3Dimentional Single Digit Nanofabrication: organization of nanostructures with dimensions below 10 nm

Stefano Cabrini,
Nanofabrication Facility Director

Interdisciplinary Instrumentation Colloquium, 28 February 2018

BERKELEY LAB

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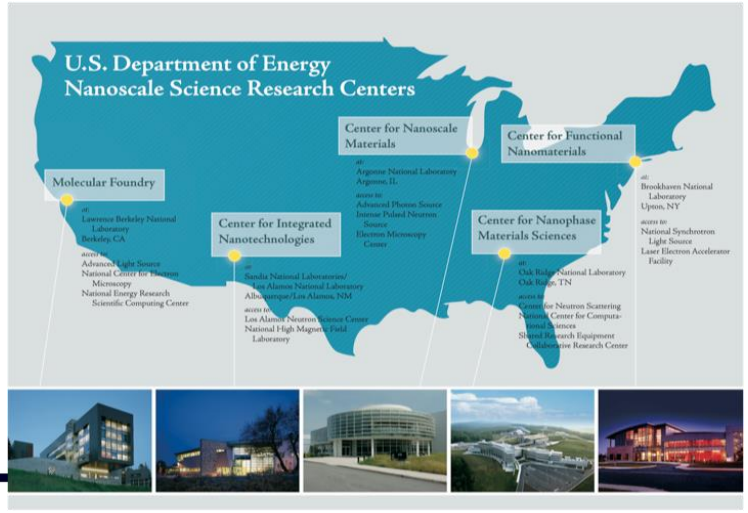

U.S. DEPARTMENT OF ENERGY

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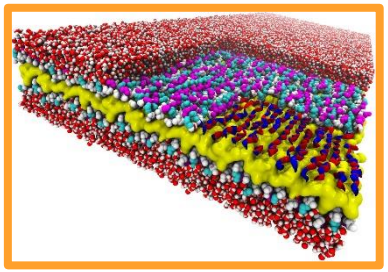
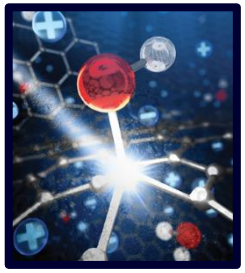
Characterization		Fabrication	Theory	Synthesis		
NCEM National Center for Electron Microscopy	**Floor 1** Imaging and Manipulation of Nano-	**Floor 2** Nano-fabrication	**Floor 3** Theory of Nano-structured Materials	**Floor 4** Inorganic Nano-structures	**Floor 5** Biological Nano-structures	**Floor 6** Organic and Macro-molecular Synthesis
Electron microscopy and nano-characterization	Characterization and manipulation of nanostructures	Advanced lithographic and thin-film processing techniques	Guiding understanding of new principles, behavior and experiments	Science of semiconductor, carbon and hybrid nanostructures	Bio-materials; new probes for bio-imaging; synthetic biology techniques	Soft materials: organics, macromolecules, polymers and their assemblies

Scientific Research Themes

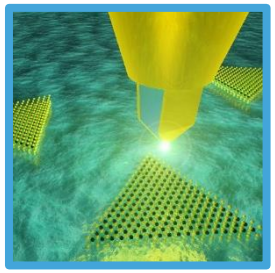
Reaffirmed and updated during annual strategic planning



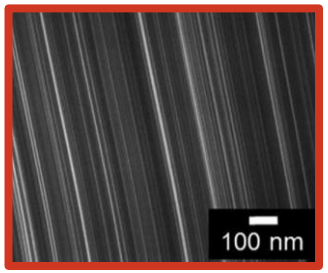
Combinatorial Nanoscience



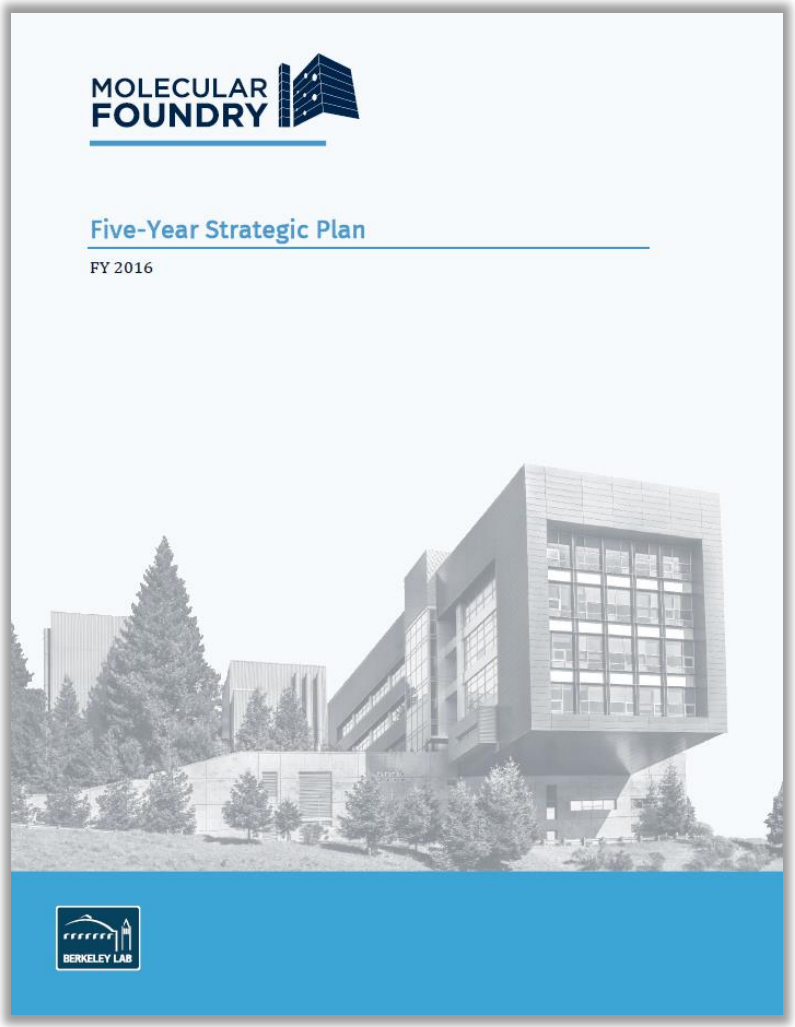
Functional Nanointerfaces



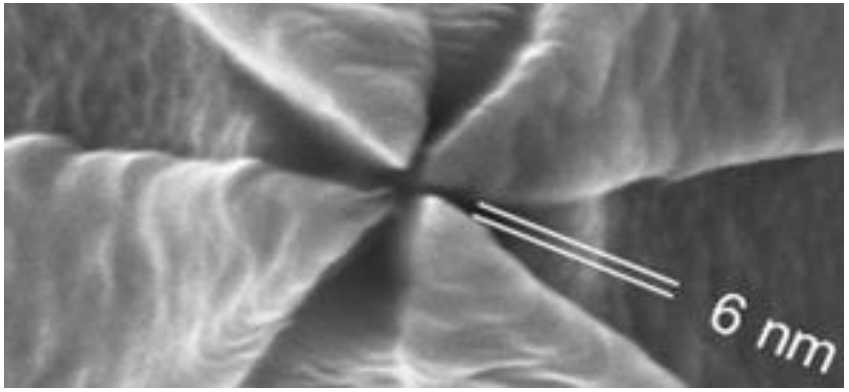
Multimodal Nanoscale Imaging

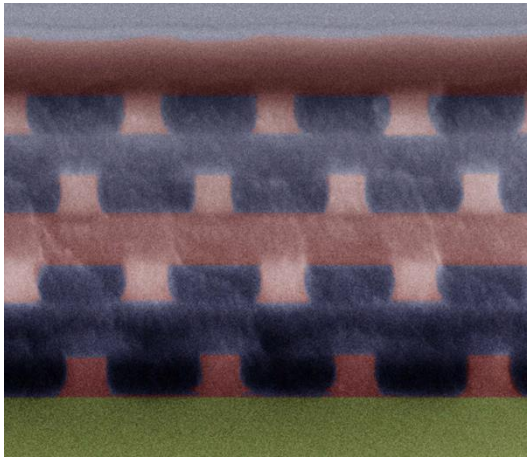


Single-Digit Nanofabrication and Assembly



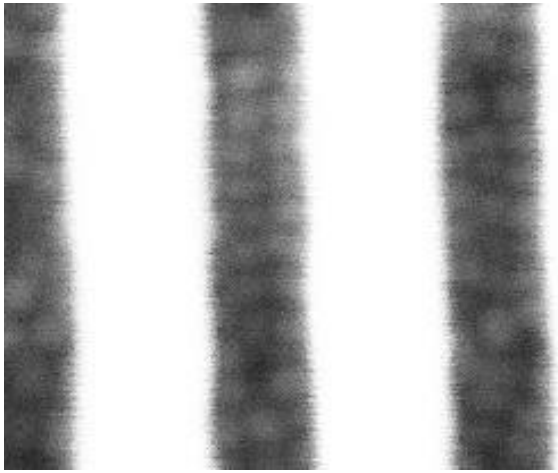
http://foundry.lbl.gov/research/



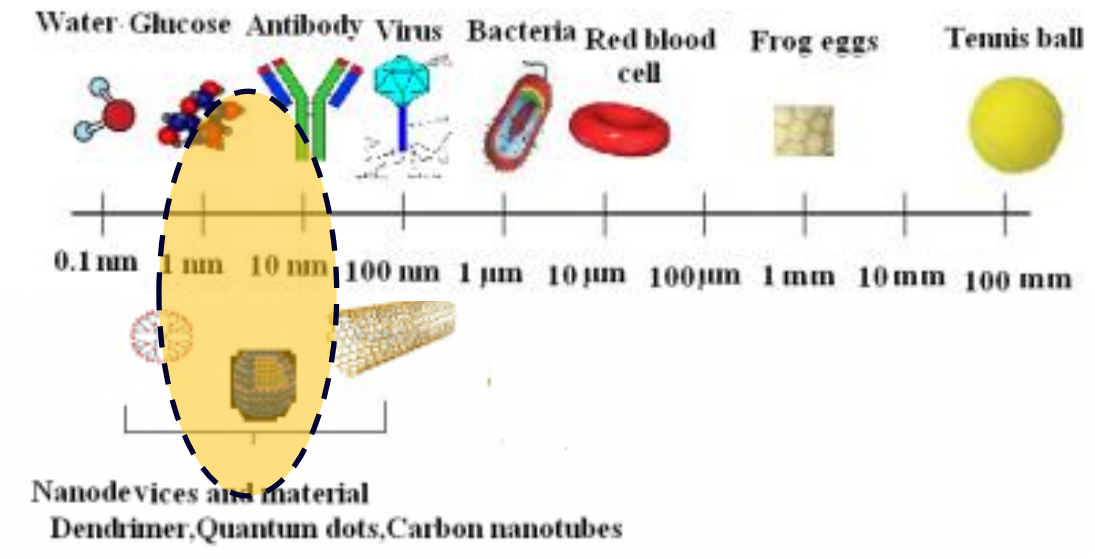


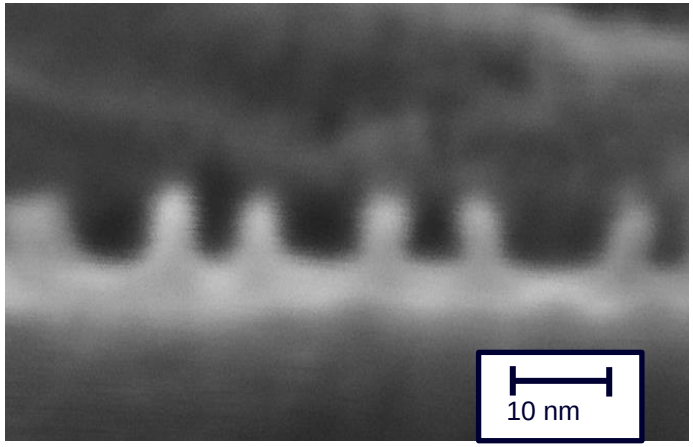
Outlook

- SDN: organization of the nanomaterial below 10 nm
- Nanofabrication 2D: 6nm features.
- Controlling the patterning in 3D: Photonic Crystals
- 3D Plasmonic
- Directed self-assembly of nanoparticles



What is Single Digit Nano?





Bridging the atomic quantum world with larger scale world

We use the term “single-digit nanofabrication and assembly” (SDN) to describe the structuring and characterization of materials whose key features are defined and resolved on a scale of 10 nm or less

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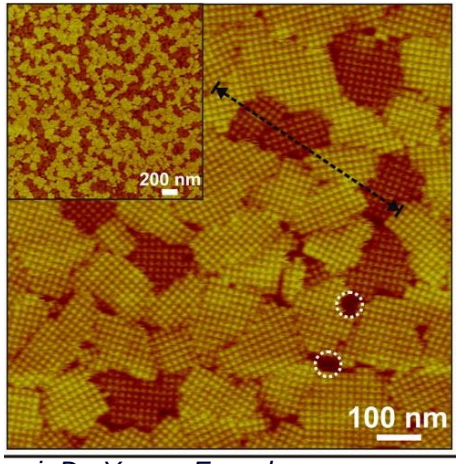
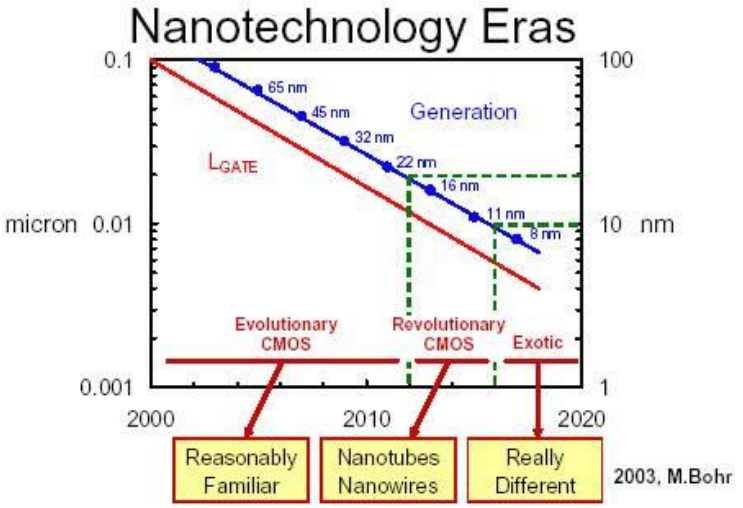
Why Single-digit nano resolution?

Protein Crystals assembly

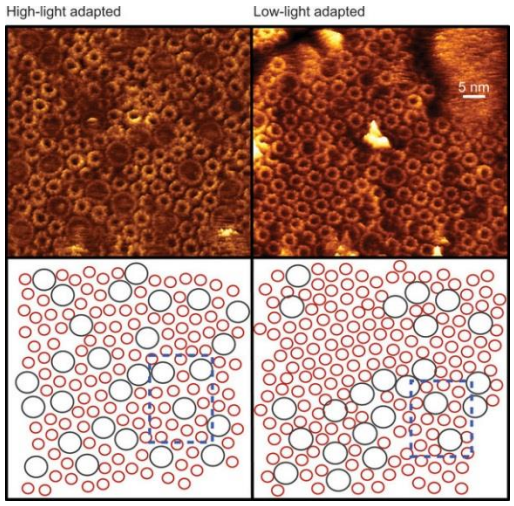


Bertozzi, De Yoreo, Foundry PNAS 2010

International Technology Roadmap for Semiconductors



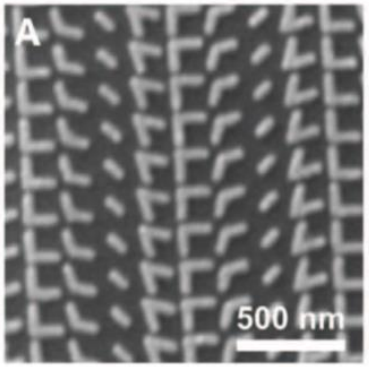
Source : 2003 International Technology Roadmap for Semiconductors



Lessons from nature about solar light harvesting

van Grondelle Nature Chemistry 3, 763–774 (2011)

New optical Phenomena



Foundry User: Xiang Zhang et al. SCIENCE VOL 339 22 2013

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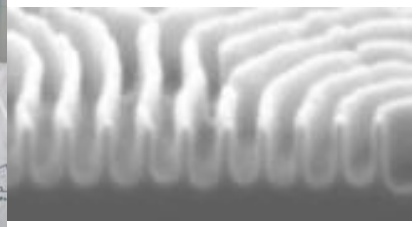
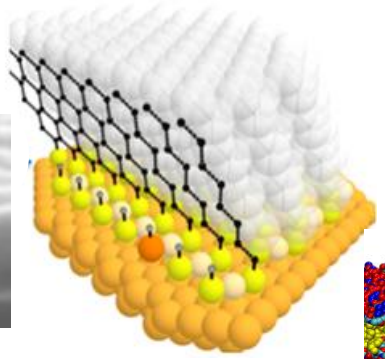
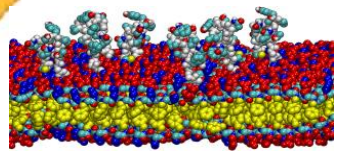
Single Digit Nano

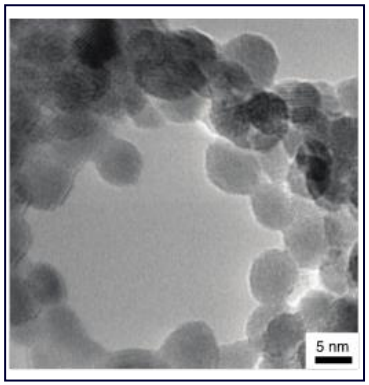




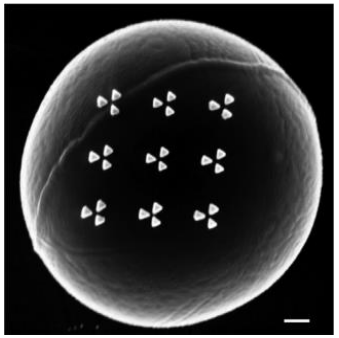


Advanced Manufacturing

Assembly Design Rules

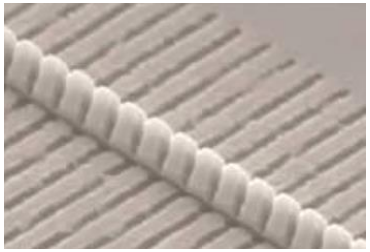


SDN



Imaging

Applications



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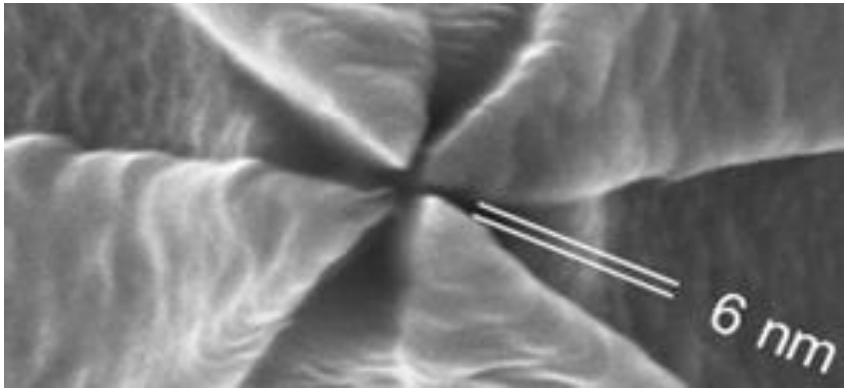

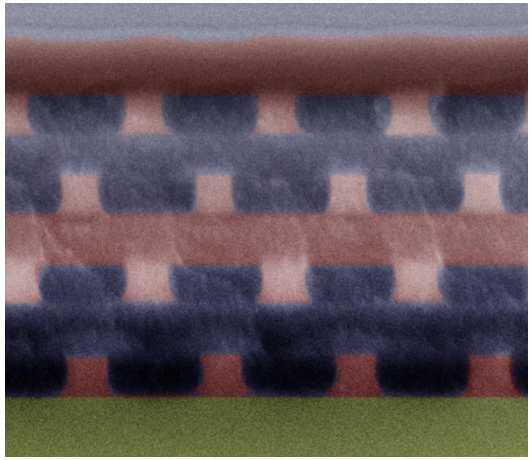

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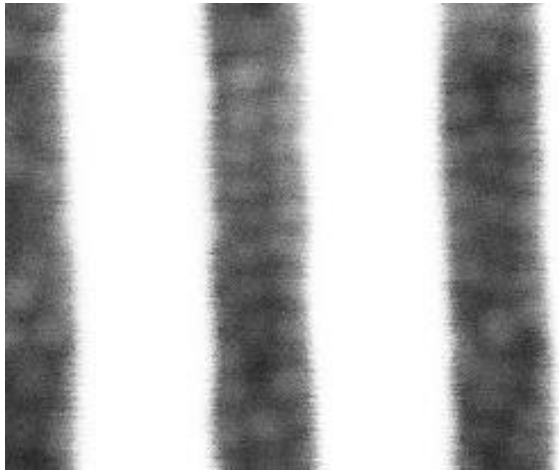
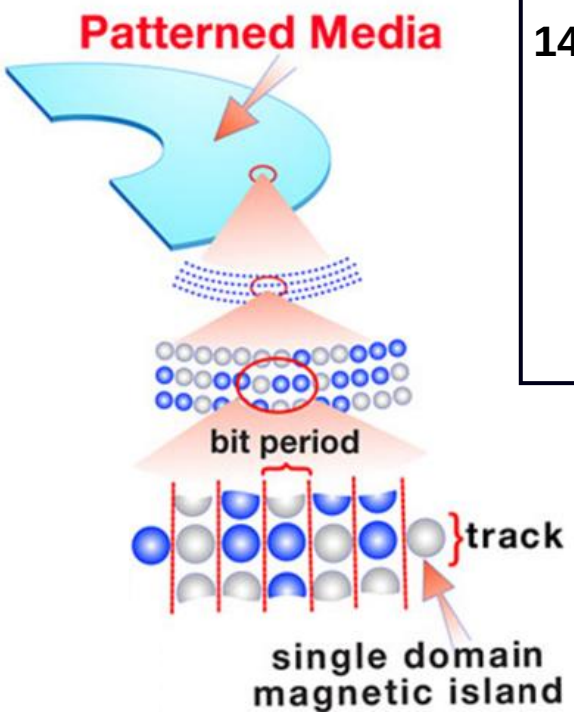
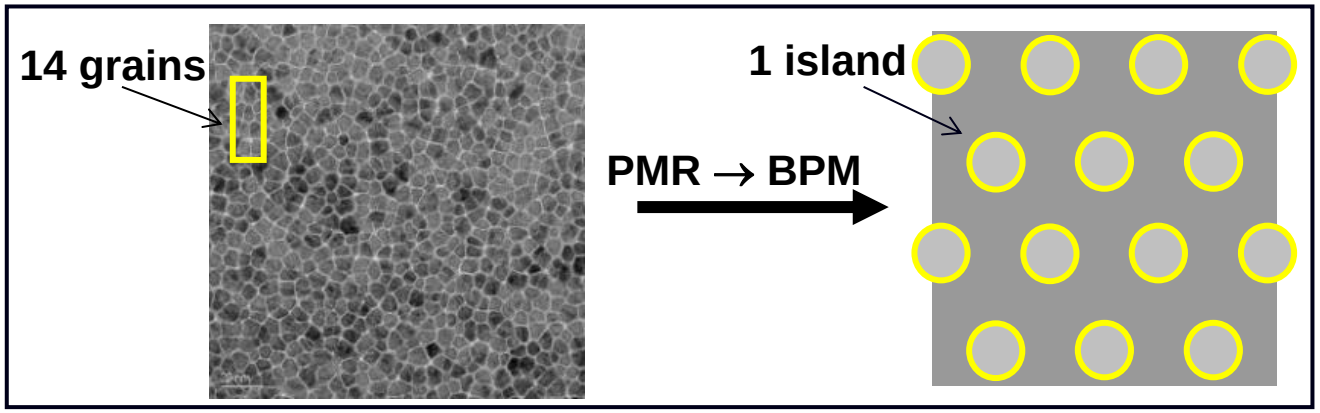


2D Patterning: Bit Pattern Media





Feature sizes vs. Areal density:

Areal density	Bit size	Pitch size
1 Tb/in^2	13 nm	25 nm
1.5 Tb/in^2	10 nm	20 nm
2 Tb/in^2	9 nm	18 nm
5 Tb/in^2	6 nm	11 nm
10 Tb/in^2	4 nm	8 nm

Griffiths, Rhys Alun, et al., *Journal of Physics D: Applied Physics* 46.50 (2013): 503001

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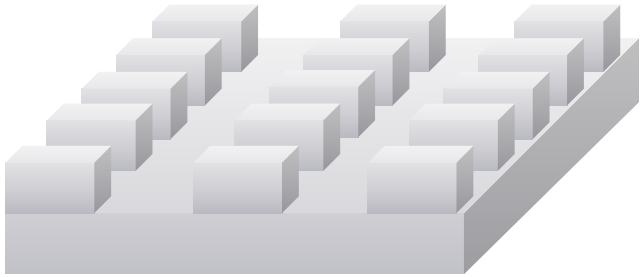
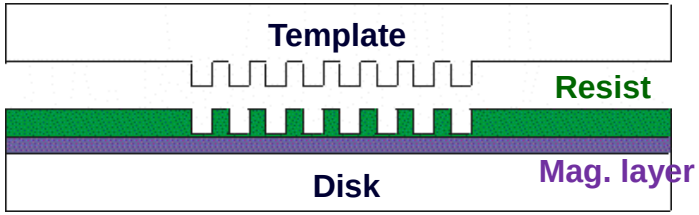
Mask Templates for Nanoimprint Lithography

Template

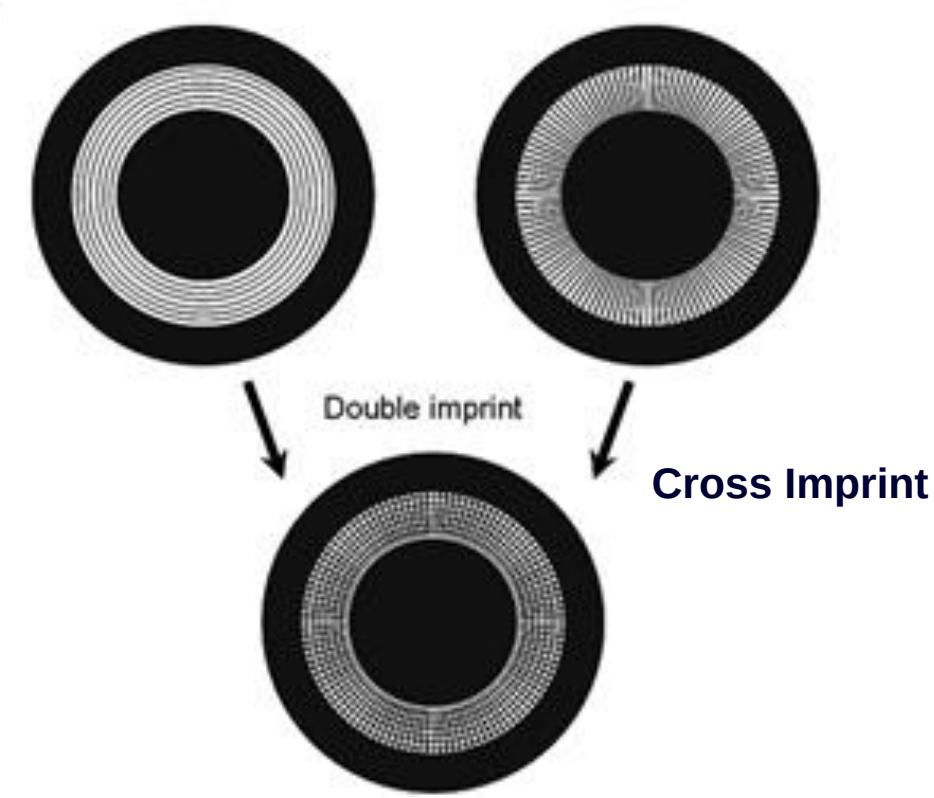


Nanoimprint Lithography



Rect. bit architecture (HGST-WD)

Concentric **Radial**



Albrecht, Thomas R., et al., *Magnetics*, IEEE Transactions on 51.5 (2015): 1-42.

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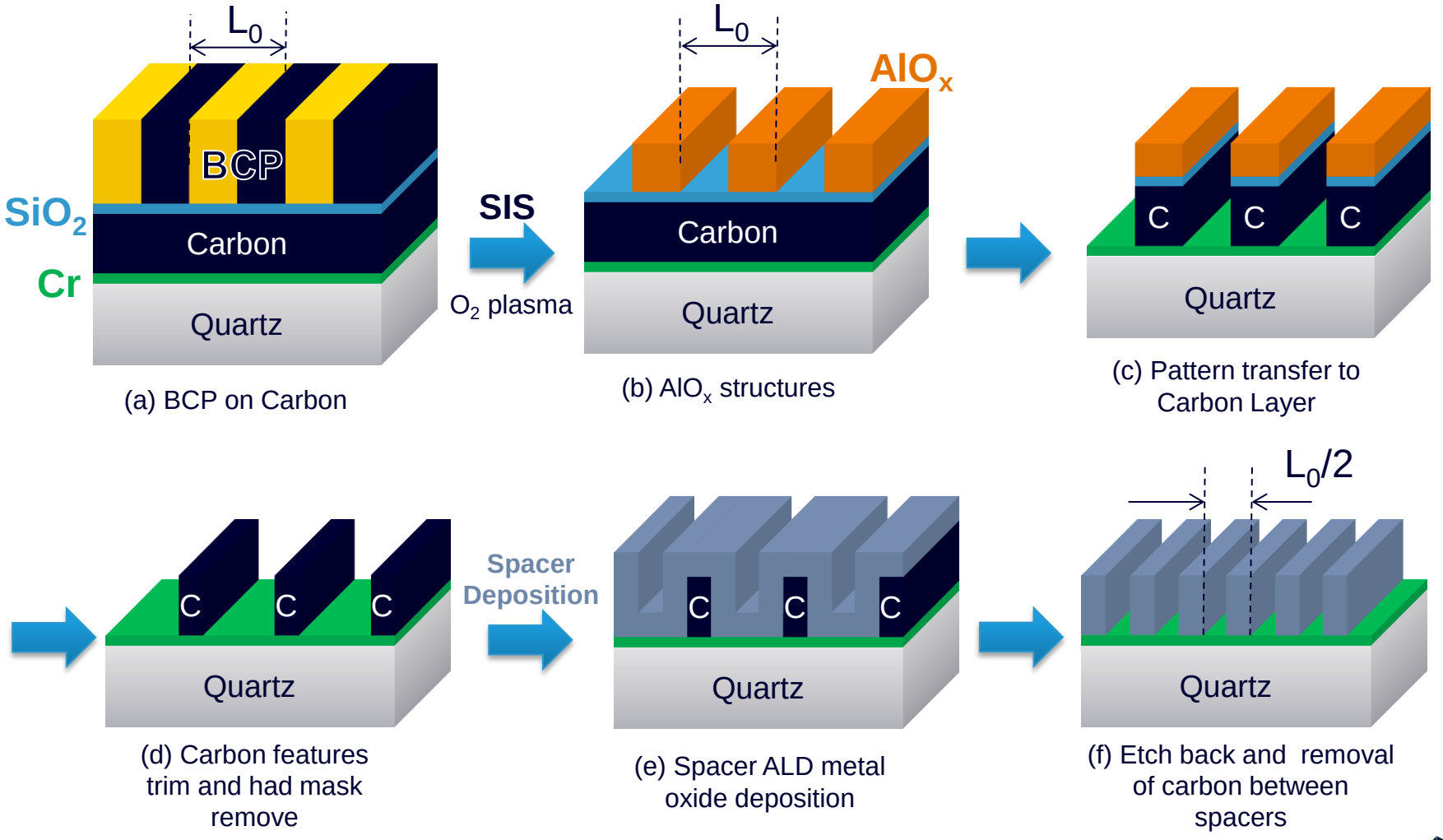
Doubling Frequency - Double Patterning



(a) BCP on Carbon

(b) AlO_x structures

(c) Pattern transfer to Carbon Layer

(d) Carbon features trim and had mask remove

(e) Spacer ALD metal oxide deposition

(f) Etch back and removal of carbon between spacers

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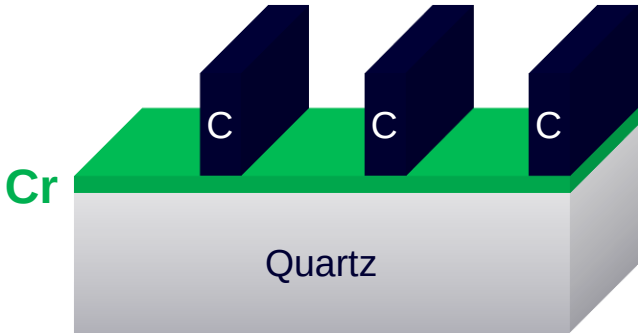
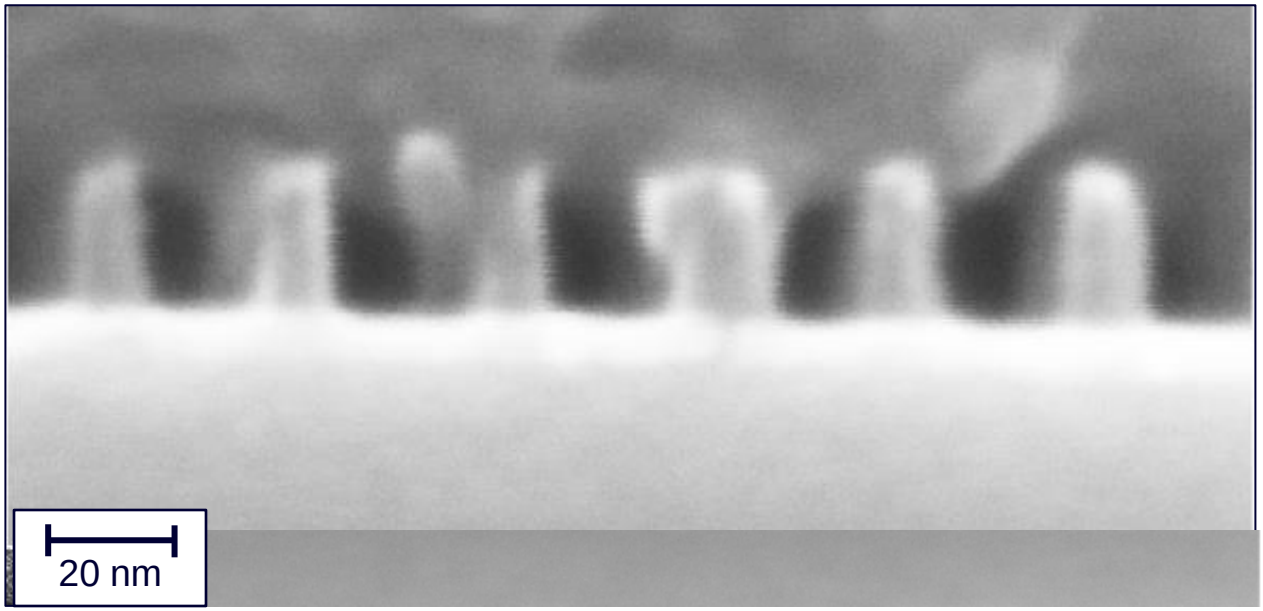
Carbon Structures trimmed





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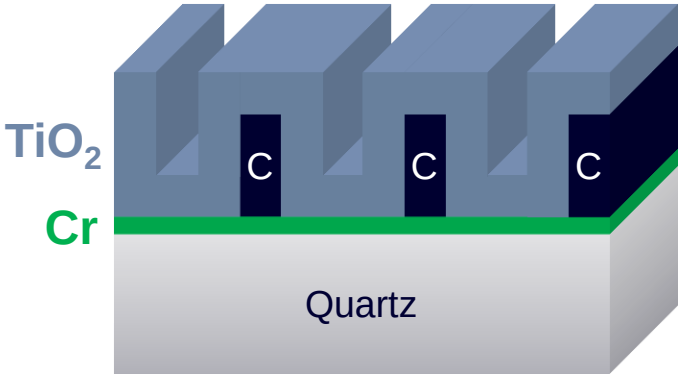
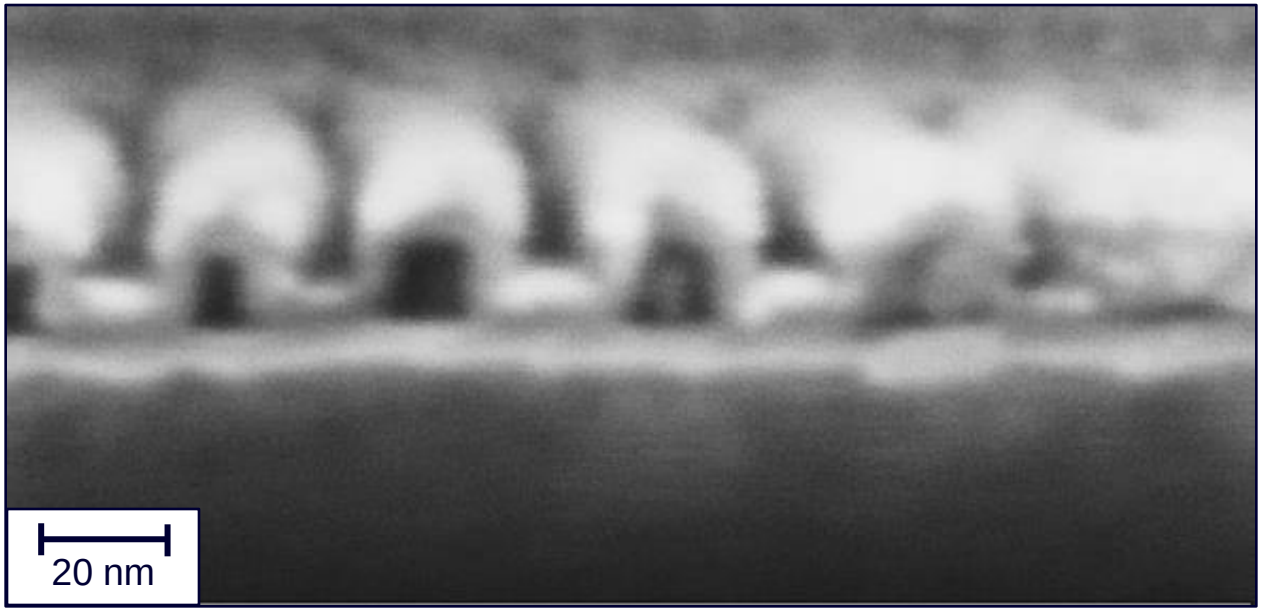
ALD coating – TiO2 Thermal





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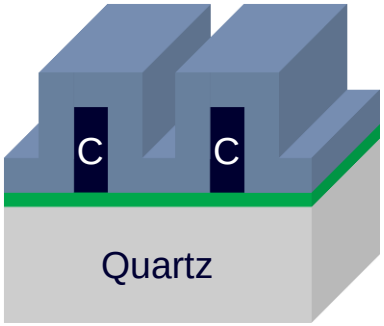
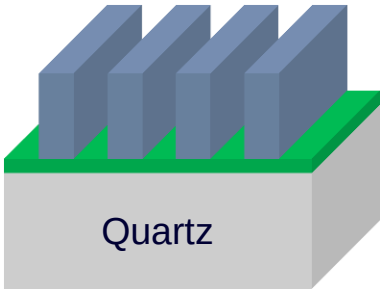
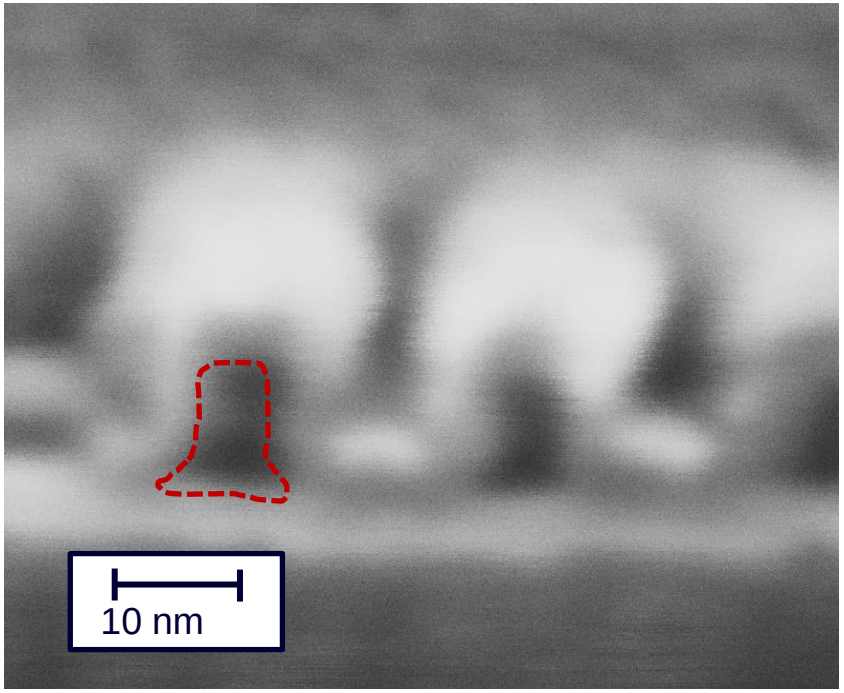
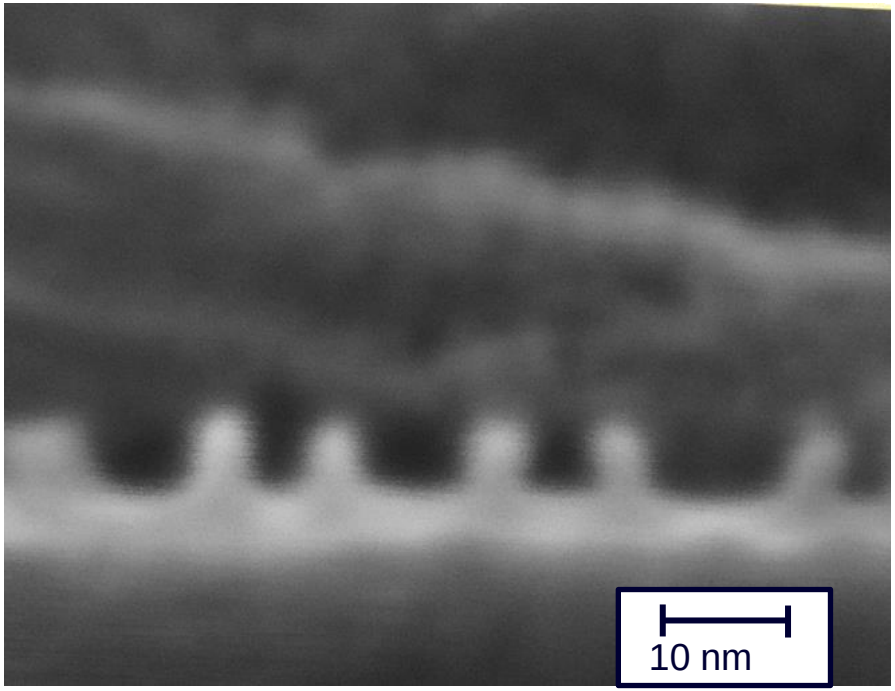
6 nm Patterned Features









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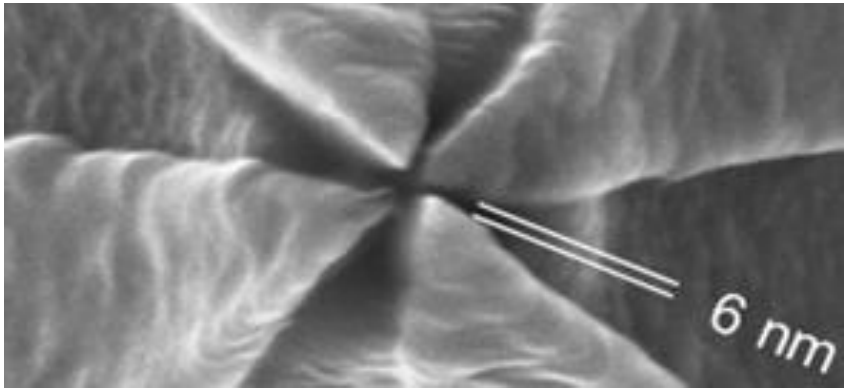

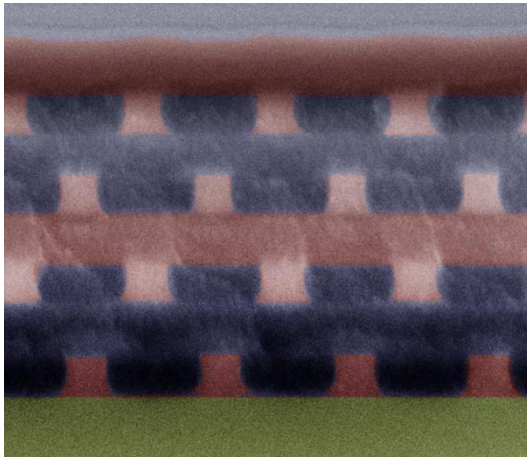

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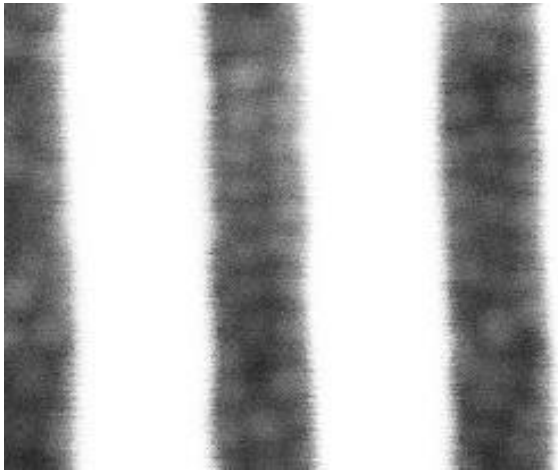
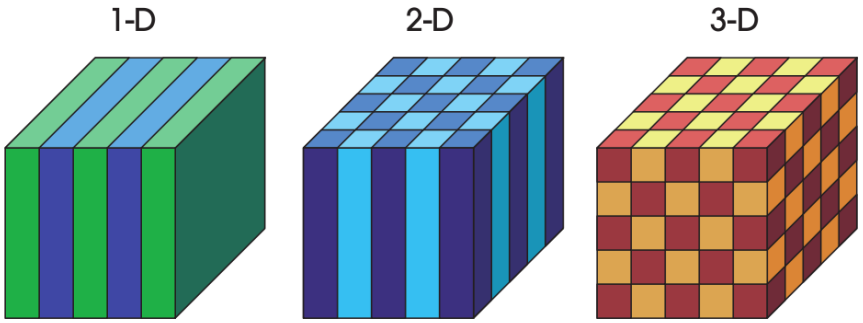


Photonic Crystals

Definition

Photonic crystals are structures in which the **refractive index** is **periodically** modulated.

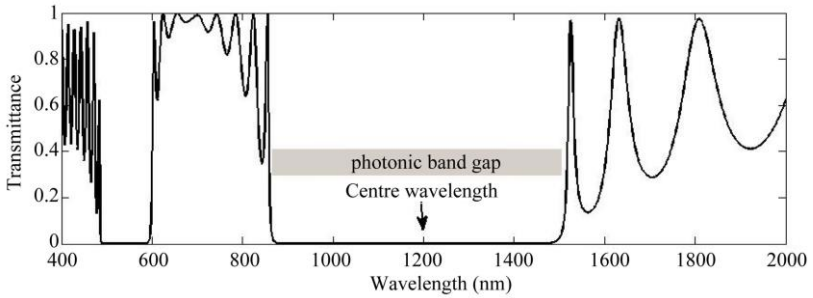


Joannopoulos et al., Princeton university press, 2008

Properties

If the length scale of the modulation is comparable with the wavelength of light

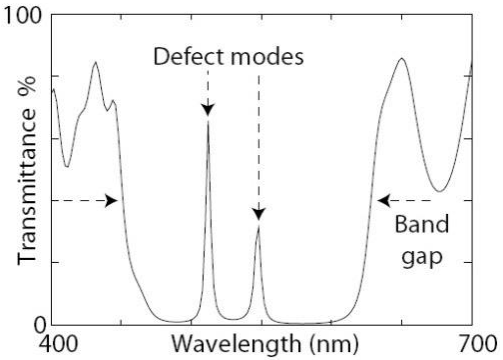
Photonic Band Gap (PBG)



Rahman et al., Optics and photonics journal, 2012

Defect in the periodicity of the structure

Defect mode in the PBG



http://imagebank.osa.org

3D Photonic crystals with defects for light guiding

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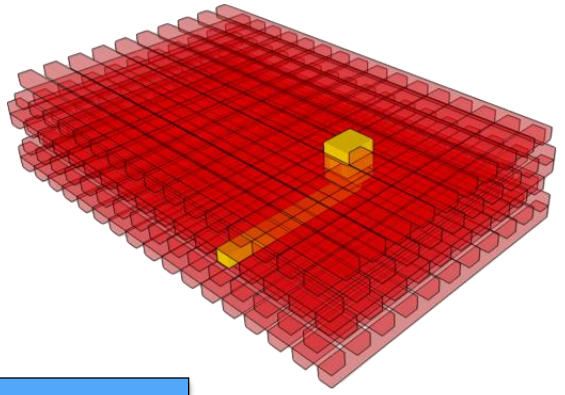
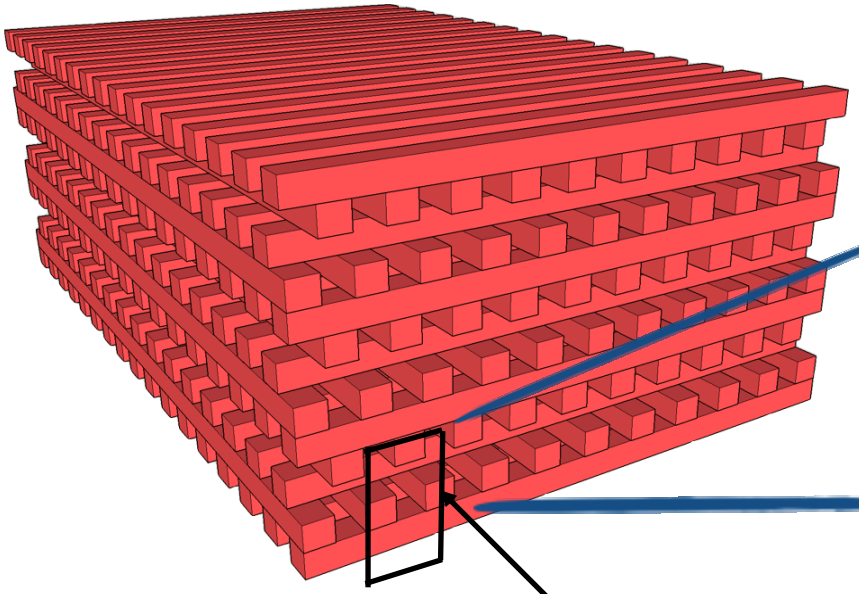
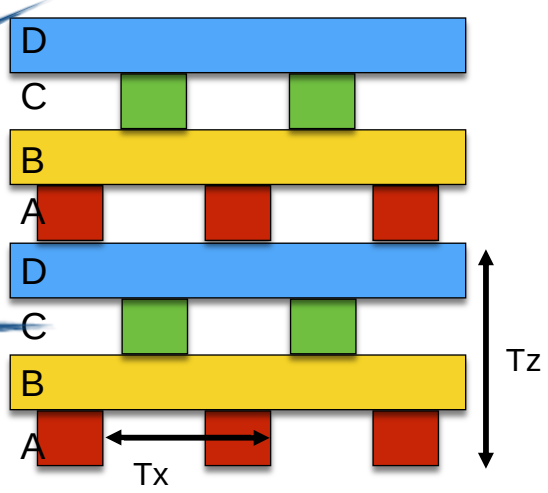
Woodpile geometry







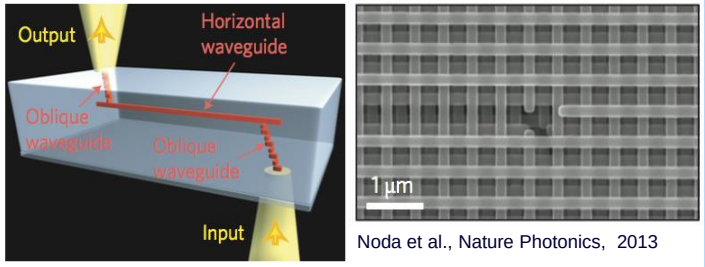
Why the woodpile?

FCC unit cell

Unit cell => 4 layers

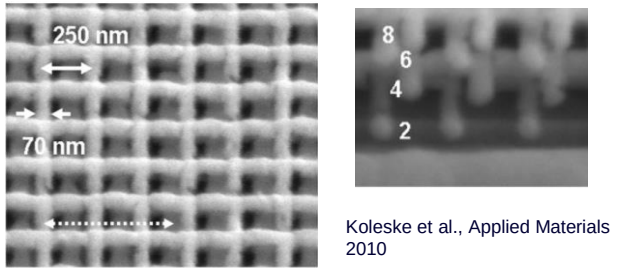
- FCC unit cell for Complete Photonic Band Gap*
- Compatible with standard fabrication techniques

IR - Kyoto University/Noda



Noda et al., Nature Photonics, 2013

VIS - Sandia Lab. / Koleske



Koleske et al., Applied Materials 2010

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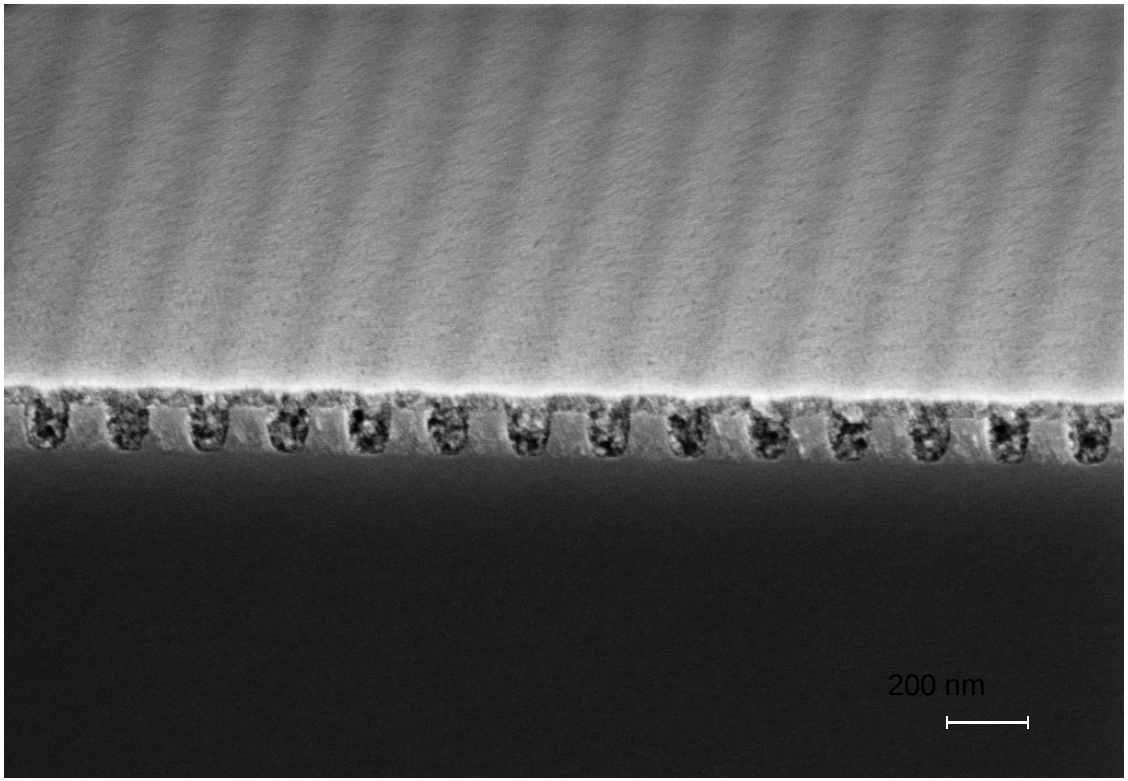
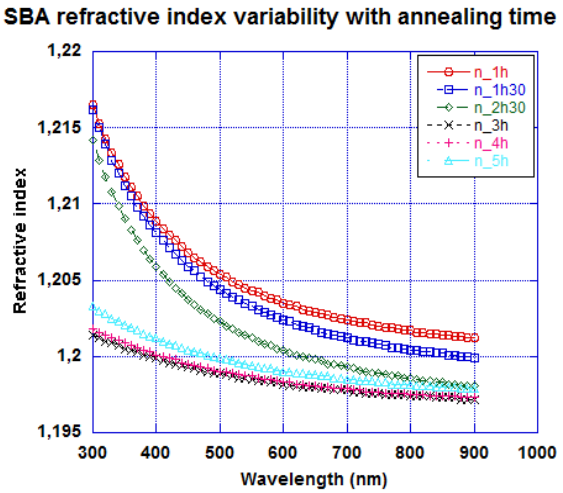
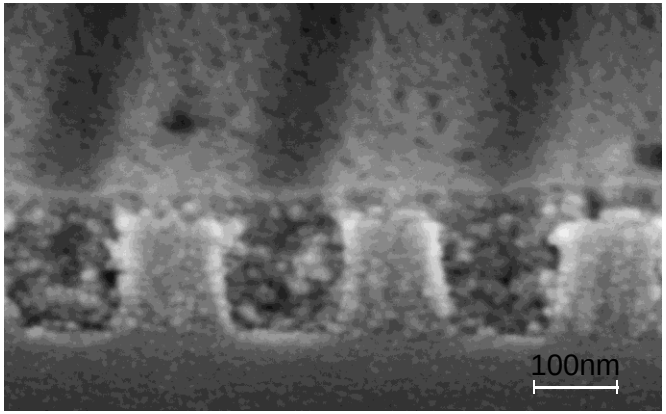
* Ho et al, Solid state communications, 1994

The SBA polymer







SEM cross sections

Self-planarization ➔ No CMP required

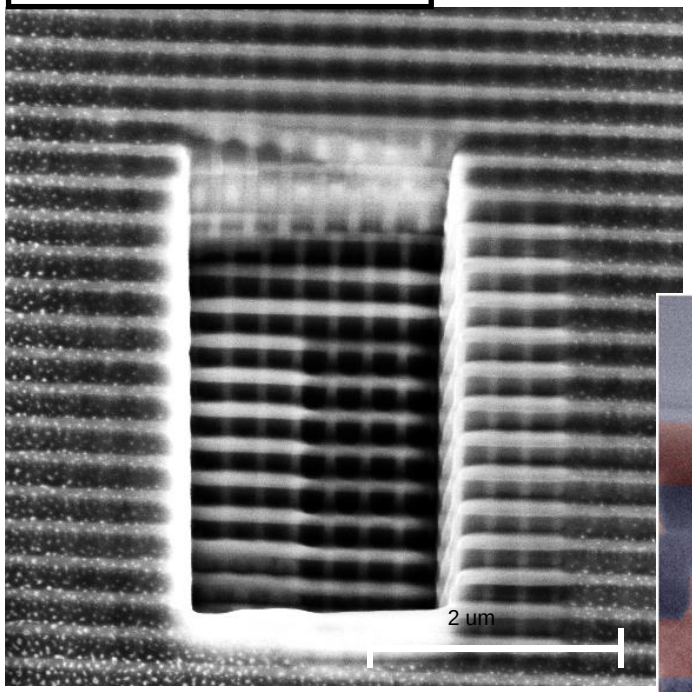
Simplification of fabrication process

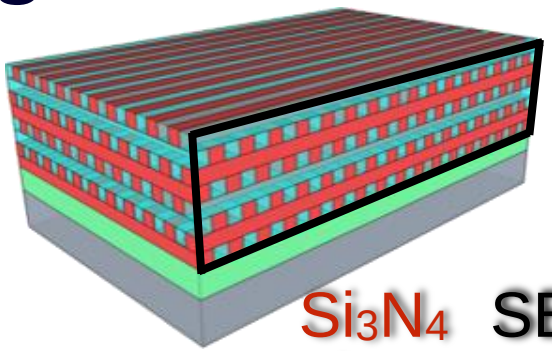
SBA Polymer spin coating and annealing at 400°C

* http://www.sbamaterials.com

Results

SEM Top - View, Milling with FIB





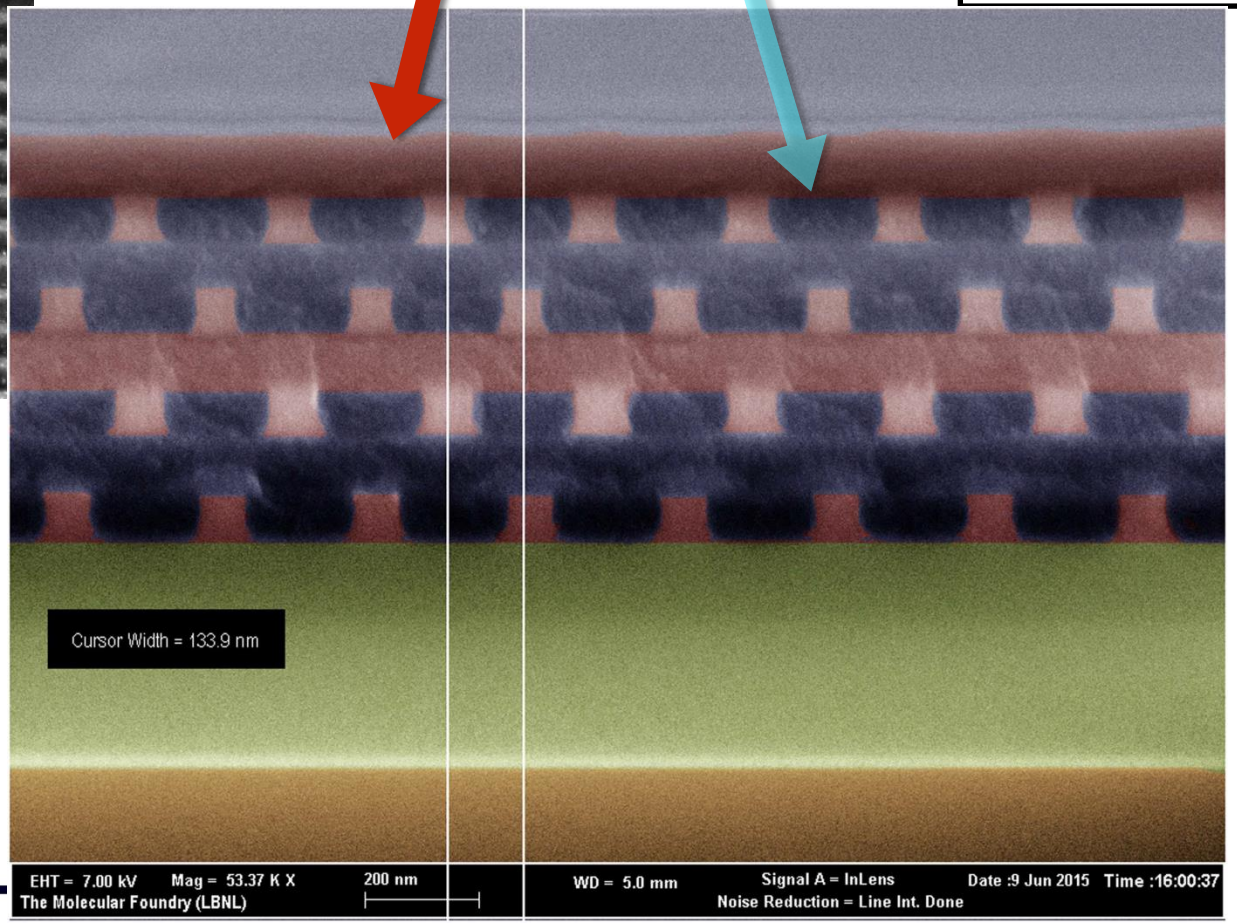
Legend

SBA Polymer

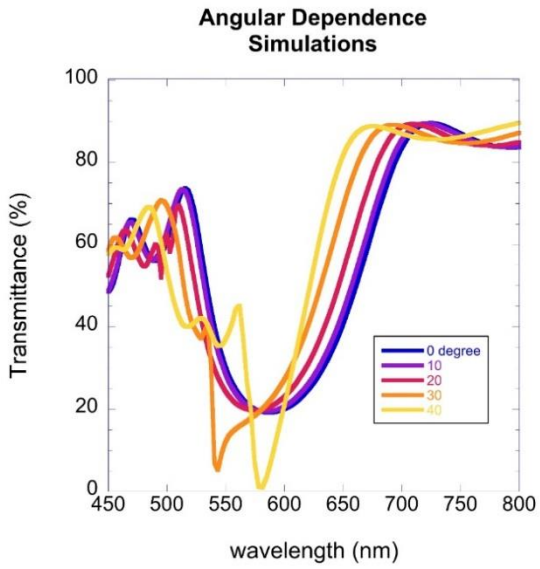
Si_3N_4

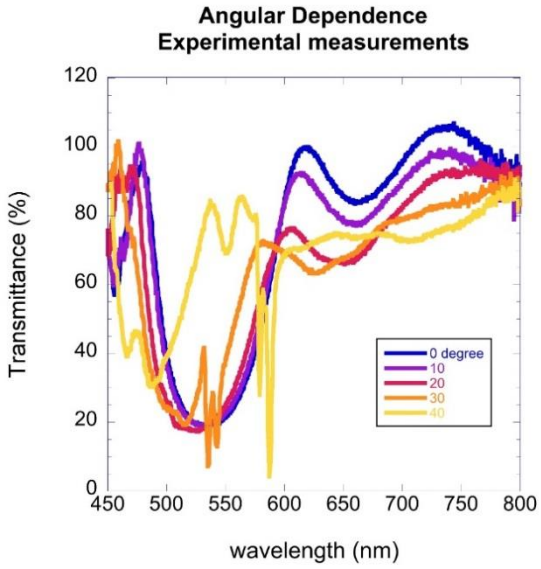
Si_3N_4 SBA polymer

SEM cross section

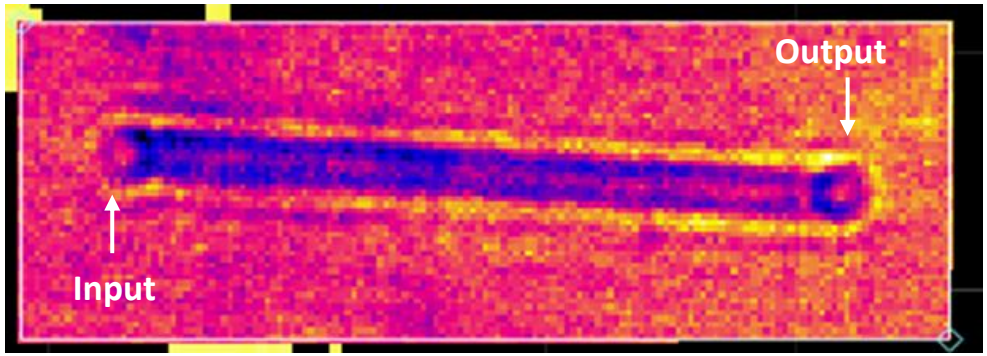


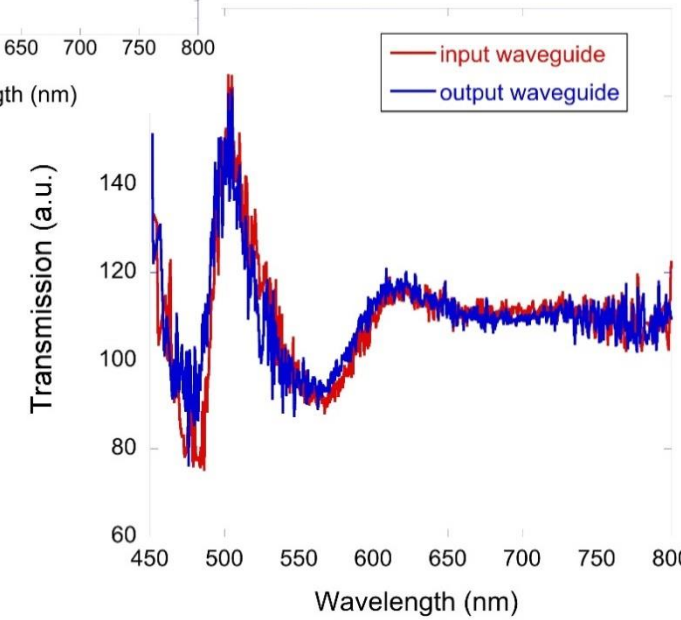
Optical Characterization



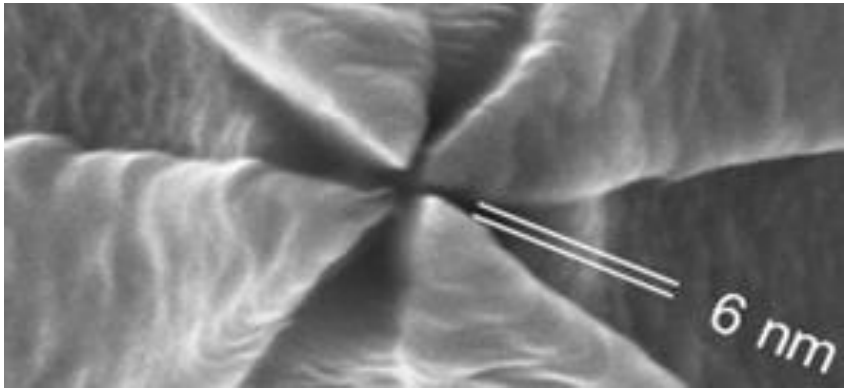


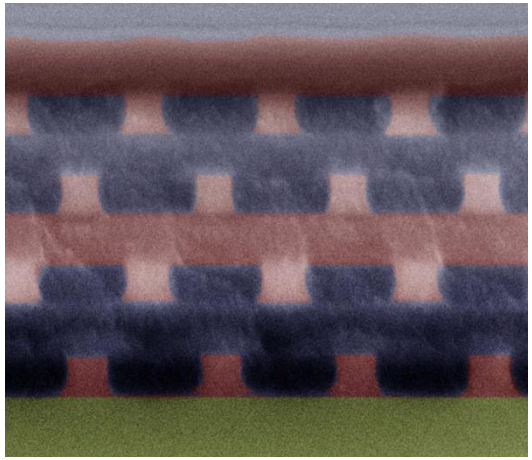
Scott Dhuey, Stefano Cabrini et al : "Three-dimensional woodpile photonic crystals for visible light applications"; 2017 Journal of Physics Communications, Volume 1, Number 1





MOLECULAR FOUNDRY





Outlook

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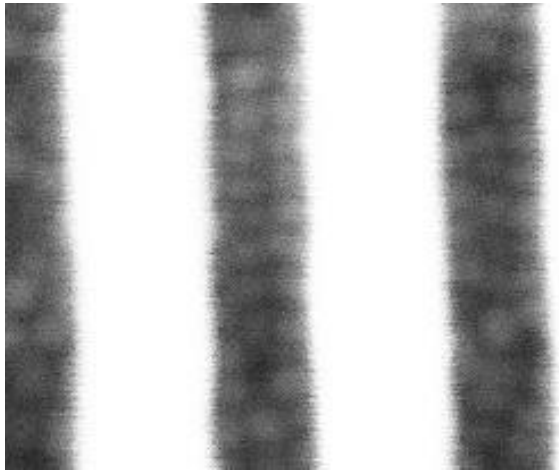
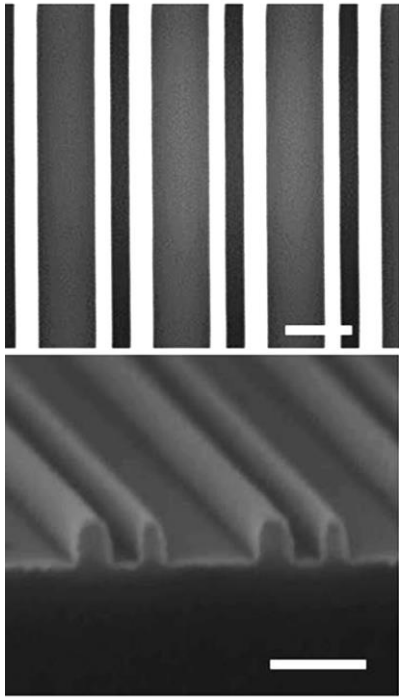
- Controlling the patterning in 3D: Photonic Crystals
- 3D Plasmonic
- Directed self-assembly of nanoparticles

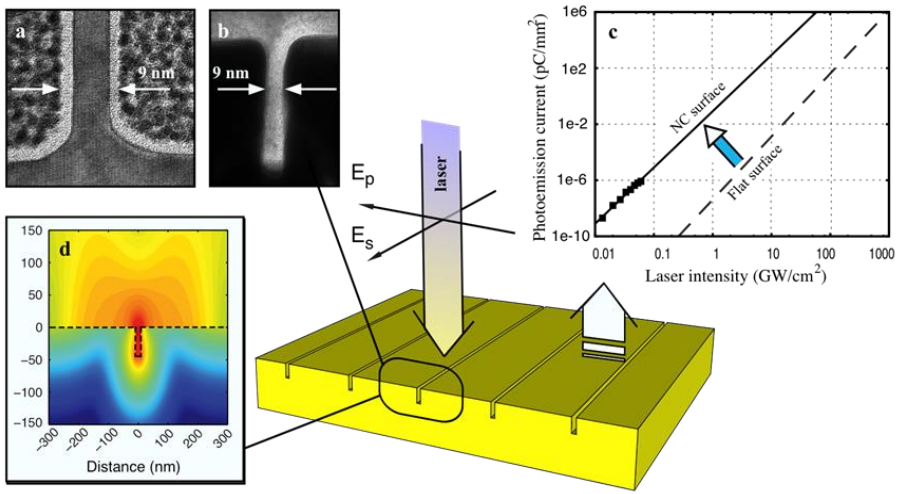


Nano Photonic Applications



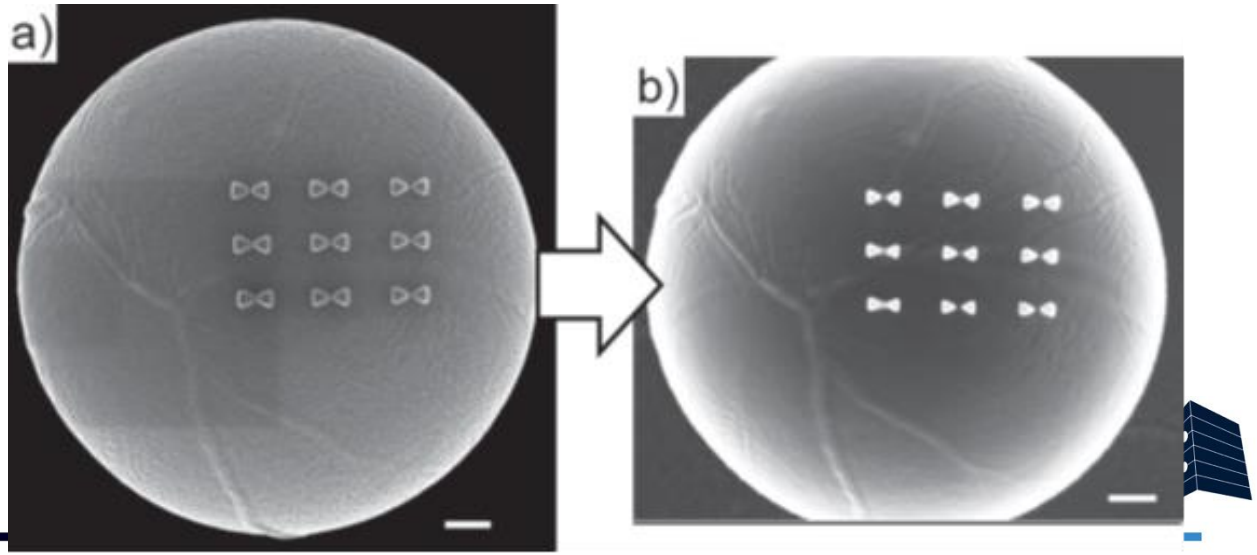
High refractive index materials for Metasurfaces: advanced photonic applications:

Enhanced Photocathode for X-ray FEL



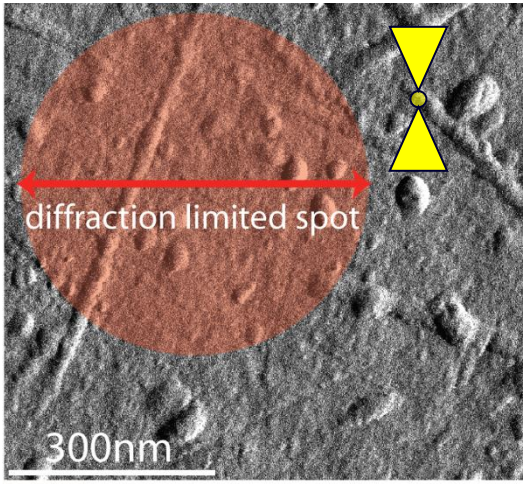
Howard Padmore, Advanced Light Source, Schuck and Cabrini; Sci. Rep. 2, (2012); Phys. Rev. Lett. 110, (2013)

Triggering and Monitoring Plasmon-Enhanced Reactions by Optical Nanoantennas

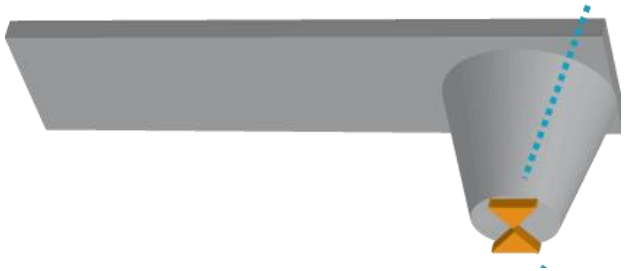


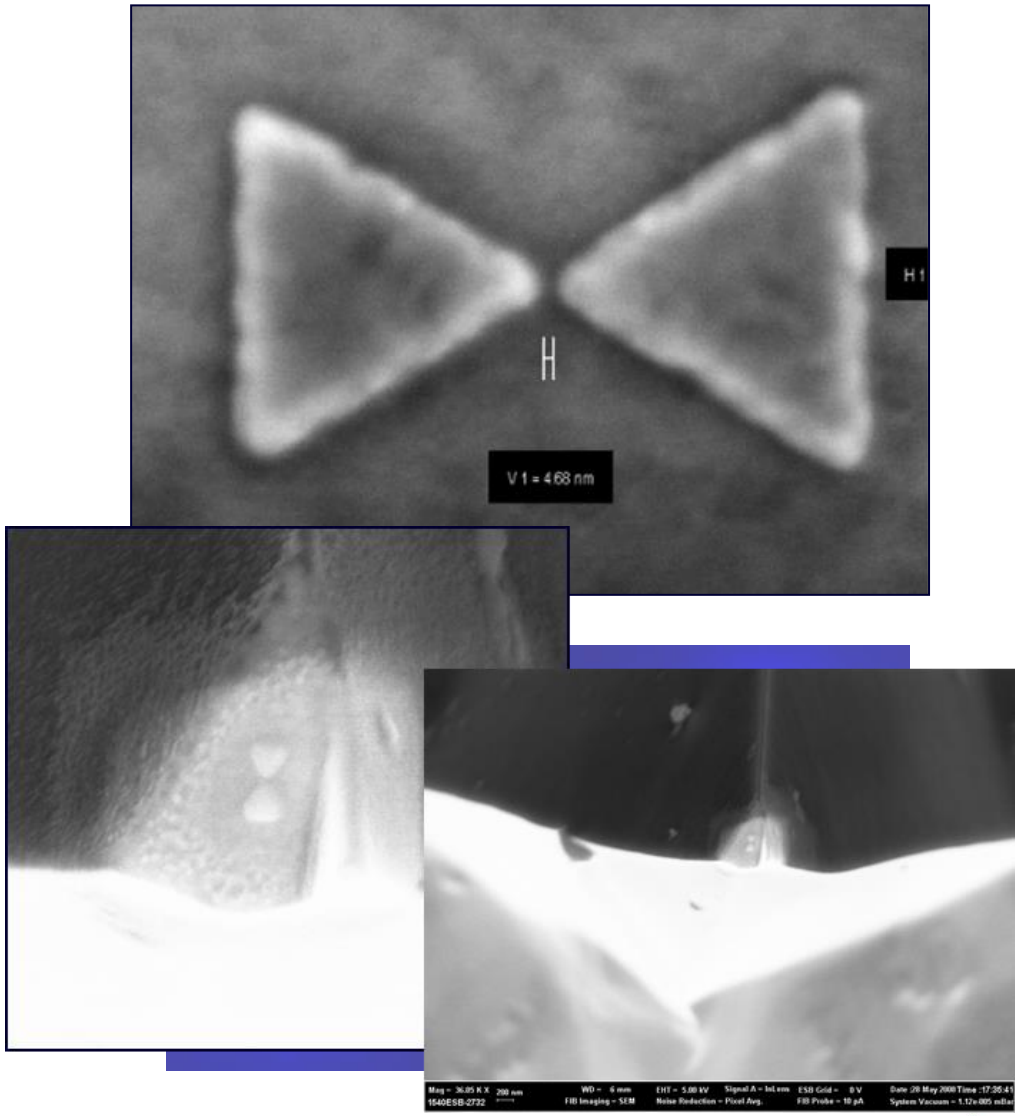
Alessandri Small 9, 3301-3307I (2013)

Significantly beating the diffraction limit.



AFM image of CNT with the resolution spot of optical microscopy compared with the Bowties focus spot

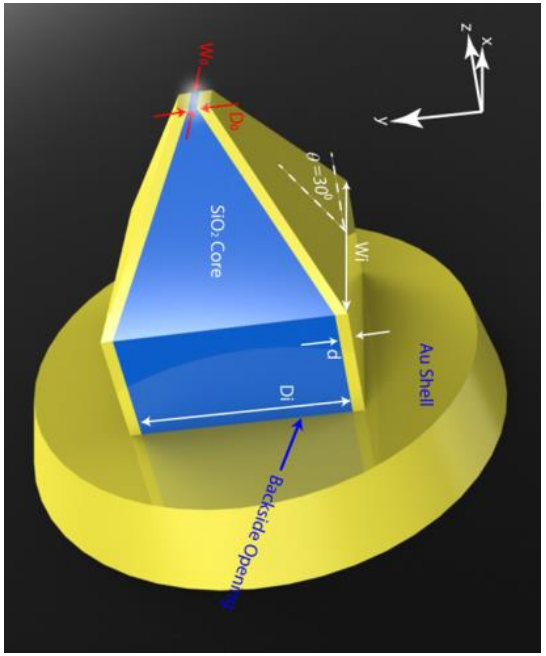




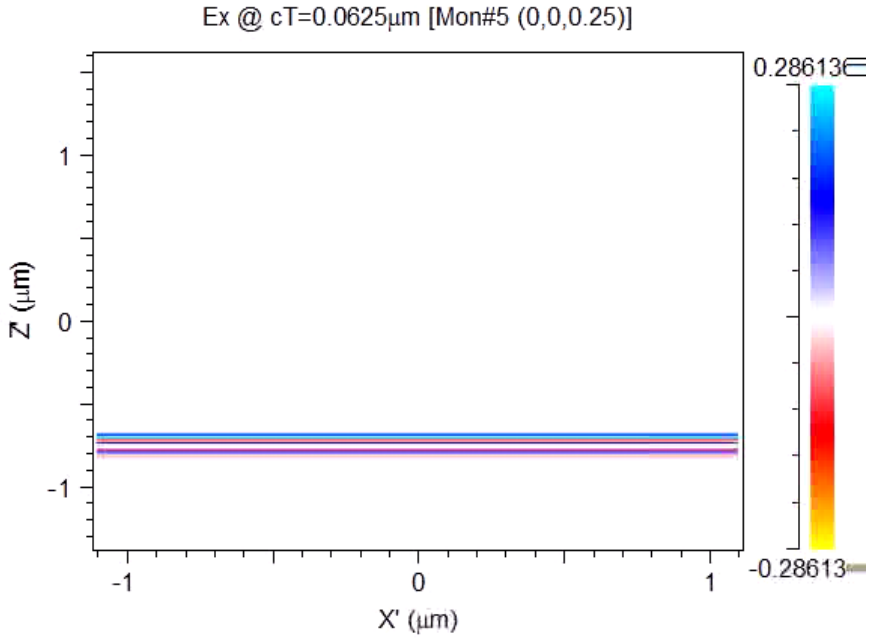
AWeber-Bargioni, S Cabrini et al: “Functional plasmonic antenna scanning probes fabricated by induced-deposition mask lithography”; Nanotechnology 21 (2010)

MOLECULAR FOUNDRY

Optical Transformers on an Optical Fiber



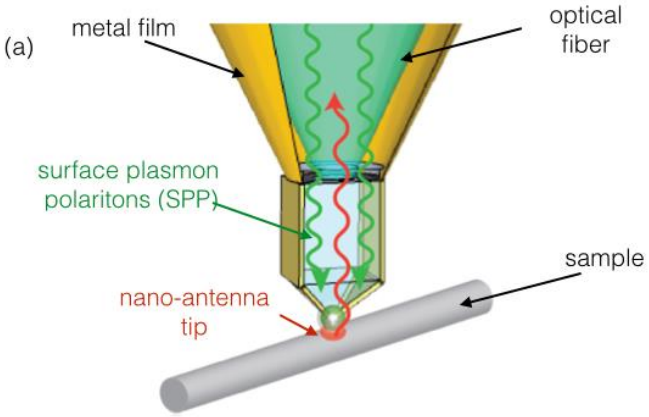
FDTD Finite-difference time-domain simulation

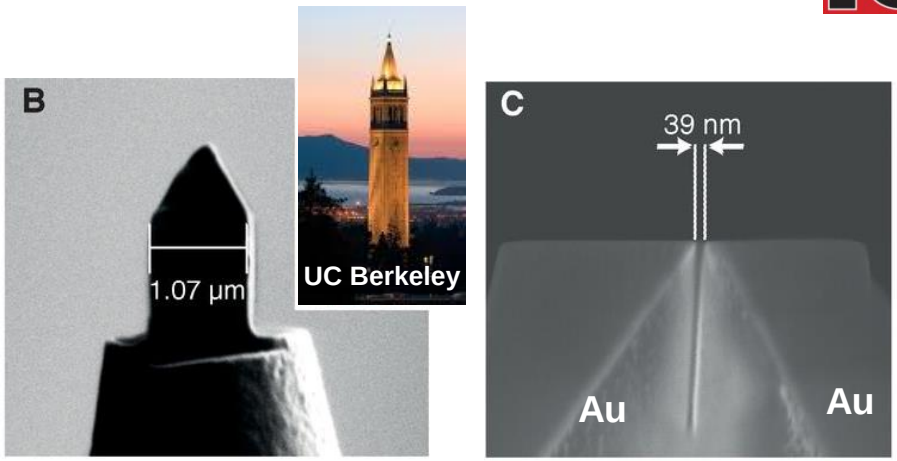


Hyuck Choo, Eli Yablonovitch et al Nature Photonics, 6, 838–844 (2012)

MOLECULAR FOUNDRY

Campanile Near-field Probes



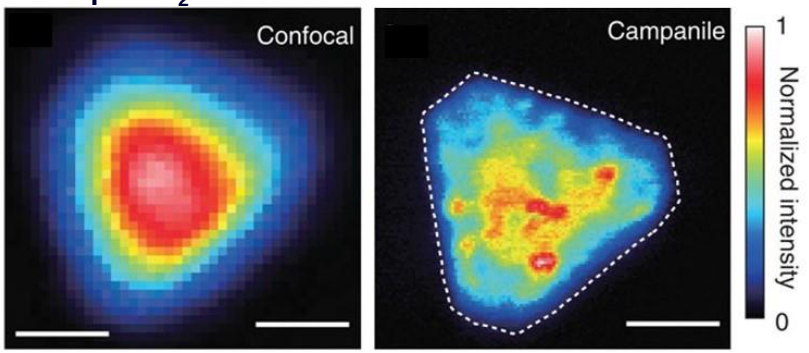


SCIENCE VOL 338 7 DECEMBER 2012

Offer numerous advantages

- Spatial resolution (gap size)
- Efficient broadband coupling
- Hyperspectral imaging at each point
- NO background signals

PL map MoS_2

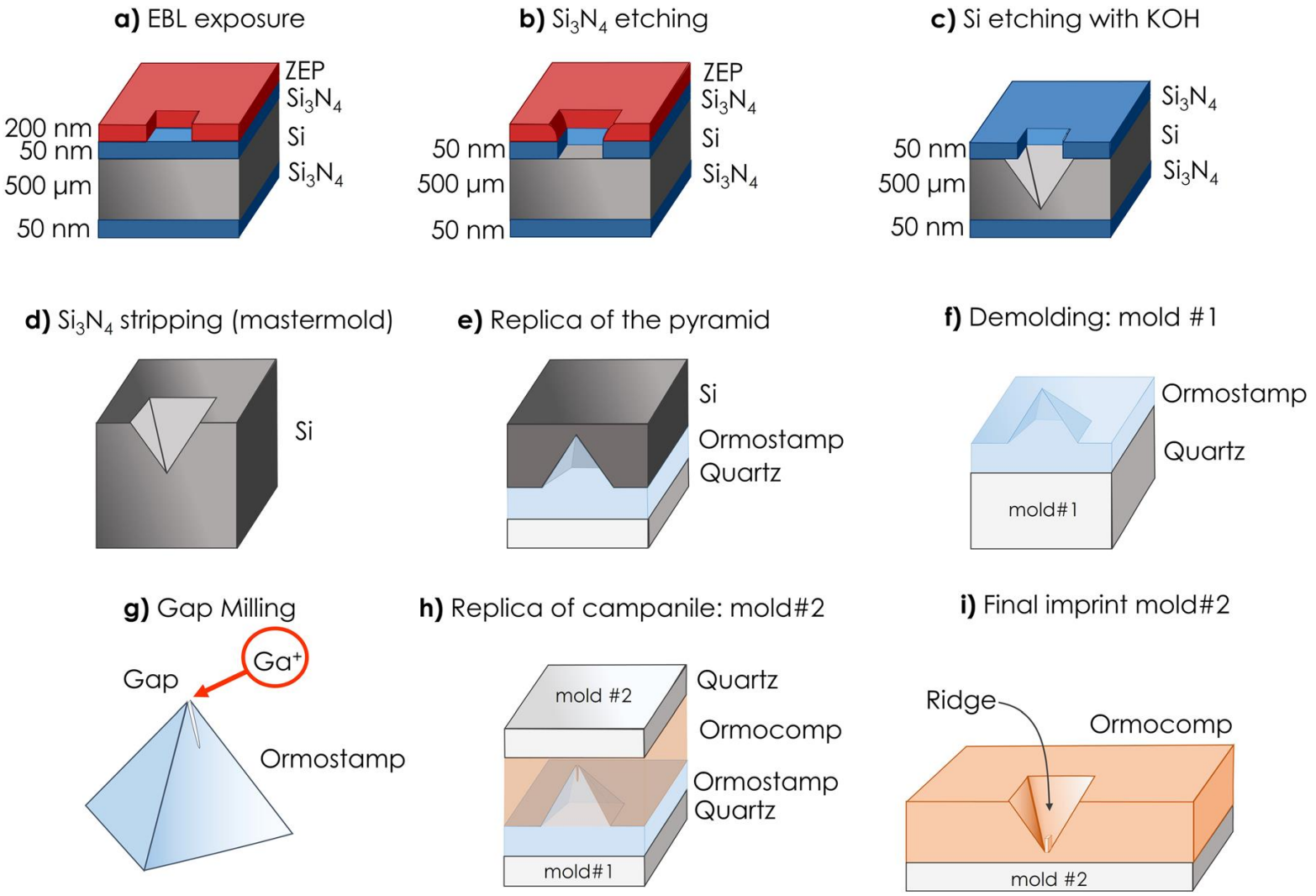


(scale bar = 1 μm)

Nature Communications 2015, 6. 7993

A. Weber-Bargioni, S. Cabrini, P. J. Schuck, et al; Science 2012:Vol. 338 no. 6112

Nanoimprinting Optical Transformers on an Optical Fiber



MOLECULAR FOUNDRY

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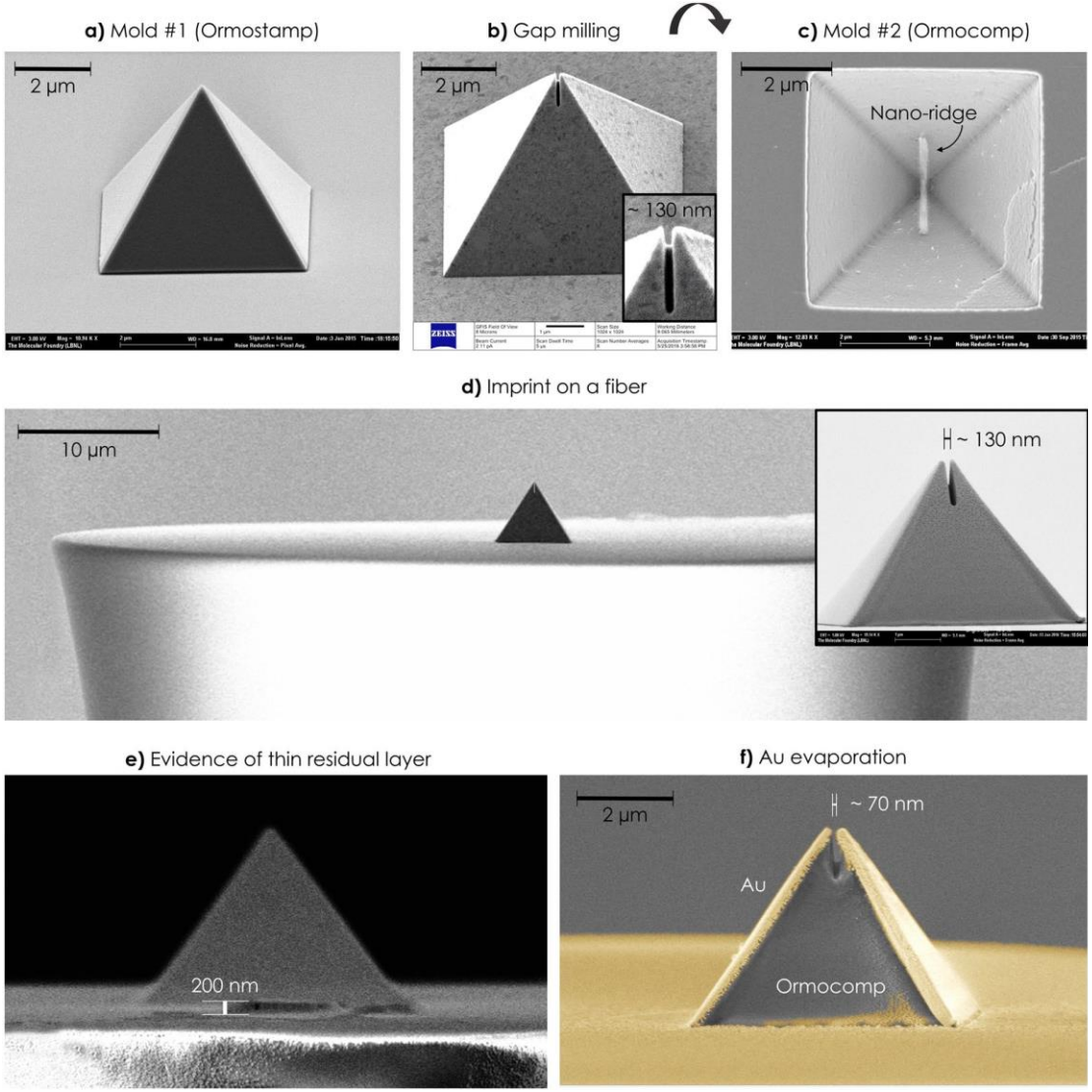
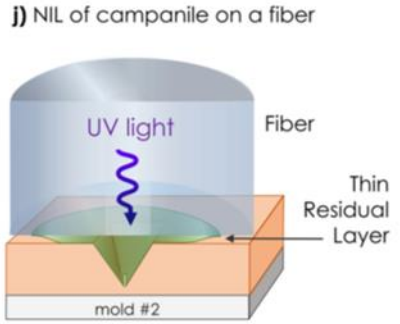
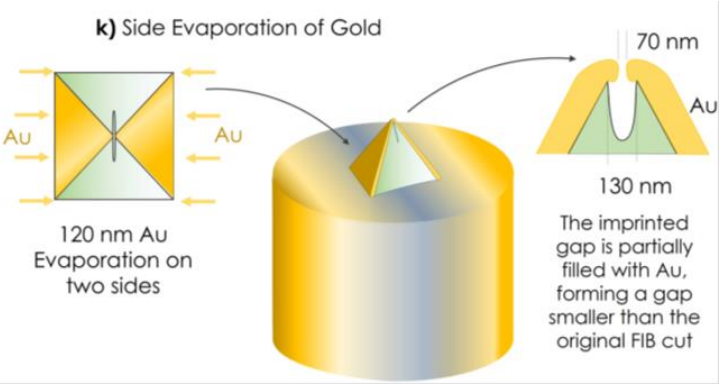


aBeam technologies

Keiko Munechika and Aleks Koshelev

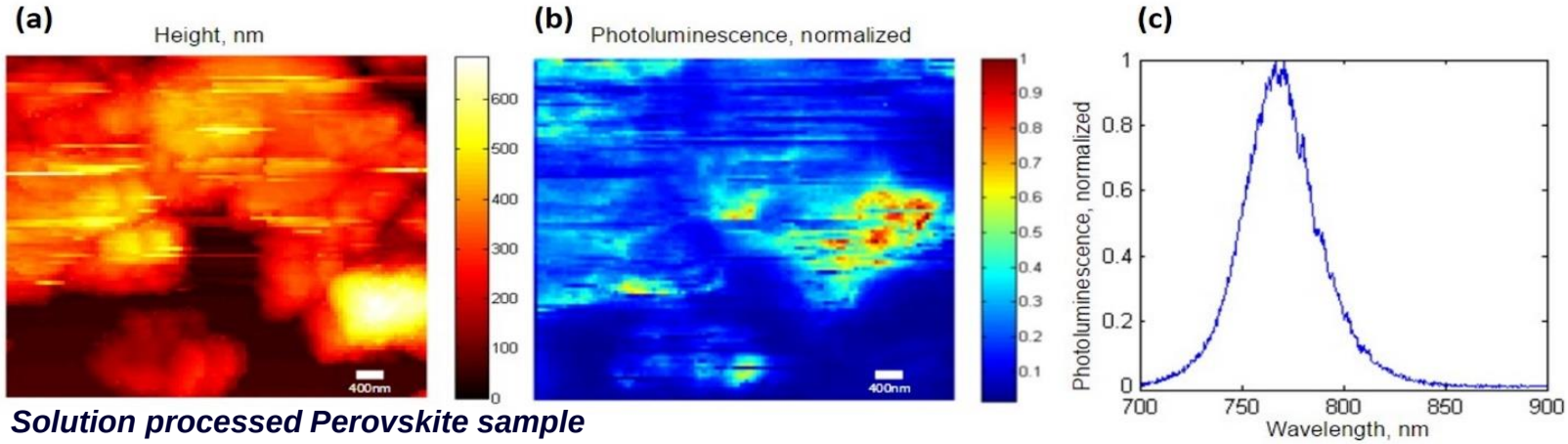




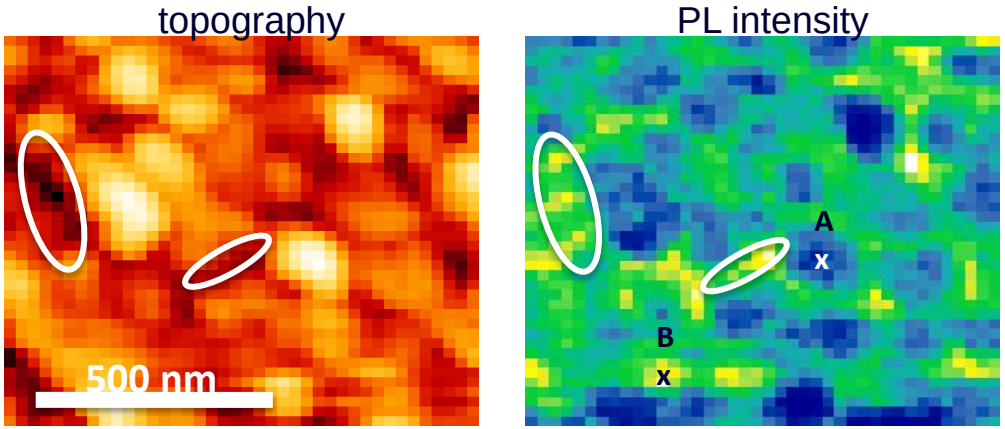
MOLECULAR FOUNDRY

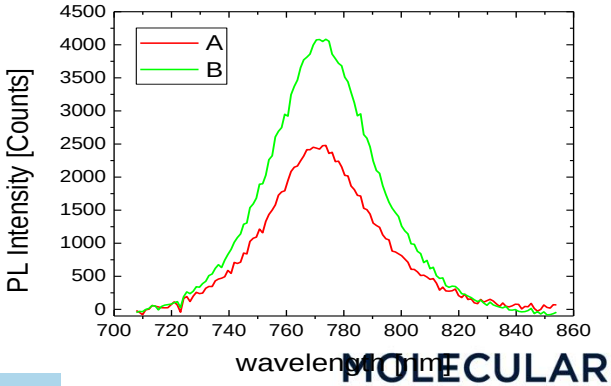
Imaging using imprinted Campanile probes

- Manufacturing yield improved > 10 fibers/day
- Imprinted Campaniles used for NSOM measurements by multiple research institutions
- Sub-diffraction features successfully imaged



Solution processed Perovskite sample

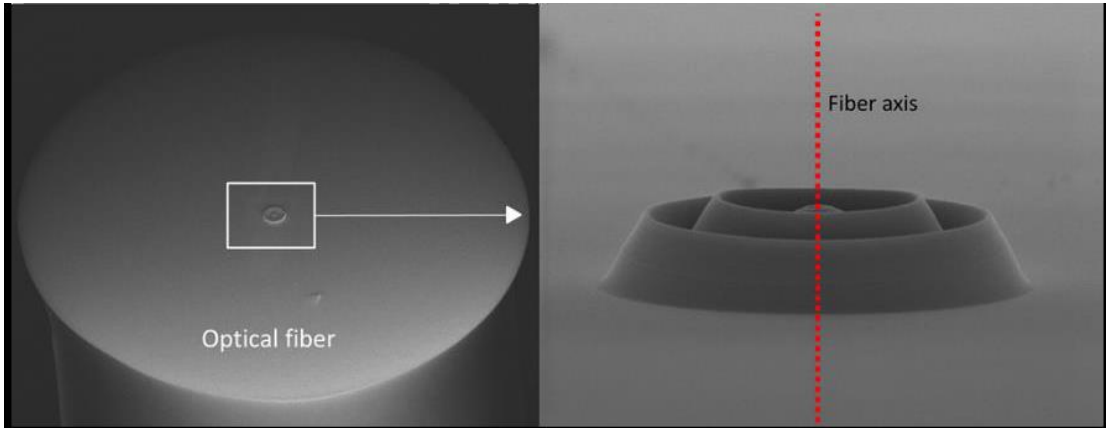


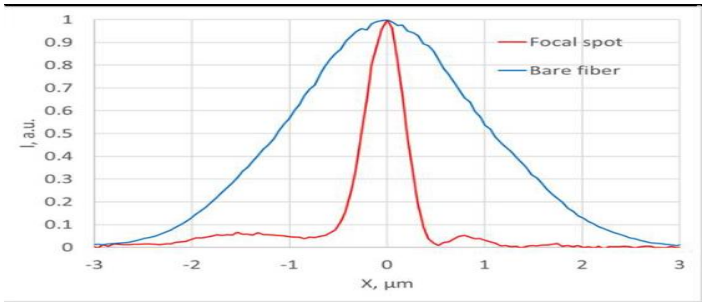


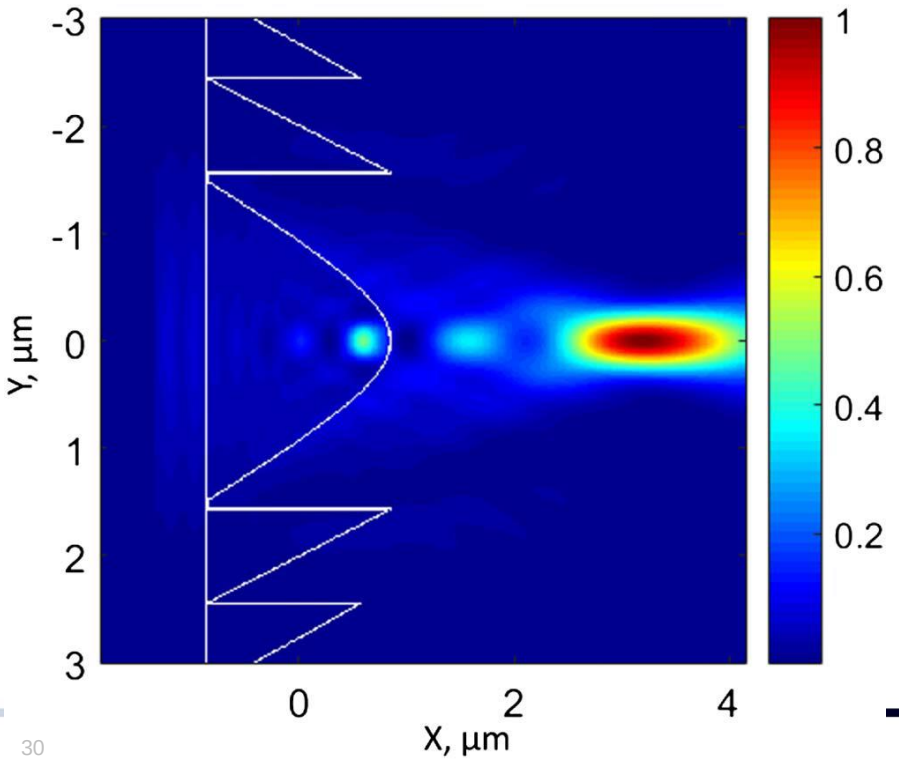
Methyl ammonium lead iodide ($CH_3NH_3PbI_3$) solar cell

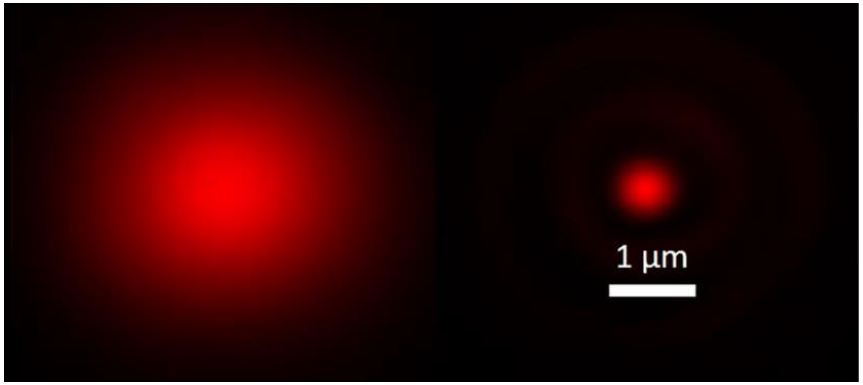
MOLECULAR FOUNDRY

High Refractive Index Fresnel Lens on a Optical Fiber





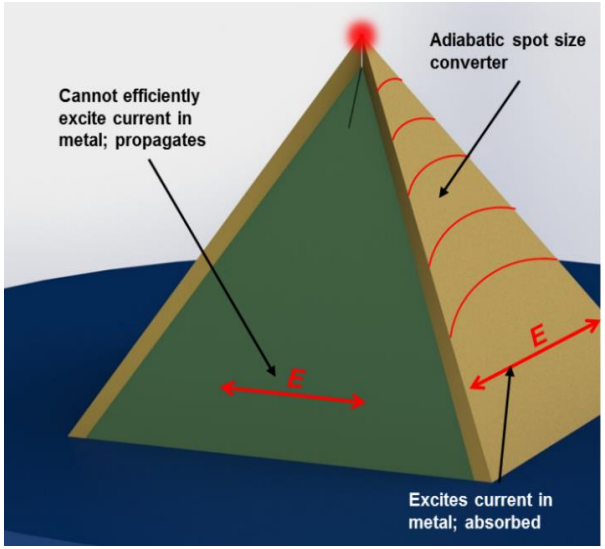


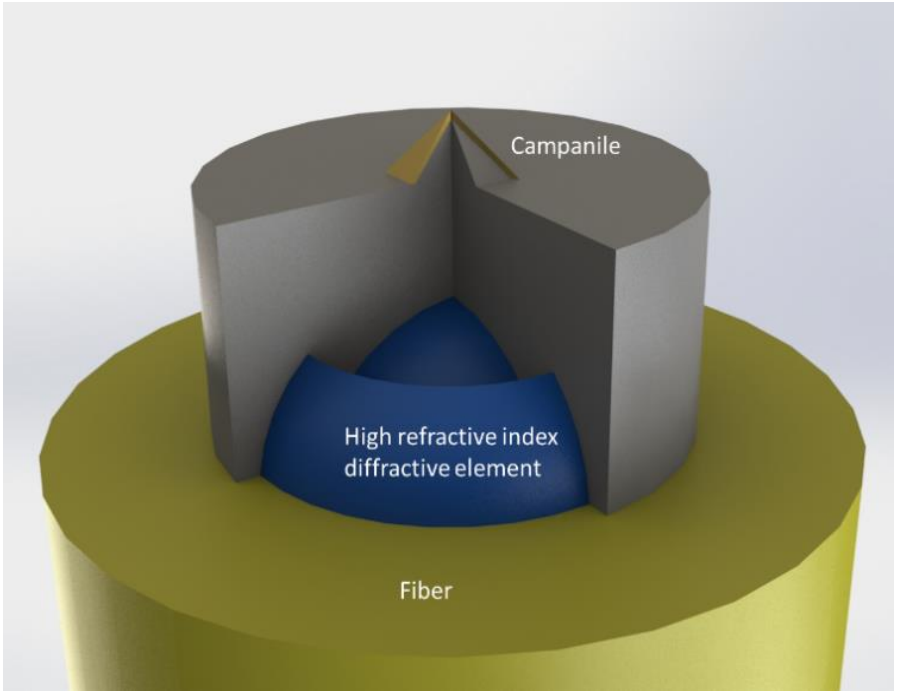


A. Koshelev, K. Munechika, Stefano Cabrini et al; Optics Letters Vol. 41, Issue 15, pp. 3423-3426 (2016)

MOLECULAR FOUNDRY

Hybrid Photonic-Plasmonic Probe

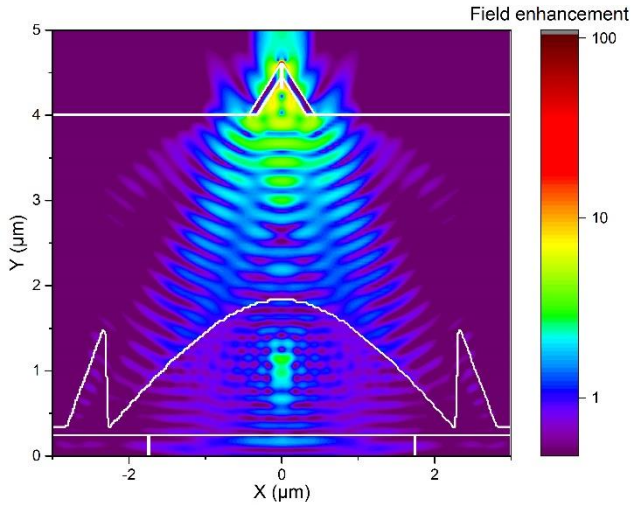




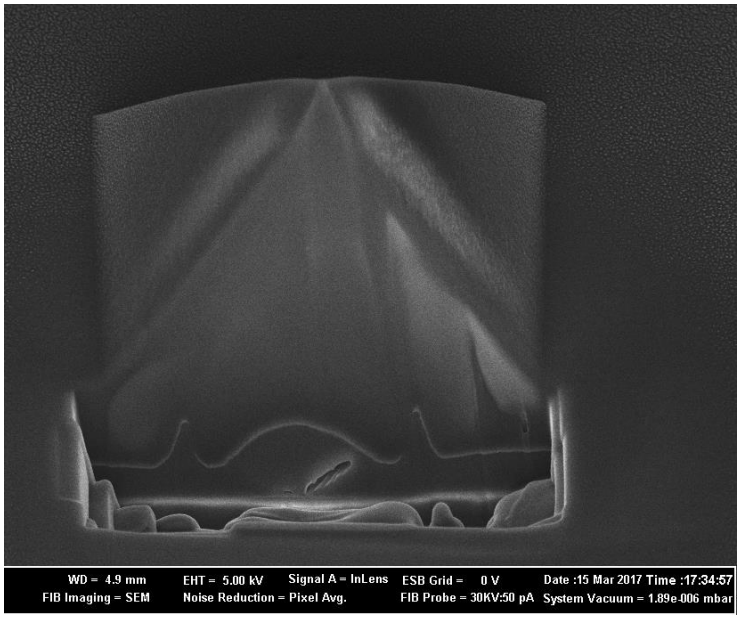
alexander koshelev, keiko munechika, stefano cabrini: “Hybrid photonic-plasmonic near-field probe for efficient light conversion into the nanoscale hot spot” accepted

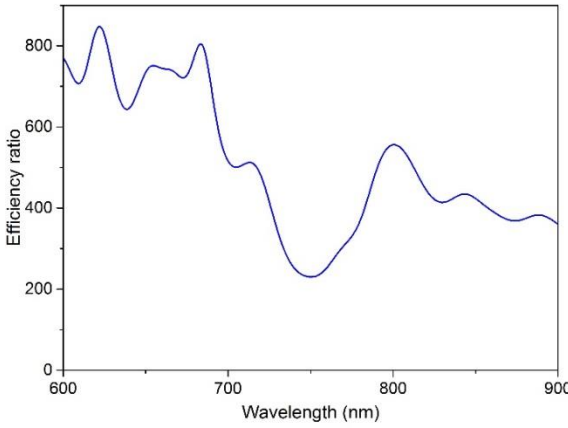
MOLECULAR FOUNDRY

Prototype Hybrid Photonic-Plasmonic Probe

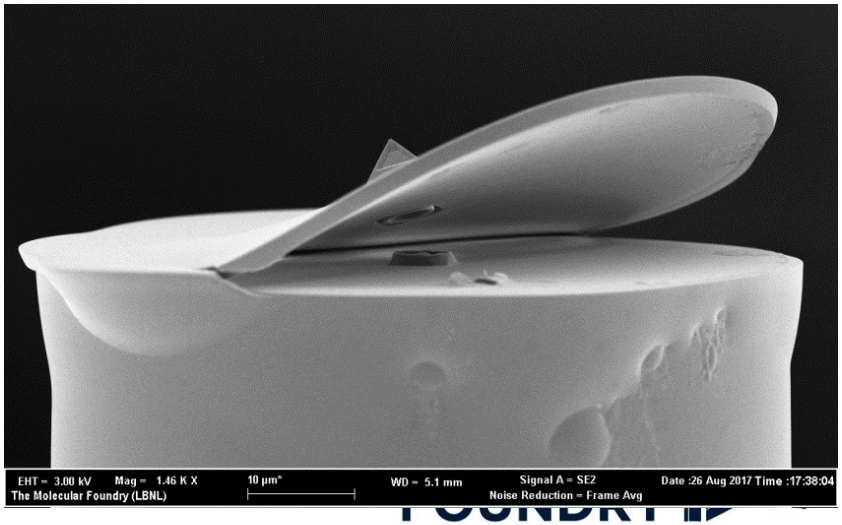


Cross section of the simulated field enhancement inside the hybrid probe in the excitation mode at 633 nm wavelength. The maximum field enhancement is 105.

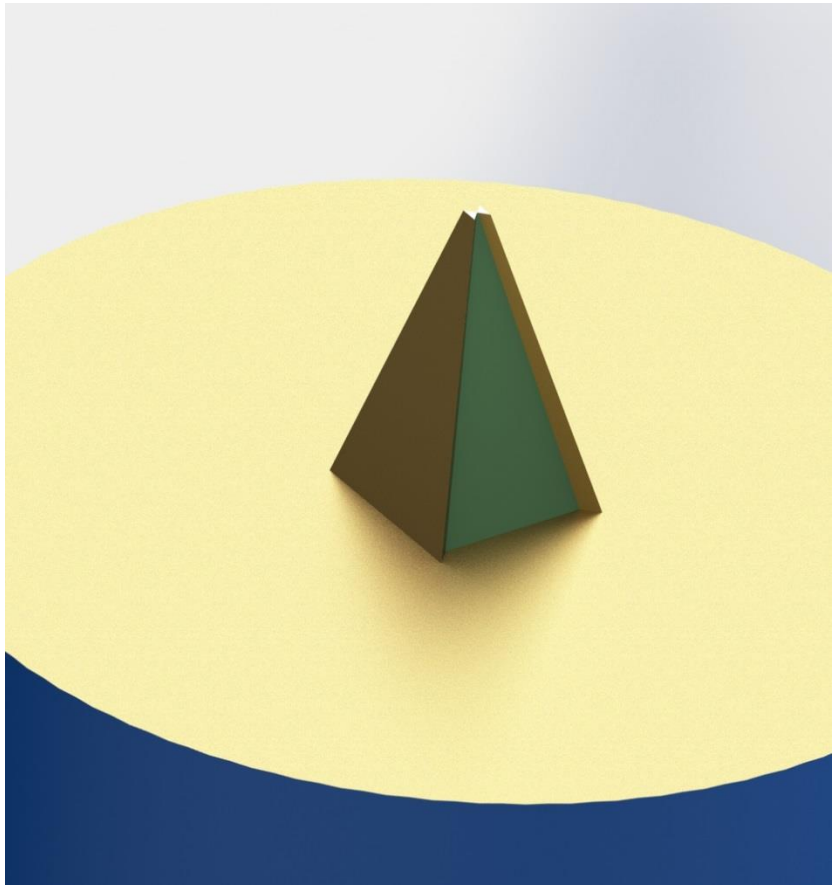




The ratio of the hybrid probe efficiency at 633 nm excitation wavelength to the efficiency of the campanile tip is about 540.

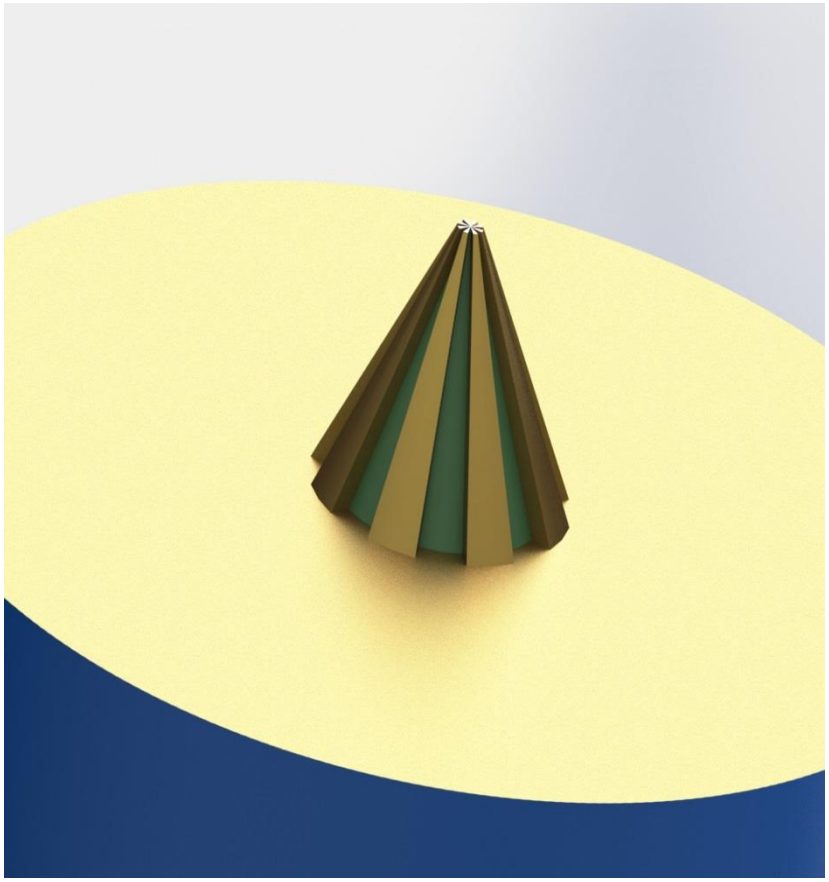


Campanile



- Rectangular geometry
- Transmits only one polarization
- One of the polarization is efficiently localized because it cannot excite electric current in the perpendicular metal stripe

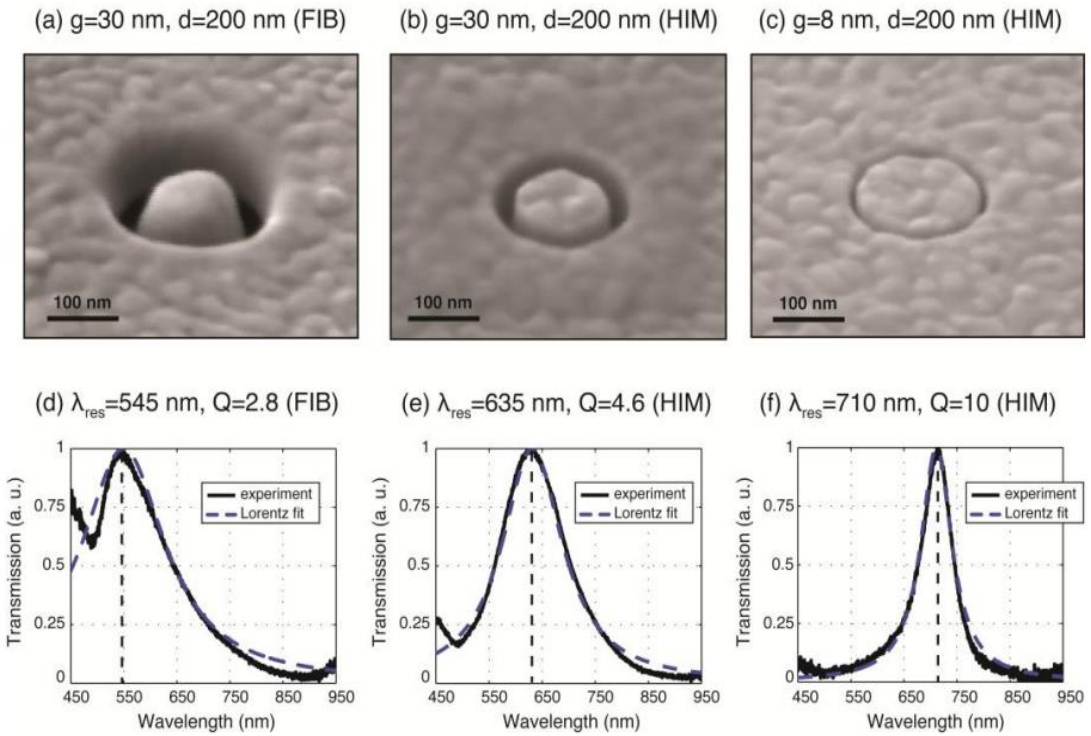
Pin-Wheel



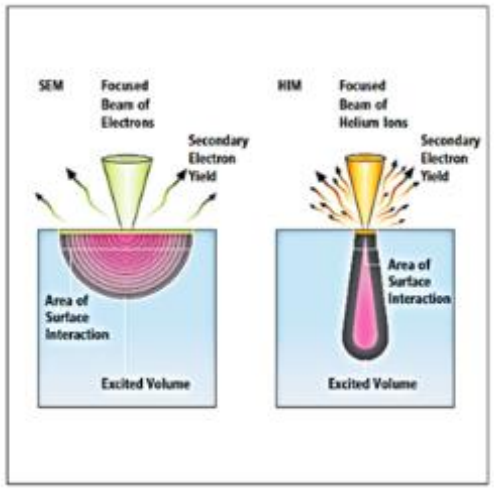
- Could potentially have circular geometry
- Potentially Polarization insensitive
- Both polarizations efficiently localized due to inability to excite current in narrow metal stripes

Coaxial Plasmonic Nanoresonators Fabricated by HIL Helium Ion Lithography

Ga⁺ FIB He⁺ FIB HIL 8 nm gap



Zeiss -ORION PLUS Helium-Ion Microscope available at the BNC lab QB3 Stanley Hall UCB



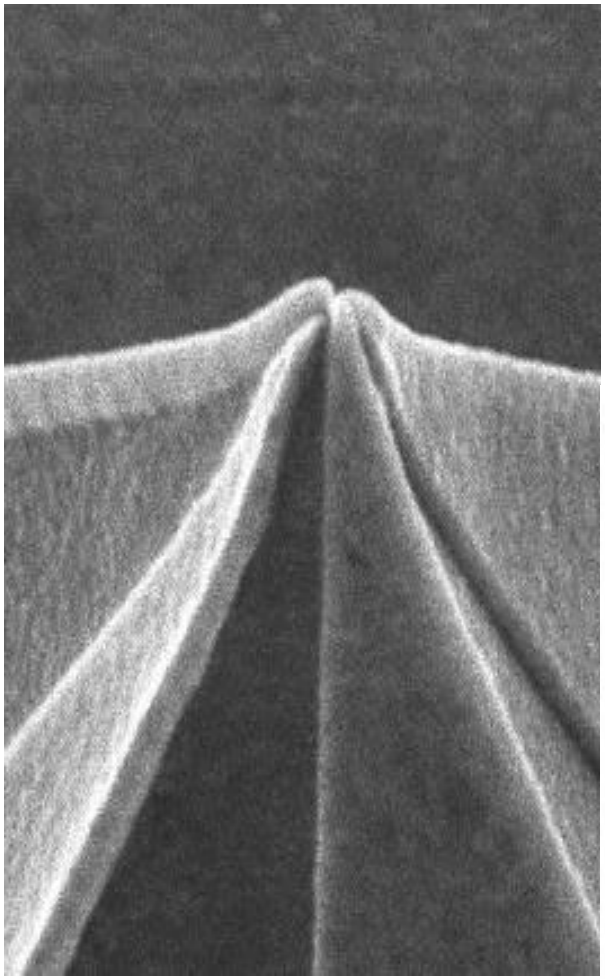
100 nm thick gold film

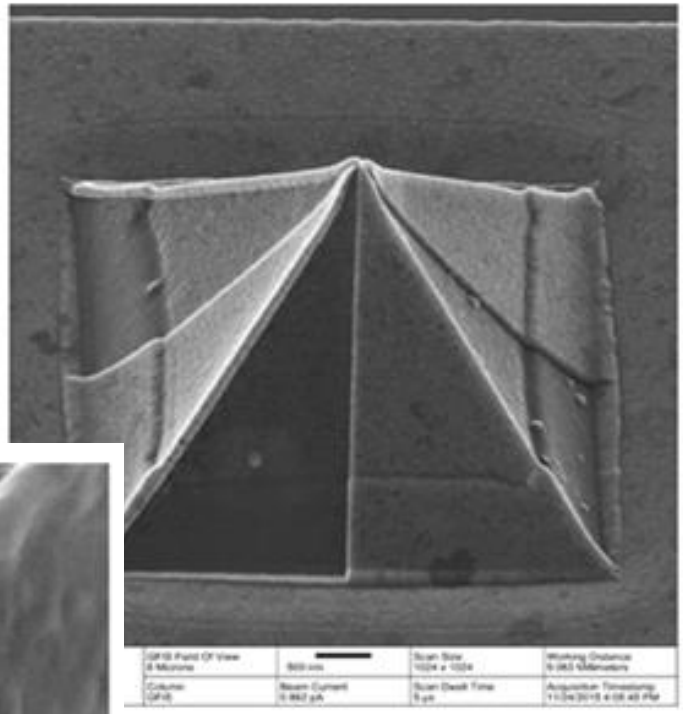
M. Melli, A. Polyakov et al; ”Reaching the Theoretical Resonance Quality Factor Limit in Coaxial Plasmonic Nanoresonators Fabricated by Helium Ion Lithography”; Nano Lett. Vol 13, Issue 6 pp 2687–2691 (June 2013)

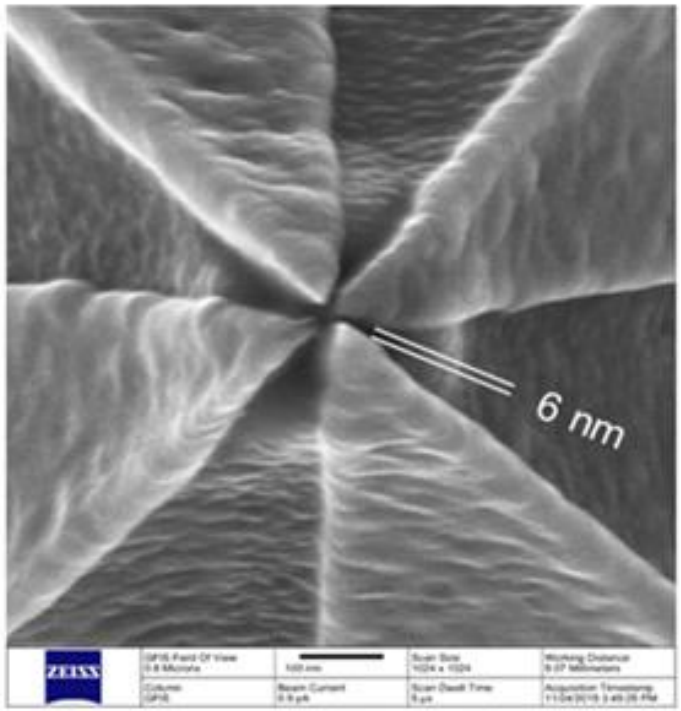
MOLECULAR FOUNDRY

Molecular Foundry

Pin-Wheel tip on SiN AFM cantilever





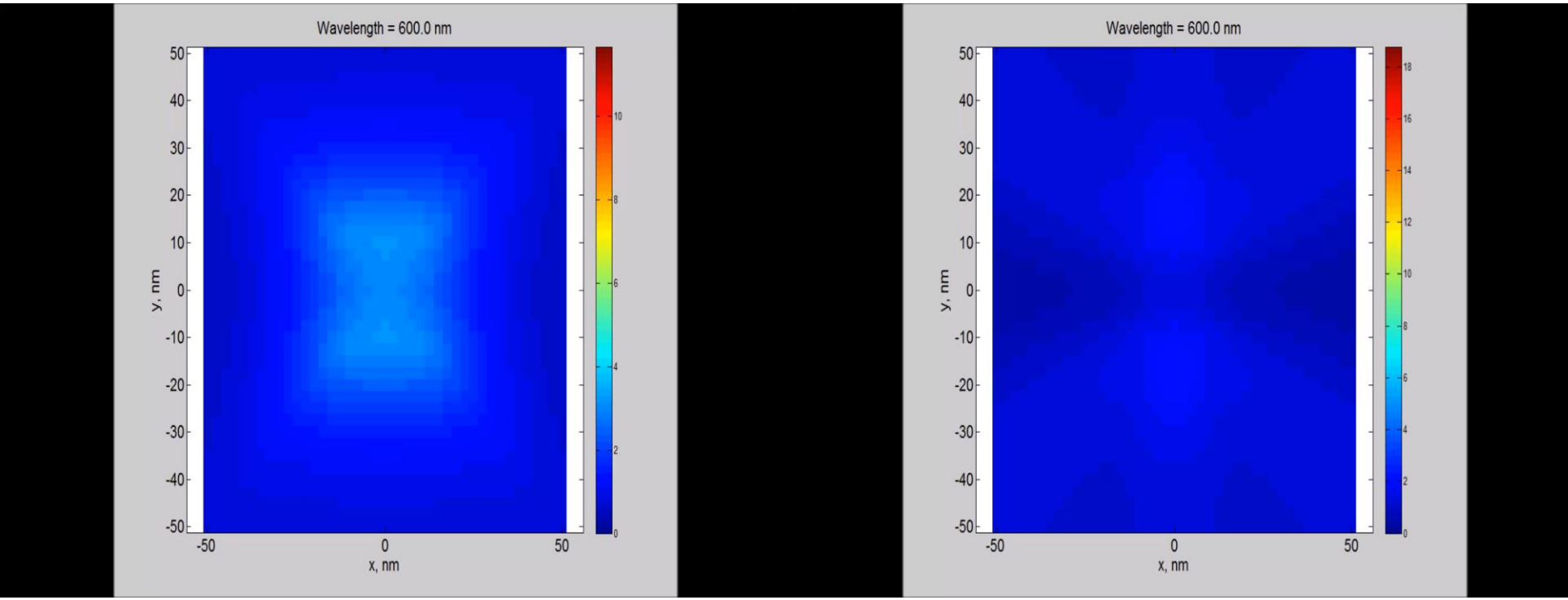


MOLECULAR FOUNDRY

Simulation: comparison of the Field Enhancement Campanile VS Pin-Wheel

Campanile

Pin-wheel

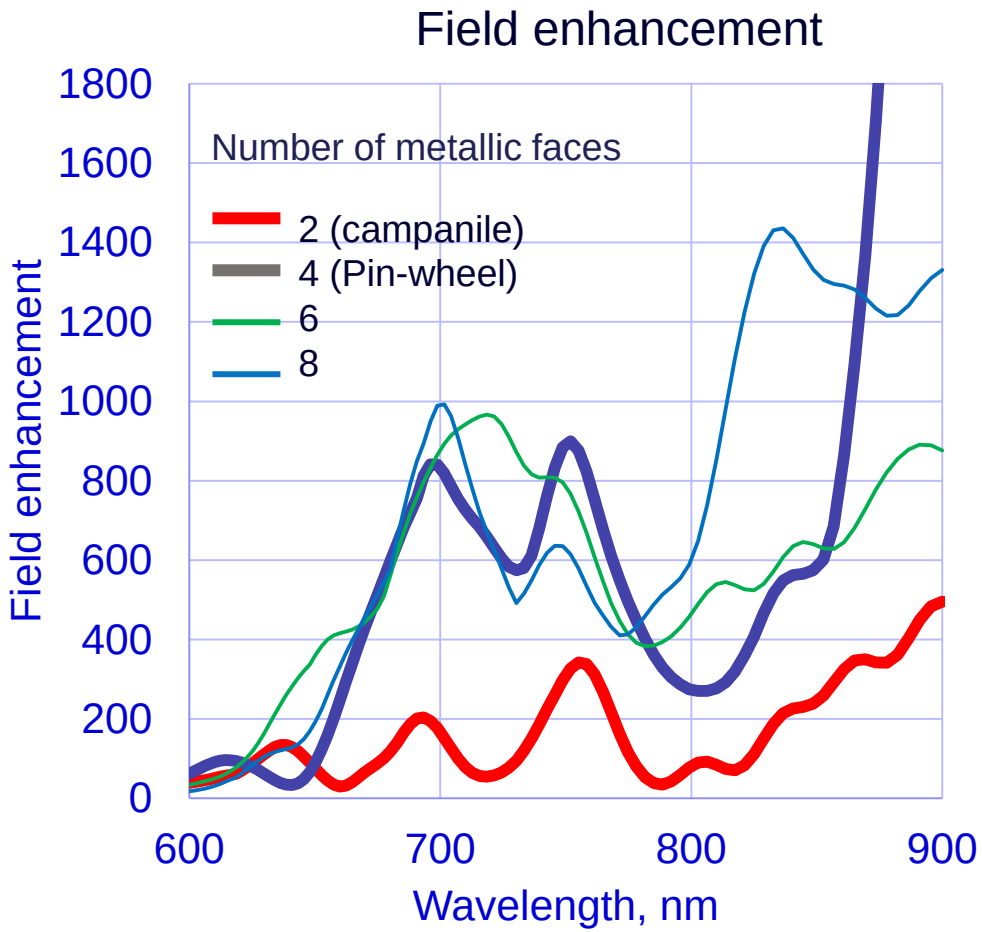


MOLECULAR FOUNDRY

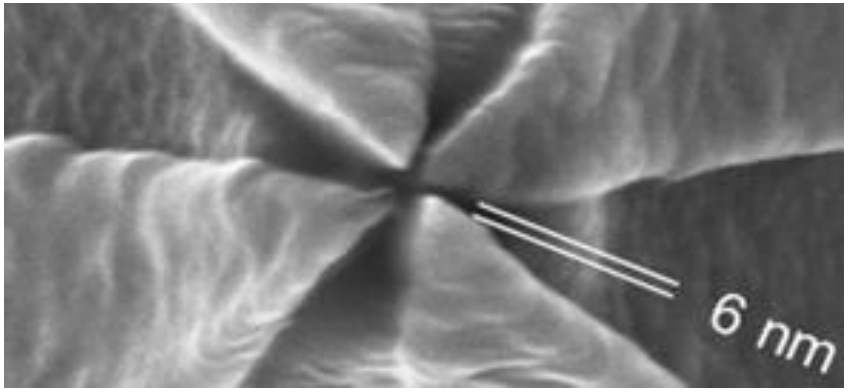
Comparison of the Field Enhancement Campanile VS Pin-Wheel

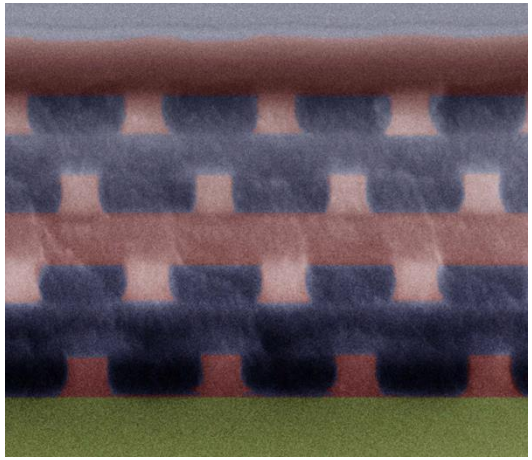
Parameters:

- Gap width 20 nm
- Gap-to-detector distance 10 nm
- Base width 5.5 um
- Height 3.8 um
- Gold thickness 120 nm



MOLECULAR FOUNDRY





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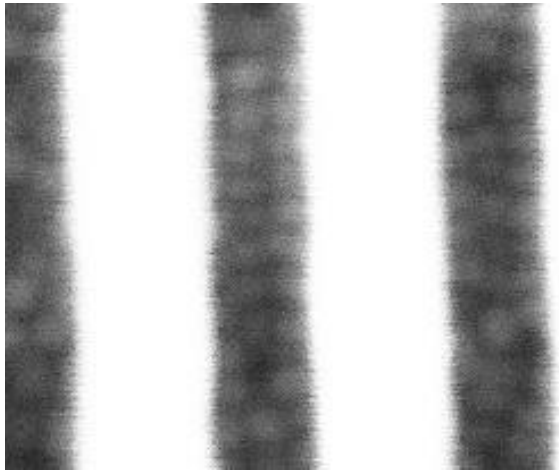
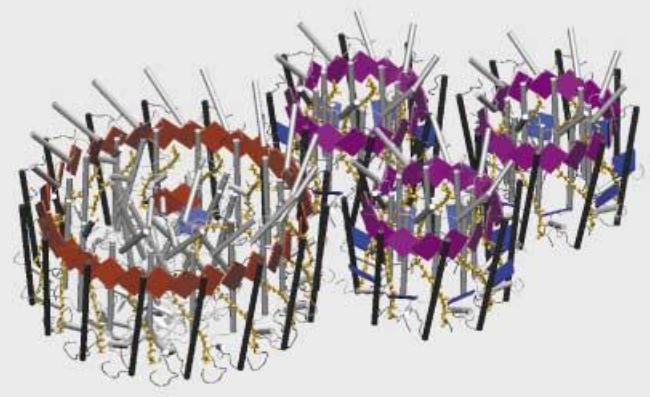
- 3D Plasmonic
- Directed self-assembly of nanoparticles



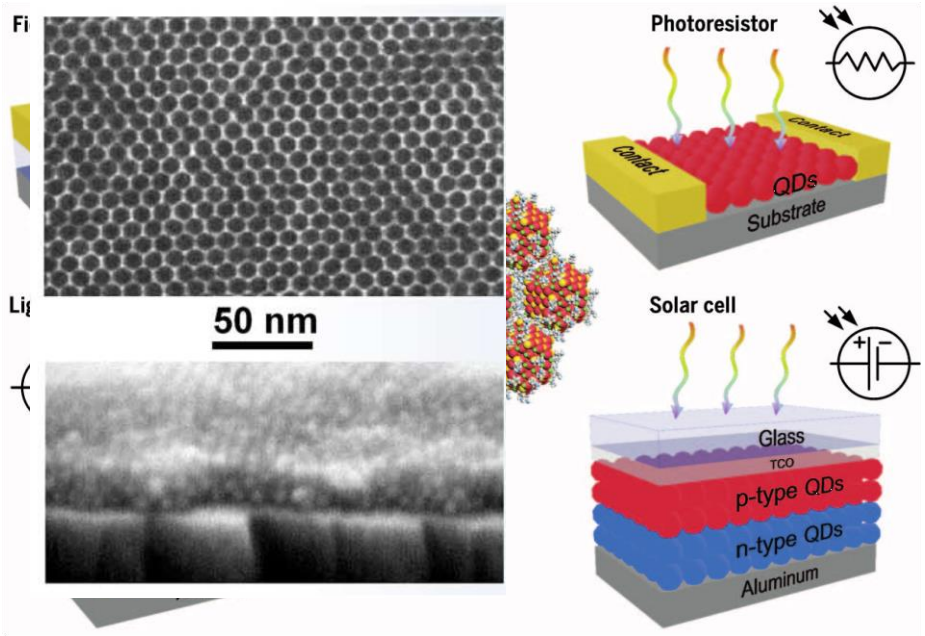
Excitonic systems

Photosynthetic Unit (PSU)



T. Ritz *et al.* The Quantum Physics of Photosynthesis ChemPhysChem 3 (2002) 243−248

Nanocrystal Solids

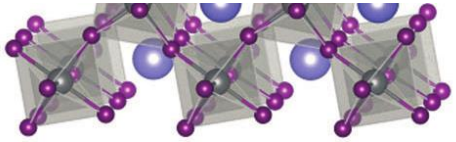


N. Kholmicheva *et al.* Energy Transfer in Quantum Dots Solids ACS Energy Lett. 2 (2017) 154−160

C. Kagan, E. Lifshitz, E. Sargent, D. Talapin, Building Devices from Colloidal Quantum Dots Science 353 (2016) 6302

MOLECULAR FOUNDRY

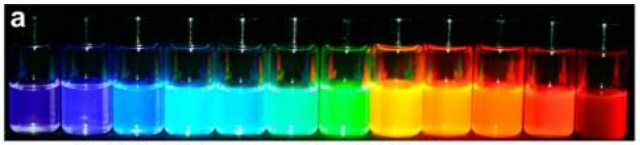
$CsPbX_3$ perovskite nanocrystals



Excellent optical properties

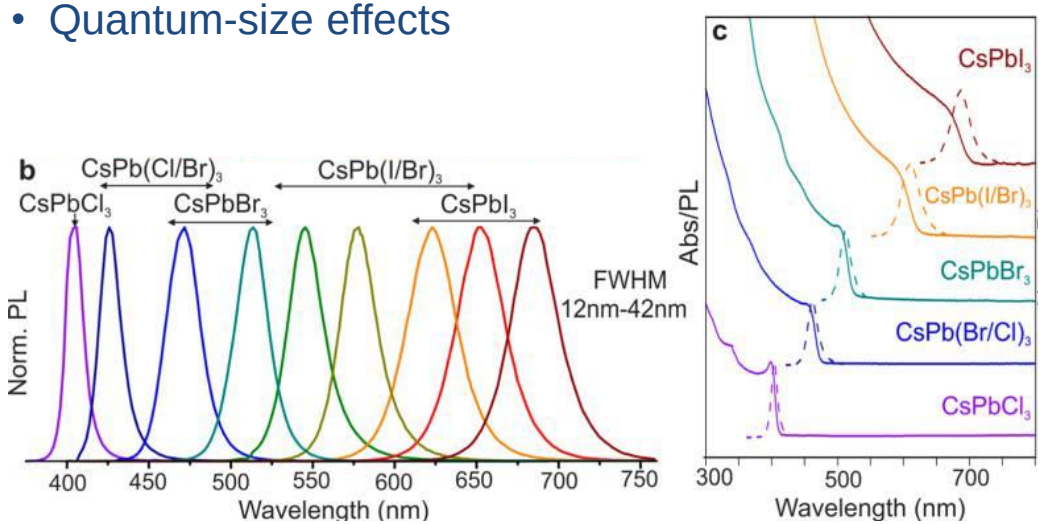
Bright photoluminescence (PL)

- High quantum yield of 50-90%
- Narrow emission line widths of 12-42 nm



Tunable bandgap energies over the entire visible spectral region by:

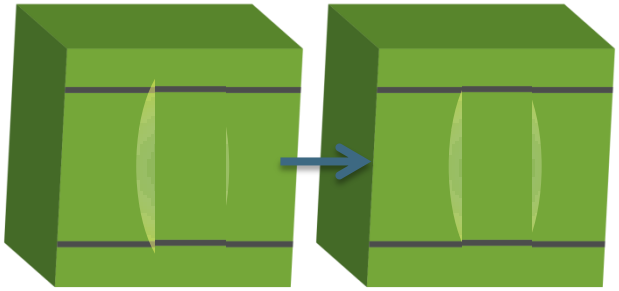
- Compositional control (mixed halide Cl/Br and Br/I systems)
- Quantum-size effects



MOLECULAR FOUNDRY

L. Protesescu *et al*. Nano Letters 15 (2015) 3692-3696

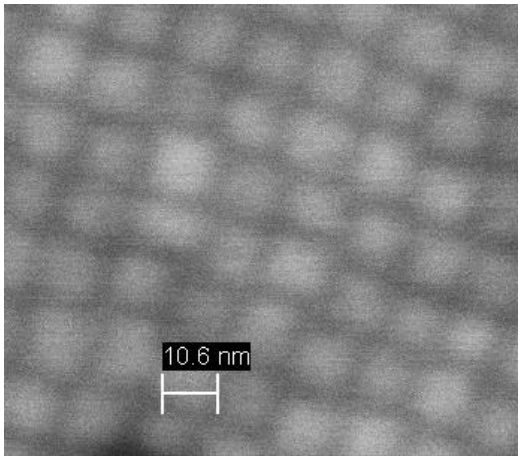
Exciton diffusion via FRET

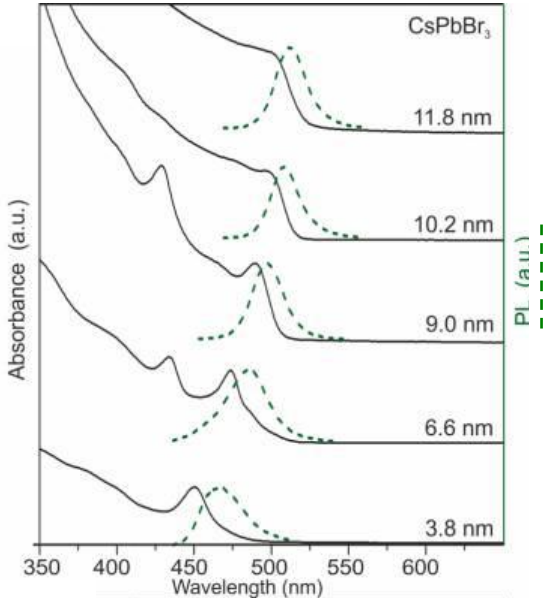


Förster Resonant Energy Transfer (FRET)

FRET efficiency:

- Spatial separation ~ R^{-6}
- Spectral overlap
- Dipole vectors alignment

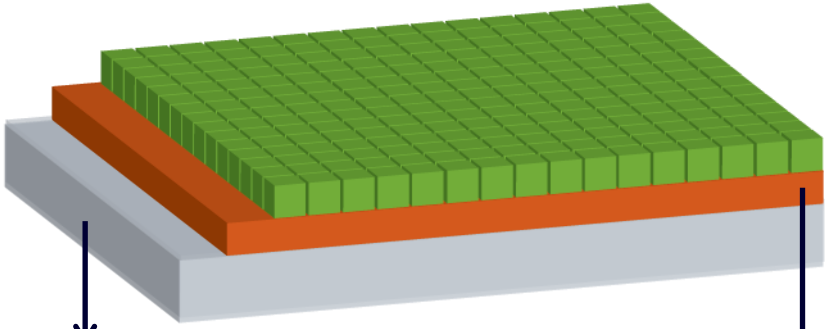




L. Protesescu *et al*. Nano Letters 15 (2015) 3692-3696

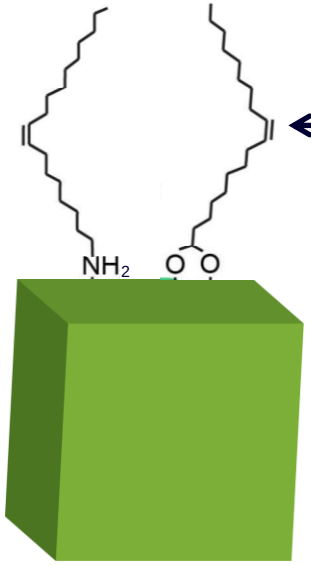
MOLECULAR FOUNDRY

Nanocrystal monolayer fabrication



Si substrate

~ 10 nm thick –CH polymer



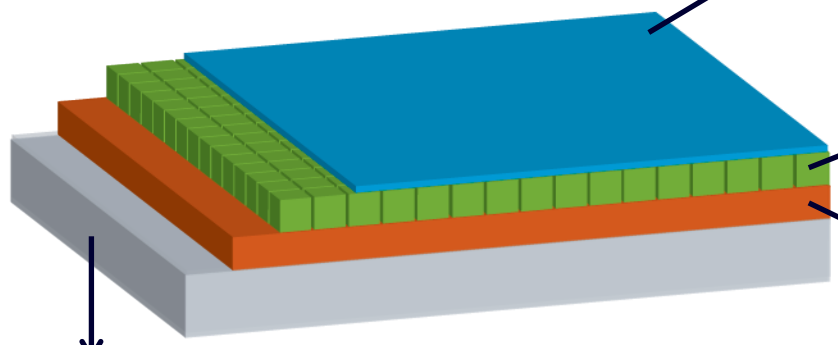
Organic ligands

$CsPbBr_3$ perovskite

Good affinity between nanocrystal ligands and substrate

MOLECULAR FOUNDRY

Nanocrystal monolayer fabrication



Prevent nanocrystal degradation during measurement

~ 3 nm thick Al_2O_3 by ALD

$CsPbBr_3$ nanocrystals

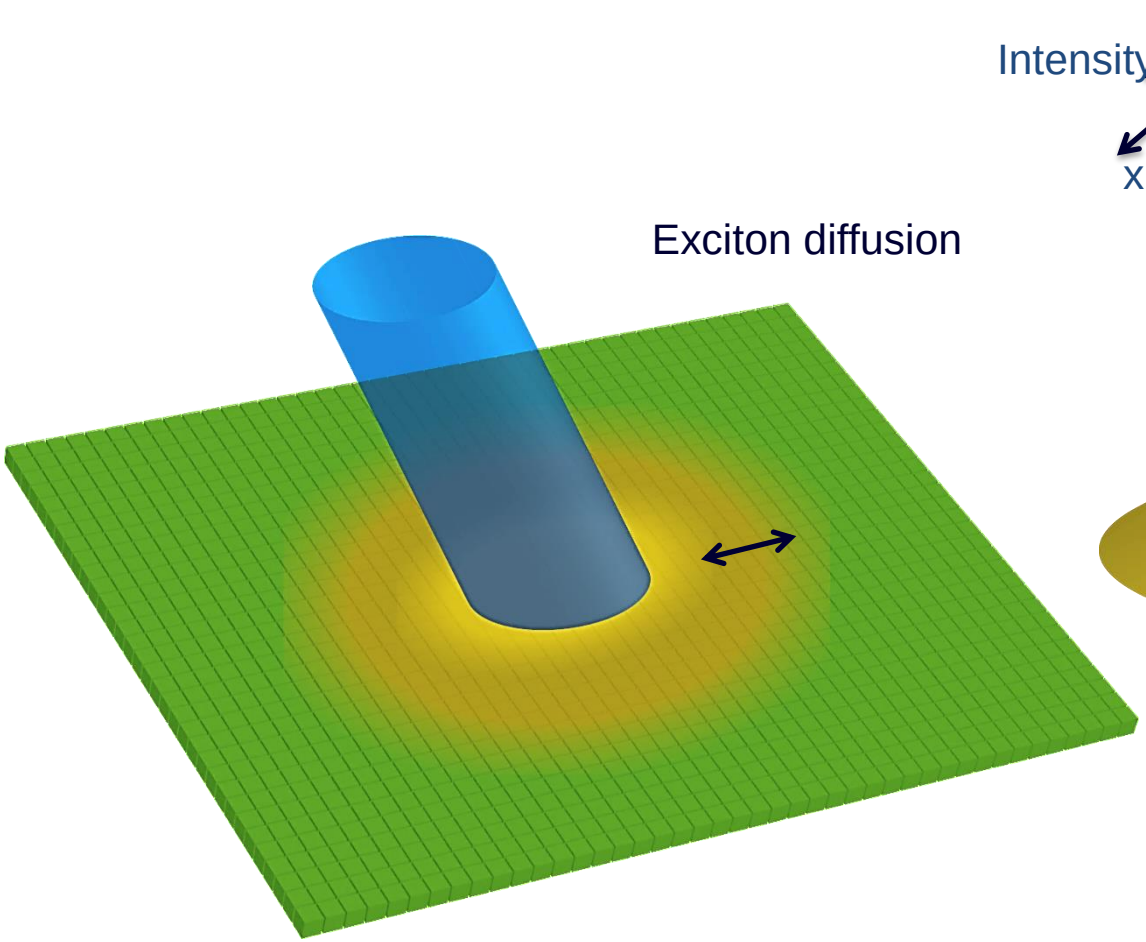
~ 10 nm thick –CH polymer

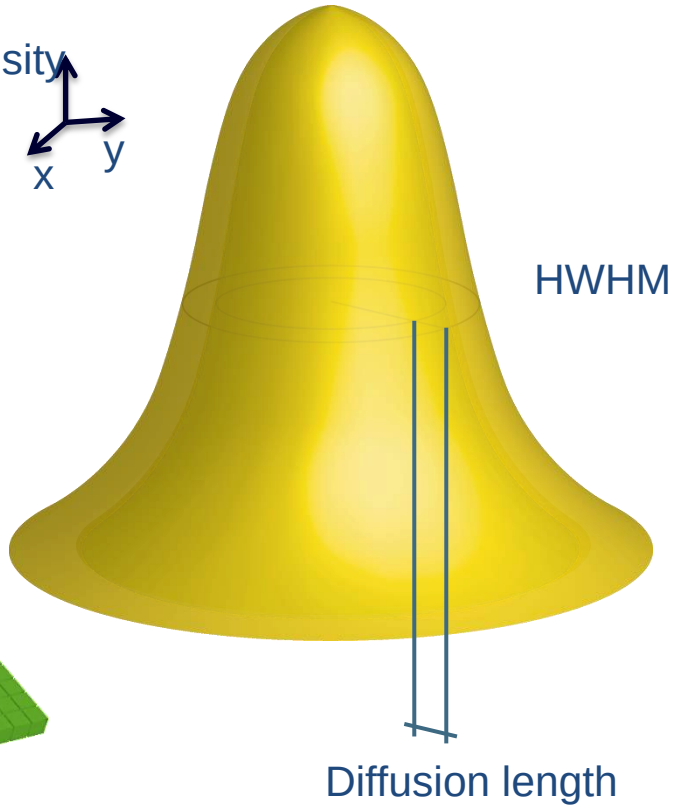
Si substrate

Good affinity between nanocrystal ligands and substrat

MOLECULAR FOUNDRY

Excited state ensemble expansion due to exciton diffusion

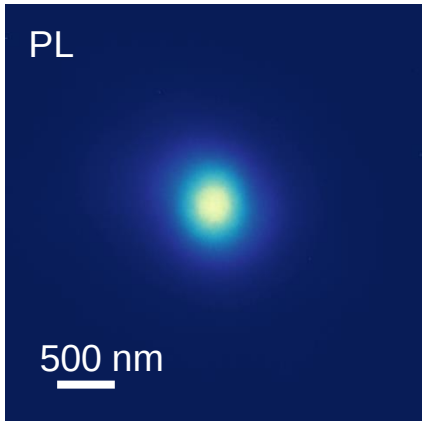


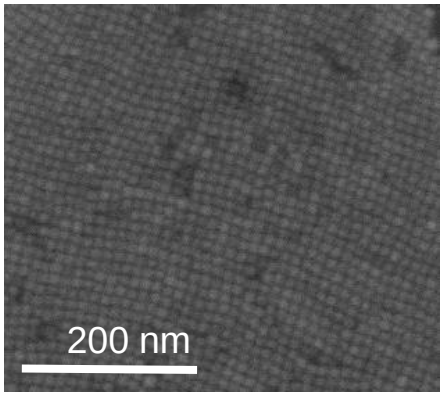


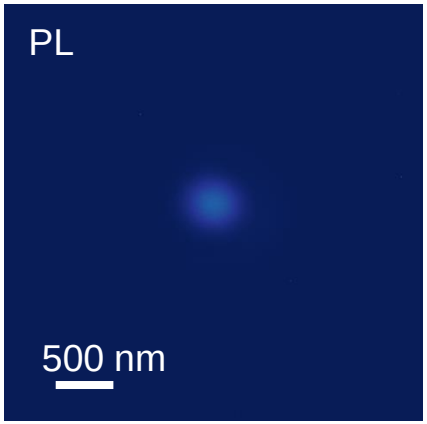
MOLECULAR FOUNDRY

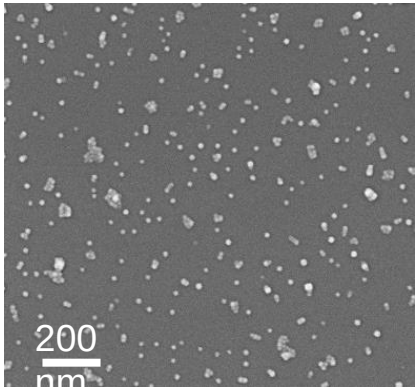
Exciton diffusion length from PL profile

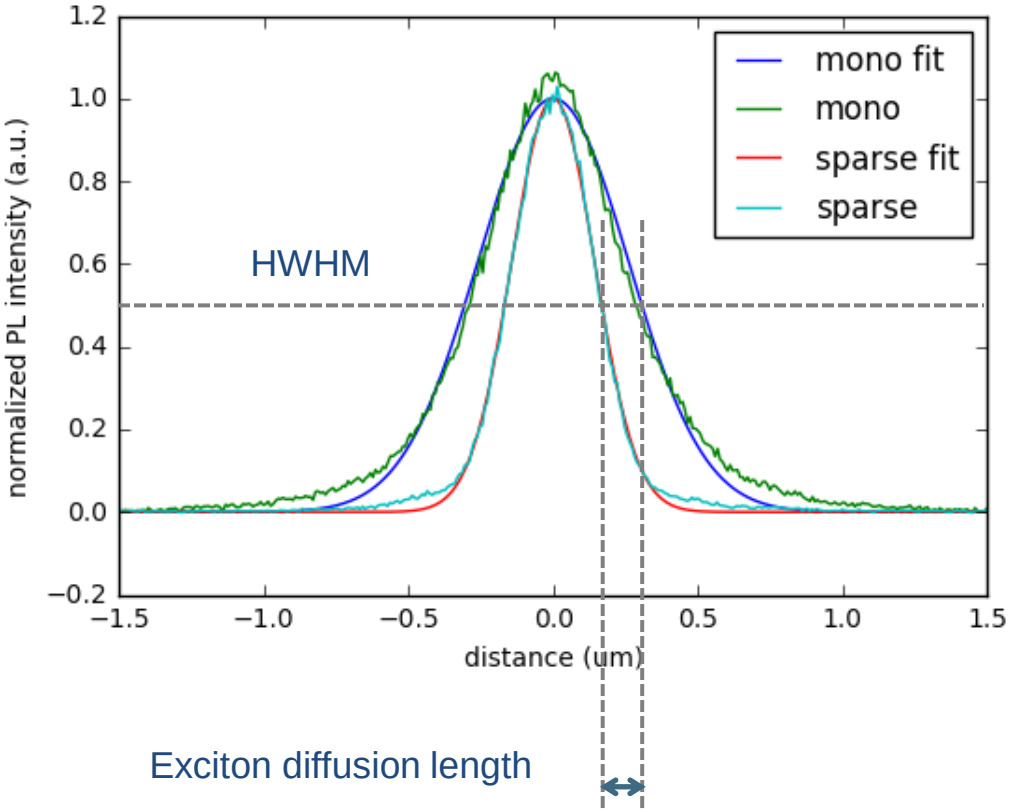
Monolayer sample











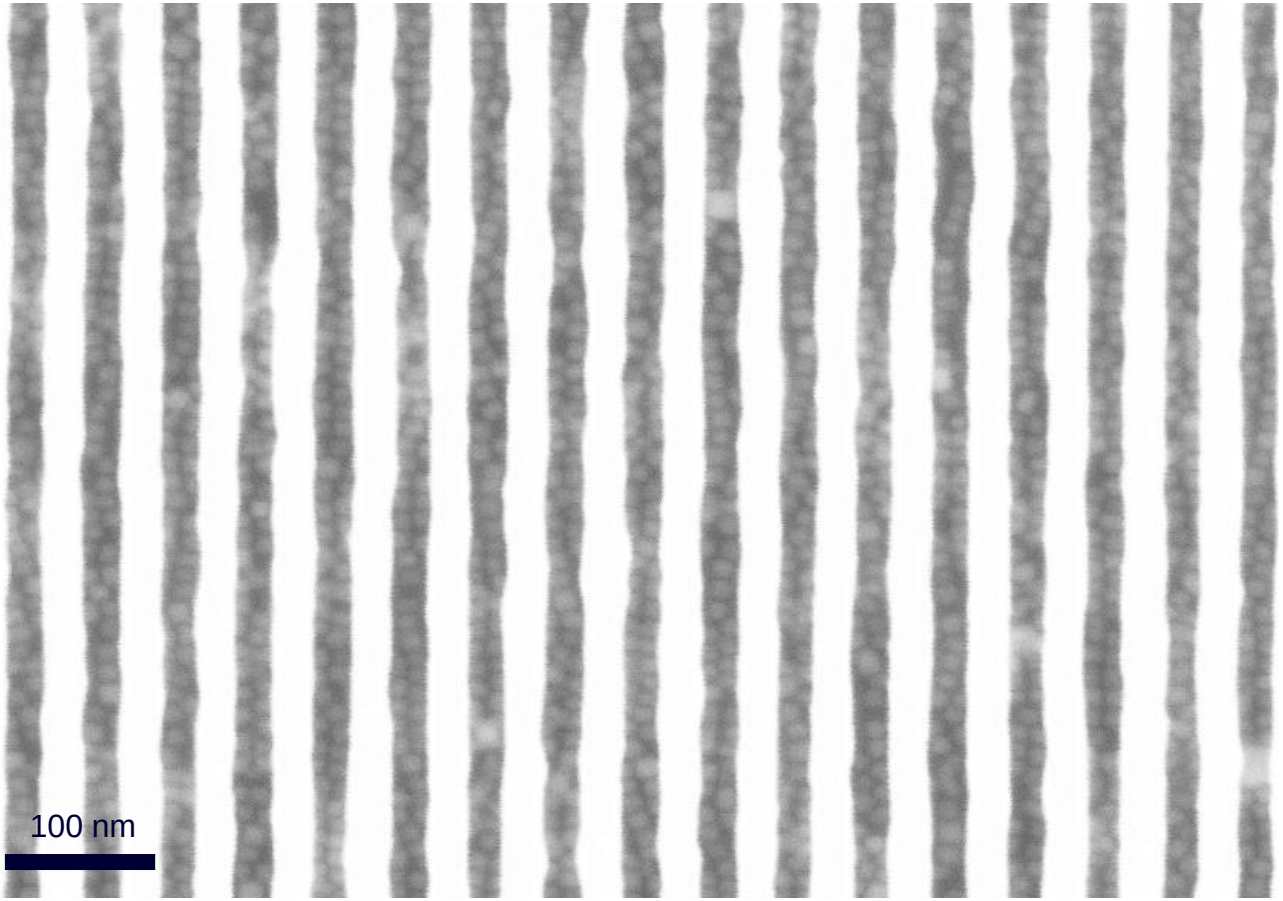
Exciton diffusion length

$L_{diff} = [\sigma^2(\tau) - \sigma^2(0)]^{1/2} = 194$ nm

Sparse sample

MOLECULAR FOUNDRY

Directed assembly of nanocrystals in patterned trenches

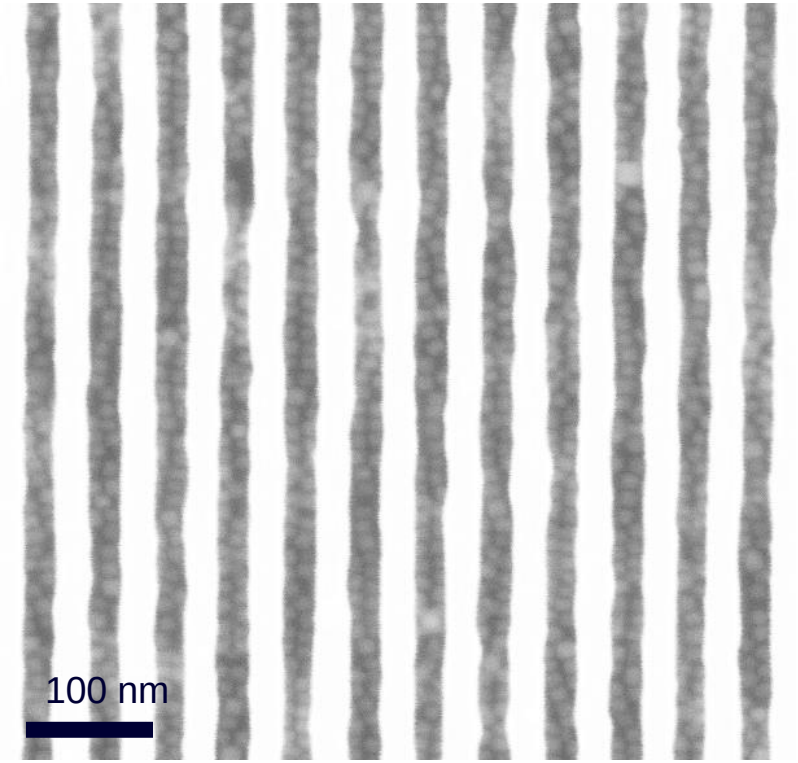


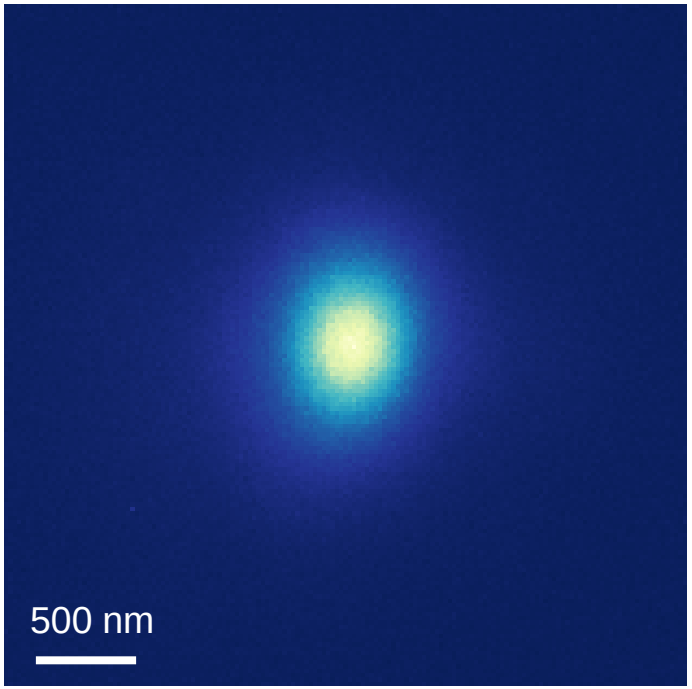
Trench width ≈ 25 nm

Nanocrystals are confined inside the trenches

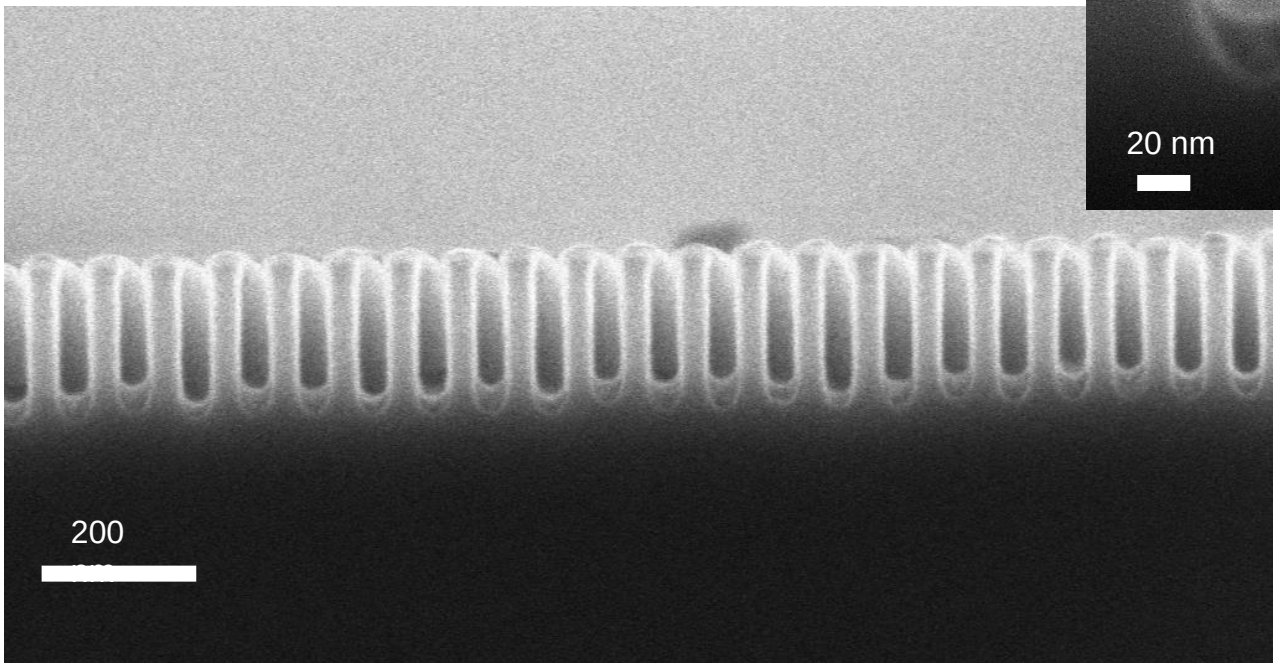
MOLECULAR FOUNDRY

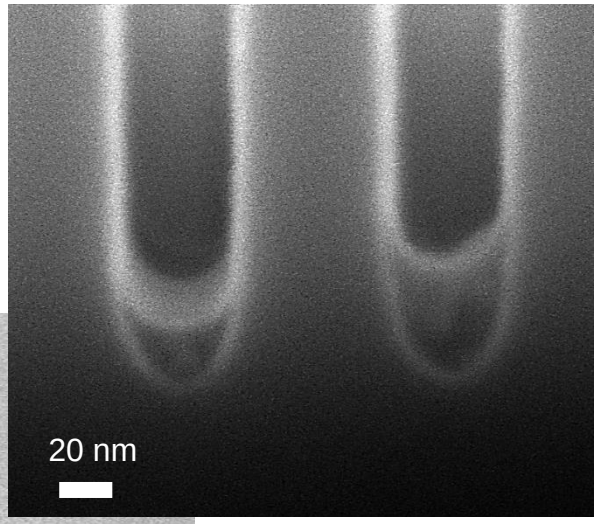
Asymmetric PL of nanocrystals assembled in patterned trenches





Nanocrystals confined inside patterned trenches

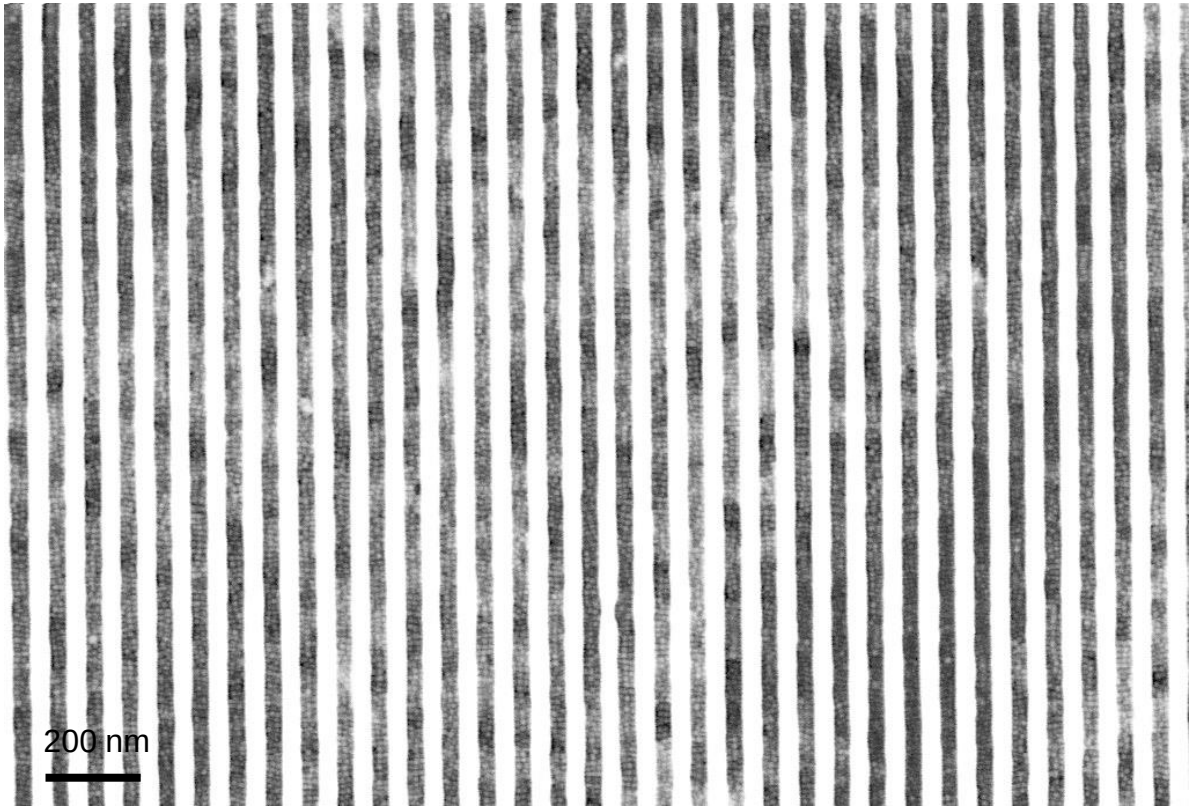


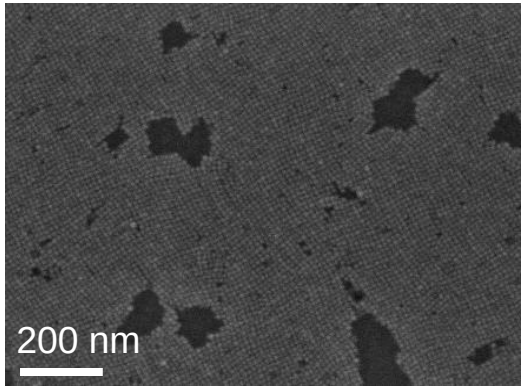


Just a few layers of nanocrystals

MOLECULAR FOUNDRY

Directed assembly extends the range of ordered structures





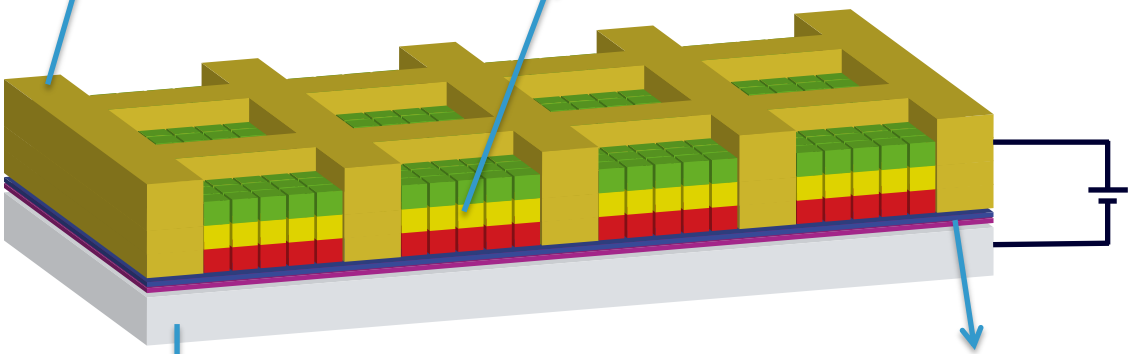
MOLECULAR FOUNDRY

Exciton manipulation: Proposed device

Perovskite quantum dots stacks

- Light absorber
- Guided exciton transport to the TMD heterojunction
- Nanoscale organization minimizes exciton quenching

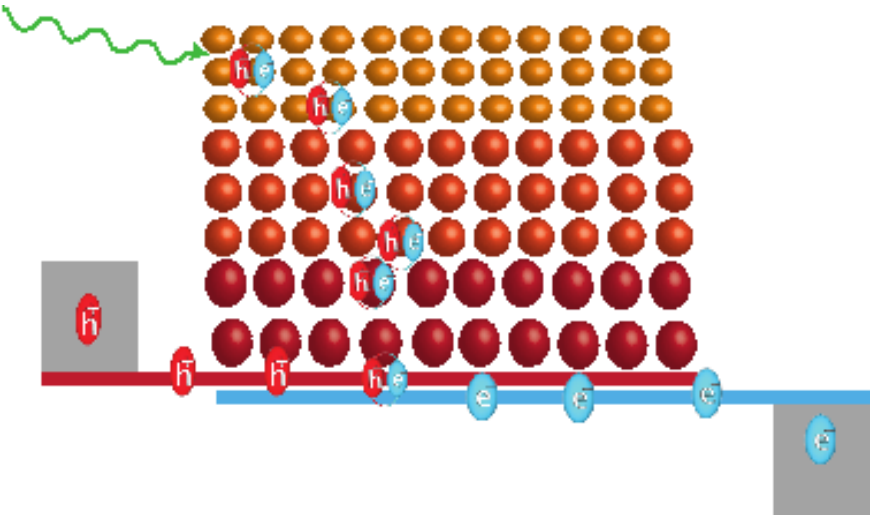
Metal electrode



Transition-metal dicalchogenide (TMD) heterojunction:

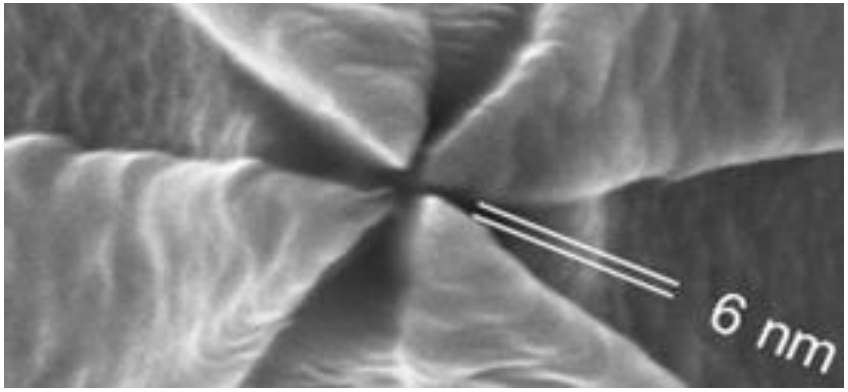
Exciton splitter

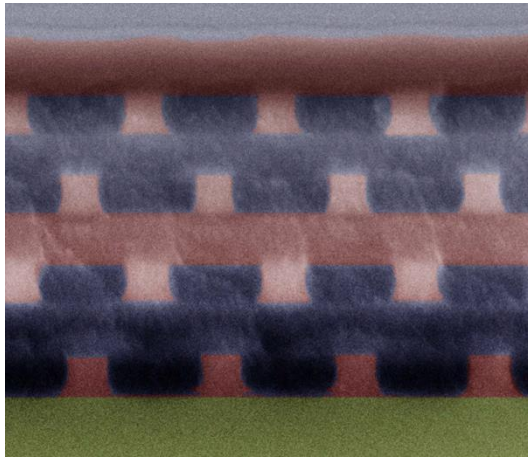
Transparent electrode



- Hierarchically organized stable colloidal quantum dots as highly absorbent antennae
- Foerster Resonant Energy Transfer (FRET) based exciton funnels that move the exitons
- Thin film “reaction” center such as 2-D Transition Metal Dichalcogenide heterojunctions

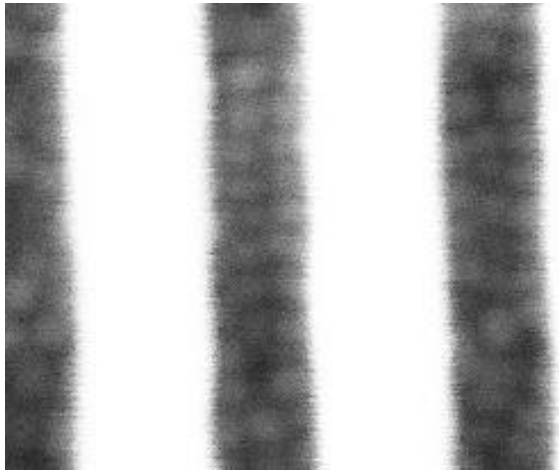
MOLECULAR FOUNDRY





Conclusion

- Molecular Foundry as User Facility for Science at nanoscale
- Organizing material at nanoscale
- Nanofabrication 2D: SDN.
- New opportunities Controlling the patterning in 3D
- Combining top down with bottom up:
  Directed self-assembly of nanoparticles



Acknowledgments

Department of Energy, Office of Basic Energy under contract no. DE-AC02- 05CH11231, DE-C0013109.

And thank you for your attention!

Adam Schwartzberg, Scott Dhuey, Michael Elowson, Simone Sassolini, Erika Penzo, Deirdre Olynick, Stefano Dallorto, Alex Weber Bargioni, Ed Barnard, Nicholas Borys, Matthew Jurow

Keiko Munechika, Aleks Koshelev, Giuseppe Calafiore, Andy Goodyear , Mike Cooke, Craig Ward , Ivo W. Rangelow, Daniel Staaks