2003) 75, 2316*

Applications of polymer photonic crystals: *deformation sensors*



Particles: rigid polystyrene beads

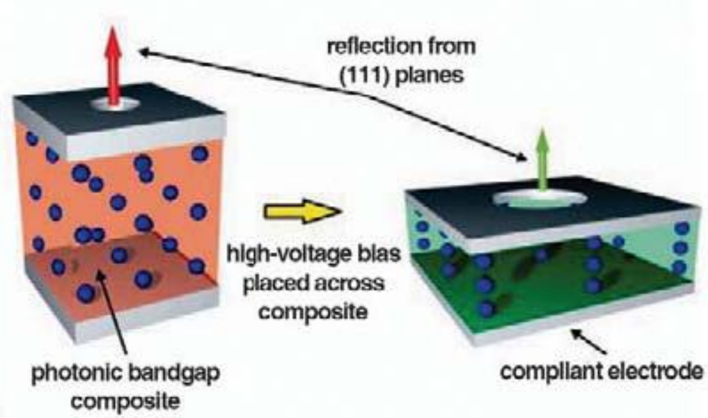
Matrix: poly(ethyl acrylate)

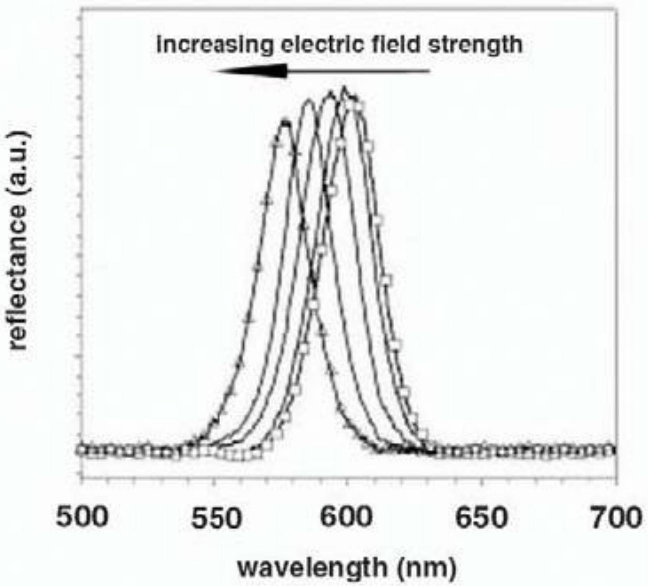
Deformation applied to elastomeric material changes its lattice constant and causes a shift in the stopband (and hence, the color of diffracted light.

Hysteresis in stretching-contraction series was minimized by cross-linking the poly(ethyl acrylate) matrix.

Viel, B., et al., *Chem. Mater*. (2007) 19, 5673

Applications of polymer photonic crystals: electric field sensors





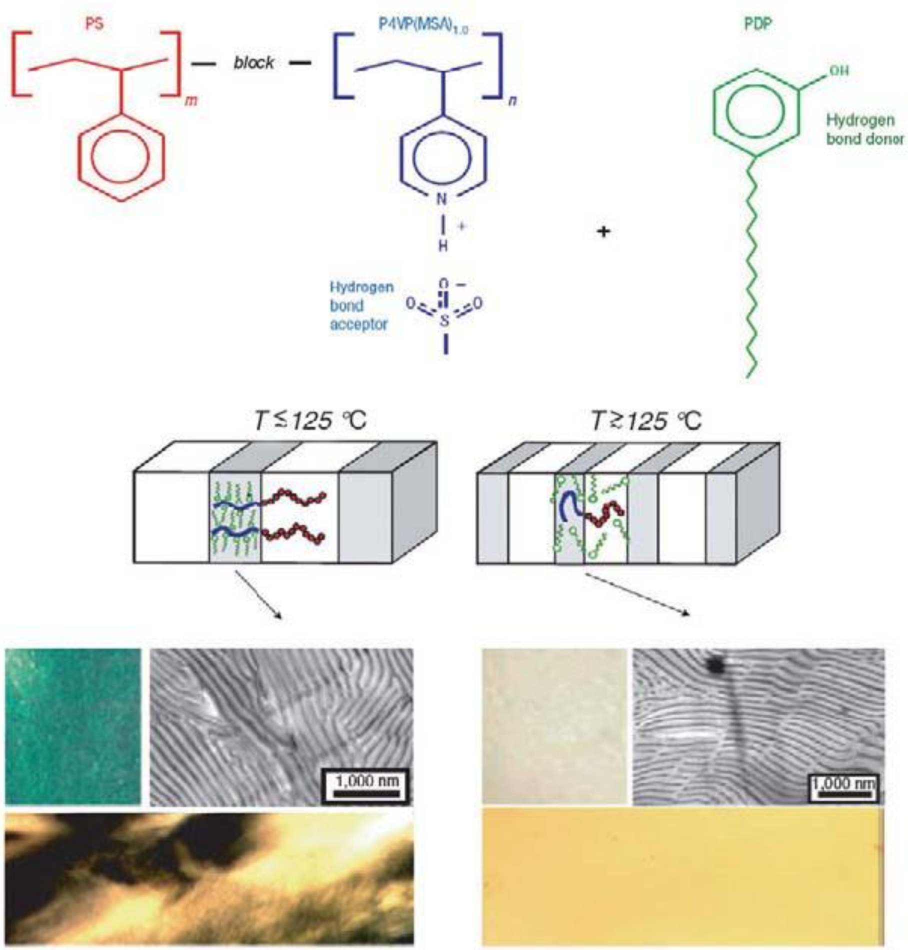
Application of an electric field to a colloid crystal fabricated in a poly(2-methoxyethyl acrylate) hydrogel loaded with Ag nanoparticles → contraction of the material in the plane perpendicular to the plane of electrodes.

The stress arises from Coulombic interactions between electrostatic charges on the opposing electrodes (via the Maxwell stress effect).

The change in interplanar distance of the the crystal led to a blue shift of the stopband

Xia, J., et al., *Adv. Mater*. (2005) 17, 2463

Polymer photonic crystals: block copolymers



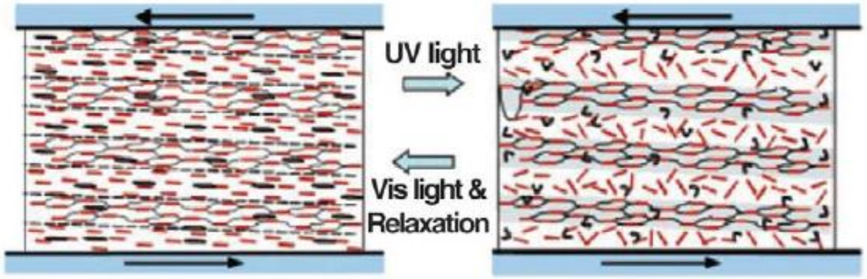
Hydrogen bonding and polymer phase behavior → large, reversible temperature-controlled switching of the stopband.

A thermal response in the optical properties of polystyrene-*b*-poly(4-vinyl pyridinium methanesulphonate) was induced by adding 3-n-pentadecylphenol.

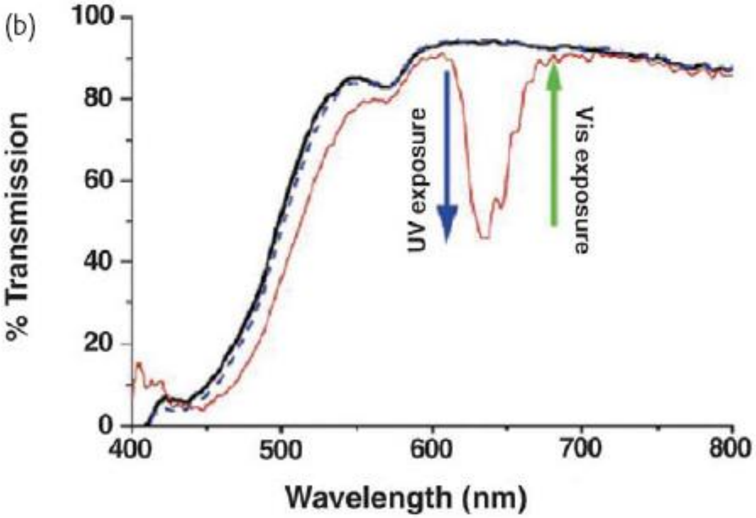
Below ~125°C, a complex of PS-*b*-P4VP (MSA) with PDP produced a supra-molecular comb-shaped architecture with a long lamellar period. The sample is green and birefringent.
Above 125°C, the hydrogen bonds broke up and PDP dissolved in both PS and P4VP(MSA) → transition to an uncolored and non-birefringent material.

Valkama, S., et al., *Nat. Mater*. (2004) 3, 872

Microfabricated Polymer photonic crystals:



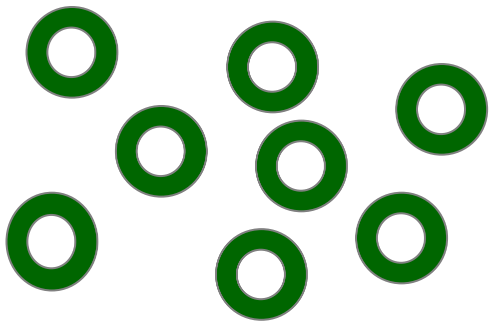
One-dimensional holographically patterned polymer-dispersed liquid crystals (H-PDLC) with primary LC molecules possessing alternating layers of nematic order and secondary LC molecules.



Opto-control of light reflection occurred by UV-irradiation: the photoisomerization of the secondary LC molecules disrupted the nematic order of the primary LC molecules and induced a refractive index mismatch in the photonic structure. The mismatch produced a stopband and a decrease in the transmission at the diffraction wavelengths.

Urbas, A., et al., *J. Am. Chem. Soc*. (2004) 126, 13580

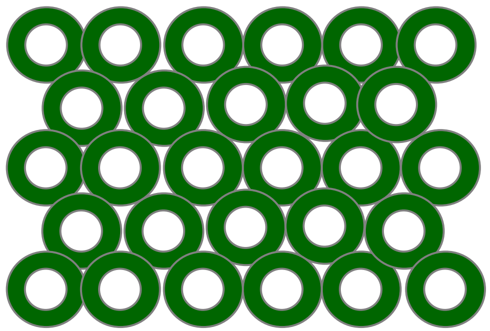
A '*CORE-SHELL*' APPROACH TO PERIODICALLY NANOSTRUCTURED MATERIALS

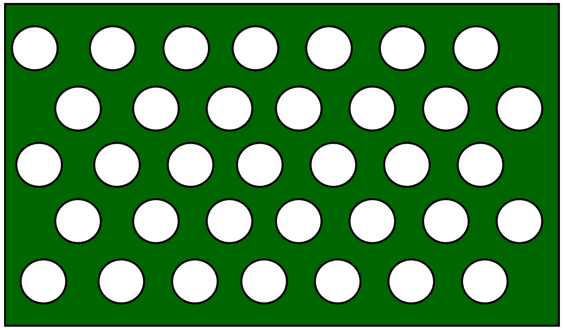


SYNTHESIS

$T_{room} < T_{g,shell} < T_{g,core}$

ASSEMBLY





ANNEALING

$T_{g,shell} < T_{annealing} < T_{g,core}$

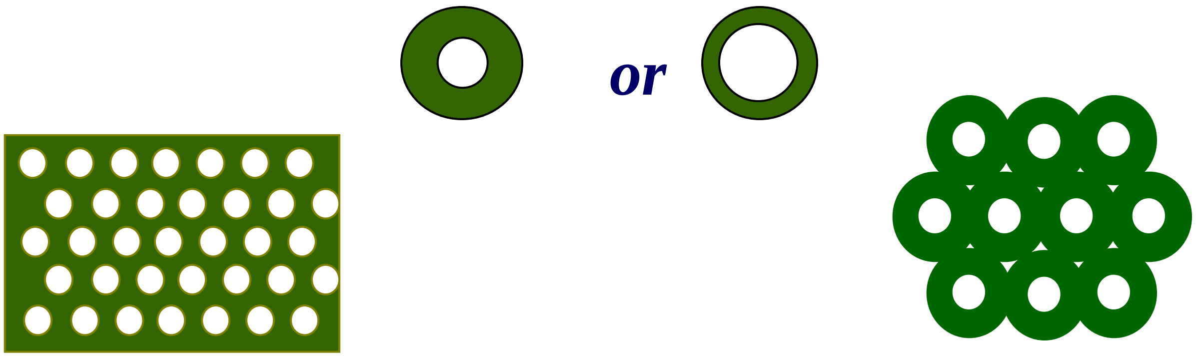
Kumacheva et al. US Patent 5952131, 09/14/99; *Adv. Mater. 11*, 231 (1999); *Macromolecules 32*, 4122 (1999)

'Structural' variables of core-shell strategy

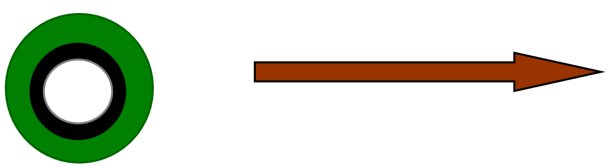
- **Variation in particle size, core radius and shell thickness**

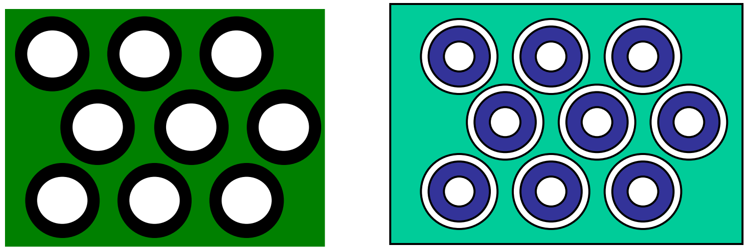
Particle number density: 10^{12} - 10^{16} cm^{-3}

- **Different size ratio between core radius and shell thickness**

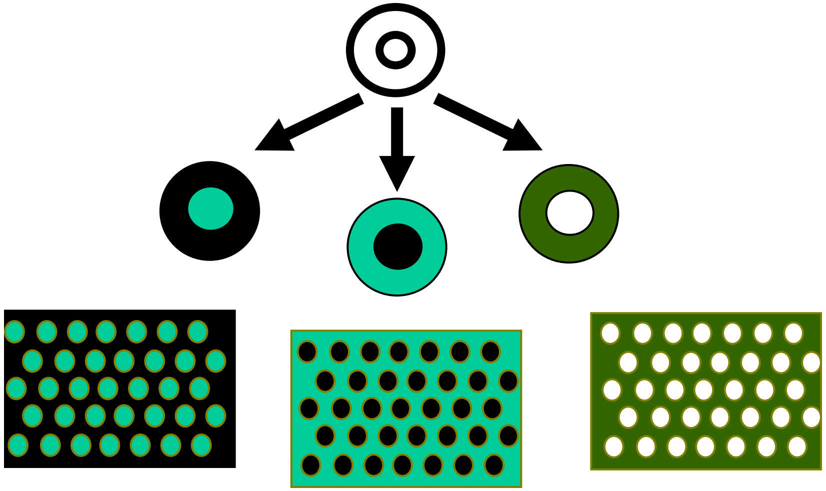


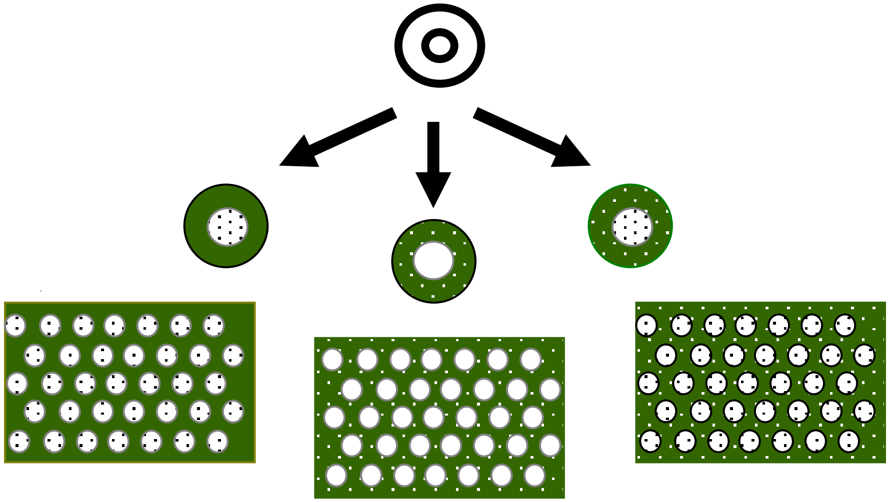
- **Multilayer (multiphase) particles**





'Compositional' variables of core-shell strategy





- Various combinations of core-forming material and shell-forming polymers

- Various organic functionalities:
  fluorescent dyes, organic chromophores, nonlinear optics species

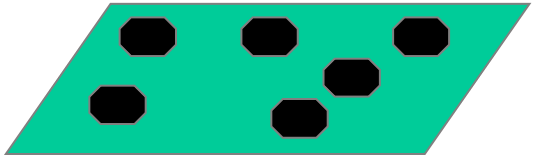
- Inorganic nanoparticles

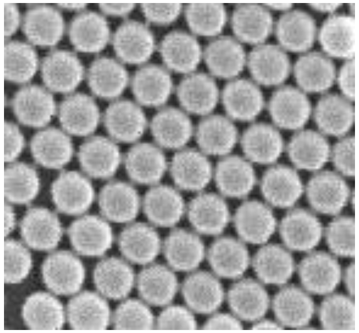
- acrylic polymers
- fluoropolymers
- styrene polymers
- polyacrylamide
- polypyrrole
- polyaniline
- poly(ferrocene silane)
- SiO_2
- TiO_2

Core-shell particles:	PM-1 + PM-2 +LMW	2^3 = 8 *materials*
	PM-1 + PM-2 +LMW-1+ LMW-2	2^4 = 16 *materials*
Three-layer particles:	PM-1 + PM-2 + PM-3 + LMW-1+ LMW-2	2^5 = 32 *materials*

Requirements

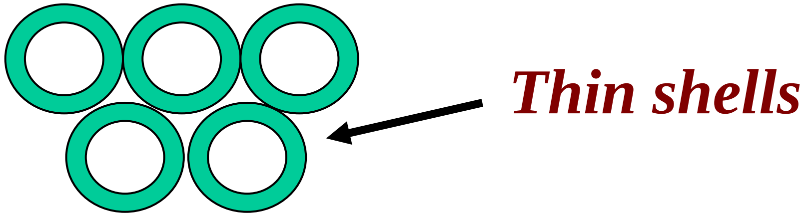
- **Narrow size distribution (for both cores and shells)**

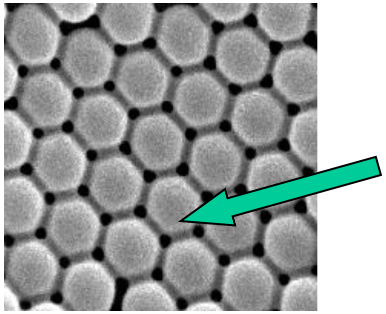




PDI = 1.05 ± 0.02

- **Sufficient thickness of shells for producing void-free materials**



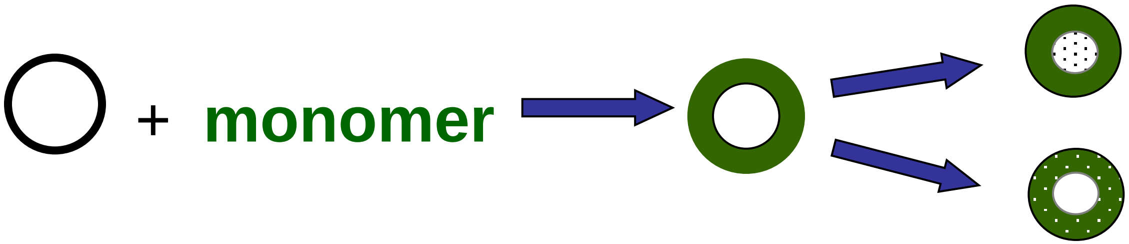


- **No diffusion between particle cores and shells**

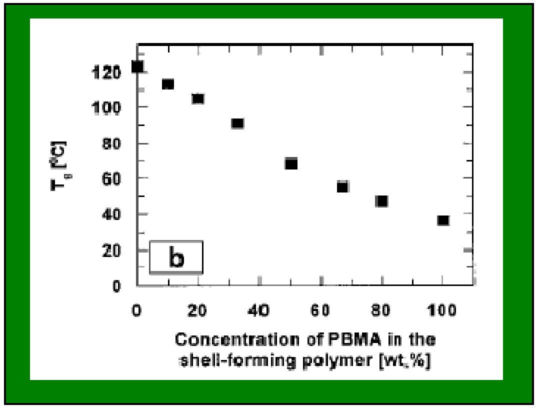
Production of core-shell particles

Interfacial polymerization

INTERFACIAL POLYMERIZATION



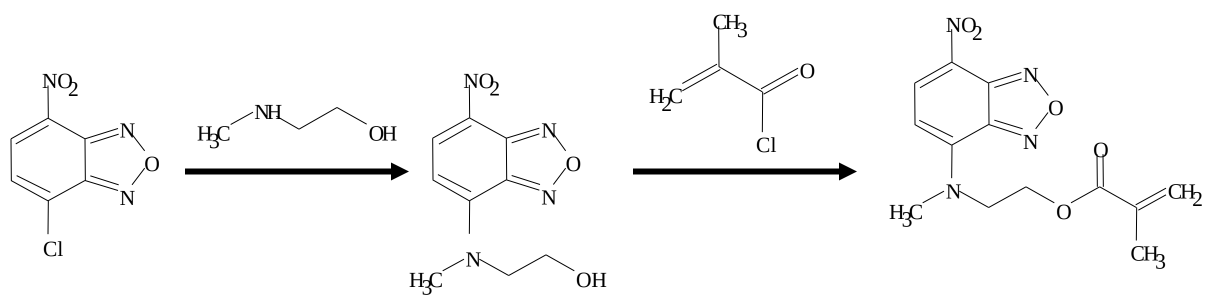
LMW : fluorescent dyes
chromophores



Latex cores: **poly(methyl methacrylate)**

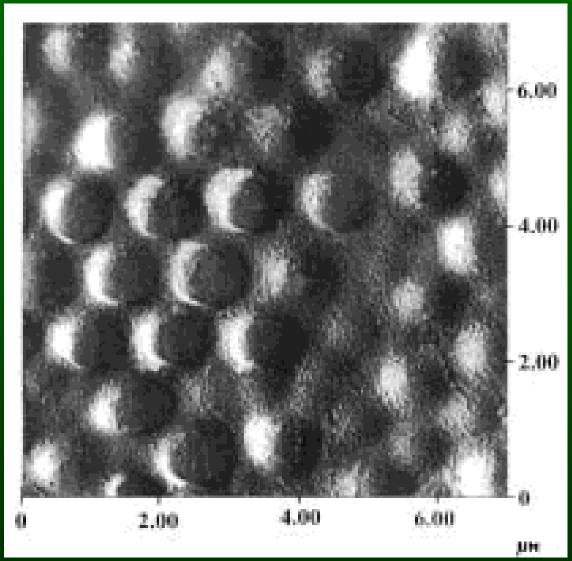
Latex shells: **poly(methyl methacrylate)/**
poly(butyl methacrylate) copolymer

Fluorescent dye: **4-amino-7- nitrobenzo-2-oxa-1,3-diazole (NBD)**

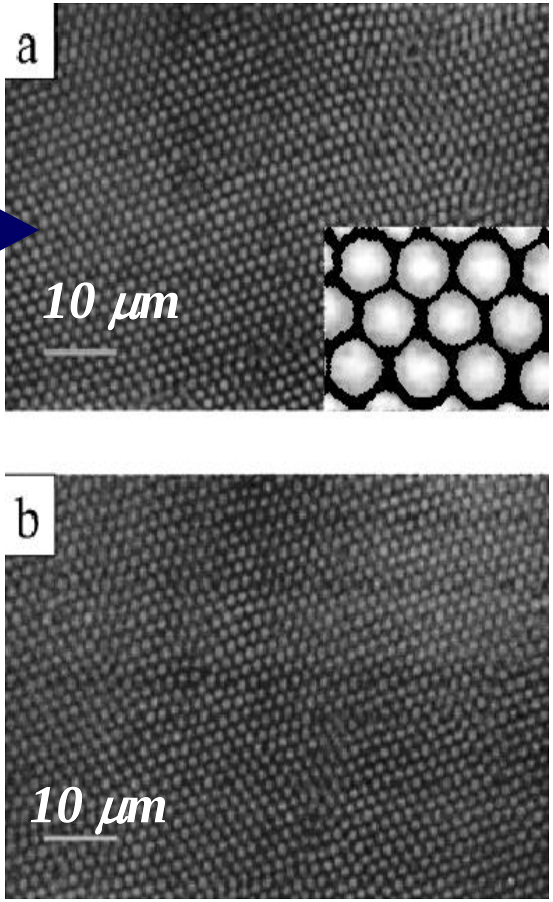


Nanostructured polymeric material

AFM



Laser Confocal Fluorescent Microscopy



Surface

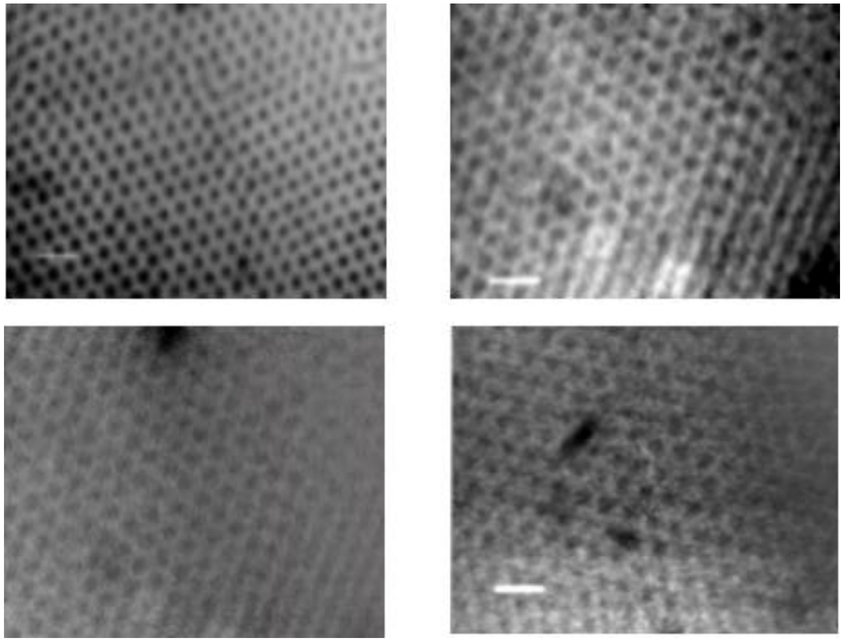
100 μm below the surface

Kalinina, O.; Kumacheva, E. *Adv. Mater.* ***11***, **231 (1999); US Patent 5952131, 09/14/99;**

Nanostructured material with inverse structure

C A + C

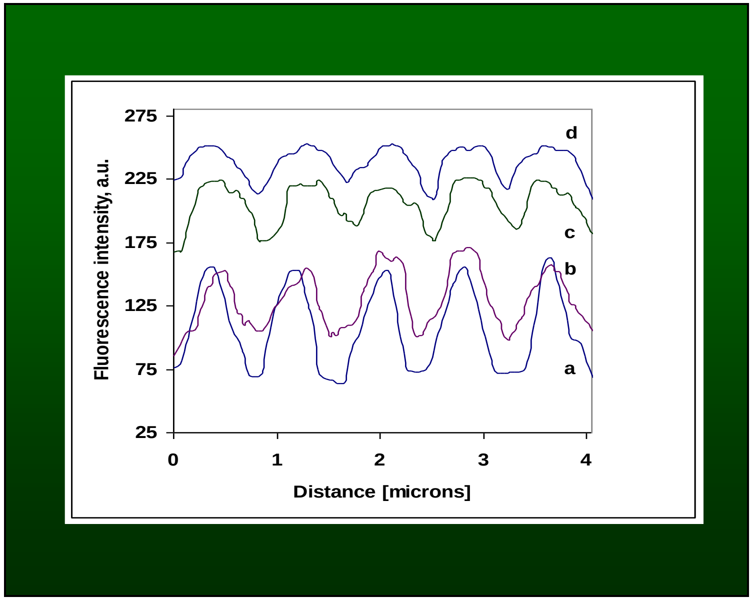
C A



C

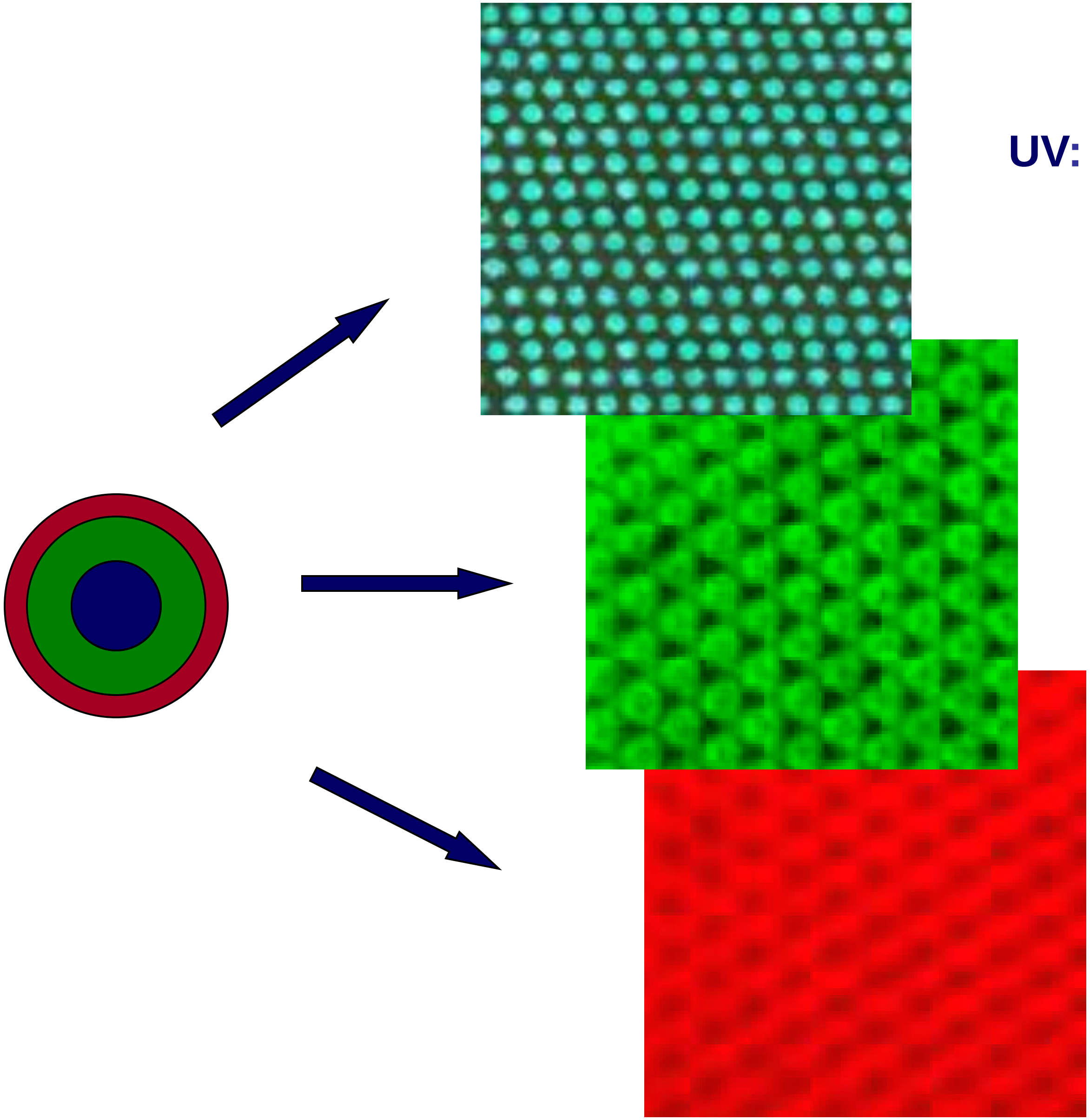
CA: covalent attachment of NBD to shell-forming polymer

C: cross-linking of shell-forming polymer



Kalinina, O.; Kumacheva, E. Chem. Mater. 13, 35 (2001), *Macromolecules*, 26, 126, 2003

"Multicolor" Nanostructured Material



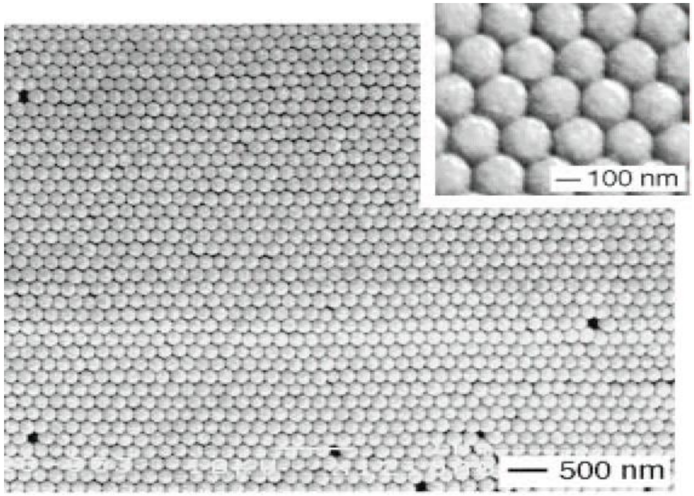
UV: 364 nm

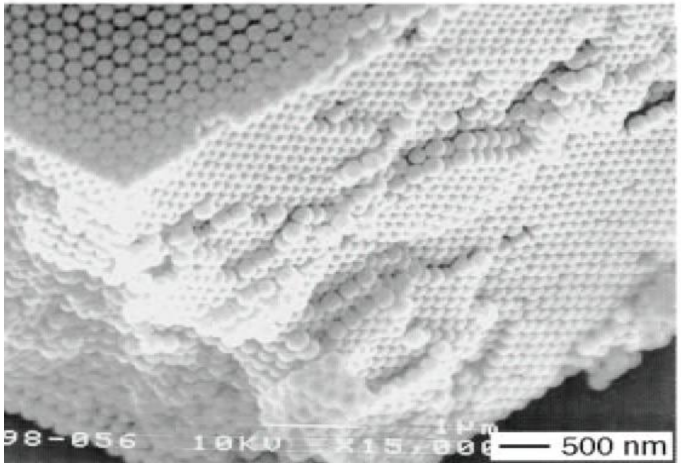
Vis: 488 nm

Near- IR: 633 nm

Colloid Crystallization

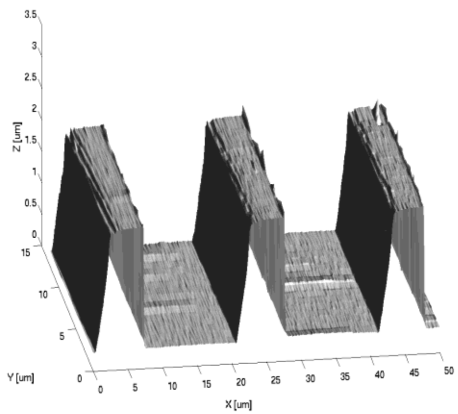
Colloid Crystallization



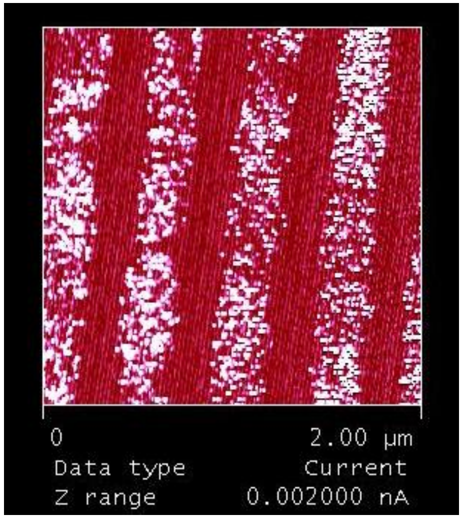


Crystallization on *patterned substrates*

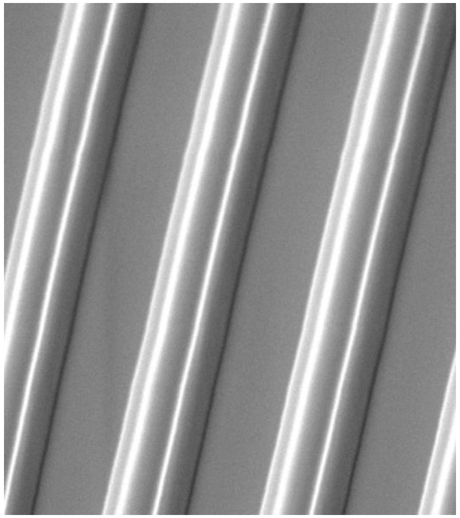
AFM



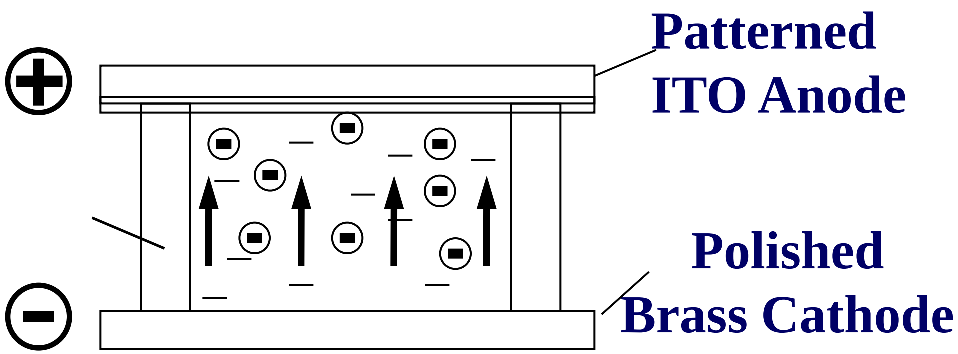
Conductivity



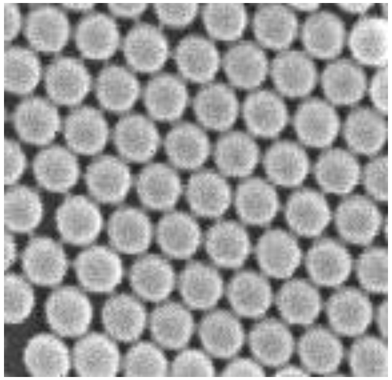
SEM



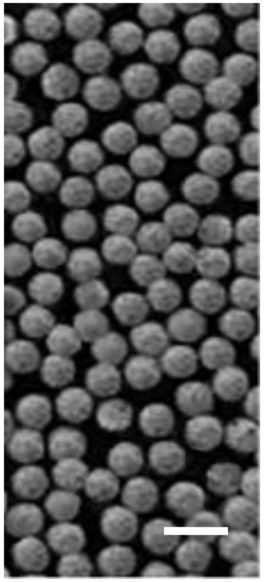
ELECTRODEPOSITION:



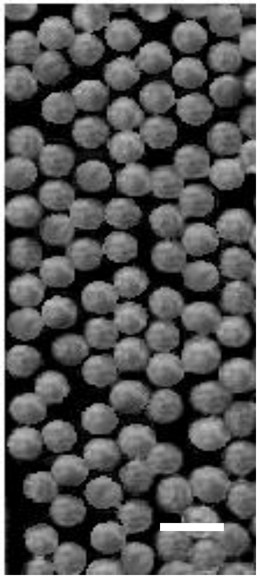
Colloid spheres



Electrodeposition on patterned substrates

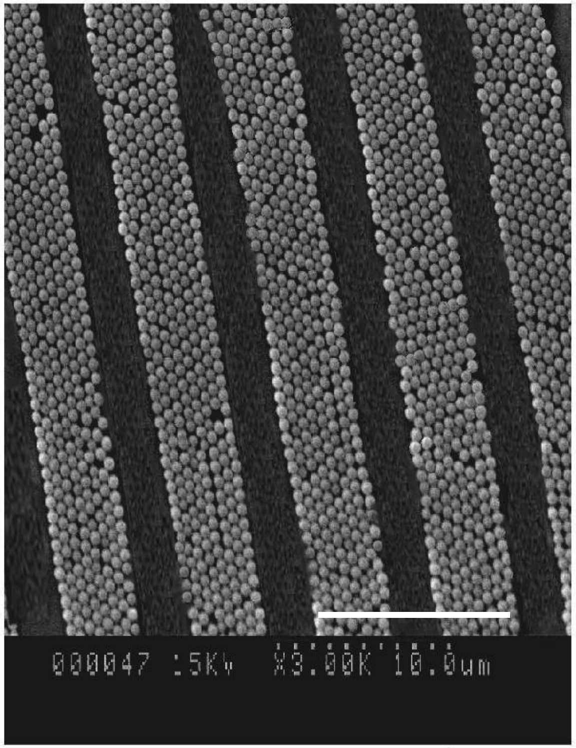


blank substrate



patterned substrate, $L = 5.5\ \mu m$

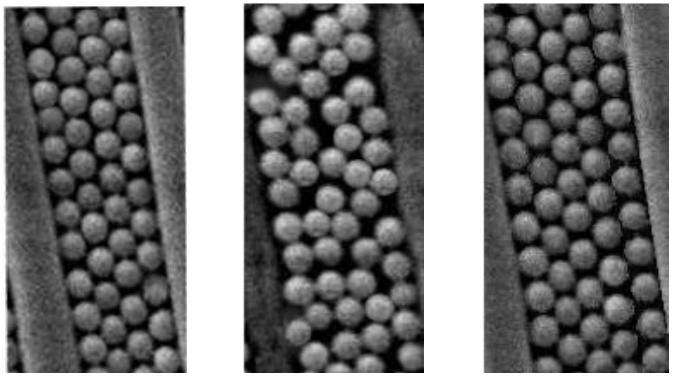
patterned substrate, $L = 4.2\ \mu m$



$$L/D = [(n-1)\cos 30^{o} + 1]$$

Crystallization on patterned substrates

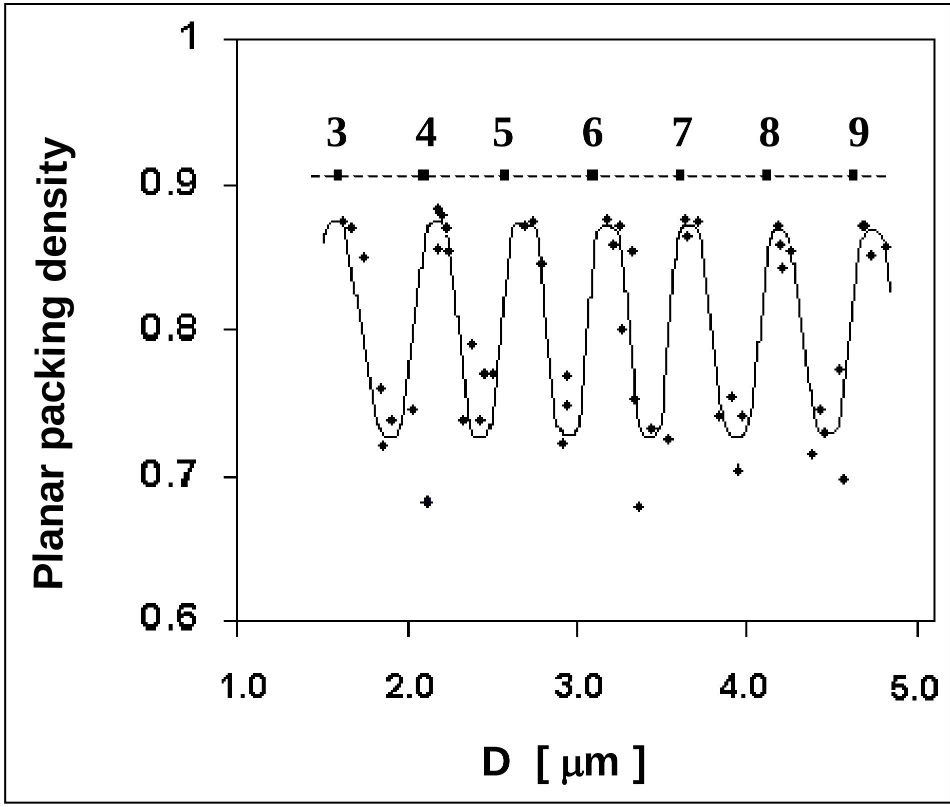
Increasing confinement



2.22 → 2.51 → 2.72 μm

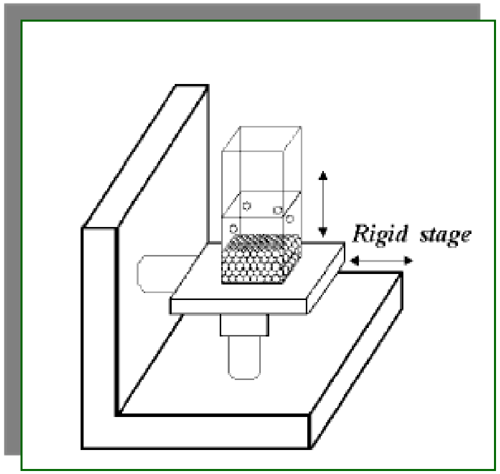
Order-disorder-order transition:

$$D_c = 2R\,[(n-1)\cos 30^{o} + 1]$$



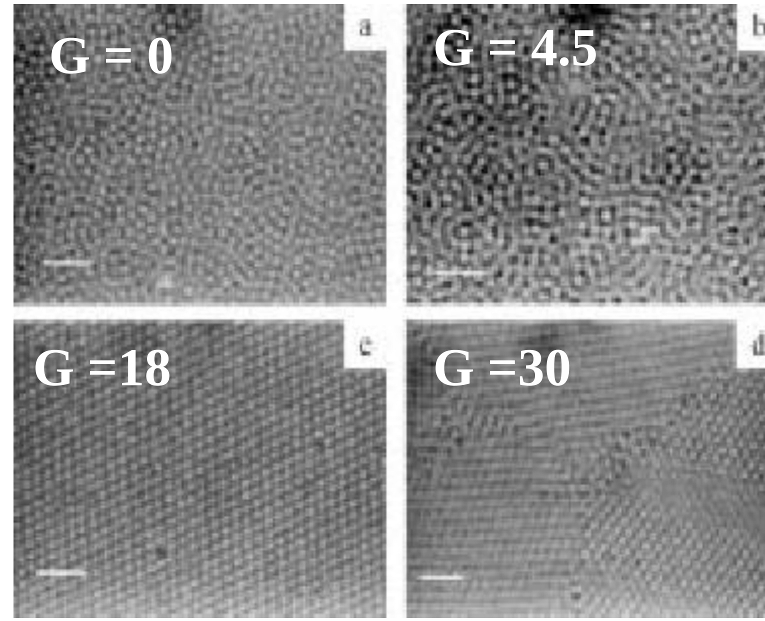
Periodicity 0.52 ± 0.02 μm

Colloid crystal growth *under oscillatory shear*

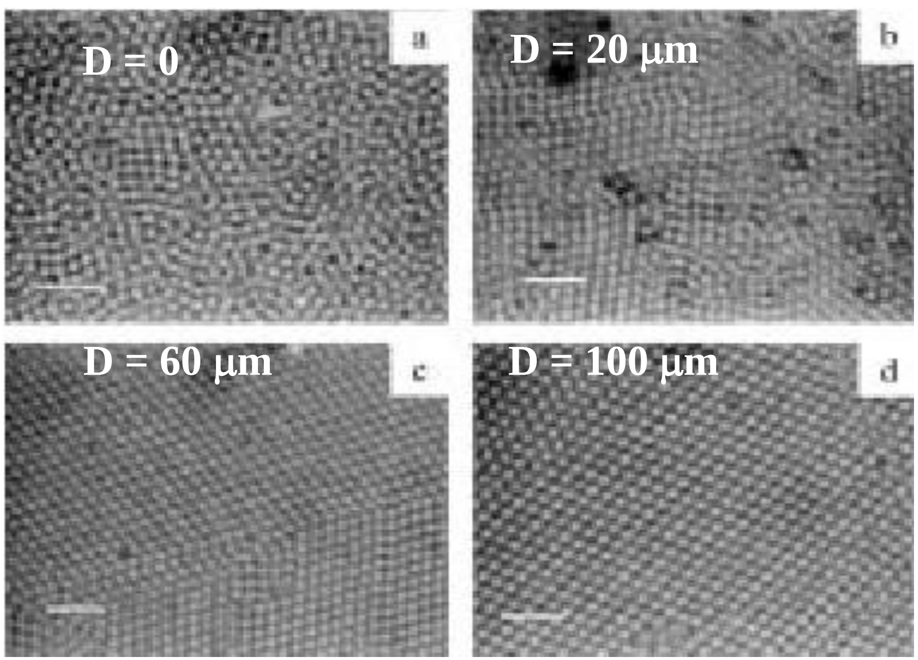


$$G = A\omega^2/g$$

$$\omega = 2\pi f$$



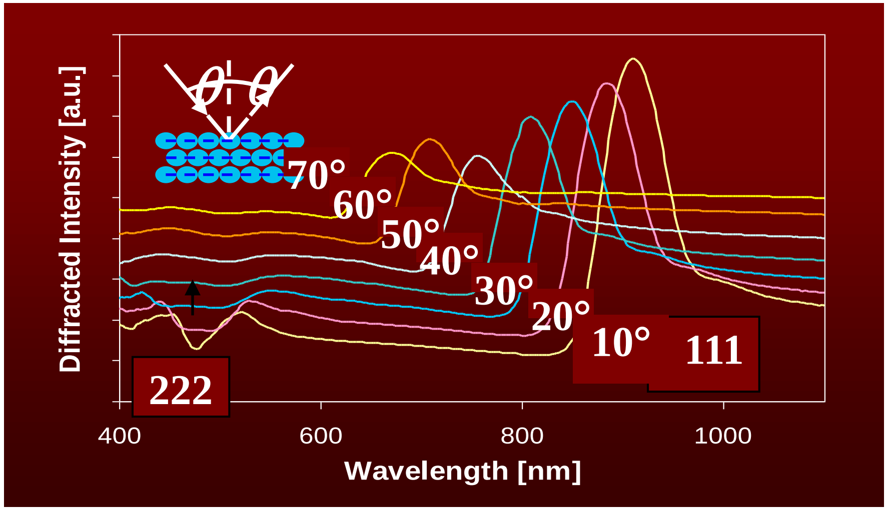
Effect of G

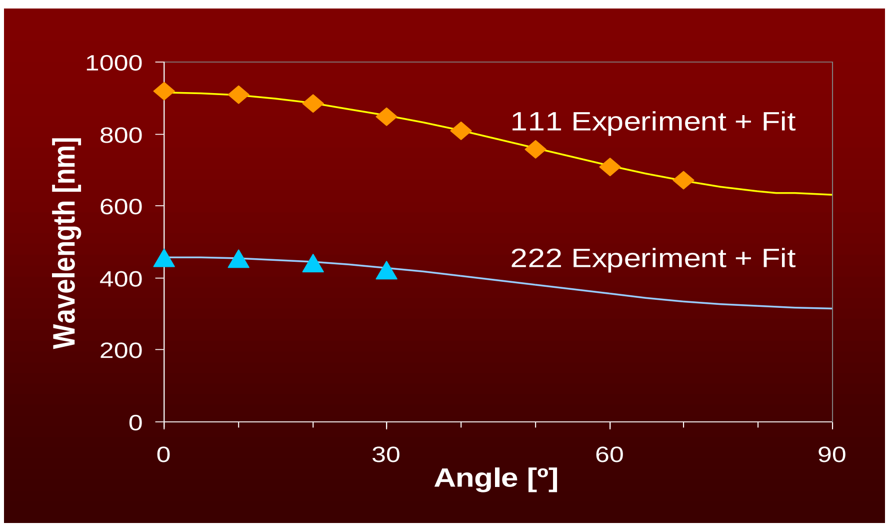


Self-healing

Kumacheva et al. *Adv. Mater.* 14, 221-224 (2002)

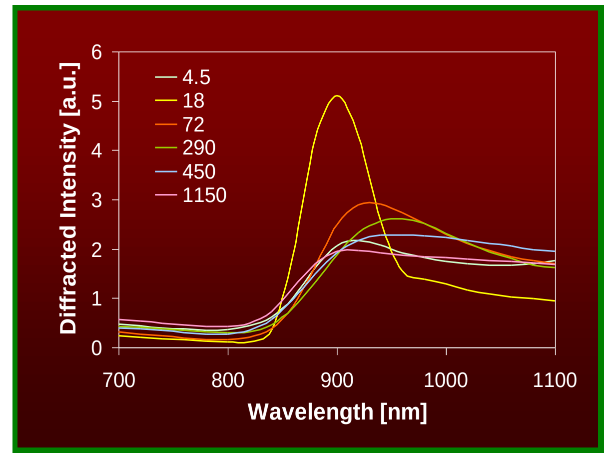
Colloid crystal growth under oscillatory shear





d = 405 nm ; n_{eff} = 1.38, précision: 0.5 %

- **Peak position is predicted accurately by Bragg's law**
- **Sphere spacing and effective refractive index were obtained with high accuracy**



Best samples exhibit the most intense Bragg diffraction

$$\lambda_B = \frac{2\, d_{hkl}}{m}\sqrt{n_{eff}^2 - \sin^2\theta}$$

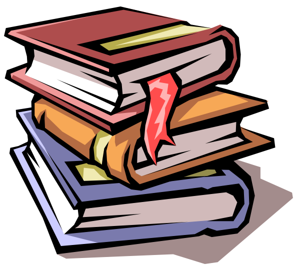
$$n_{eff} = \sqrt{n_{air}^2\phi + n_{spheres}^2(1-\phi)}$$

Allard, M et al. *J. Quant. Electronics* 34, 27-36 (*2002*)

Applications

- Materials for Optical data Storage
- Materials for the Recording of Biometric Features
- (Multilayer Dielectric Resonators)

3D Optical Data Storage



versus

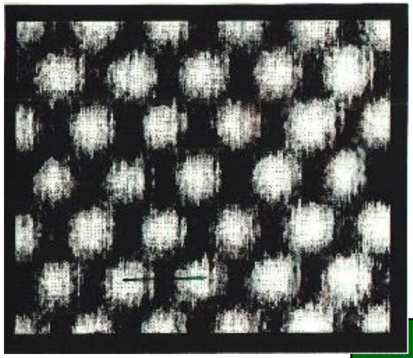
I think there is a world market for maybe five computers.

Thomas Watson,
Chair of IBM, 1943

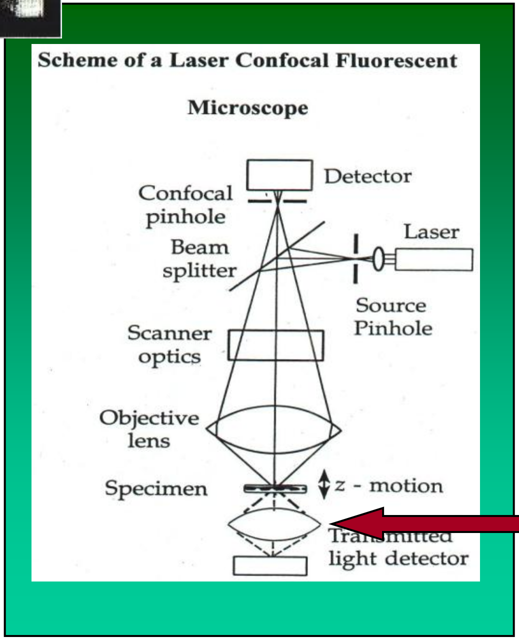
640 K ought to be enough for anybody!

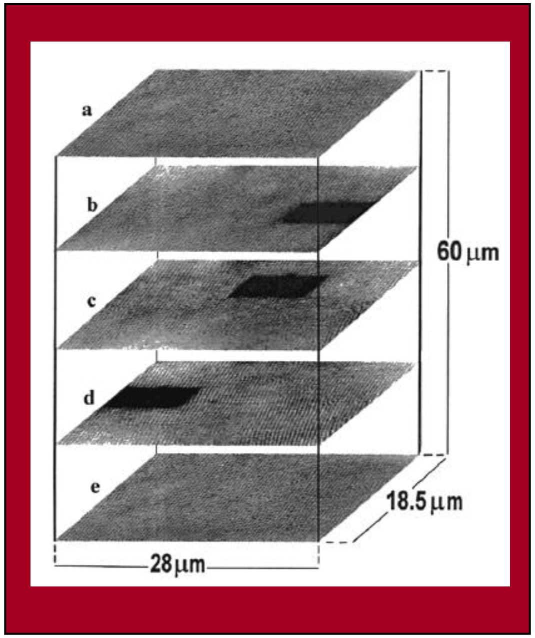
Bill Gates, 1981

Three-dimensional optical data storage

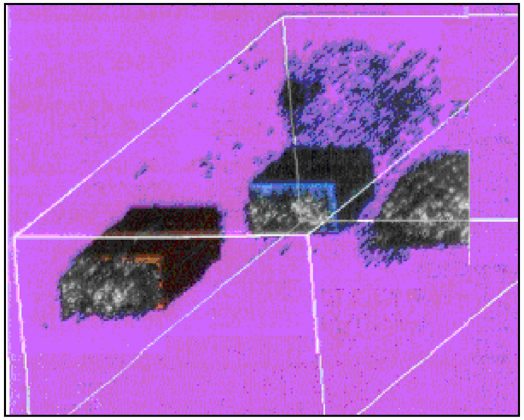


Polymer photonic crystal





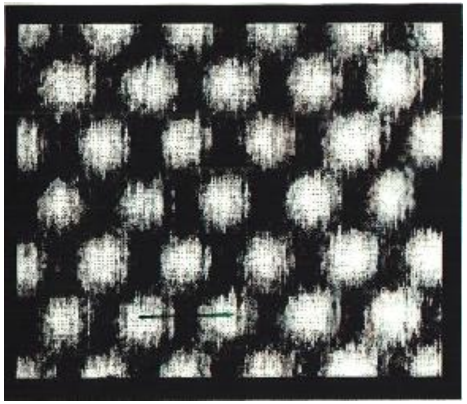
The first attempt to "write" in 3D nanostructured materials



Laser Confocal Fluorescent Microscopy:
a specific plane can be imaged and photochemically changed

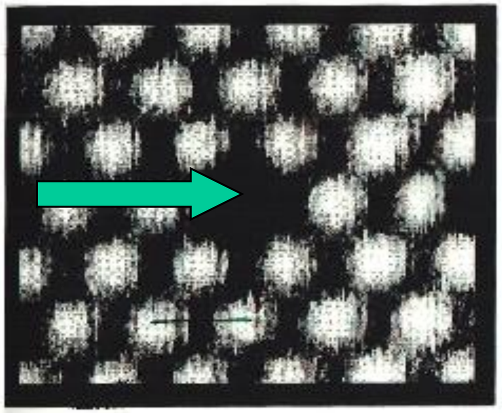
Kumacheva et al. ***Adv. Mater.*** ***11*****, 231-234 (1999)**

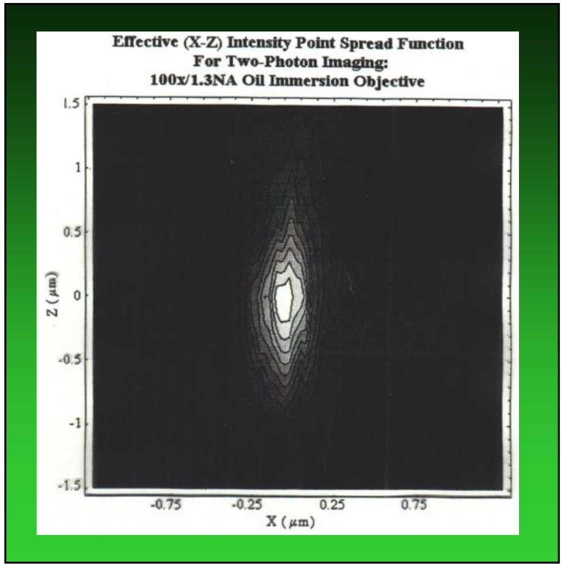
Three-dimensional optical data storage

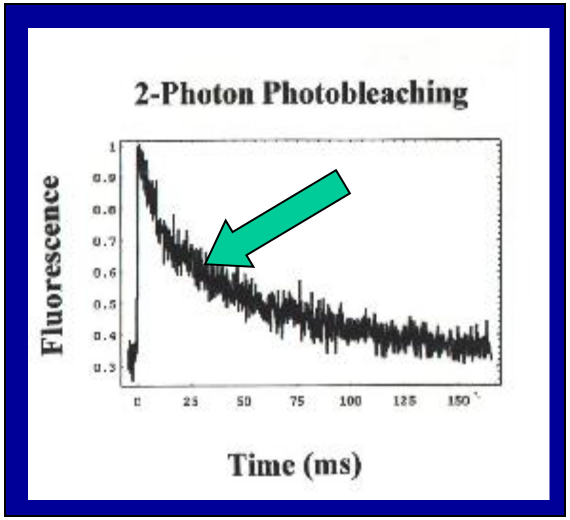


Domain size 0.5 μm
λ_{abs} = 470 nm

Writing in 3D!!







2-photon cross-section:
L = 0.5 μm
λ_{abs} = 840/2 = 420 nm

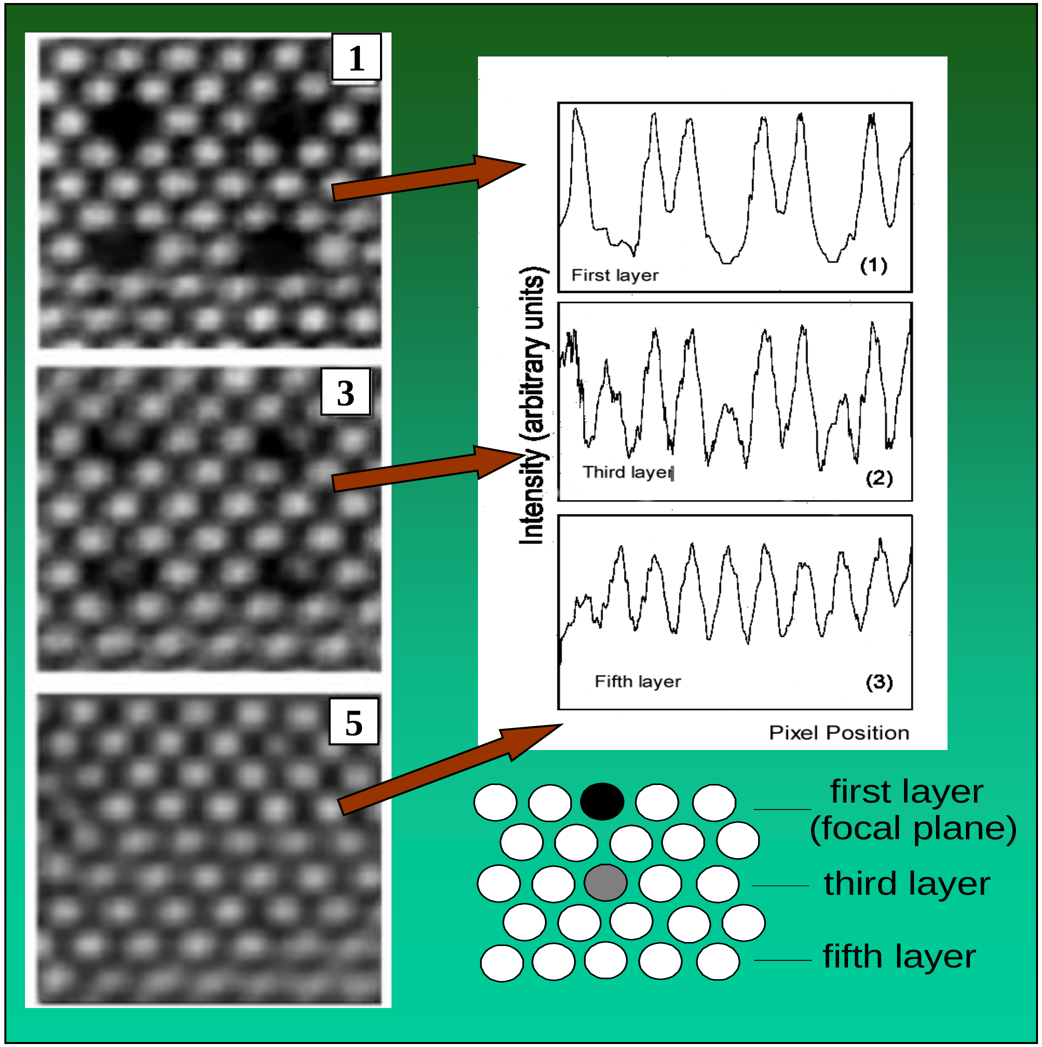
Three-dimensional optical data storage

Depth Discrimination: 2.5 μm

Storage density:

6 x 10^{12} bits/cm^3 (3D)
versus
3.5 x 10^8 bits/cm^2(2D)

B. Siwick et al. J. Appl. Phys. **90, 5328 (2001)**

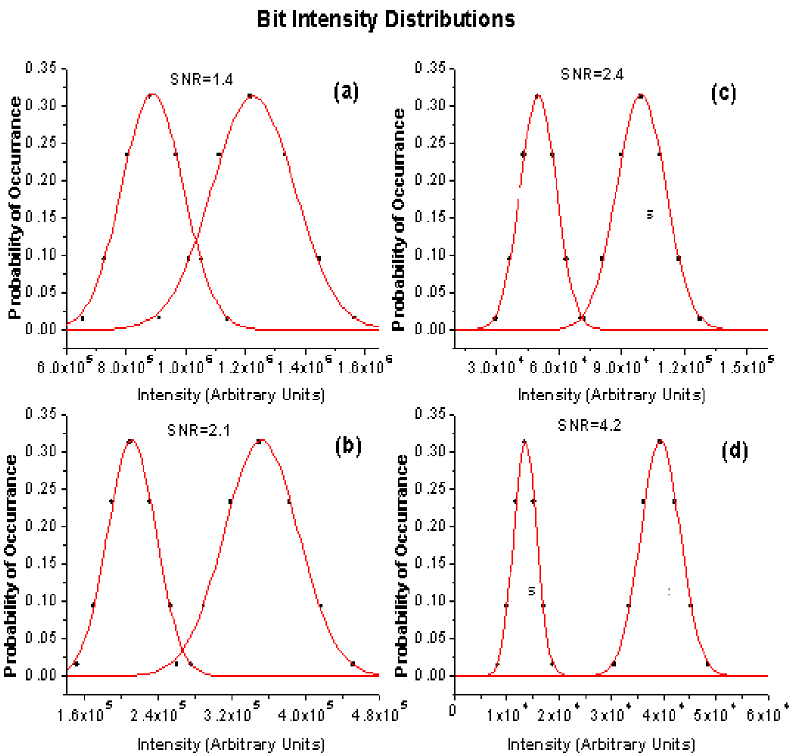


Homogeneous versus Nanostructured Materials

Homogenous

Homogenous ("windowed" bit pattern)

Dwayne Miller:



Distribution of 1's (photobleached) and 0's (unphotobleached) intensities for a bit-pattern

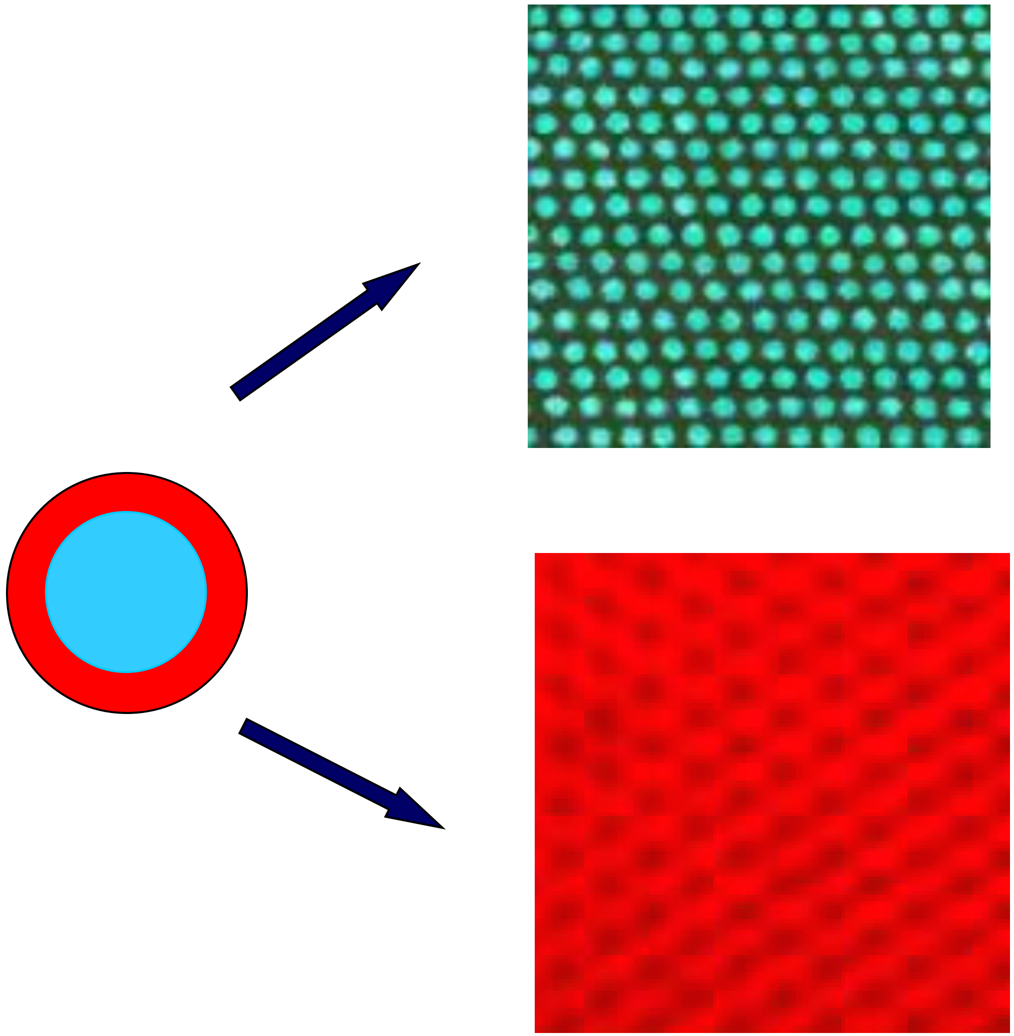
Image quality for the bit pattern photobleached into the nanostructured material is approximately twice as good as in the homogenous material.

Nanostructured

Nanostructured ("windowed" bit-pattern)

Materials for the Recording of Biometric Features

"Multicolor" Nanostructured Material

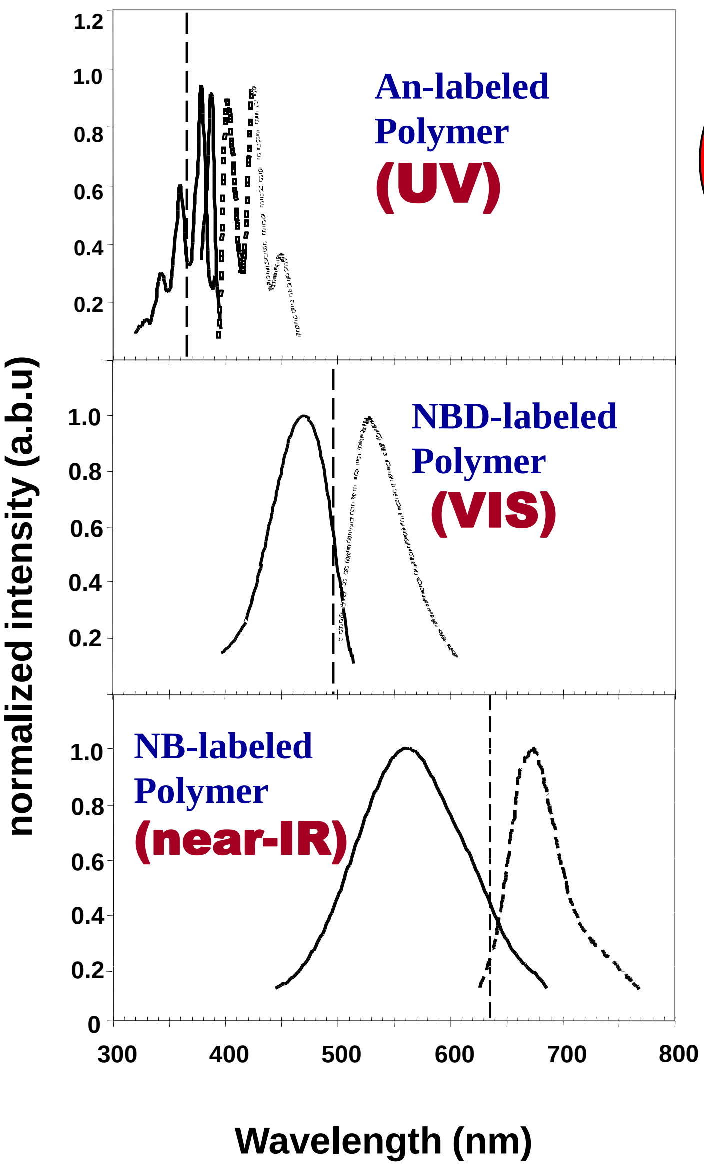


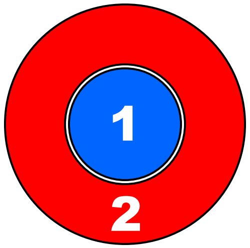
UV: 364 nm

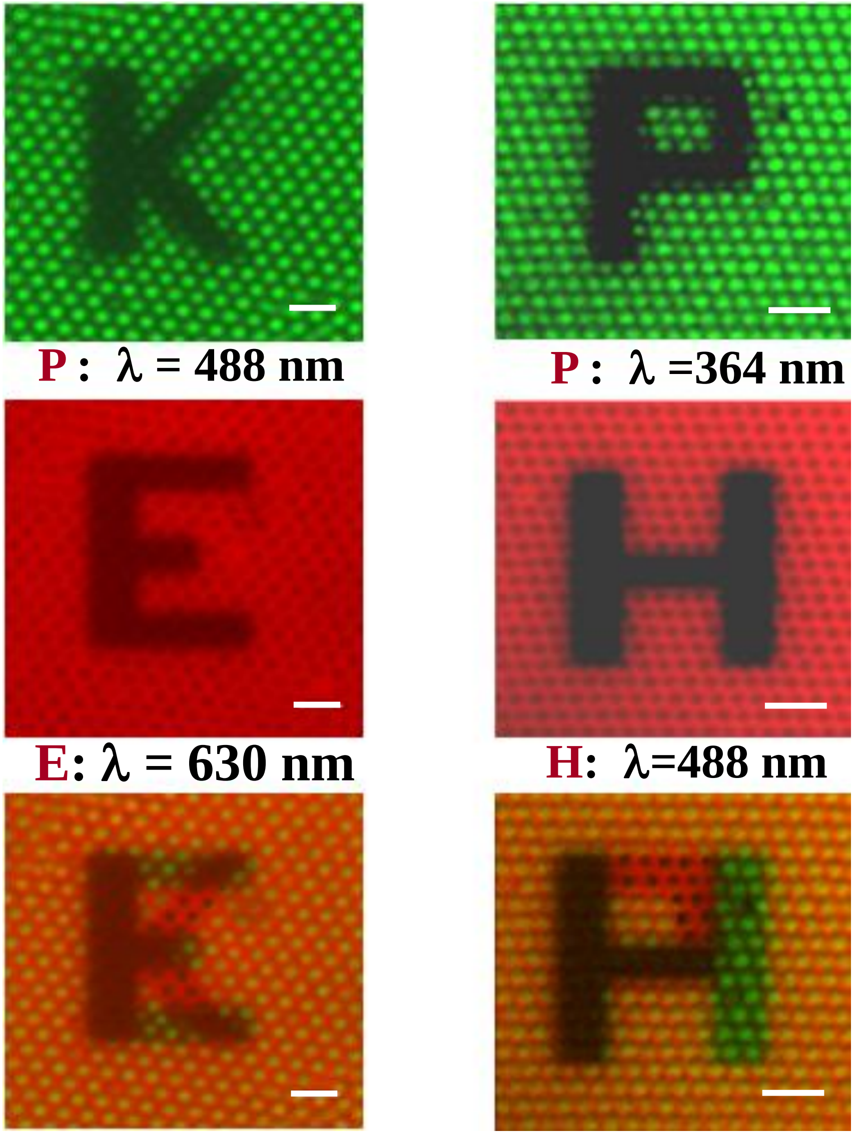
Near- IR: 633 nm

Pham et al. Adv. Mater. 16, 516-520 (2004)

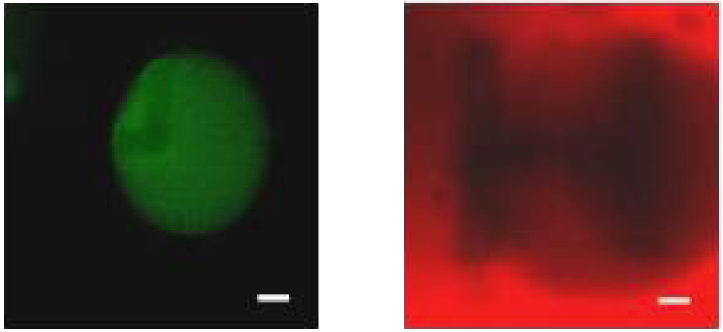
Security Writing



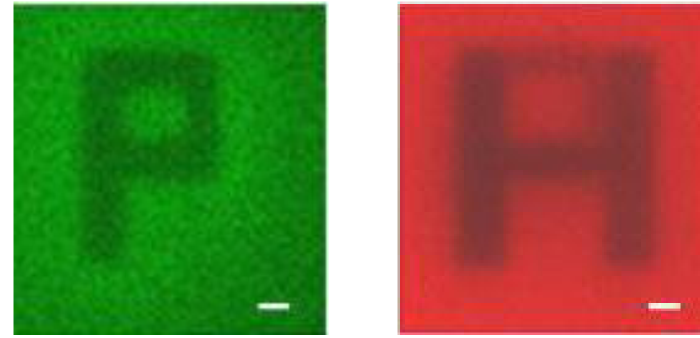




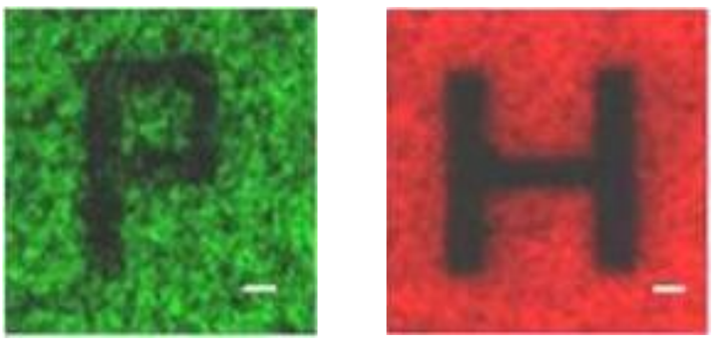
Security Writing



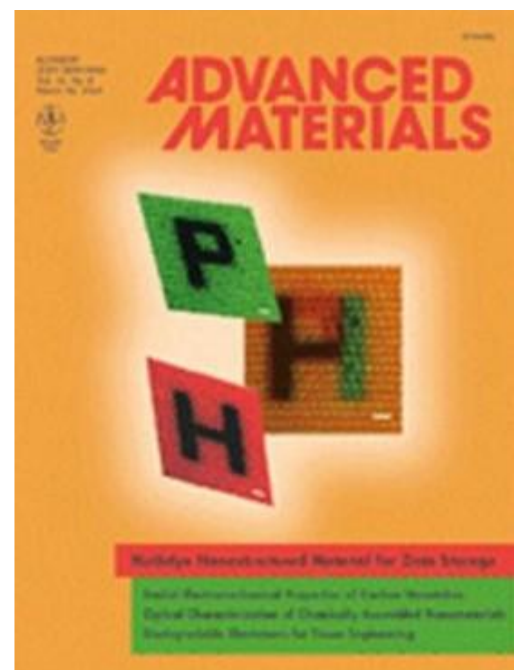
Solution of *two* dye-labeled polymers



Solution of *a single* polymer and *two* dyes



Mixture of dye-labeled particles



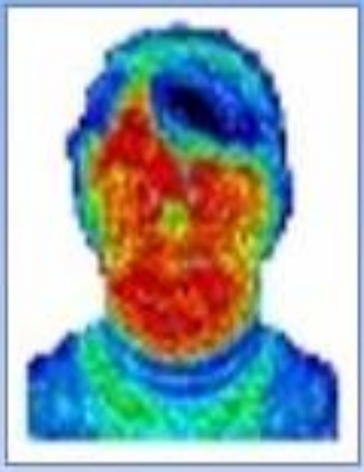
Advantages of nanostructered material

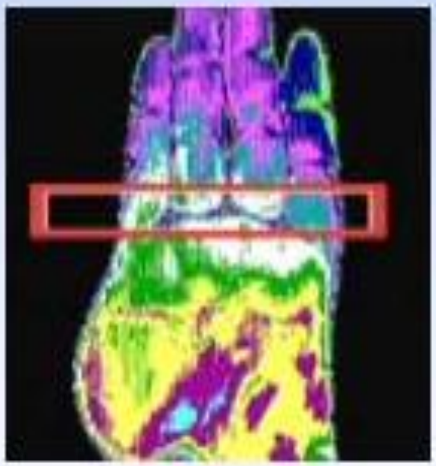
2^2 writing modes for two dyes
(2 modes: 1 or 0 for one dye)

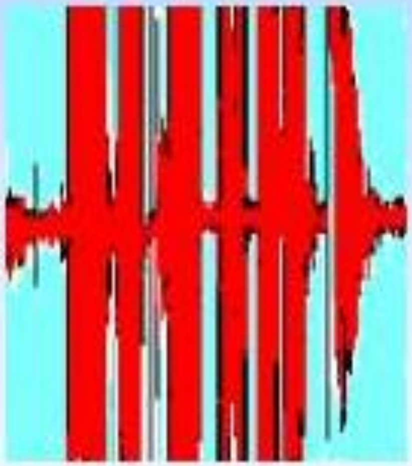
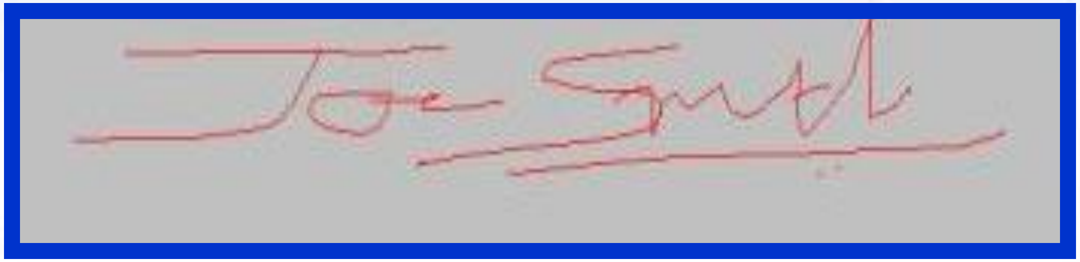
Resolution: 10^8 dpi *versus* 10^5 dpi

Biometrics: utilizes "something you are" to authenticate identification: photographs, fingerprints, retina patterns, hand geometry or signature dynamics.

The user's biometric information is stored on a smart card, the card is placed in a reader, and a biometric scanner reads the information to match it against that on the card. This is a fast, accurate, and highly-secure form of user authentication

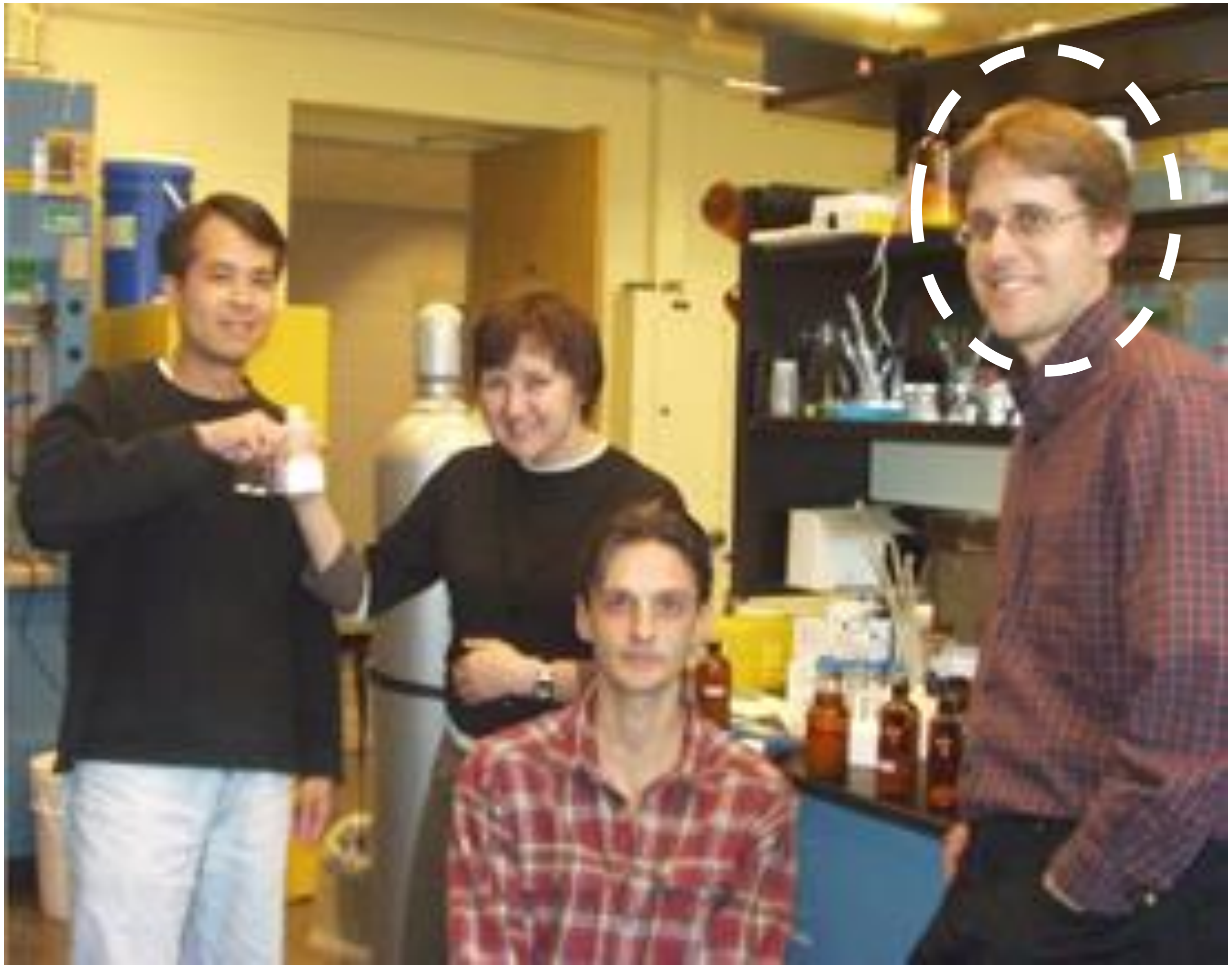



Natural Sciences and Engineering Research Council of Canada
Conseil de recherches en sciences naturelles et en génie du Canada
Canada

December 2004

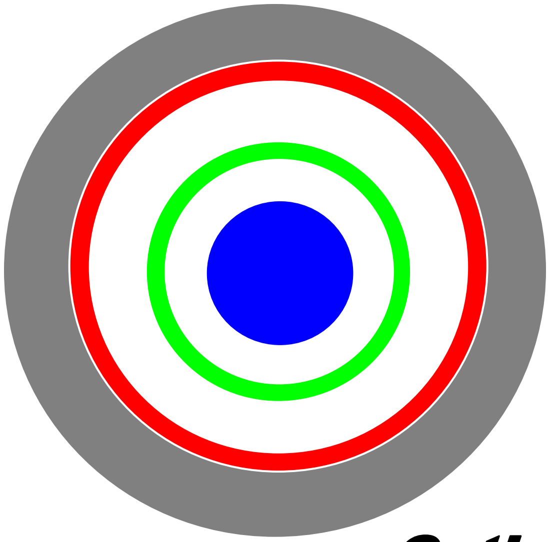


Hung Pham **Ilya Gourevich** **James Jonkman**

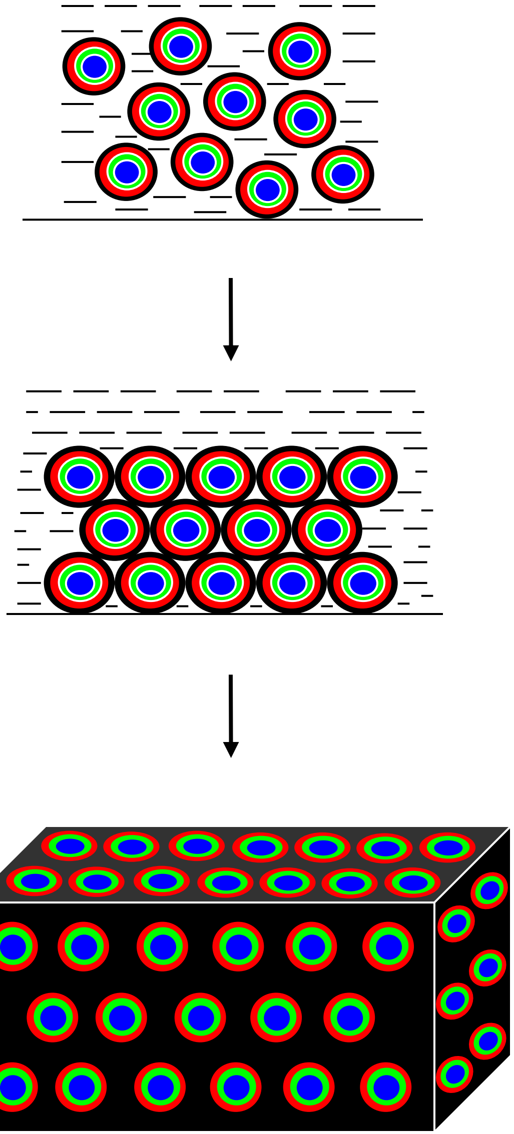
NEXT GENERATION: “Three-color” Material

2^n modes in information encoding

3 dyes: 8 modes



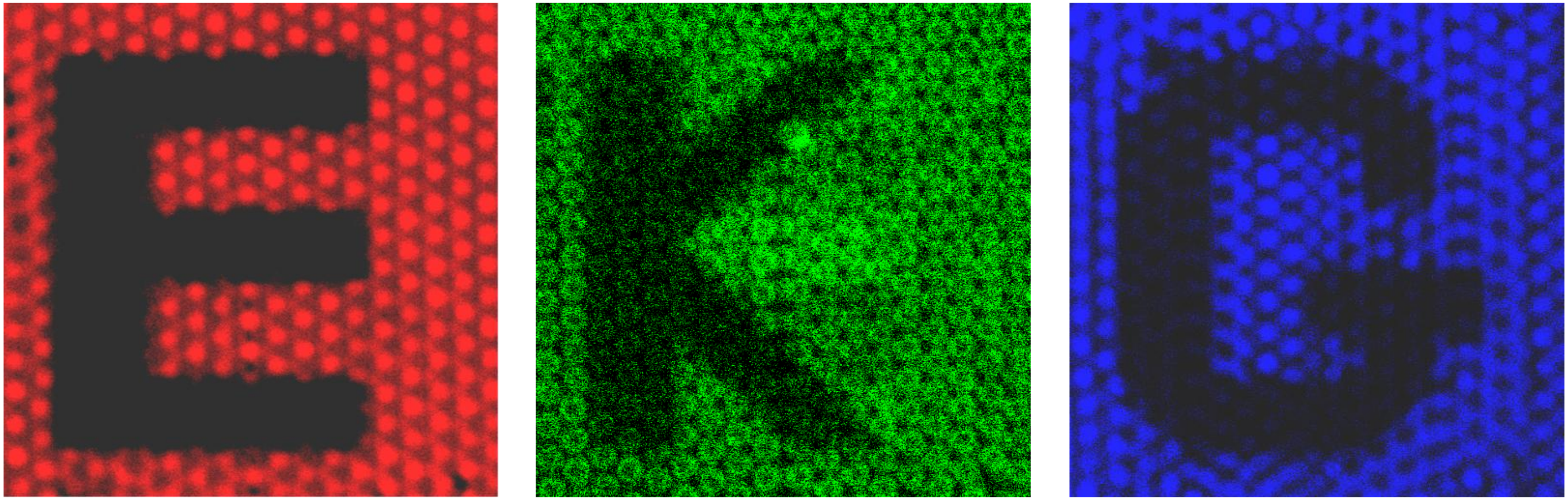
Optically inert non-labeled elastomeric shell



- Same polymer composition for all but the outmost layer (PMMA)
- Last layer: poly (MMA-BMA), T_g = 5 ^oC

Writing on the same location

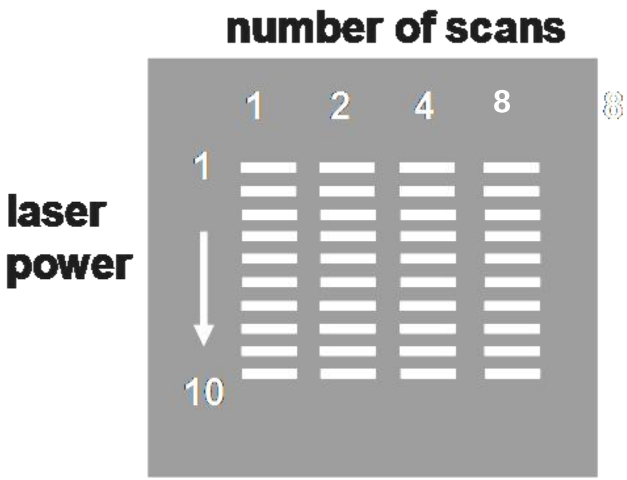
Eugenia Kumacheva Group

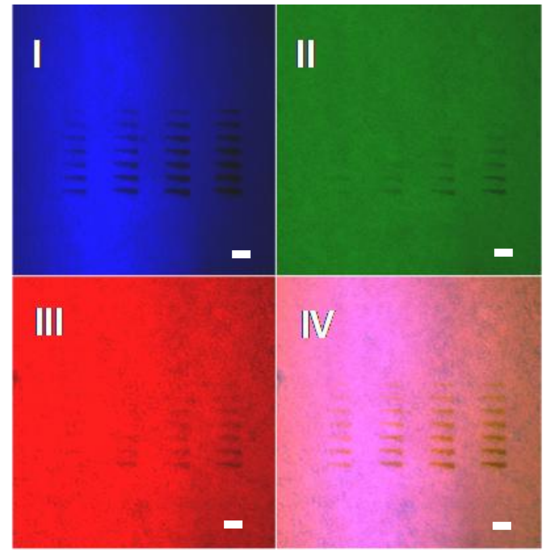


2^n modes in information encoding

3 dyes: 8 modes

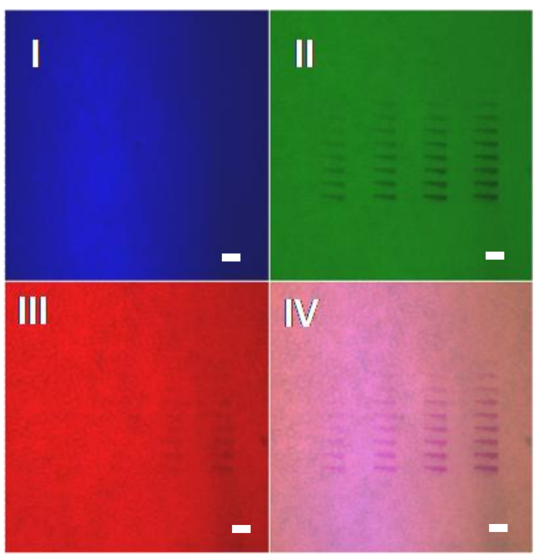
Writing in the same location

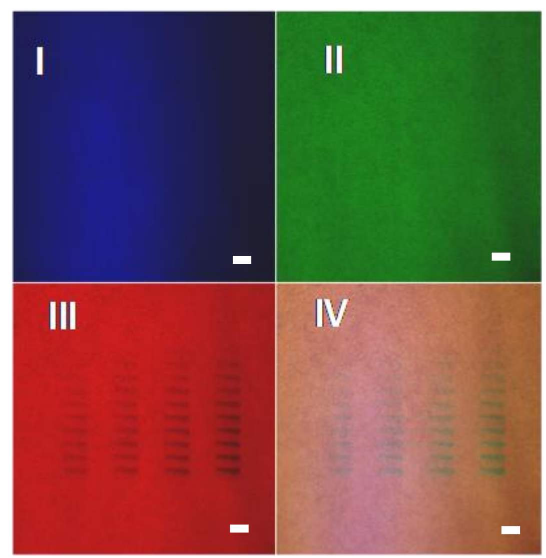




λ =354 nm

λ =488 nm





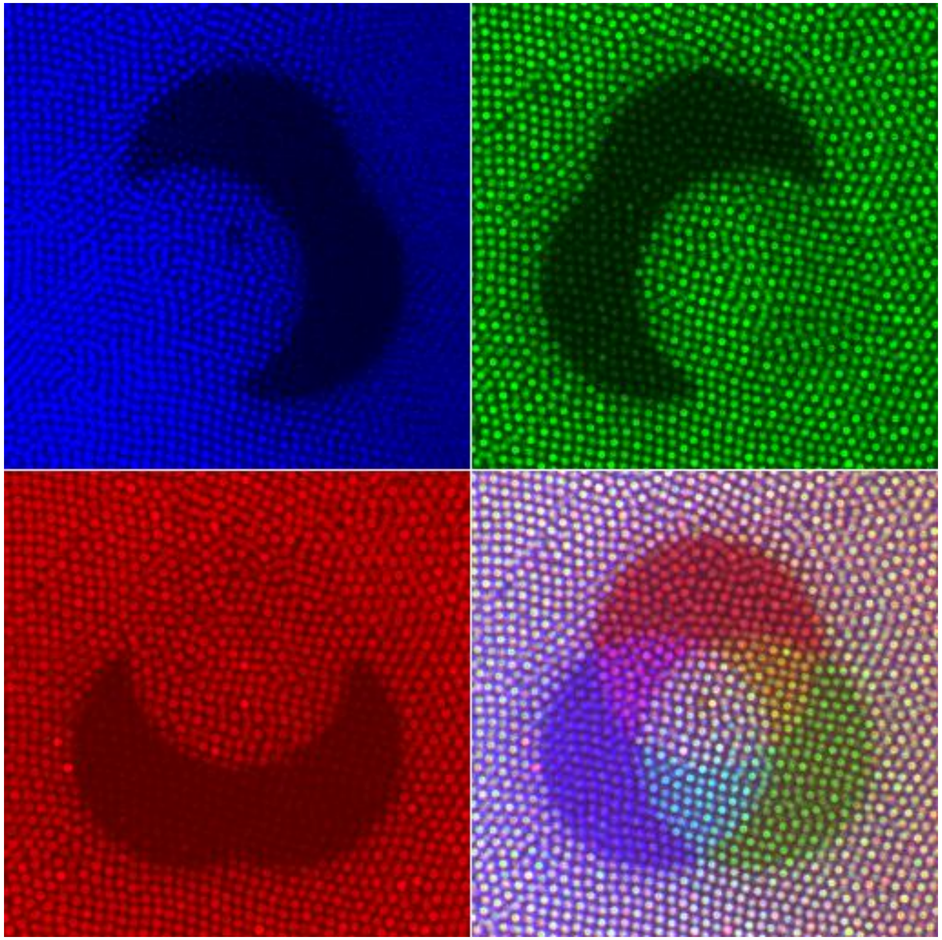
λ =633 nm

Encryption of Biometric Features

Scale bar

50 μm

REAL RGB Picture



The same picture recorded in the polymer

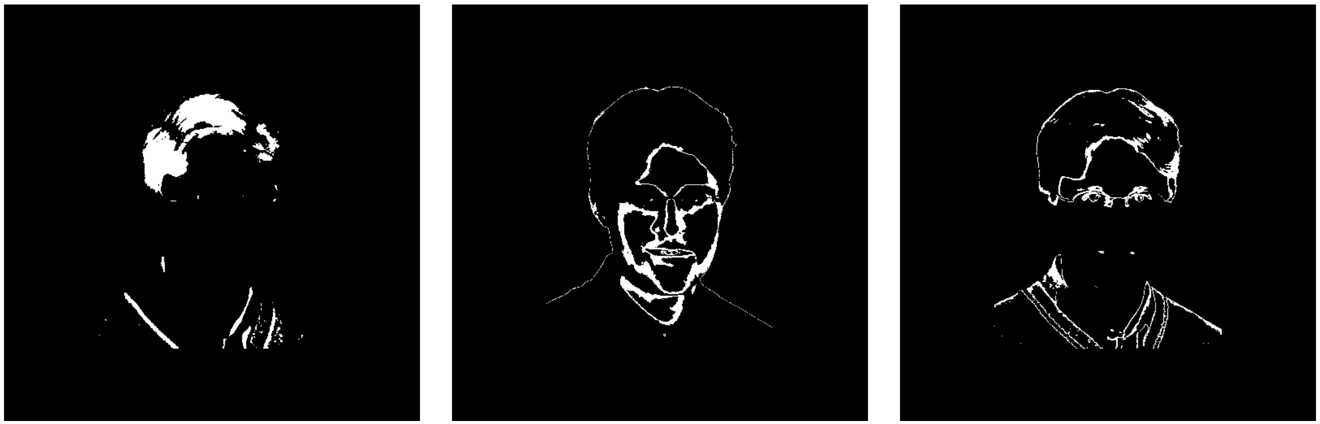
James Jonkman

- Split a 24-bit color digital photograph of **James** into the red, green and blue component images

- Each component **monochromatic** image comprising 256 gray scale levels was further split into **8 binary images**, each comprising 32 shades of gray

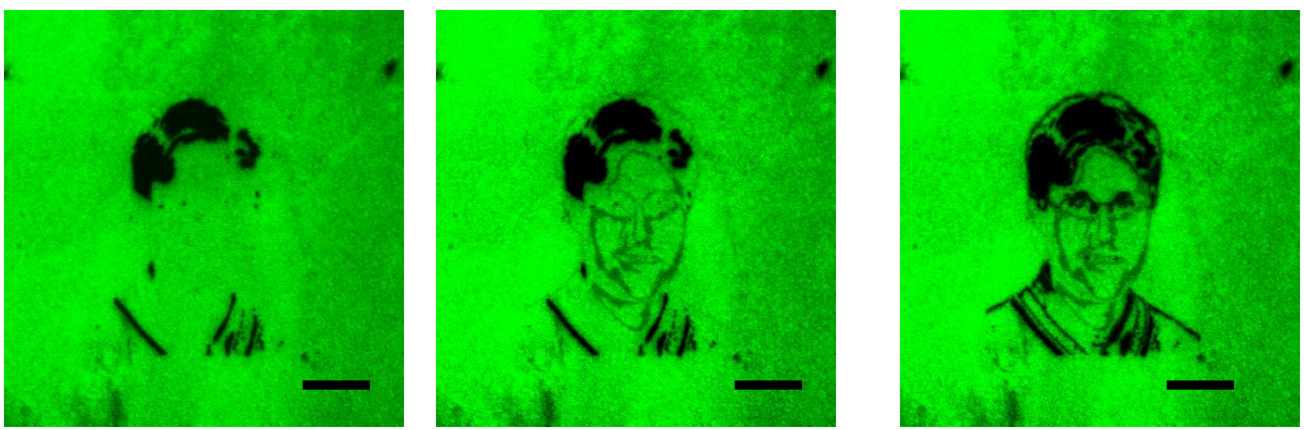
- Each binary image acted as the non-zero coordinates (as a ‘mask’)

Writing with Grayscales



0 - 31 | 32 - 61 | 62 - 91

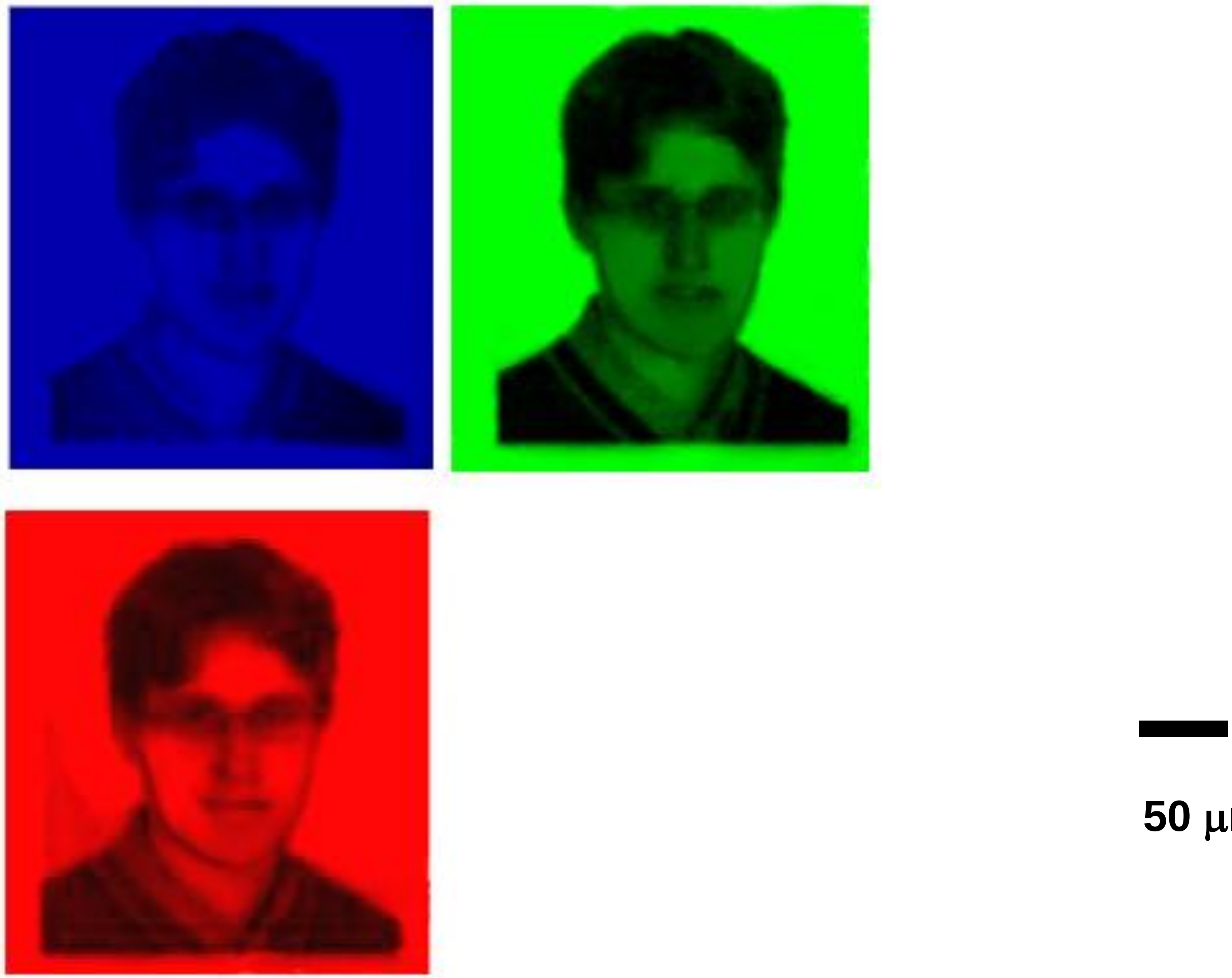
Binary images ('masks')



Monochromatic images (recorded by using 'masks')

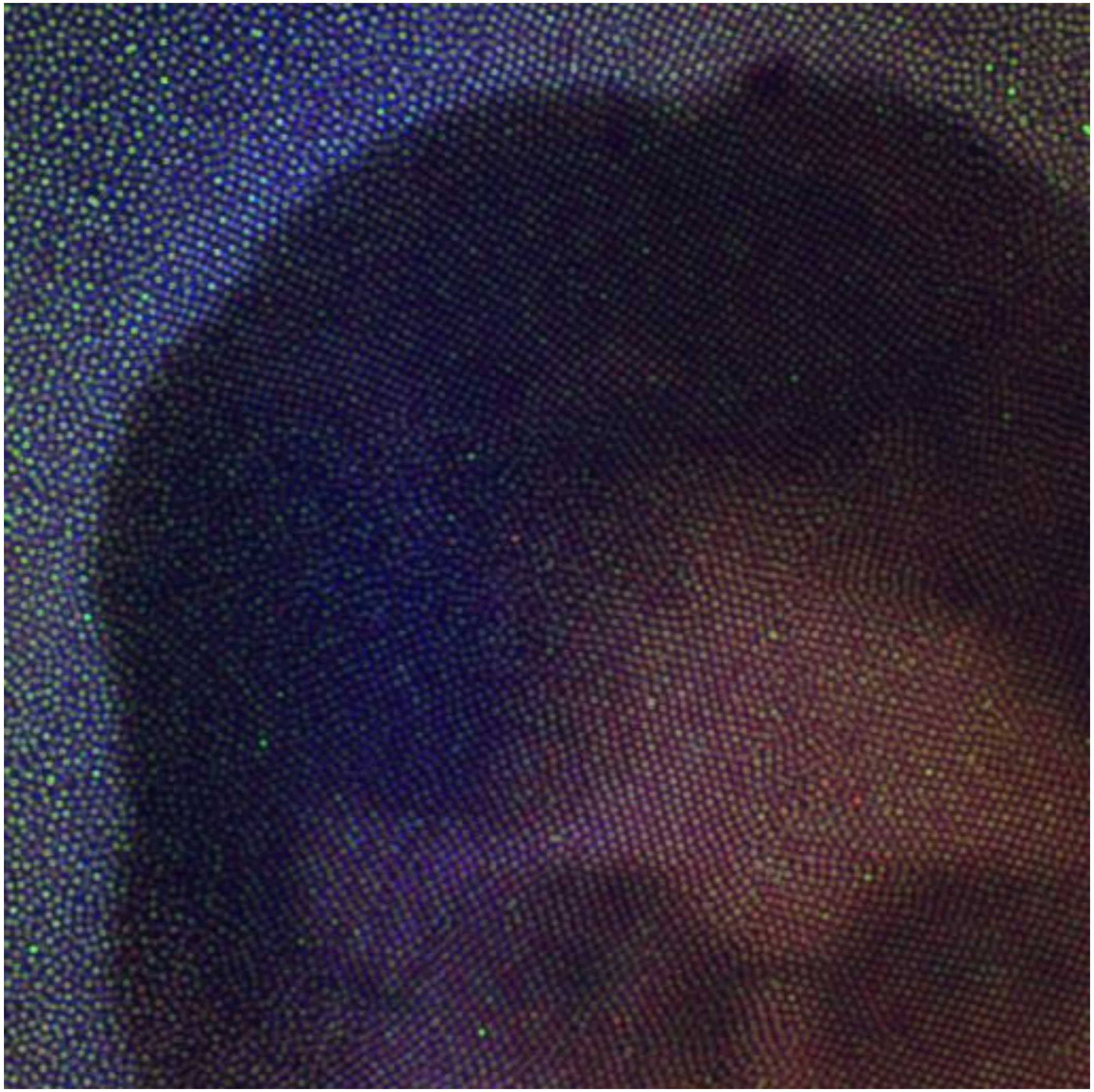
Scale bar 50 microns

Recording Pictures in RGB format

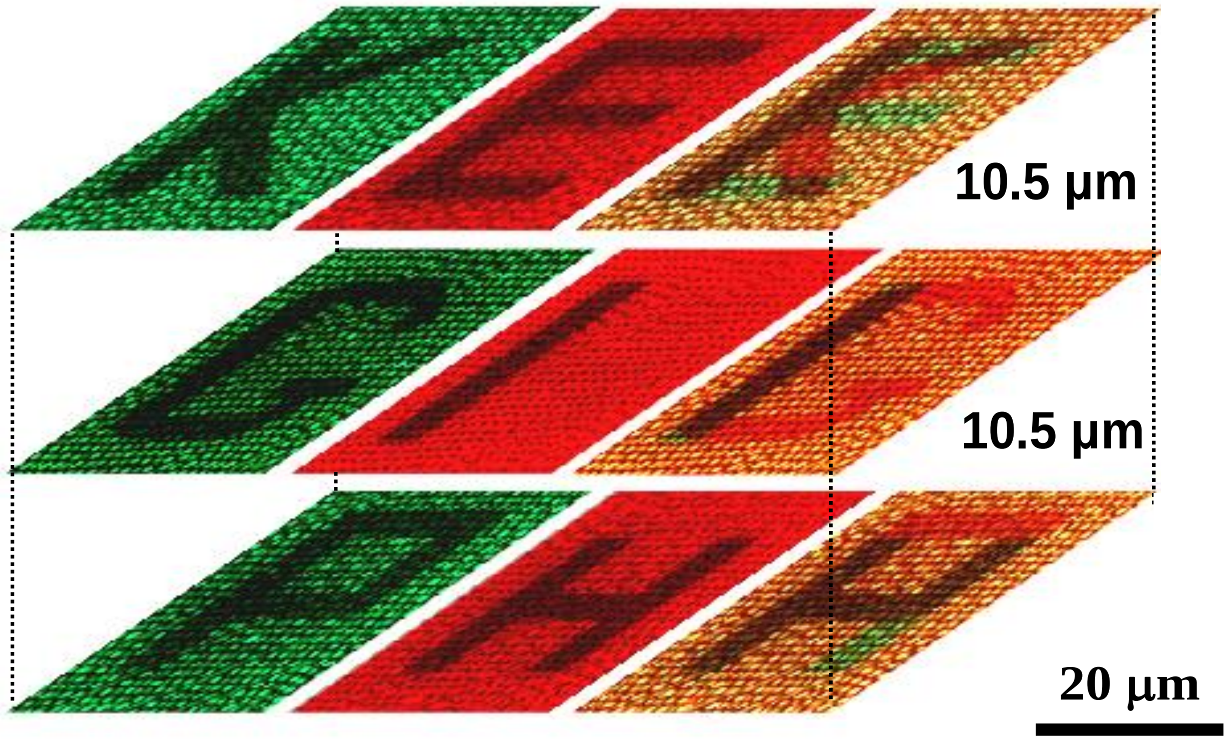


50 μm

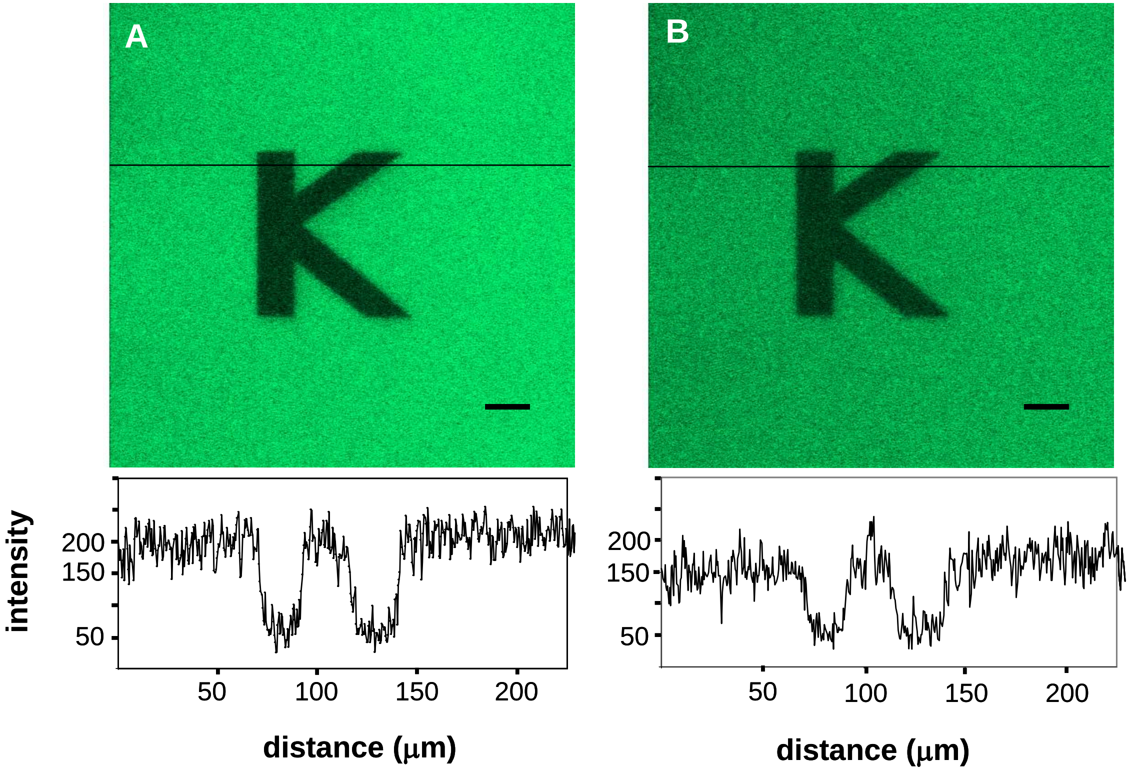
THIS IS NOT A DIGITAL PHOTOGRAPH!



Security Writing information in 3D



Security Writing: Destructive Readout information



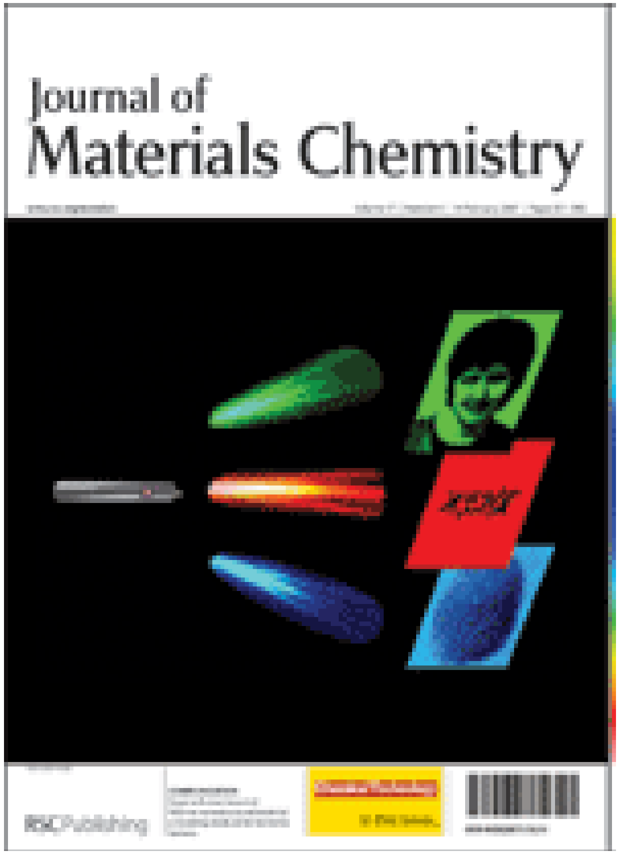
BEFORE

AFTER
scanning it 2000 times

After 2000 scans fluorescence intensity decreases by 25%
The recorded patterns can be read every day for 4 years

Conclusions

• Two new concepts for secure encryption of biometric features in identification documents and smart cards



- **For 2D : up to 8 modes of recording**
- **For 3D : an unlimited number of modes.**

Can take photographs every 5 years

- **New concept of 'printing' pictures in RGB format**

Gourevich, I. et al. *Chem. Mater.* 16, 1472-1479 (2004)
Pham, H. H et al. *J. Mater. Chem.* 17, 523-526 (2007)

Multilayer dielectric resonators (with J. Sipe)

- **N layers**
- **Average refractive index n**

- **The reflectivity at an interface between two layers**

$$R = 2\Delta n/n^2$$

- **Reflectivity grows as**

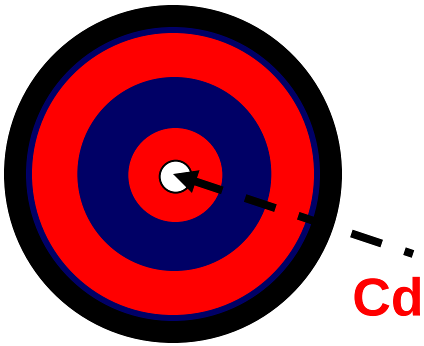
$$2N\Delta n/n^2$$

until it approaches unity and light is completely rejected from the material

- **Each multilayer microsphere behaves as a photonic crystal in the radial direction**

D. Brady, G. Papen, and J. E. Sipe, *J. Opt. Soc. Am. B10*, 644 (1993)

Multilayer dielectric resonators

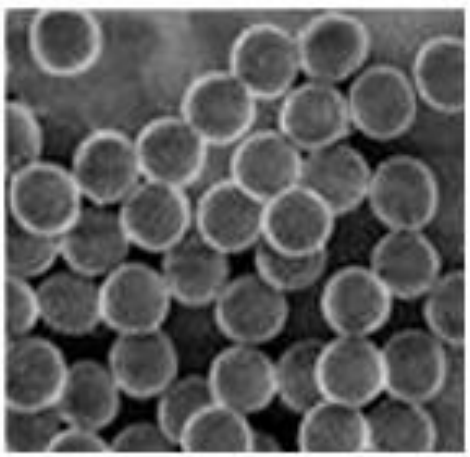


high **n** Poly(styrene-vinyl carbazole) n = 1.64

low **n** Fluorinated Acrylates n = 1.36

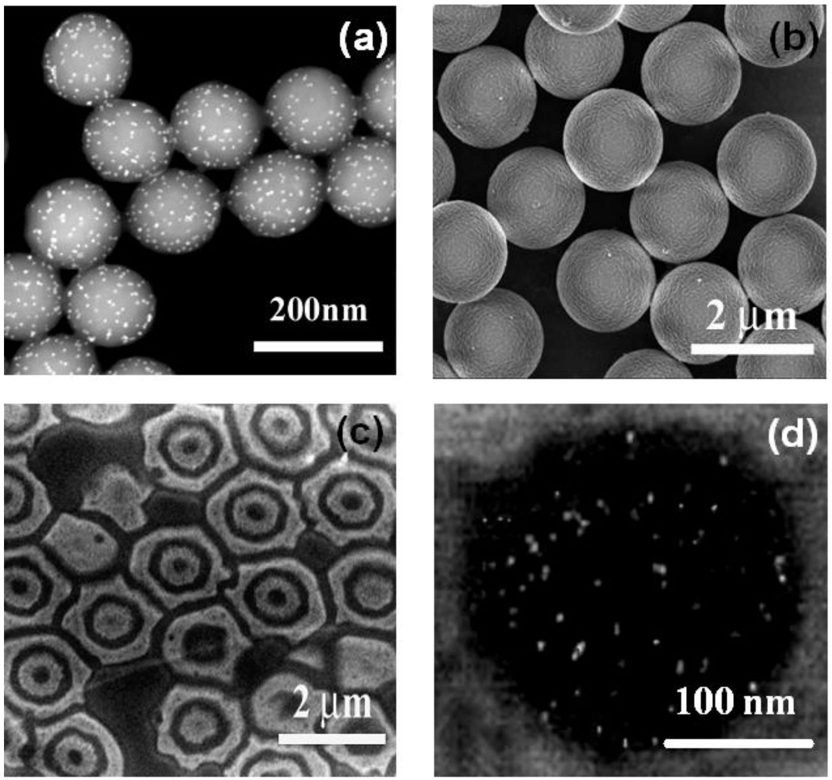
CdSe-CdS QDs

N = 4



N = 4

CdSe-CdS QDs



Conclusions

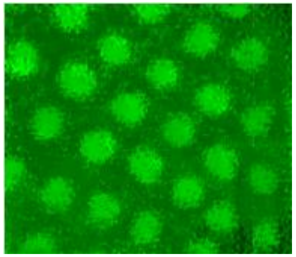
1. Core-shell particles have been used as multicomponent building blocks for nanostructured materials with periodic structures.

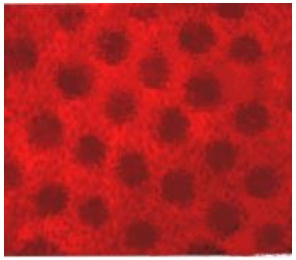
2. The structure of the core-shell particles was varied to produce complex structural and compositional patterns in nanostructured materials

Core-shell particles:	PM-1 + PM-2 +LMW	*materials:*	$2^3 = 8$
	PM-1 + PM-2 +LMW-1+ LMW-2	*materials:*	$2^4 = 16$
Three-layer particles:	PM-1 + PM-2 + PM-3 + LMW-1+ LMW-2	*materials:*	$2^5 = 32$

3. The extent of order in the nanostructured materials was controlled by assisted assembly of colloid particles

4. Various high tech applications of our materials, such as 3D memory storage, optical limiting and switching, 3D ultrasensitive strain sensors, and security paper and labels can be achieved





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- ♦ Prof. Ted Sargent (Univ. of Toronto)
- ♦ James Jonkman (University Health Network)

Funding:

Canada Research Chair Fund
NanoIP Program
NSERC Canada CRD grant
Xerox Research Centre of Canada
Premier Research Excellence Award
Chorafas Foundation Award
Nortel Networks Corporation
Ontario Research Challenge and Development Fund

Every intelligent fool can make things bigger, more complex, and more violent.

It takes a touch of genius - and a lot of courage to move in the opposite direction.

Albert Einstein (1879-1955)