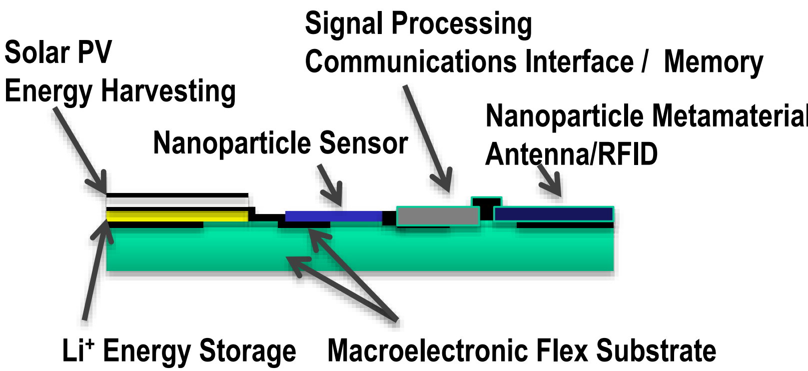
Functional Hybrid Materials using Additive-Driven Self Assembly and Nanoimprint Lithography: Towards Solution Based Nanomanufacturing



Jim Watkins
Center for Hierarchical Manufacturing – NSF NSEC
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University of Massachusetts, Amherst




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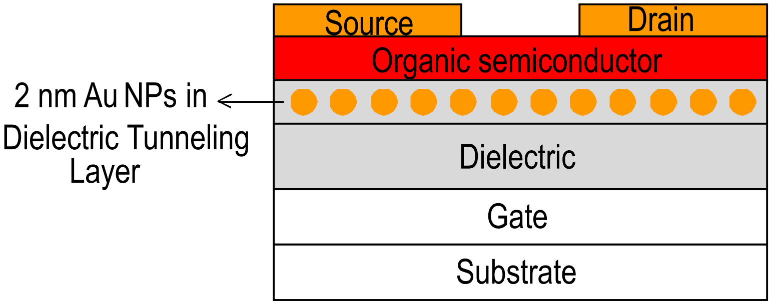
Today's Discussion

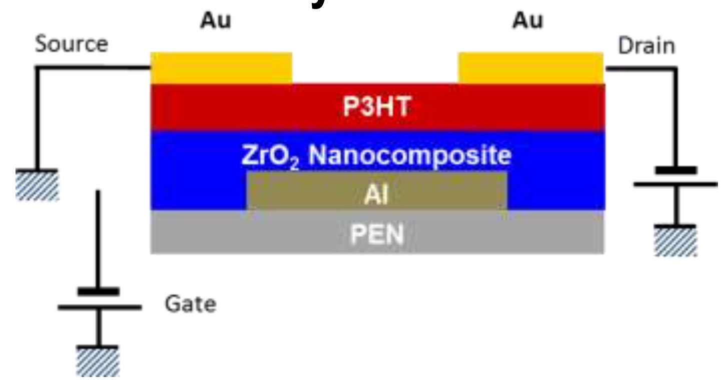
- A Few Target Devices and Designs
- Scalability and Transitions to Roll-to-Roll
- Printing "Intelligent" Devices: Is it Possible?
- Imprint Lithography for Functional Nanostructures
  (polymers/hybrids/crystalline metal oxides/metals)
- Additive Driven Self-Assembly for Functional Materials
- The Center for Personalized Health Monitoring and the New
  Advanced Print and Roll-to-Roll Manufacturing Demo Facility at UMass

Target Devices and Device Layers from Our Lab

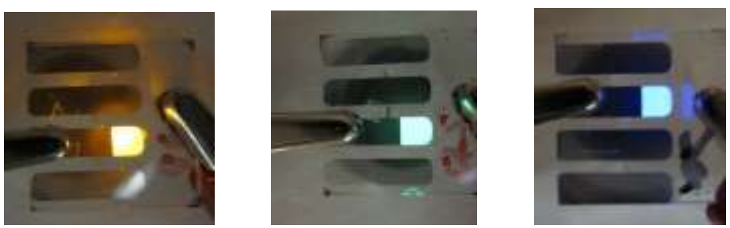
Printed Electronics / Memory



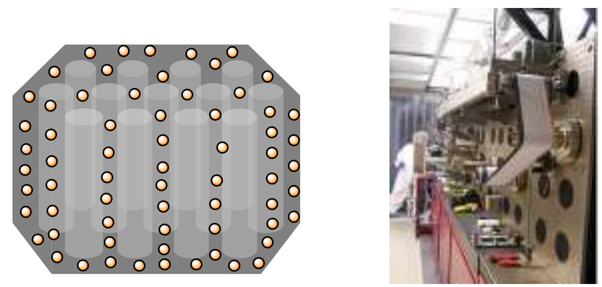
NP/Polymer Dielectrics



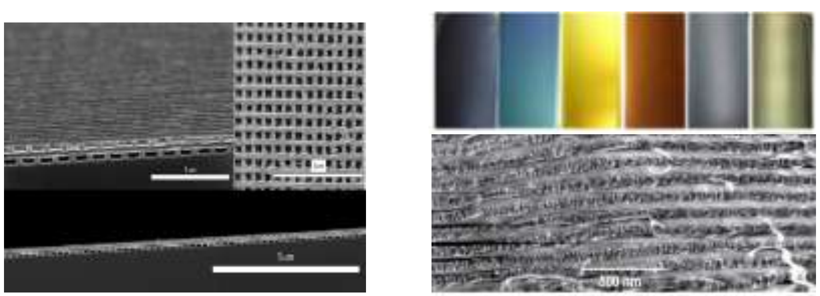
QD-Based LECs



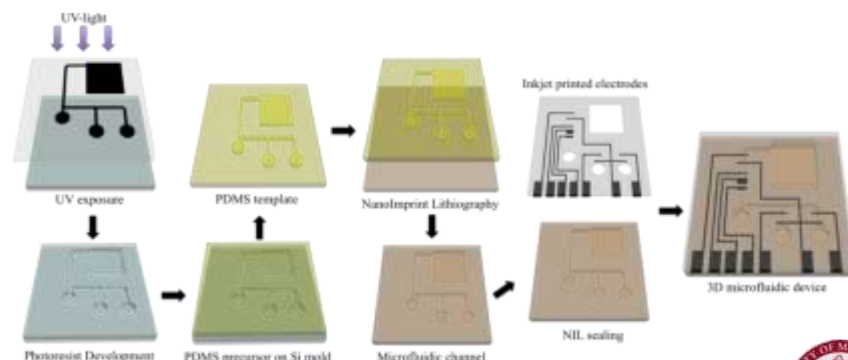
Nanostructured SuperCaps and Batteries



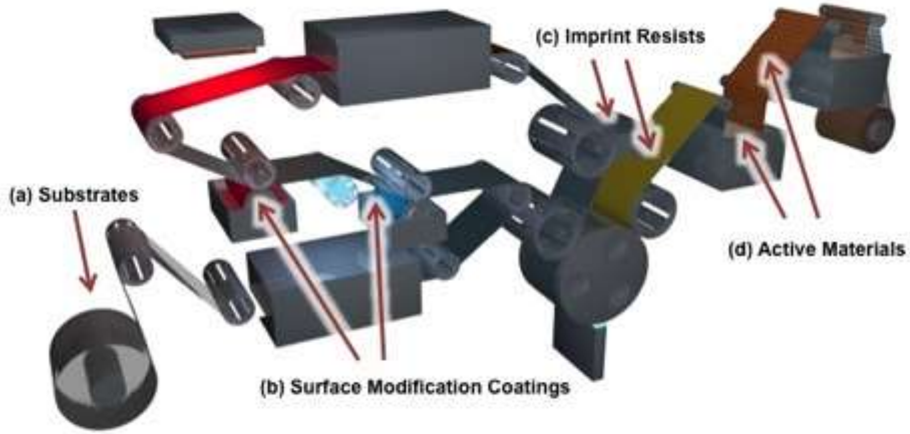
Photonics

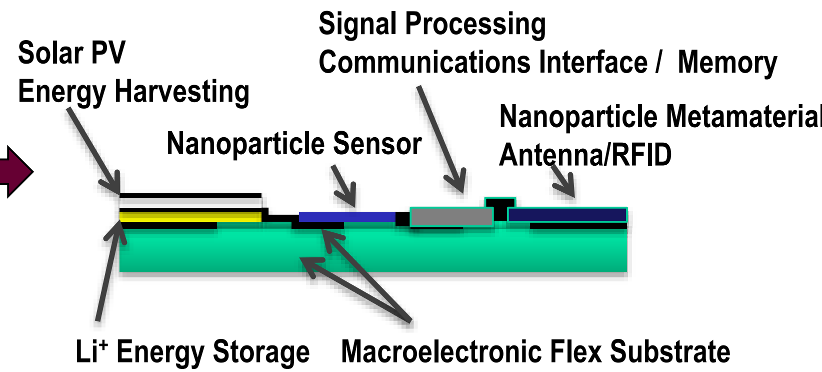


Printed Microfluidic Biosensors



One Solution: Low-Cost Capable Devices by Combining Printed Electronics and Nanostructured Device Layers



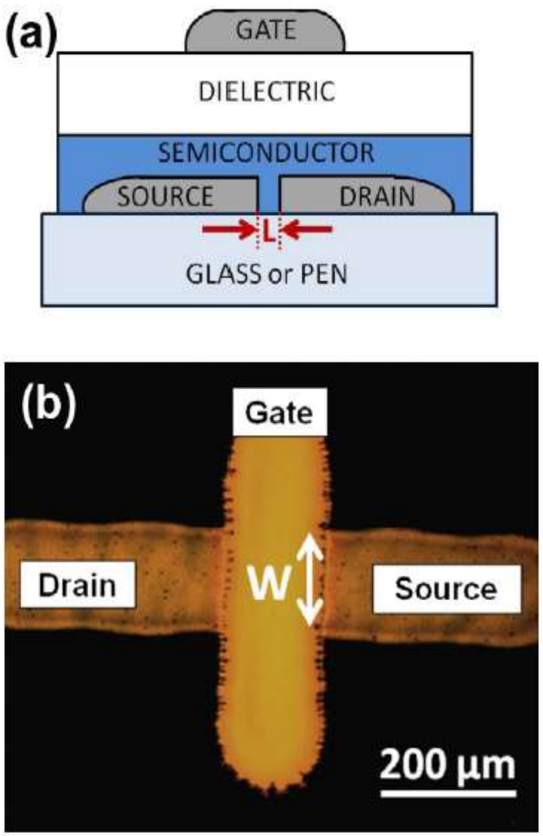


Challenges include:

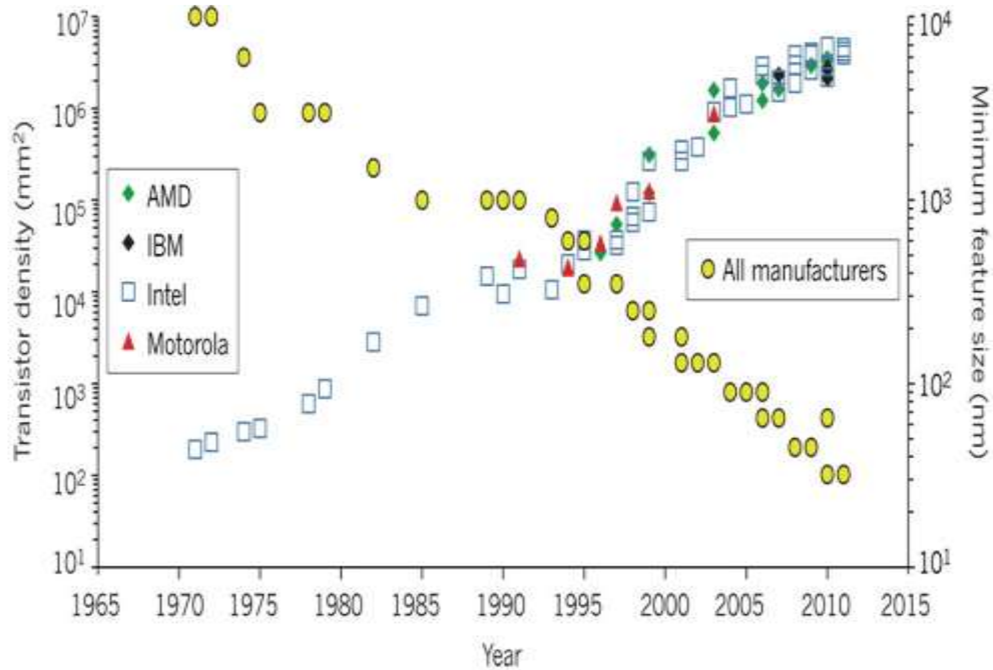
1. Materials (mobility, lifetime, tune-able μ, ε, n)
2. Strategies for incorporation of inorganic device layers
3. Solution and additive-based processing
4. Increased integration density (smaller feature size)
5. Improved layer-to-layer dynamic alignment
6. Manufacturing tools and demonstration facilities

Next Generation Printed Electronics: One Fundamental Challenge is Integration Density

Ink Jet Printing / Laser Anneal



10s of Micron CDs = Pre 1970s Electronics



Microelectronic Engineering 111 (2013) 242–246

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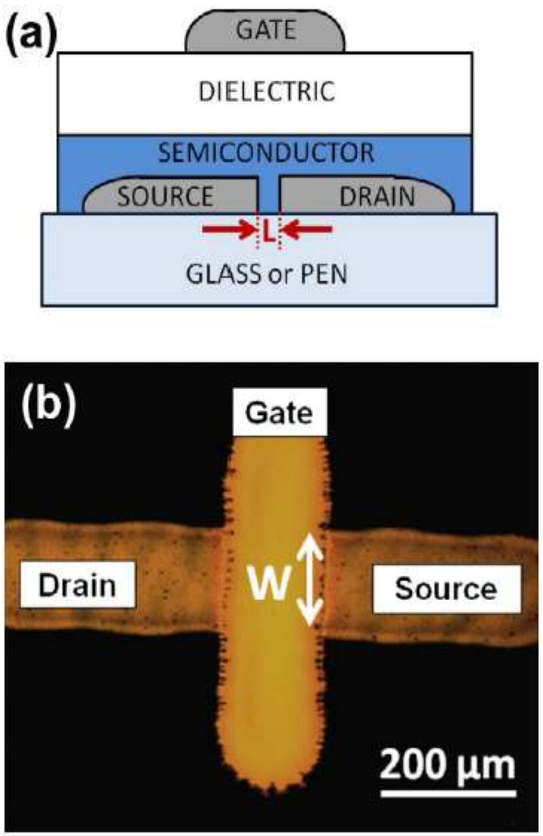
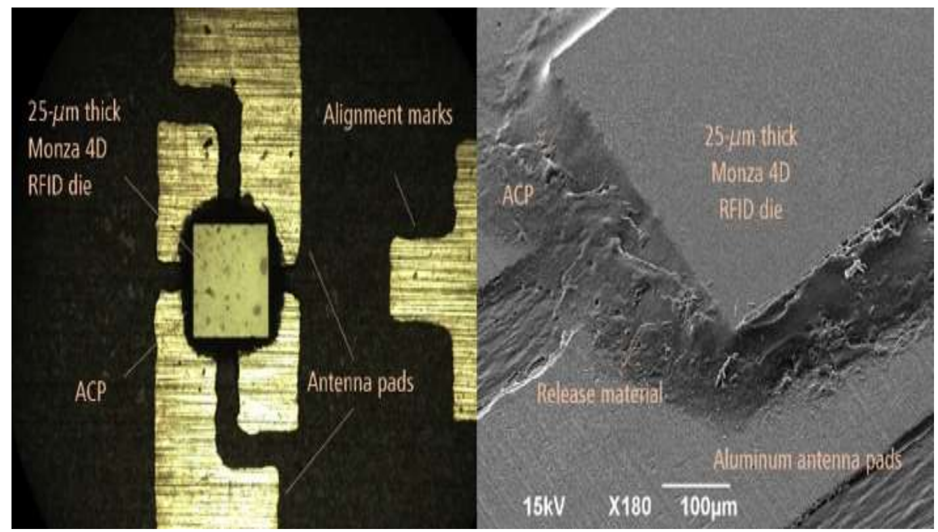
Next Generation Printed Electronics: One Fundamental Challenge is Integration Density

Ink Jet Printing / Laser Anneal



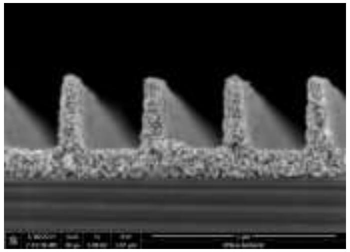
Near Term Issue: Sub-50 micron Contacts for Hybrid Integration

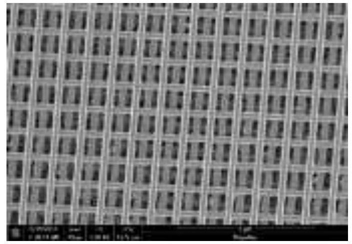


Microelectronic Engineering 111 (2013) 242–246

Our Tool Box: Materials, Device Layers, and Approaches

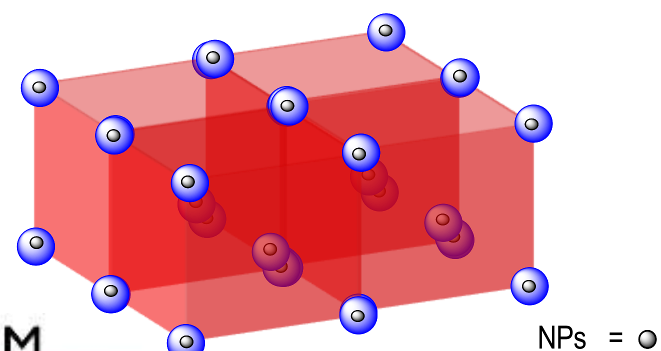
Nanoimprint Lithography Revisited: Direct "Printing" of 2-D and 3-D Hybrid and Inorganic Nanostructures



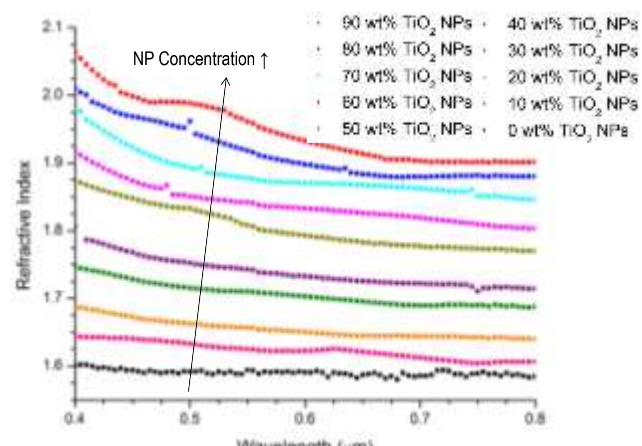


Scalability: (R2R NIL, Ink Jet/Photonic, Hybrid Coating, Pick and Place, more)

Periodic Nanocomposites and Metamaterials by Self-Assembly



Tunable Hybrid Materials



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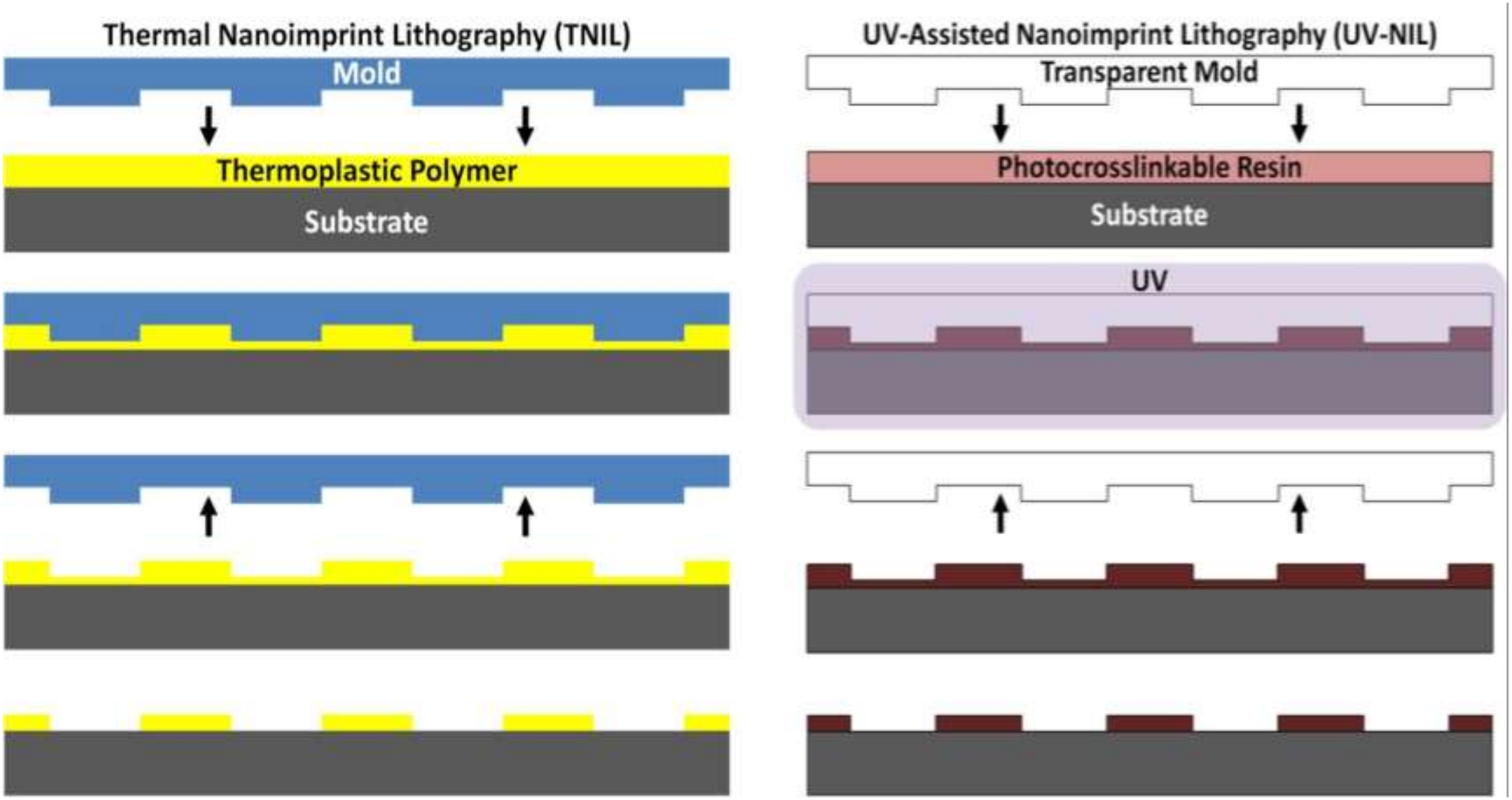
Nanoimprint Lithography: Two Modes

Thermal: Emboss thermoplastic or thermoset using heat, pressure

UV-Assisted: Contact UV-curable resin with master, photocure



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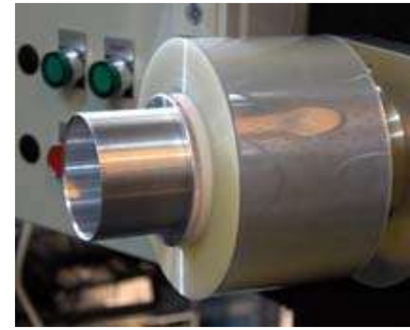
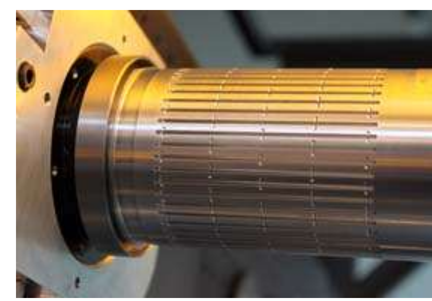
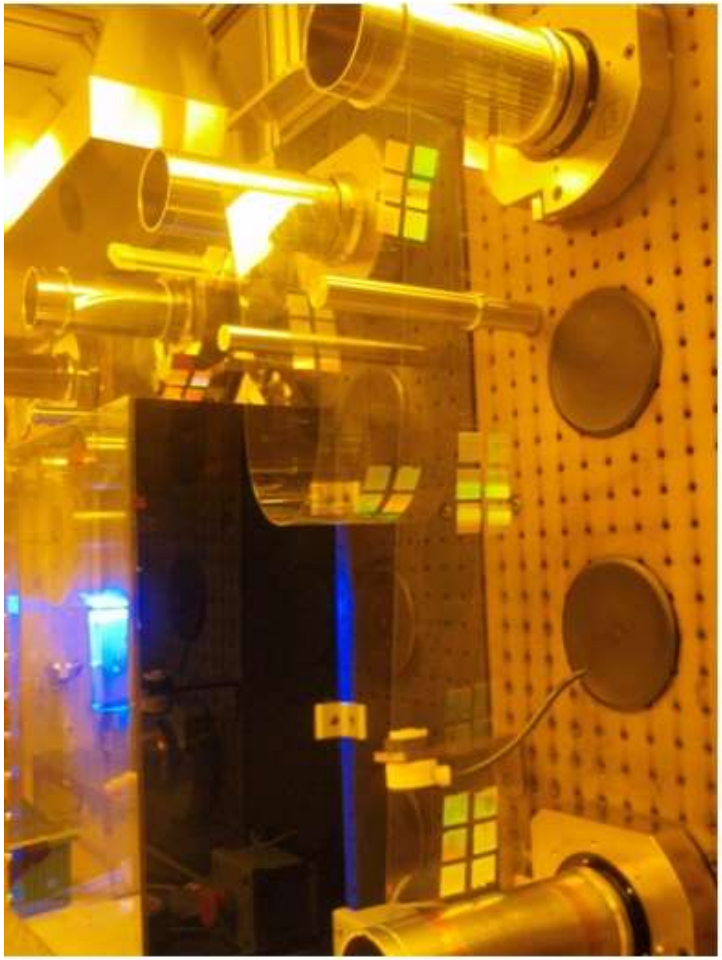
UMass / CHM R2R NIL Tool

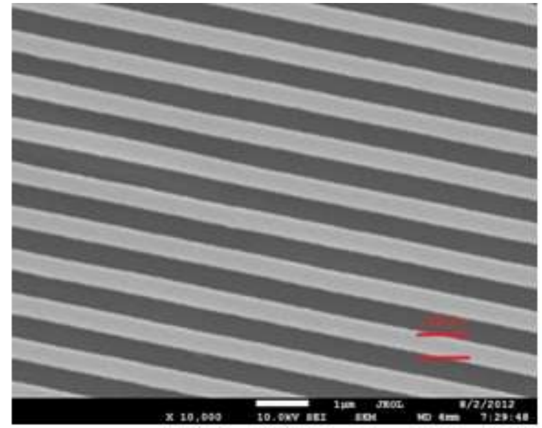
UMass NANOemBOSS R2RNIL constructed with Carpe Diem Technologies (Franklin, MA)
Profs. Ken Carter and Jonathan Rothstein Test Bed Coordinators



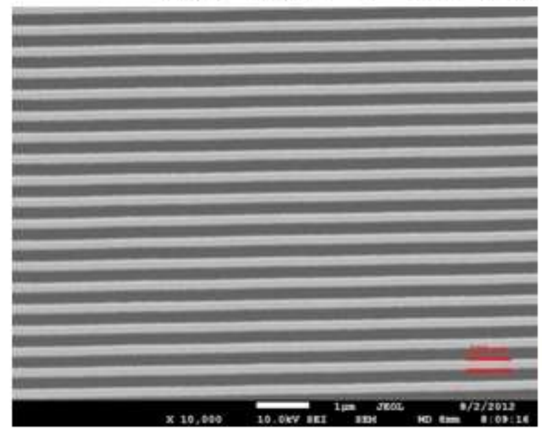


R2RNIL – 500 nm to Sub-100 nm Gratings

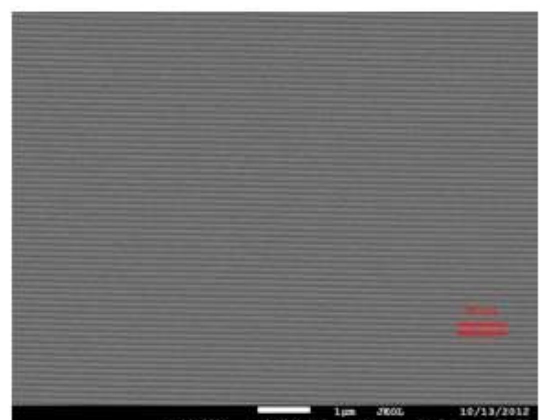




500 nm



230 nm



70 nm

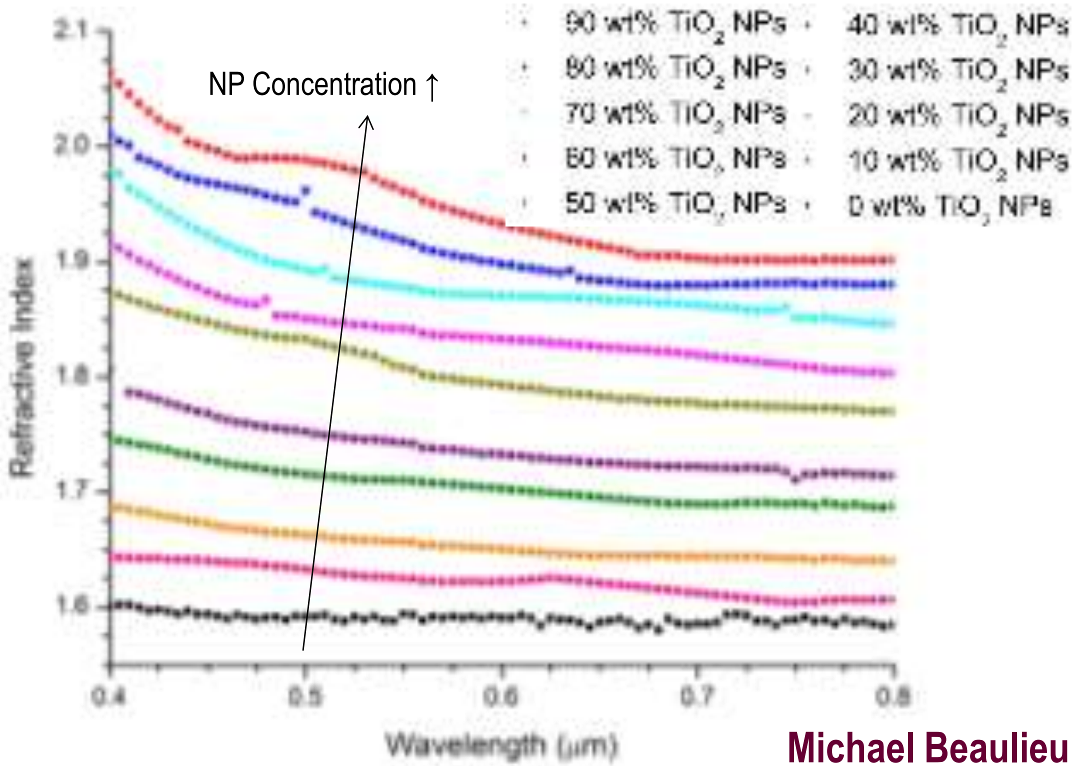
John, Tang, Rothstein, Watkins,, Carter *Nanotechnology*, **2013**,

NIL - Intermediate Assessment

- NIL Offers Very High Pattern Resolution
- R2R NIL Offers High Rate Continuous Patterning
- Current NIL Resists Offer Limited Functionality
- Can We Imprint Directly into Useful Materials?

Polymer / TiO_2 NP Hybrid Resists with Tunable Refractive Index

- Anatase NPs 5-25 nm / smooth films
- RI Measured with VASE, films thicknesses 150 nm to 350 nm
- RI Manipulation with Excellent Transparency
- RI Matching for Transparent Composites / RI Tuning for Light Management



Michael Beaulieu et al., ACS Photonics 2014

% TiO_2 Nanoparticles	50	60	70	80	90
RMS (nm)	5.41	5.10	4.85	4.70	4.97

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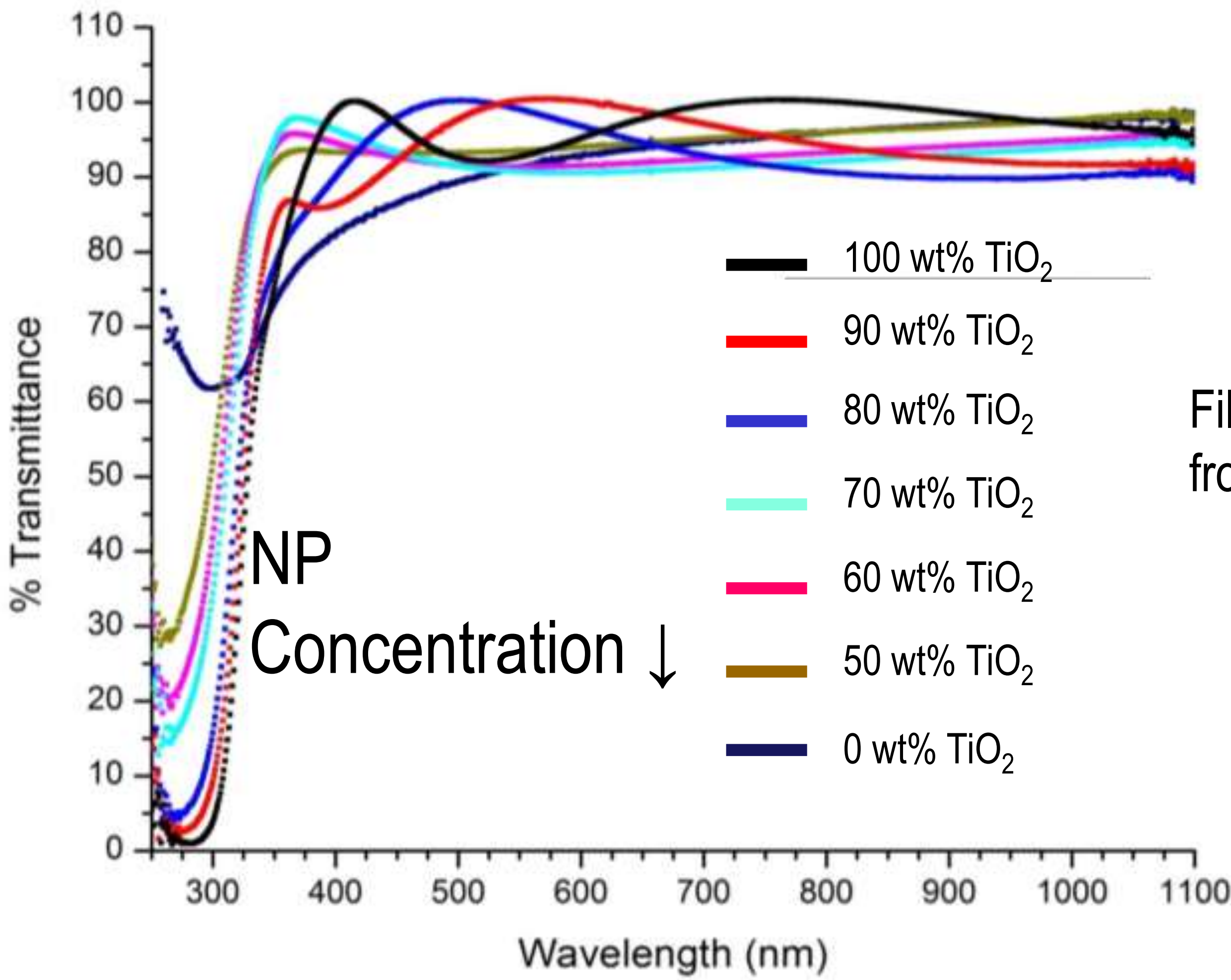
Transmittance of Planar Nanocomposites

- The planar nanocomposite films are greater than 90% transparent from 400 nm to 800 nm

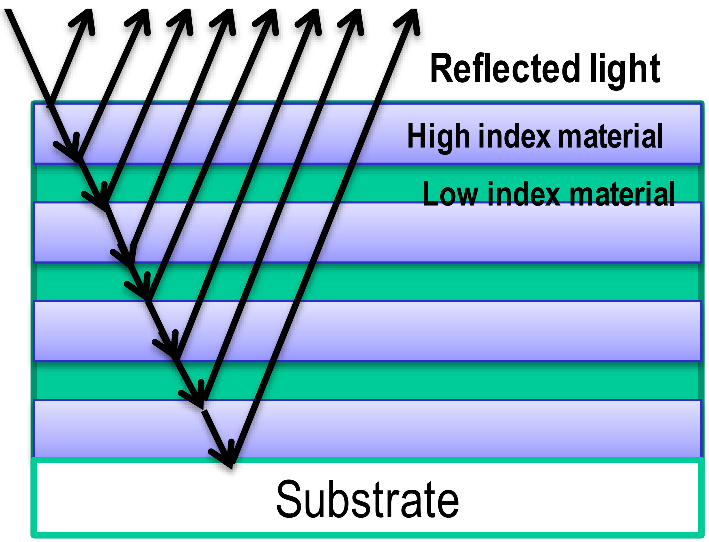
.



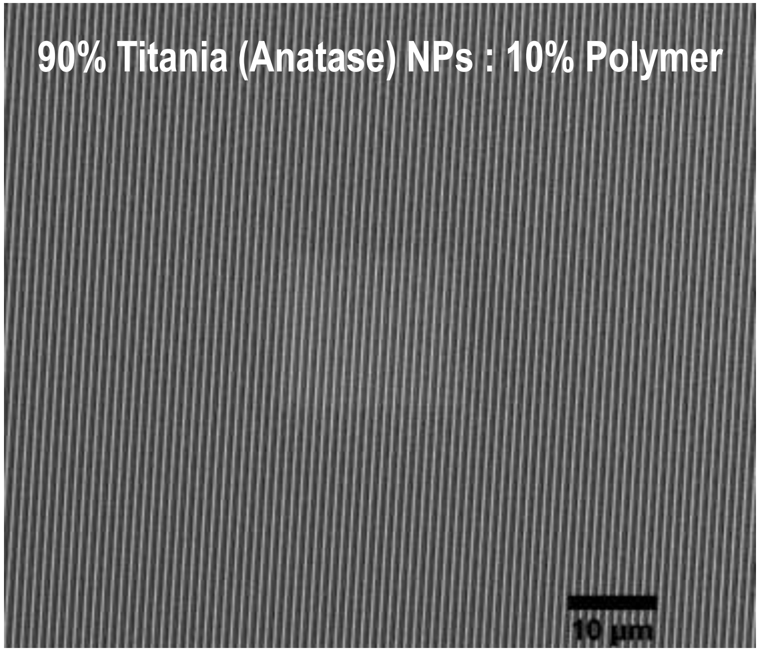
Film thickness ranged from 200 nm to 400 nm.

Solution Coatable Patterned and Planar Hybrid Device Layers
Example: Tuned Material Properties, Patterns by Nanoimprint Lithography

Wavelength Selective Bragg Mirrors



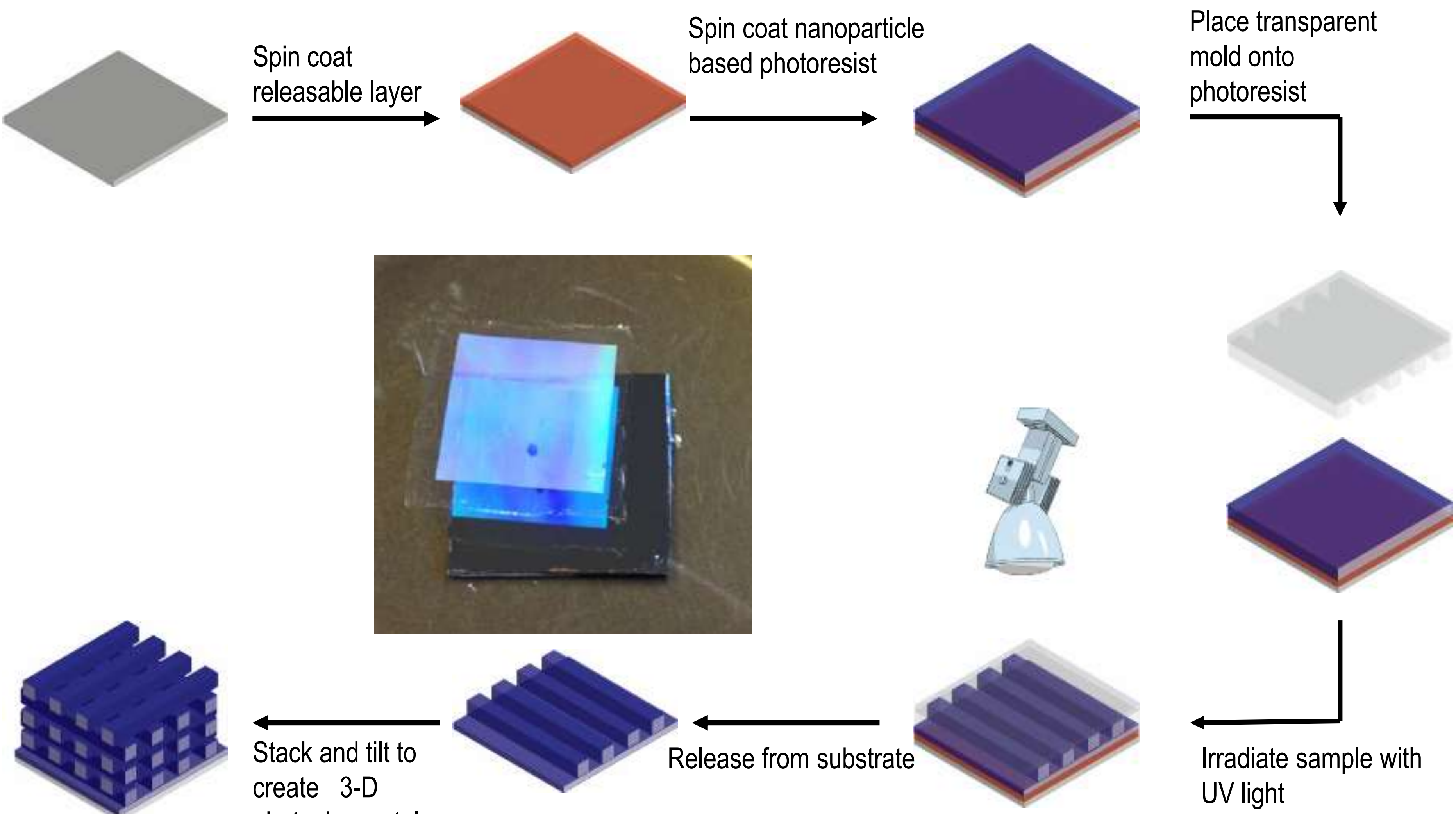
NIL Patterning of Composites



U.S. Appl. 13/900,248

We can create, coat and pattern smooth polymer/NP and NP films
Ranging from 100% polymer to 90% stabilized NPs
metal oxides/high k /high RI / low RI
Crystalline NPs / structures –Low Temperature Processing

3-D Patterning of Nanocomposites
Print-Lift-Turn-Stack



(Beaulieu, M. R et al., ACS Photonics 2014)

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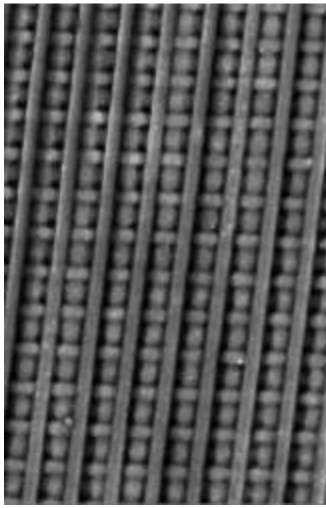
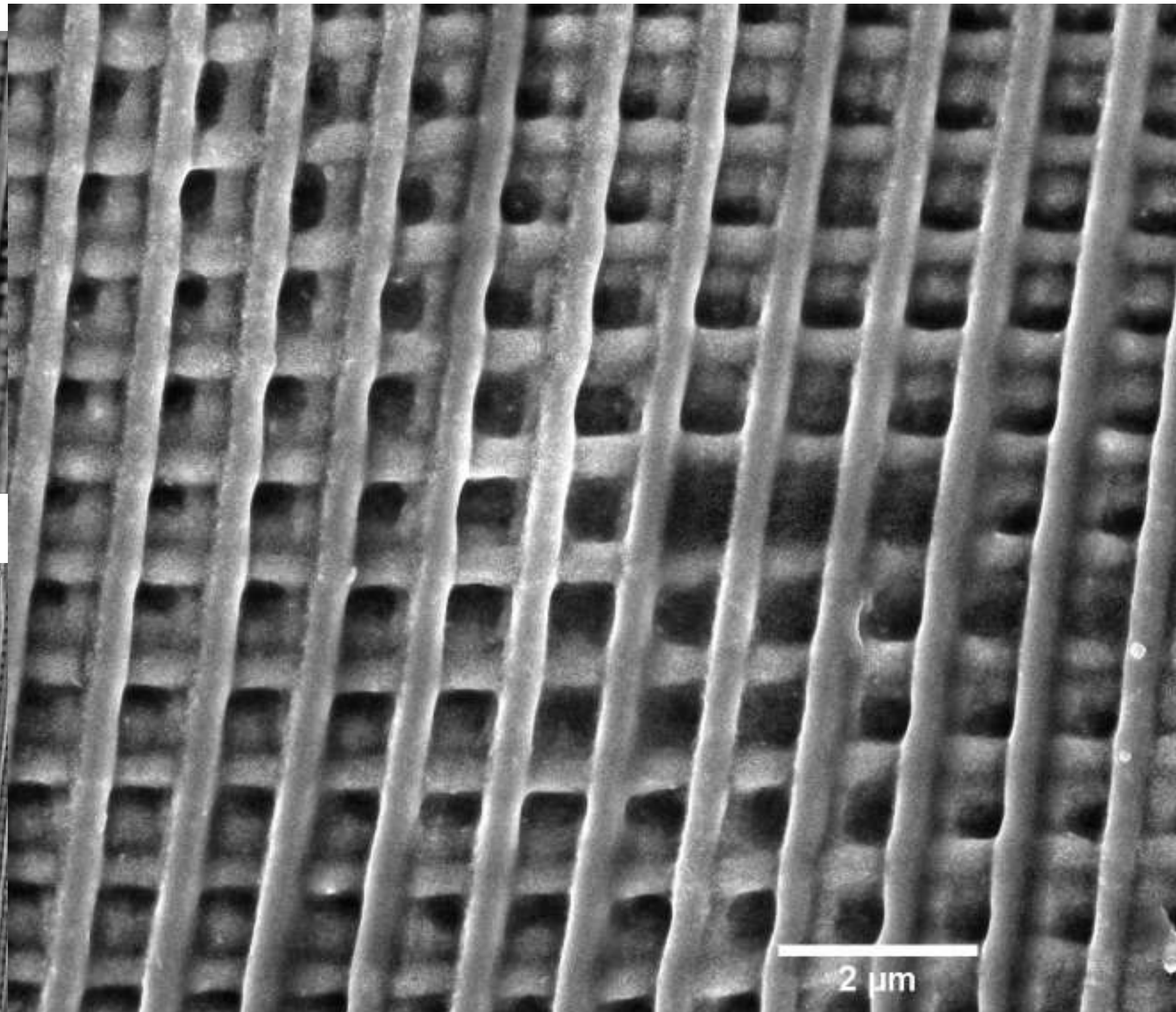
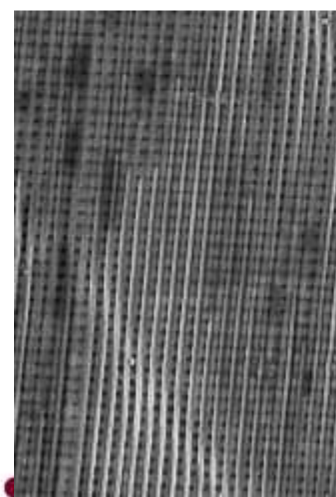
3D Patterning: Tetralayer

- SEM Images: 50% TiO_2, 50% NOA60



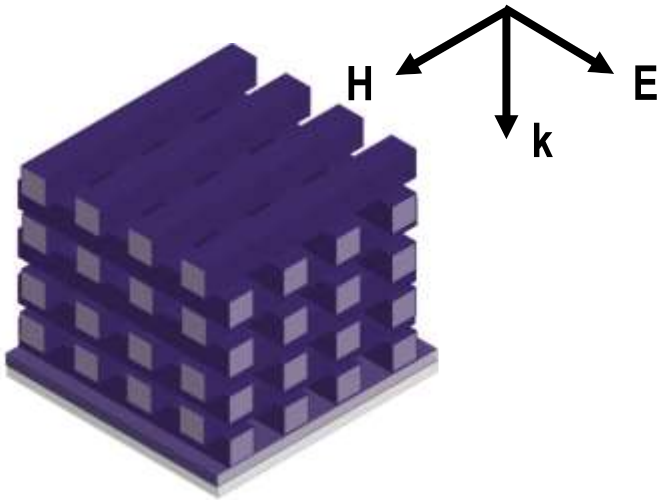




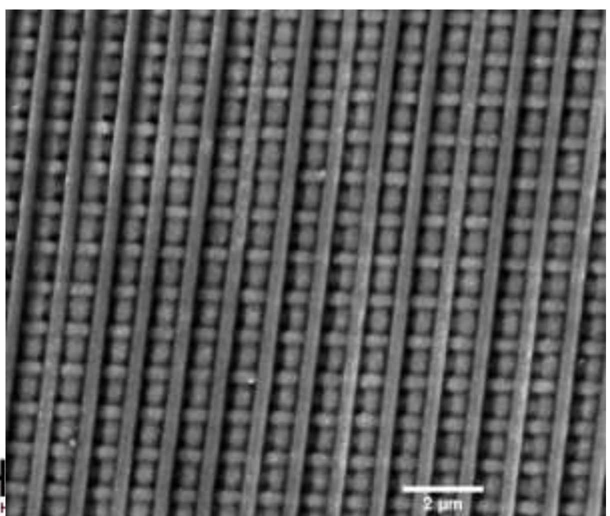
Printable Photonic Log Pile Structures

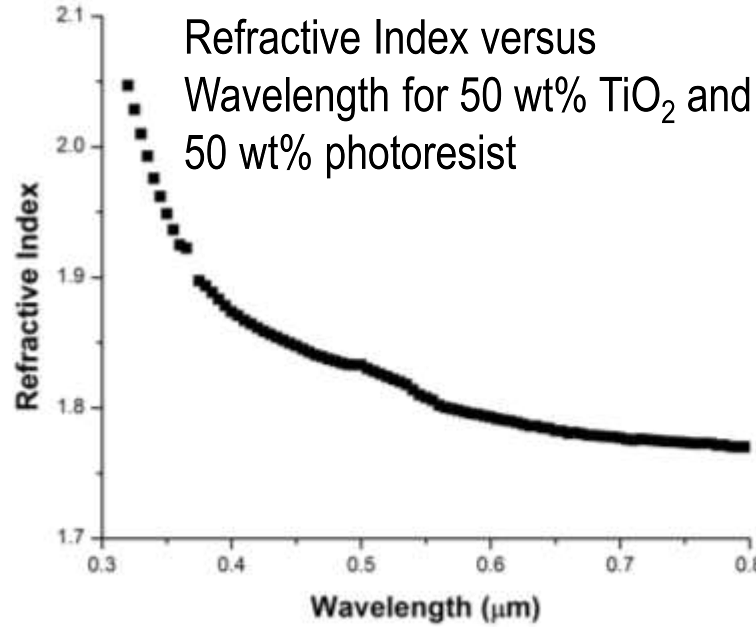
(Beaulieu, M. R et al., ACS Photonics 2014)

6-layer Photonic crystal made from 50 wt% anatase TiO_2 nanoparticles and 50 wt% photoresist

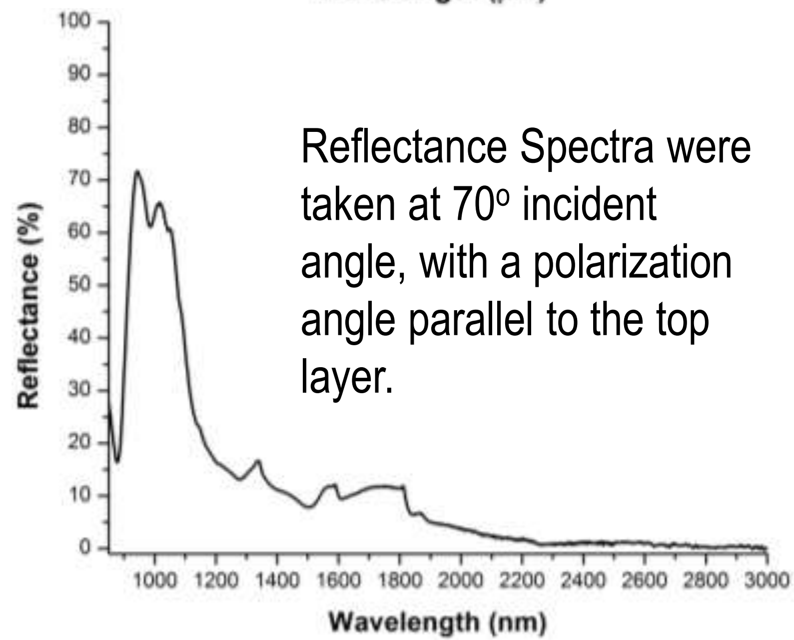


Top Down SEM View





Refractive Index versus Wavelength for 50 wt% TiO_2 and 50 wt% photoresist

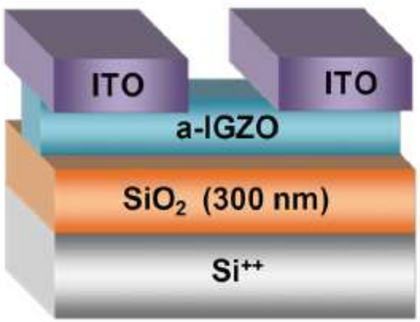


Reflectance Spectra were taken at 70° incident angle, with a polarization angle parallel to the top layer.

CH

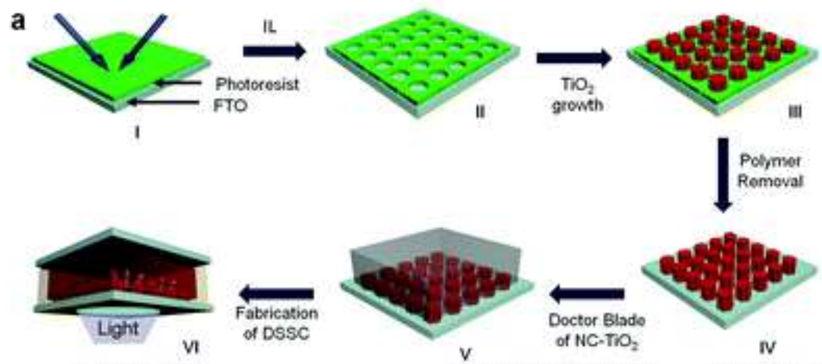
Direct Imprinting of Patterned Metal Oxides Nanostructures

Patterned ITO for transistors



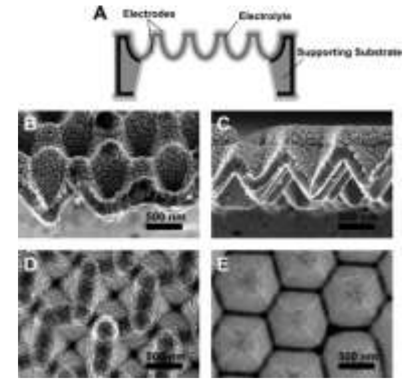
ACS Appl. Mater. Interfaces 2012, 4, 1614−1619

Patterned TiO_2 for solar cells



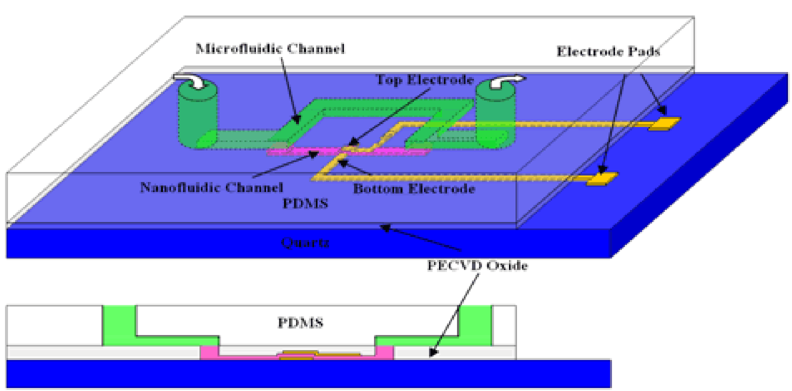
Nanoscale, 2012, 4, 4464

Patterned YSZ for SOFC

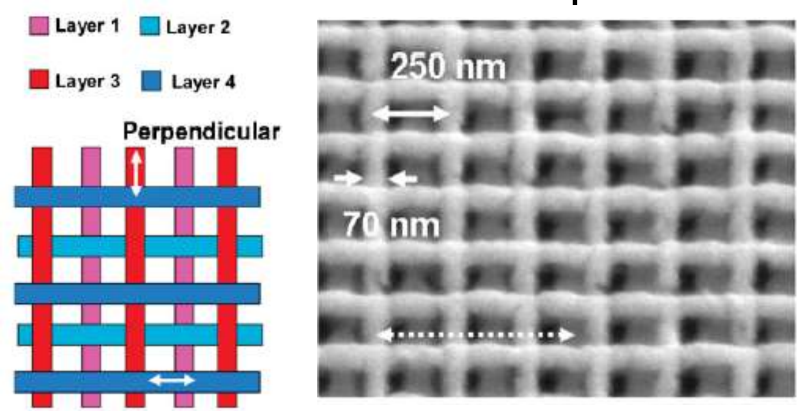


ACS Nano, 2011, 5, 5692-5696

Patterned electrodes for nanofluidics



Patterned dielectrics for photonic devices



Adv. Mater. 2010, 22, 487–491

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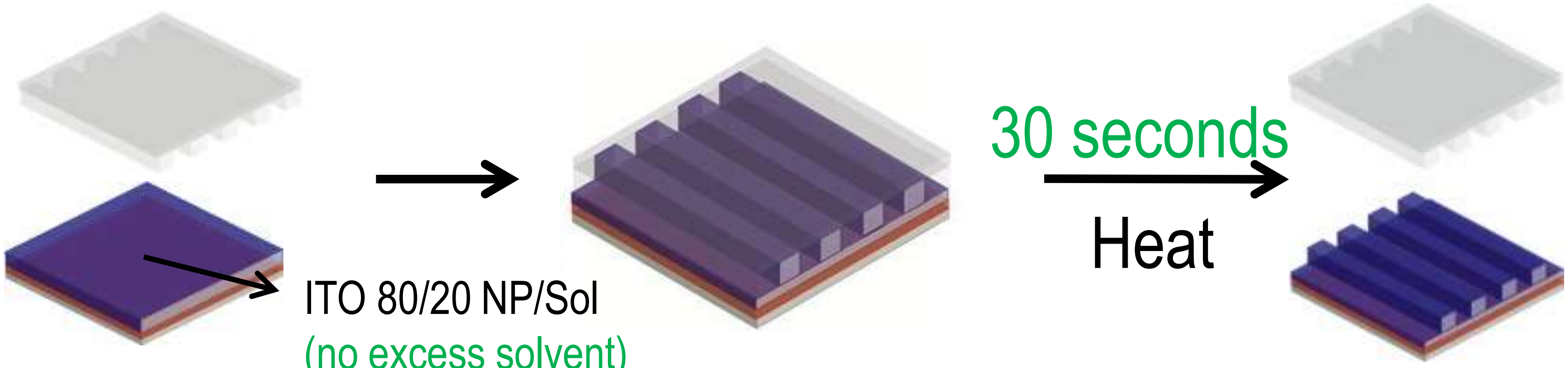
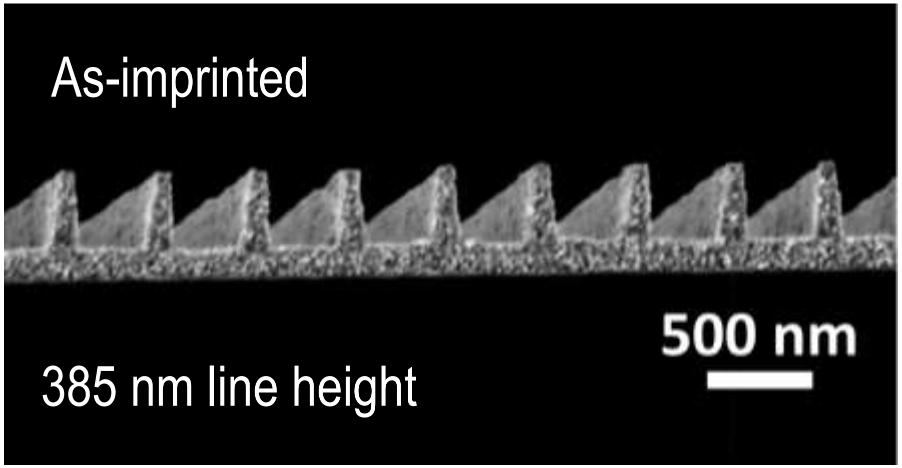
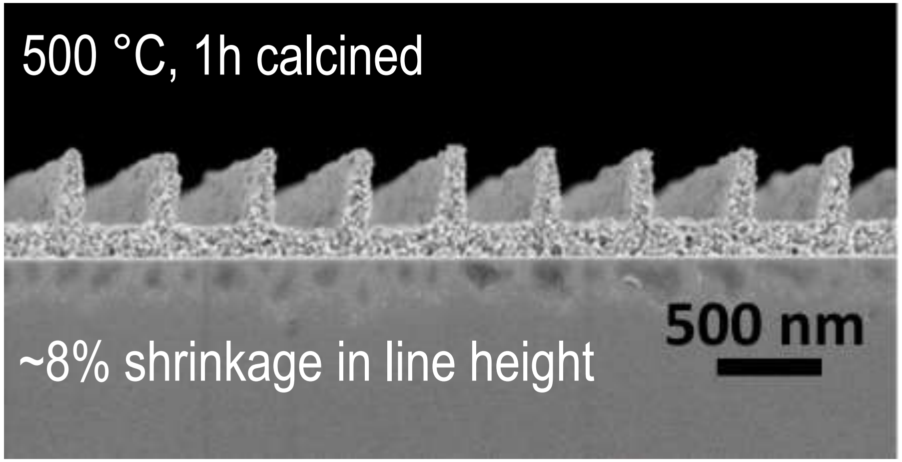
http://www.personal.psu.edu/sjf2/

Direct Imprinting of ITO NP/Sol Ink







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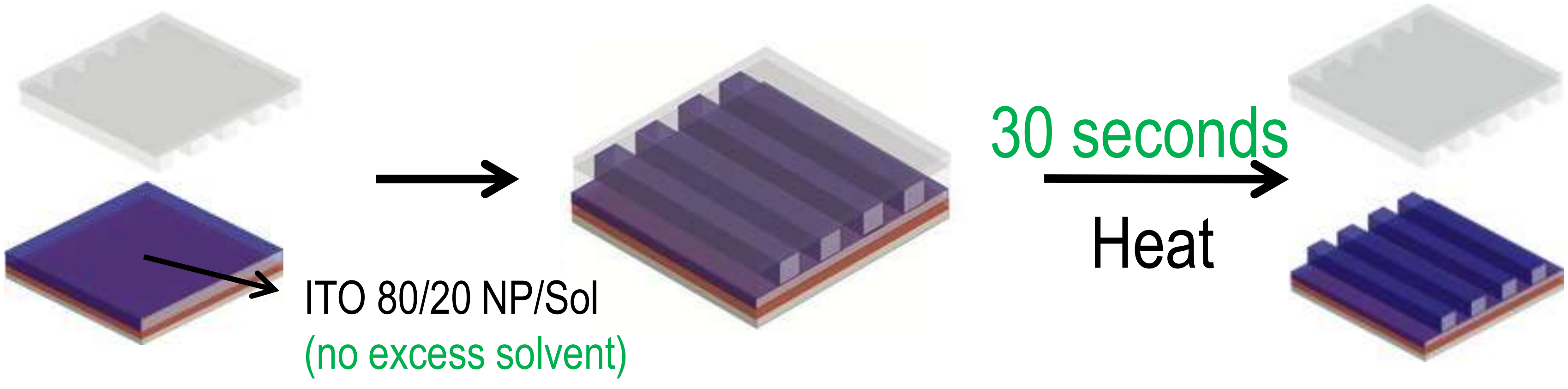

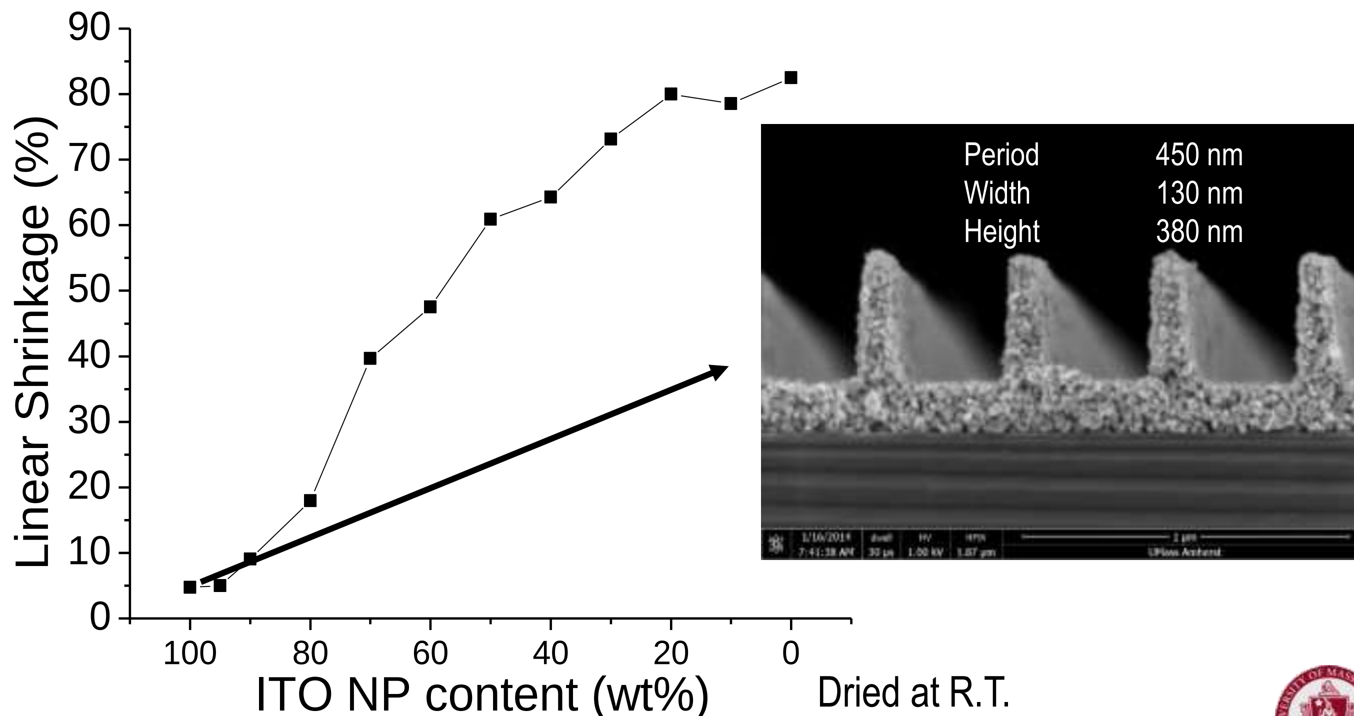

Dried at R.T.
Calcined at 500 °C

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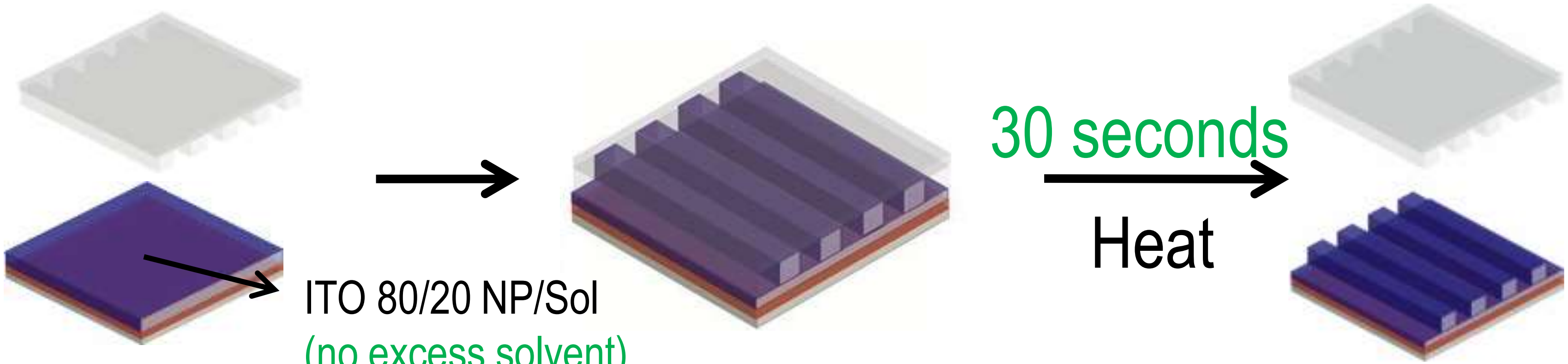
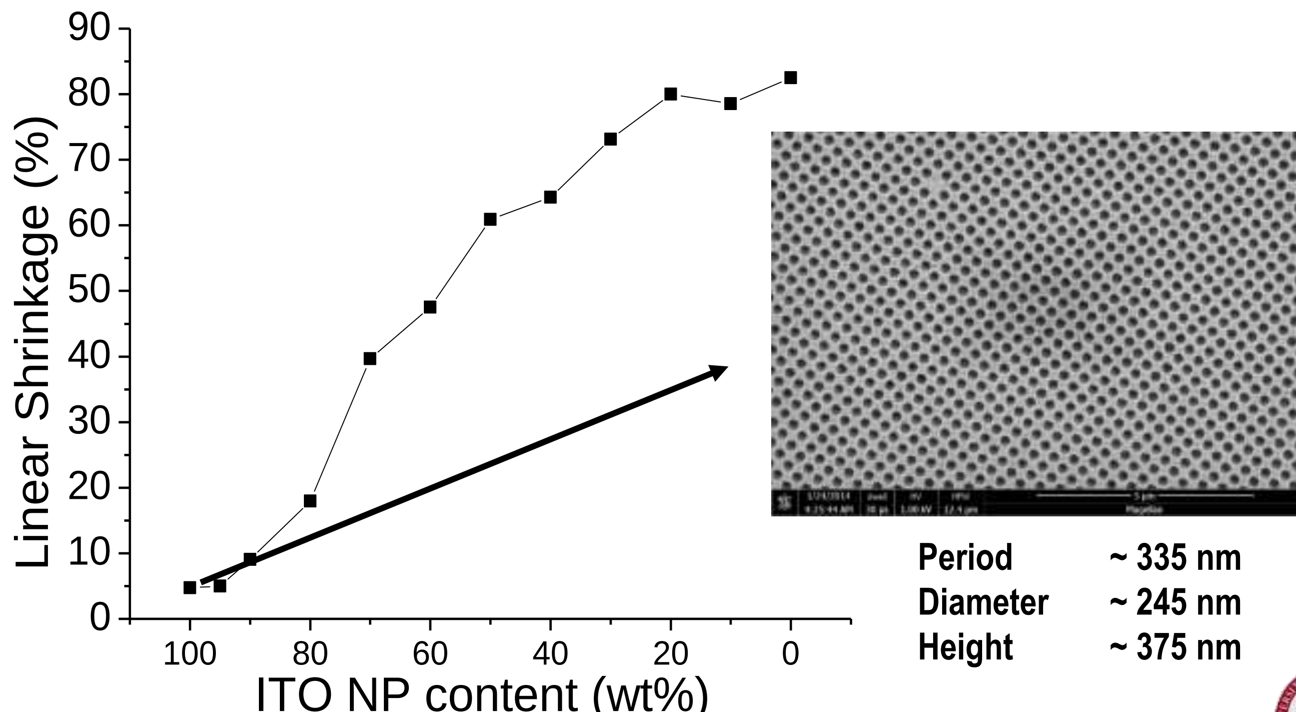
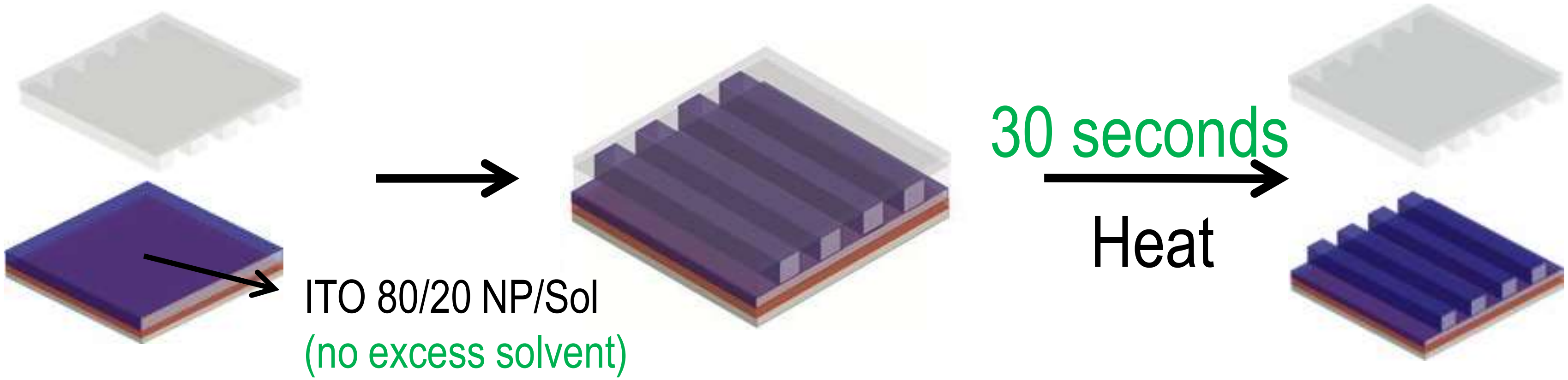
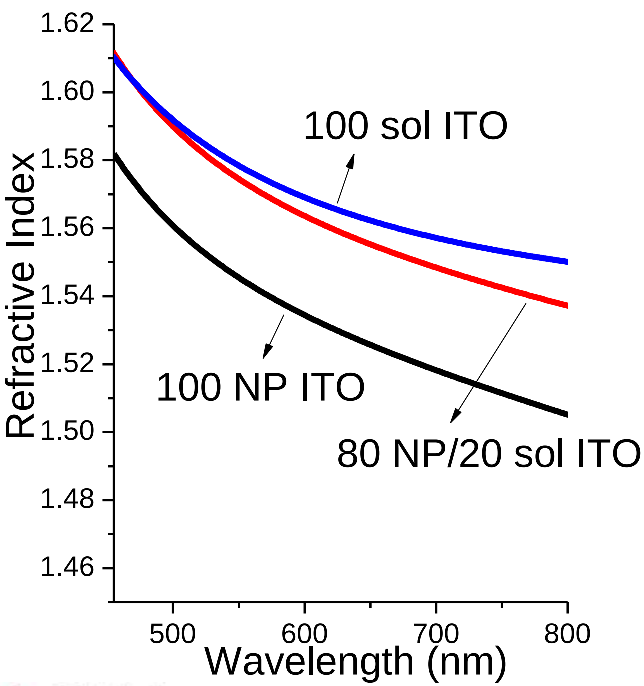
Direct Imprinting of ITO NP/Sol Ink

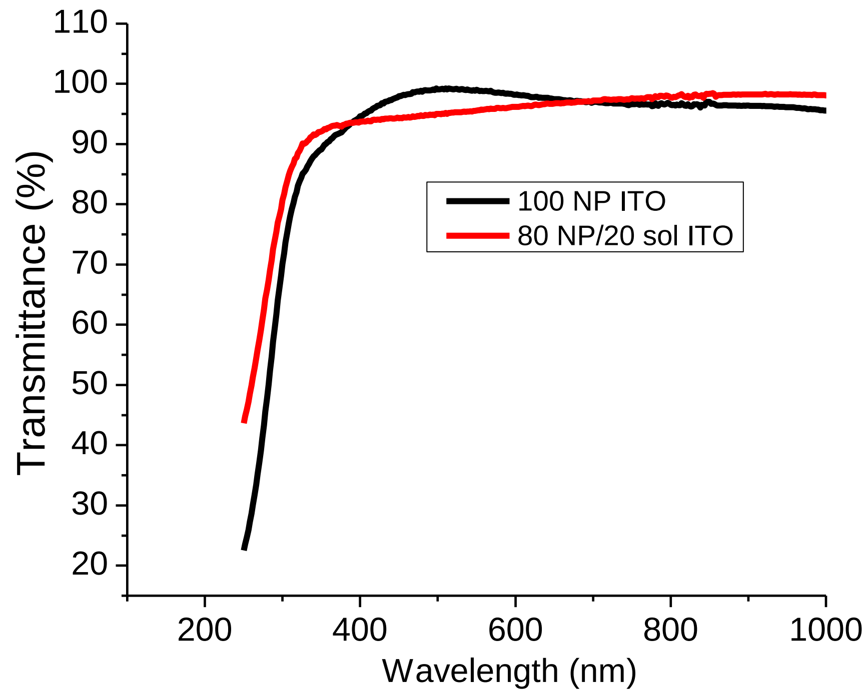




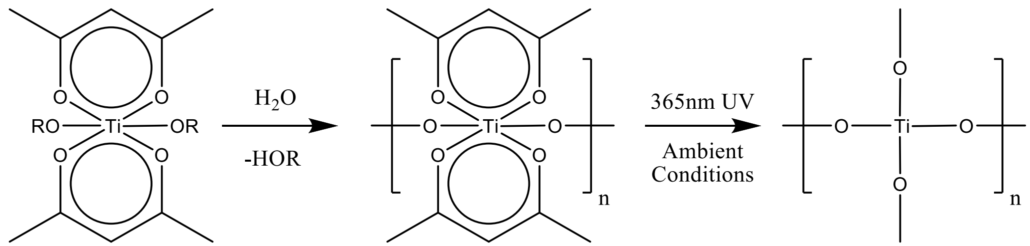
Direct Imprinting of ITO NP/Sol Ink





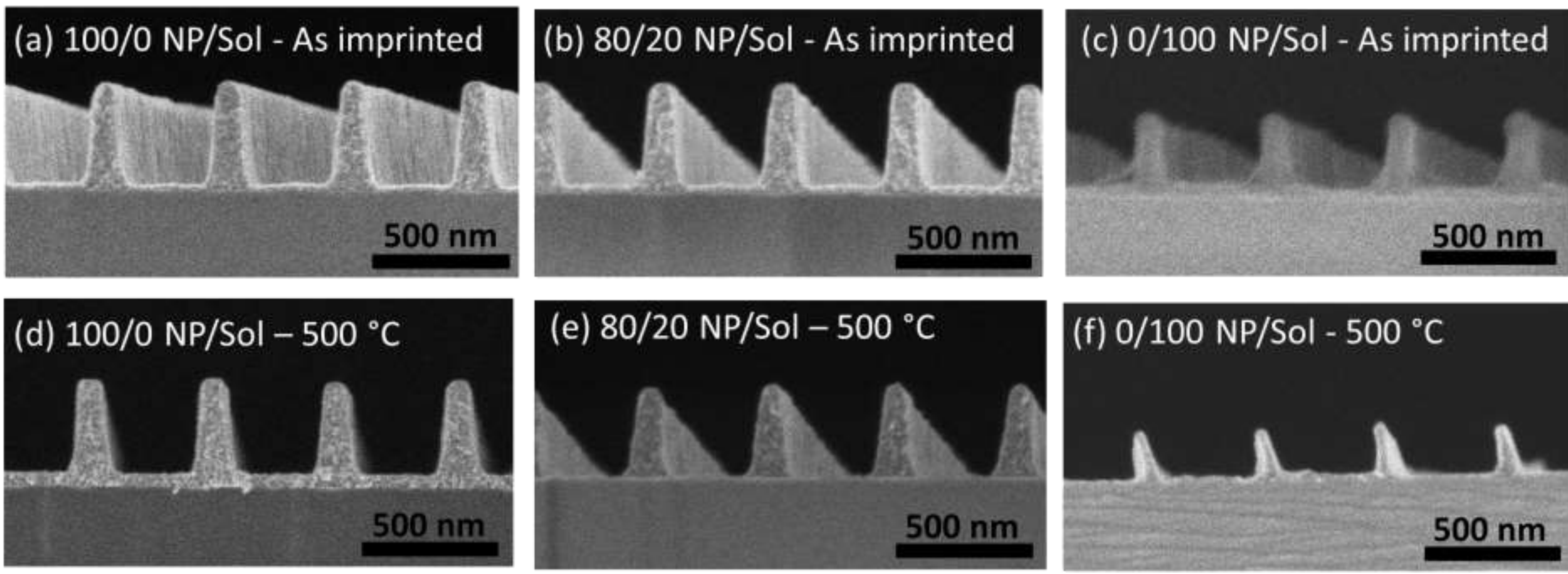


Soft-nanoimprinting of TiO_2 Nanostructures



TiO_2 nanoparticles (anatase)

UV curable TiO_2 sol-gel precursor



5% Shrinkage

11% Shrinkage

50% Shrinkage

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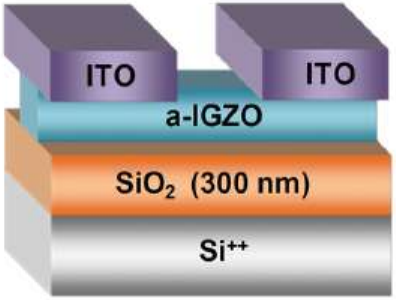
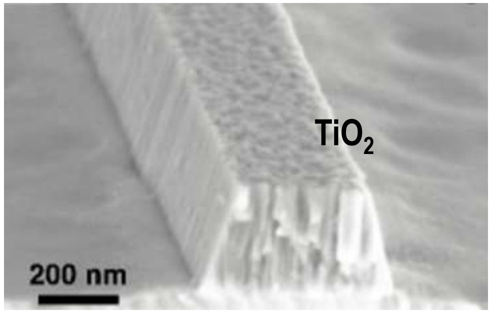
Is Residual-layer Free Imprinting for Device Fabrication Possible?

Printed Transistors



ACS Appl. Mater. Inter. **2012**, *4*, 1614

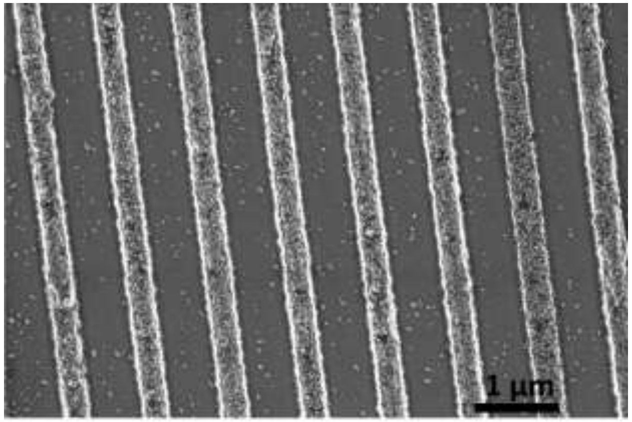
Waveguides by E-beam and Etch



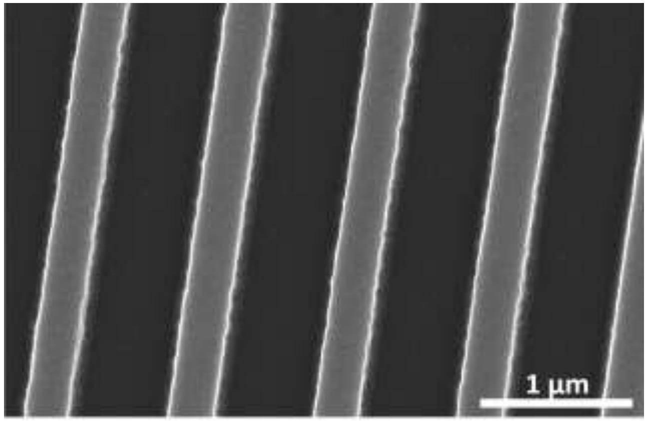
Optics Express **2012**, *20*, 23821

Yes, Isolated Metal Oxide Lines

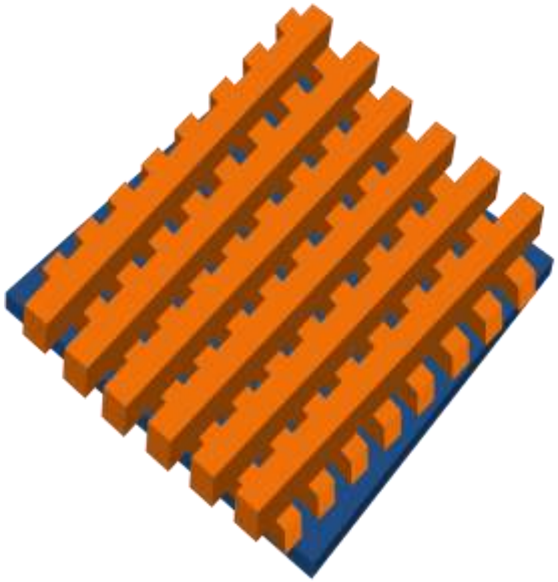
ITO

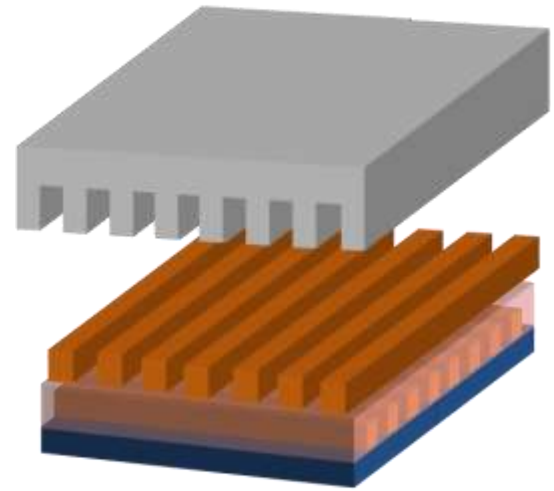


TiO_2

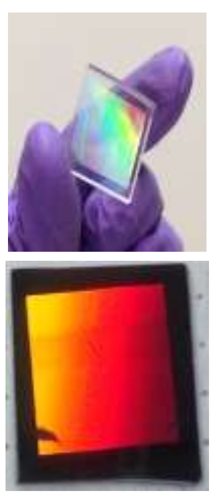


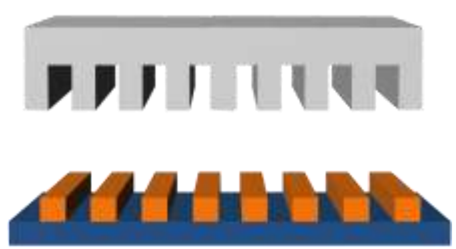
All Inorganic 3D Nanoimprinting





3D inorganic metal oxide nanostructures





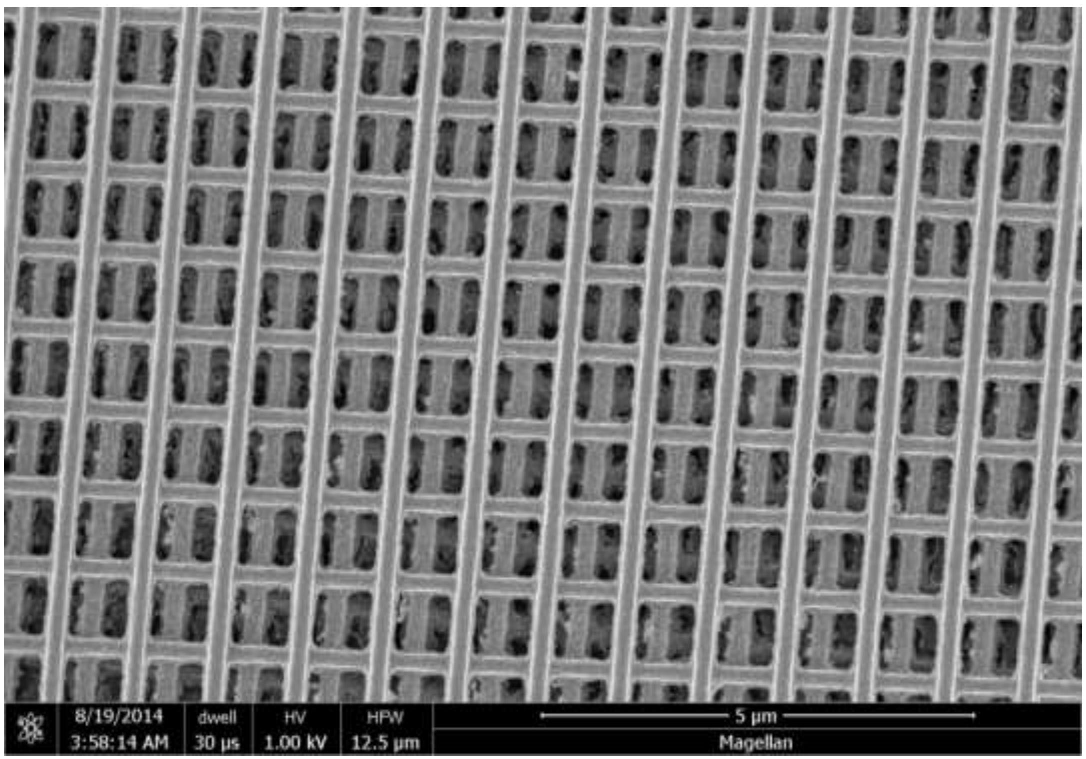
Planarized using crosslinkable polymer

R. Khotari, I. Howell

Layer by Layer Printing of Crystalline Metal Oxides

Pattern TiO_2 using NIL → Planarize using polymers

Remove planarizing layer at the end by calcination



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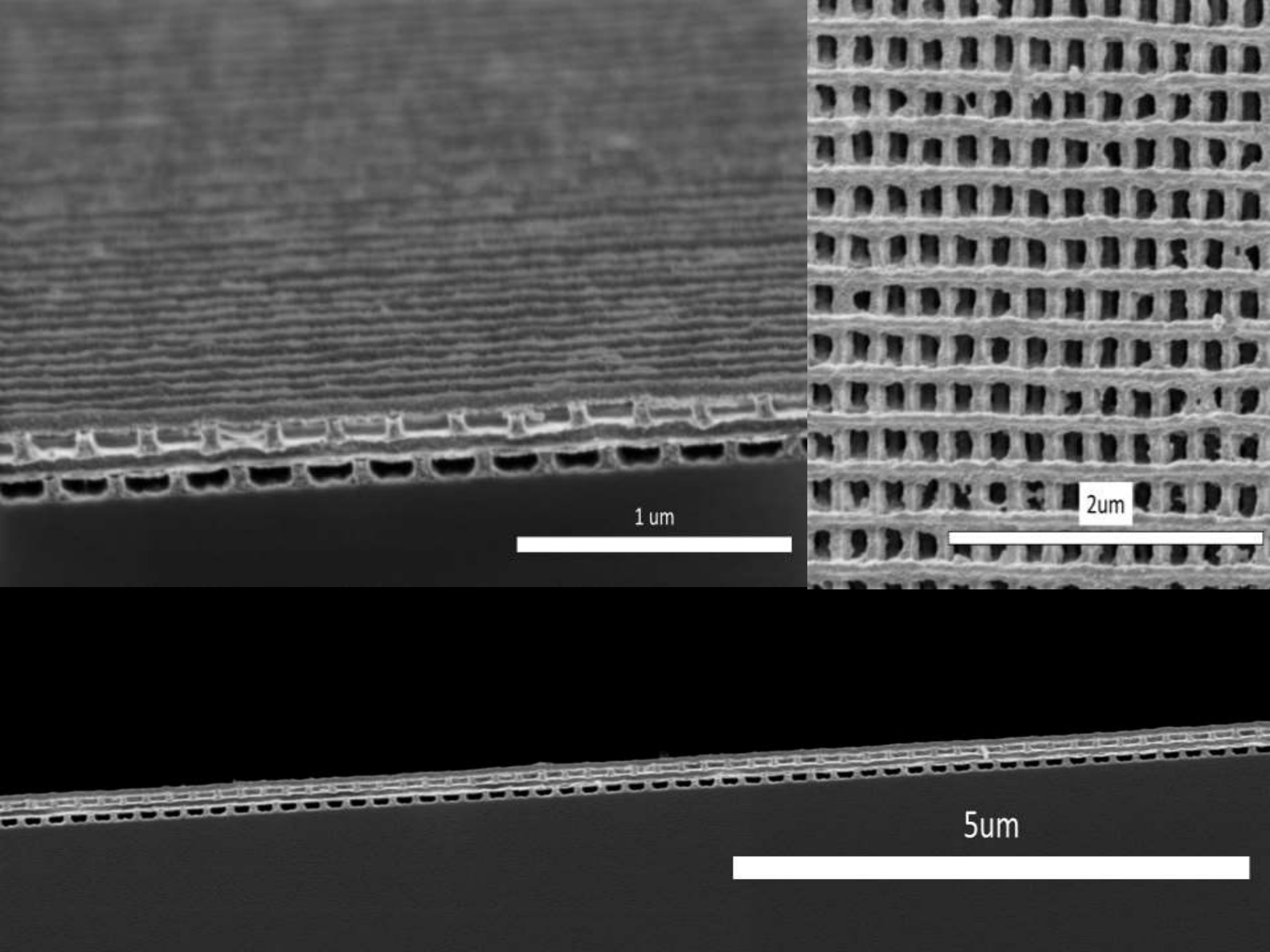

1 um
2um
5um

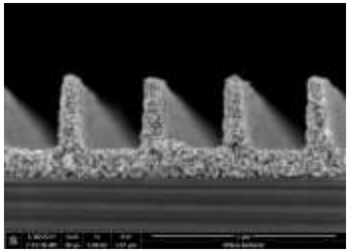
Direct "Imprinting" of Patterned Crystalline Metal Oxide and Metal Films for Devices

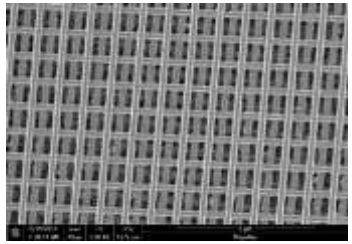
Potential Impacts

- Direct Printing of Inorganic Devices
- Have Demonstrated Conductors and Dielectrics
- Avoid Performance Limitations of Printed Organic Devices
- R2R Platform, Additive
  - low cost alternative to traditional Fabs
- Combine with Pulse Flash Lab Cure for Low T Substrates
- Versatile: Transistors to Fuel Cells
- Bring High Integration Density to Printed Systems

Our Tool Box: Materials, Device Layers, and Approaches

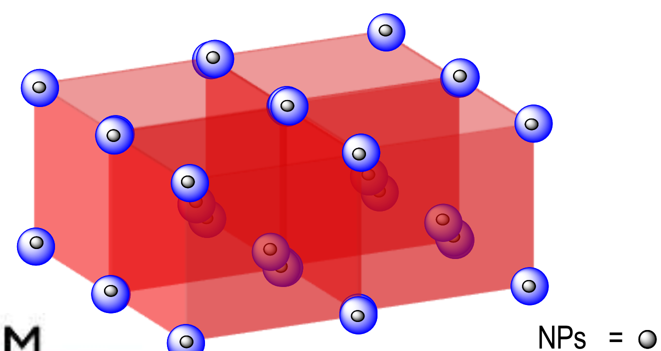
Nanoimprint Lithography Revisited: Direct "Printing" of 2-D and 3-D Hybrid and Inorganic Nanostructures



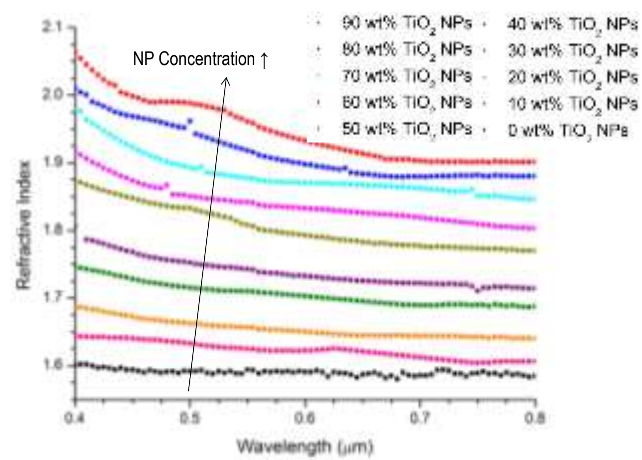


Scalability: (R2R NIL, Ink Jet/Photonic, Hybrid Coating, Pick and Place, more)

Periodic Nanocomposites and Metamaterials by Self-Assembly

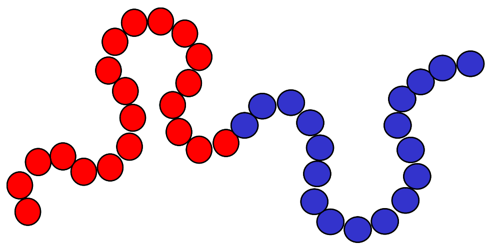


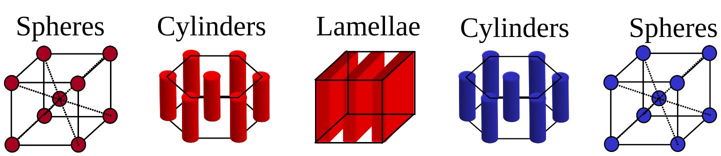
Tunable Hybrid Materials



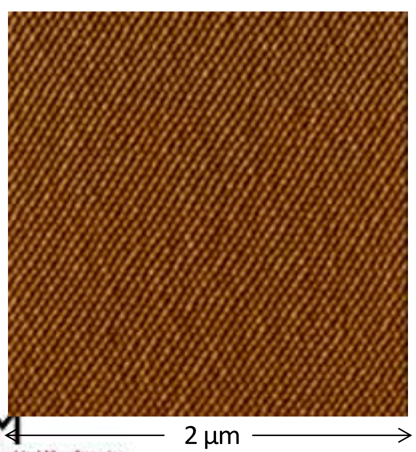
Block Copolymer Templates:
Spontaneous Assembly upon Spin Coating, Complete Control of Morphology

Linear Di-Block Copolymer Assembly

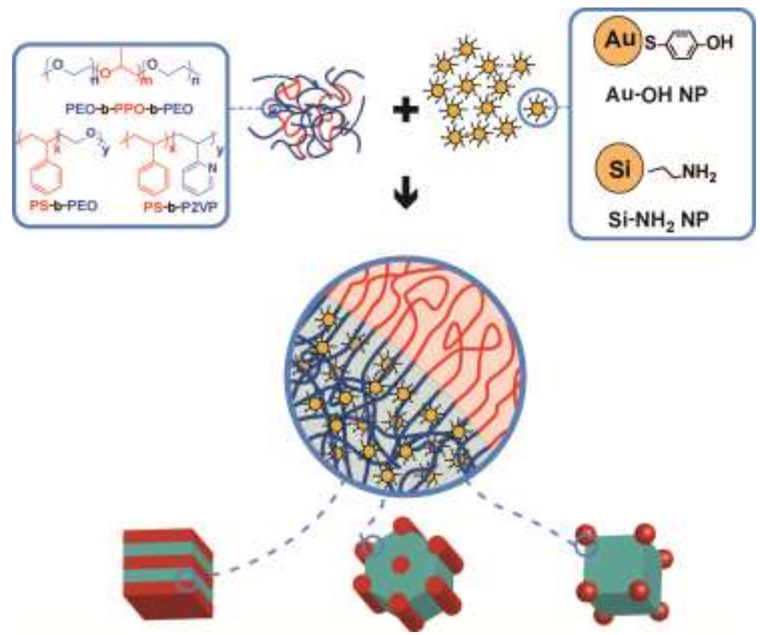


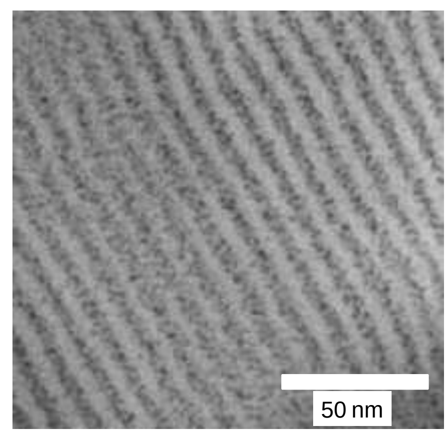


Increasing f →



Additive-Driven Assembly of Hybrids





Some Additional Questions Regarding Block Copolymer/NP Co-Assembly for Practical Device Fabrication

- Can we tailor interactions to overcome entropic barriers to well ordered systems at high additive loadings?

- Can we achieve long range order in large volume elements?

- Can we direct the placement of two or more distinctive species of NPs to different domains of BCPs by introducing orthogonal intermolecular interactions?

- Can we create ordered systems containing "large" particles?
  - quantum dots, plasmonic Au

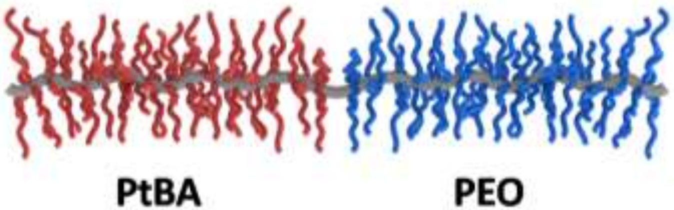
- Can we design the BCP template to be an active component or precursor to an active component within the device?

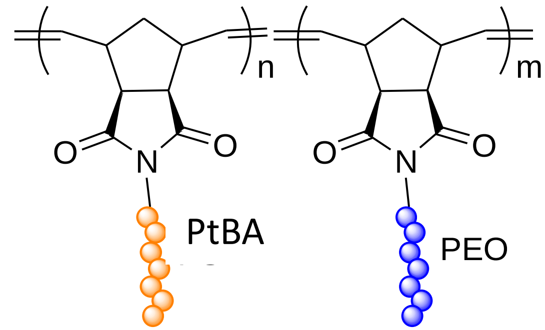
- Can we induce non-traditional but desirable morphologies?

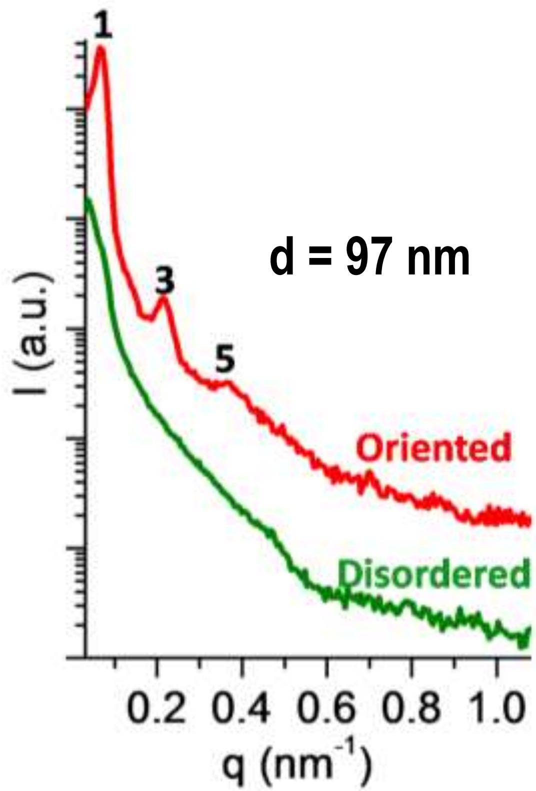
(The answer to each of these questions is yes)

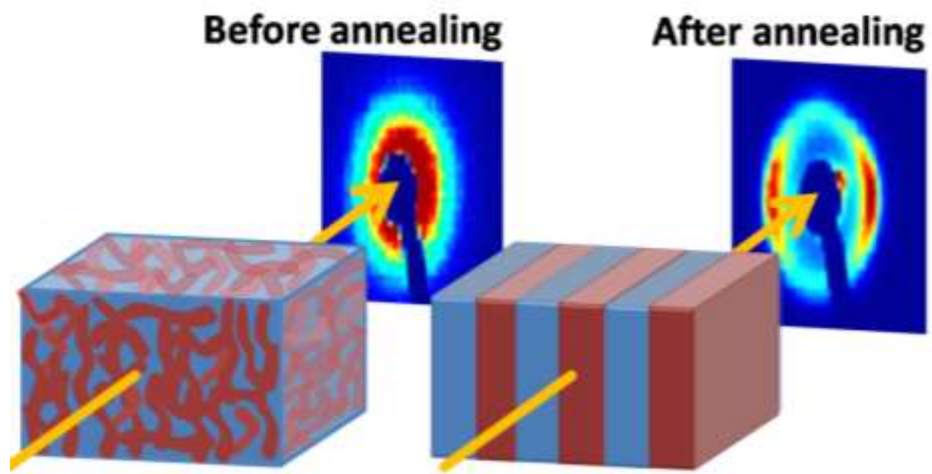
Block Copolymers for Optical Composites: Requires Large Domain Spacings and Large Volume Alignment

PtBA-PEO Brush Copolymers





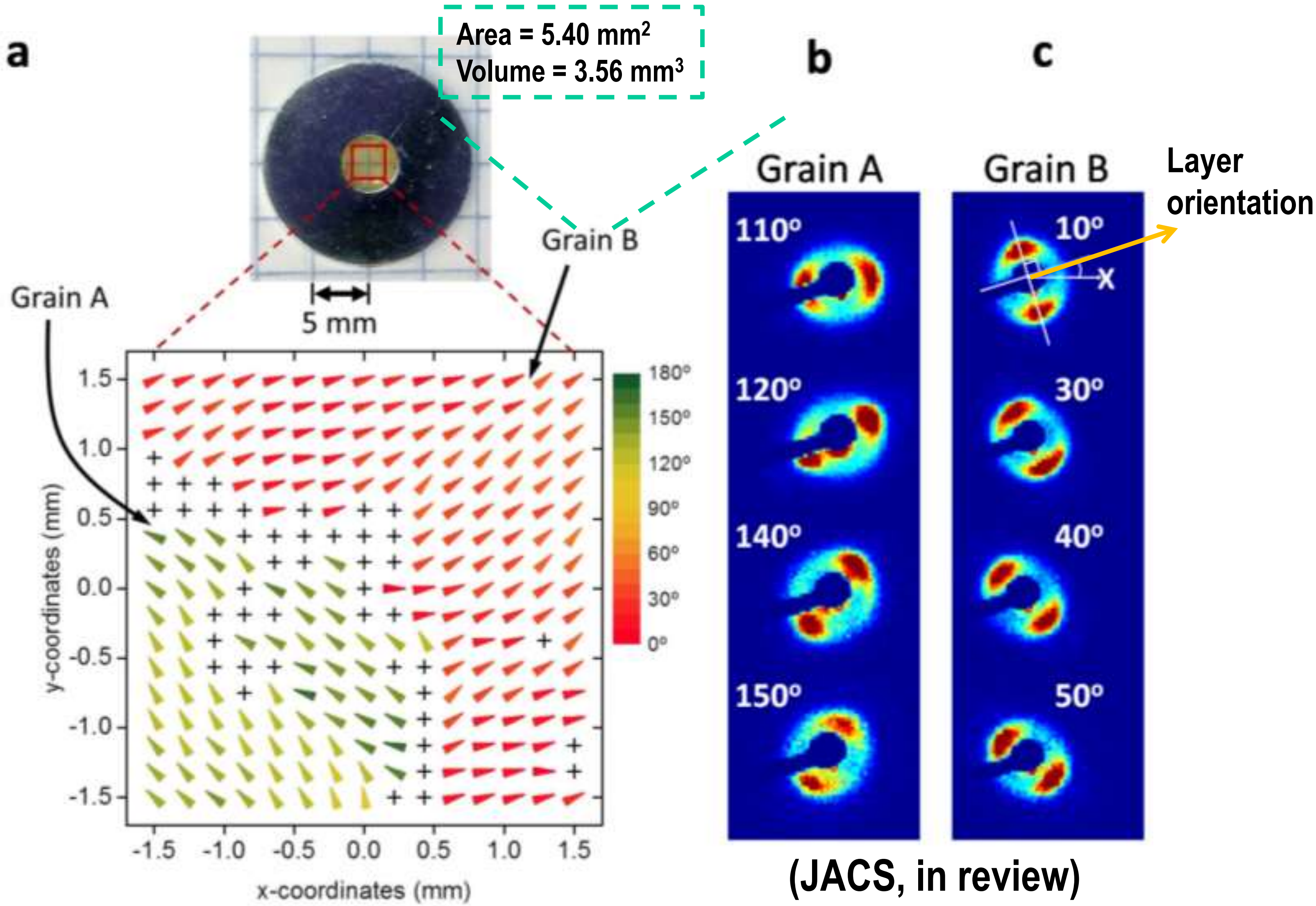




5 minutes at 110 ^{0}C

Dongpo Song et al., *J. Am. Chem. Soc.*, **2015**, 137, 12510

Spontaneous Formation of Millimeter Scale Grains in PtBA-PEO Brush Copolymers



(JACS, in review)

Mapping of the layer orientation in BBCP-A (M_n = 1,850 kg/mol, f_{PEO} = 48.4%) using continuous SAXS scan measurements. The thickness of the sample is approximately 0.66 mm.

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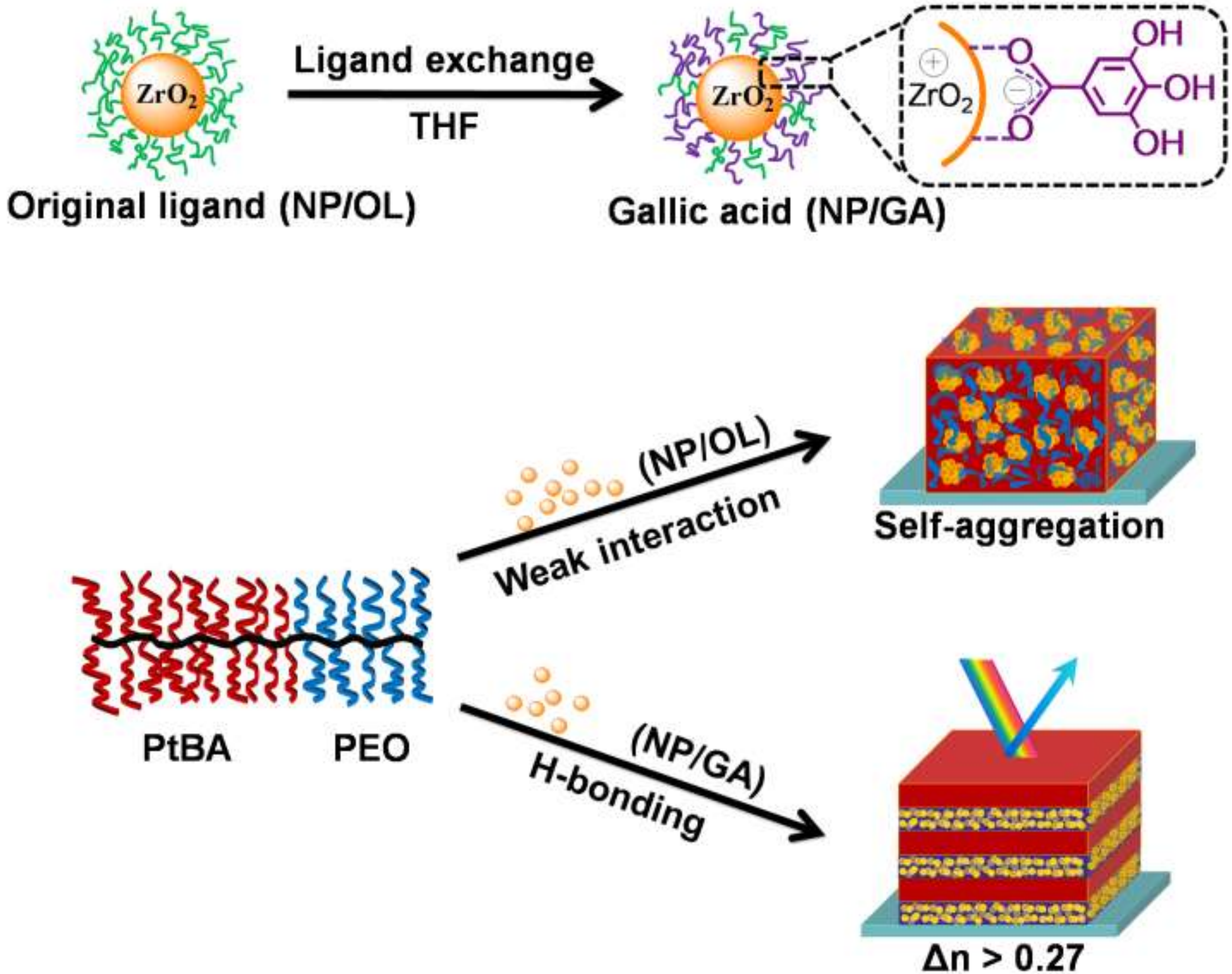
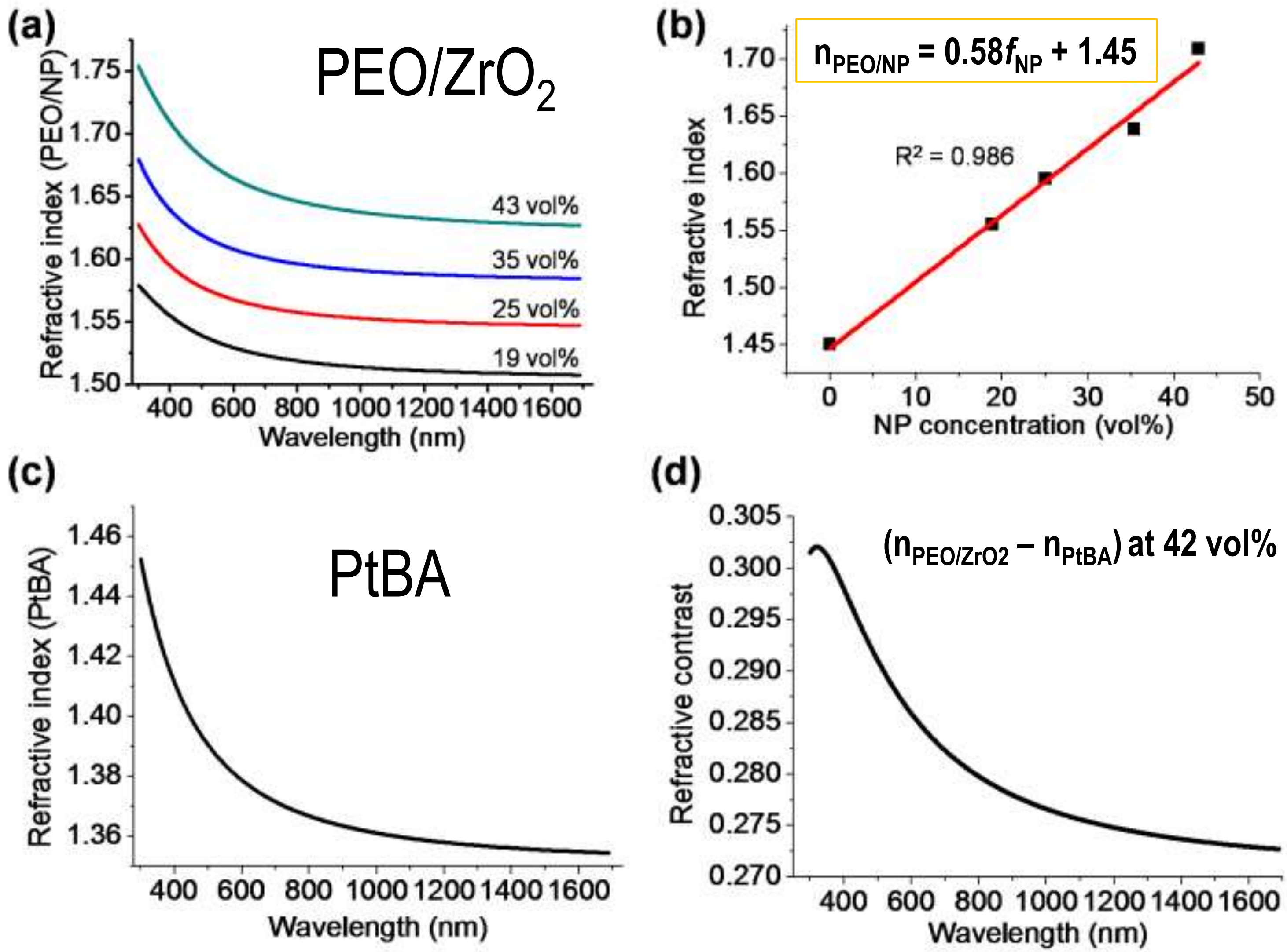
Self-assembled Photonic Hybrids with High Refractive Index Contrast



Refractive Indices of PEO/ZrO_2 Blends, PtBA, and RI Contrast



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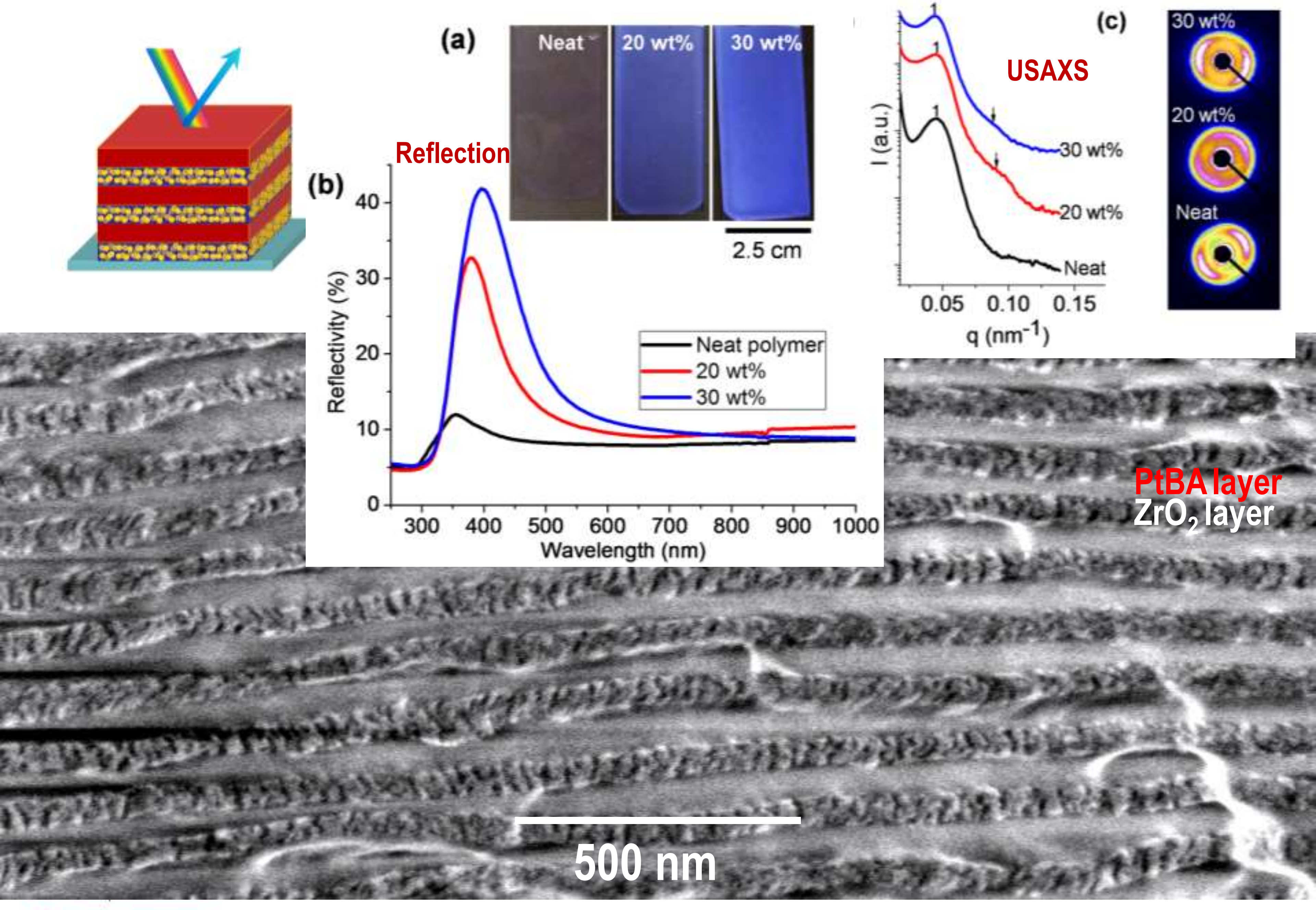
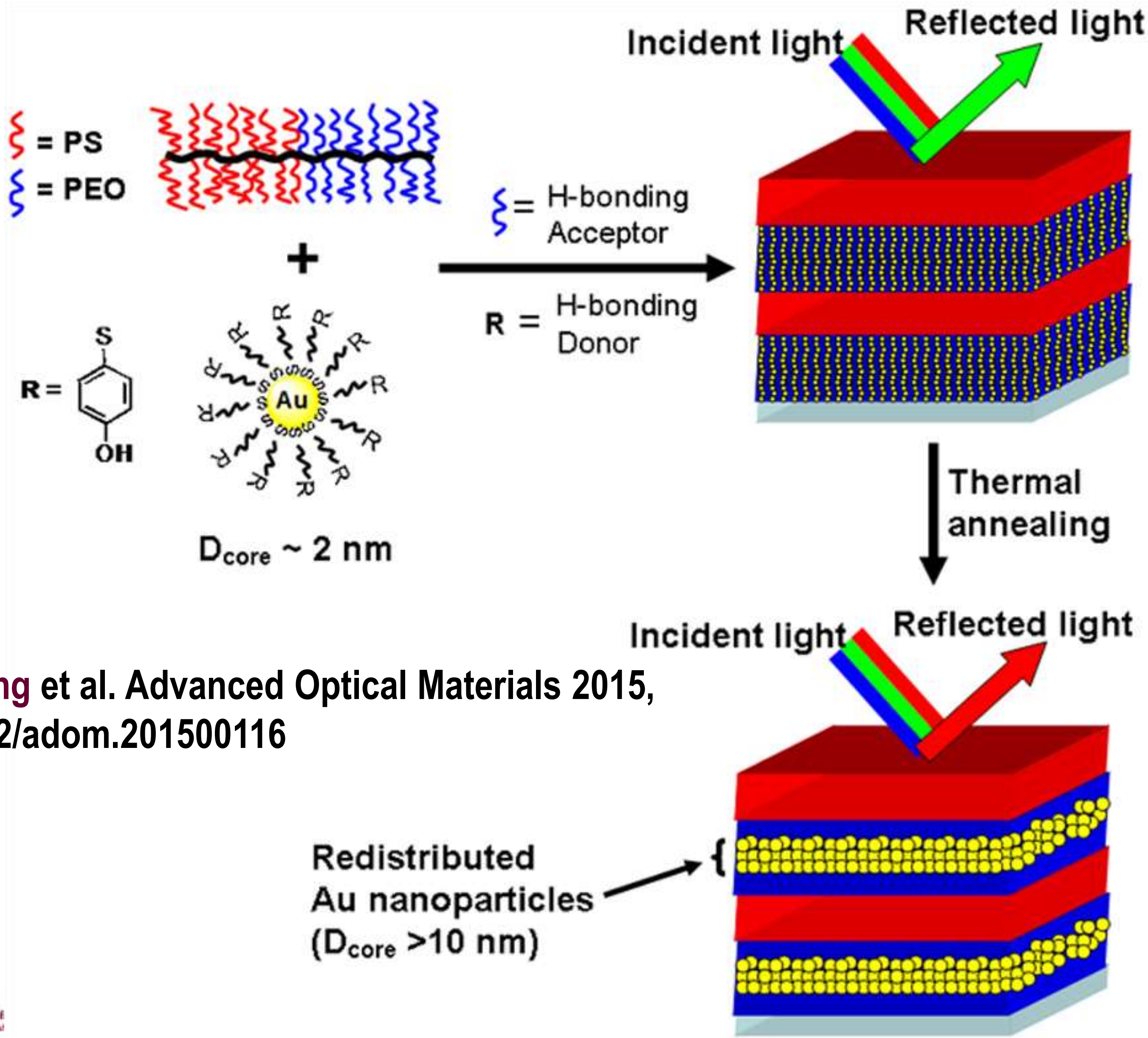
RI measured using variable angle spectroscopic ellipsometry (VASE)

Enhanced Reflection via Selective Incorporation of ZrO_2 within PEO Domains



Tunable Metallodielectrics from Self-Assembly of Brush Block Copolymers and Gold Nanoparticles



Dongpo Song et al. Advanced Optical Materials 2015,
DOI: 10.1002/adom.201500116

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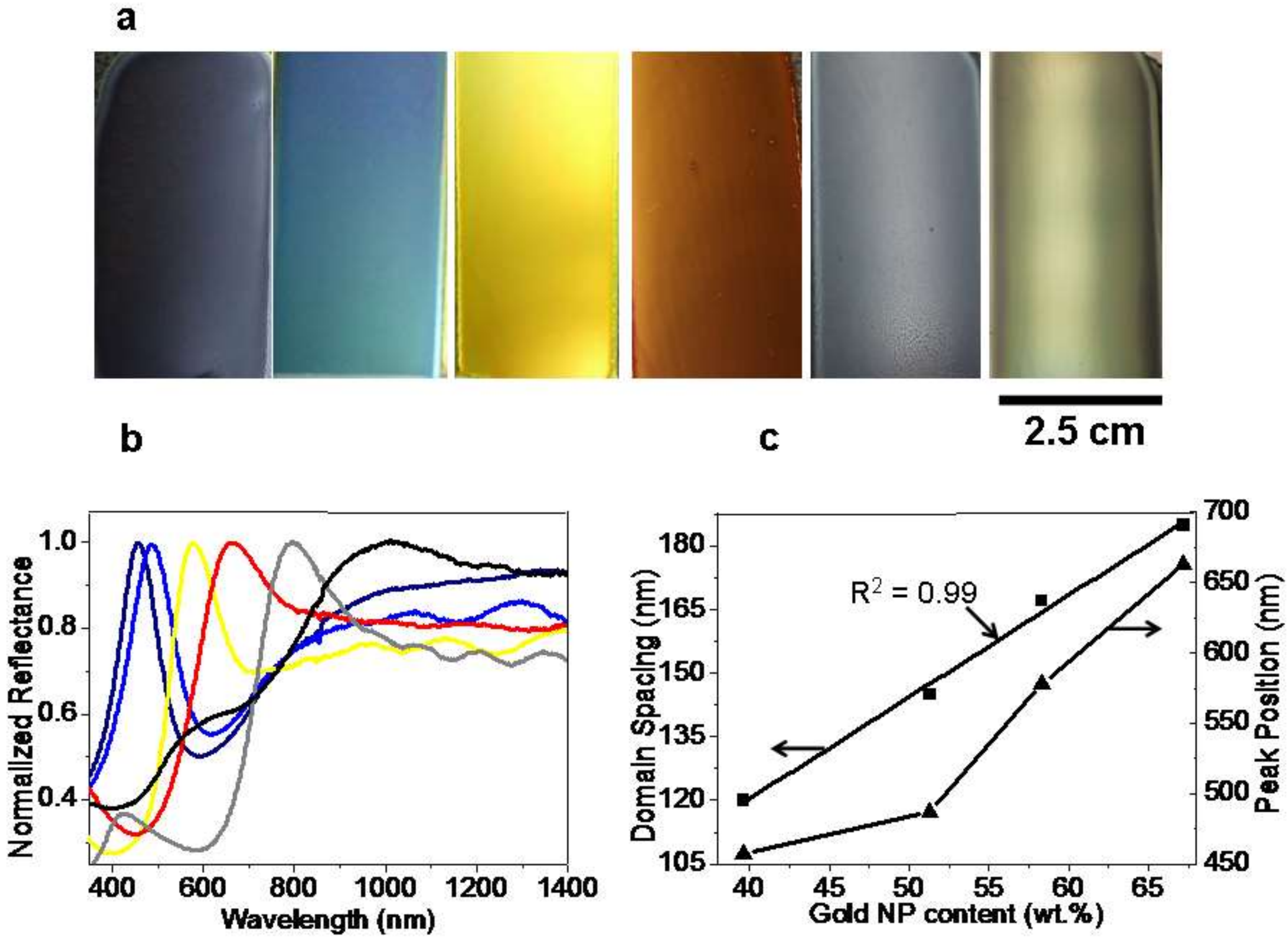
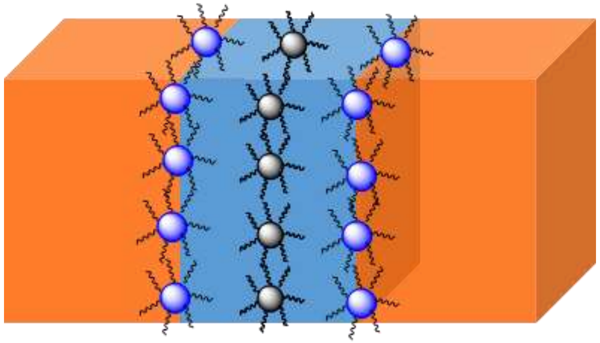
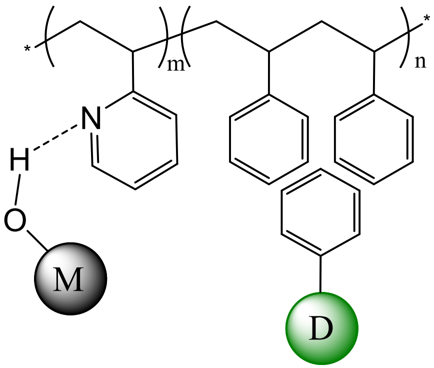
Tune-able Reflectance



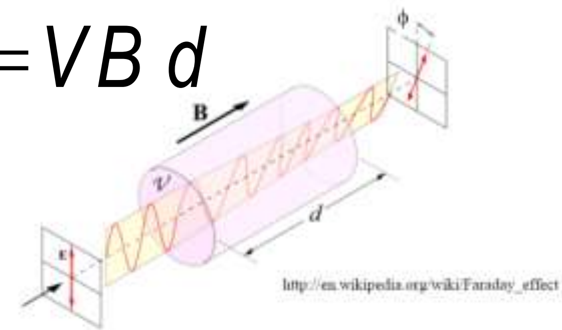
Magneto-Optic Metamaterials

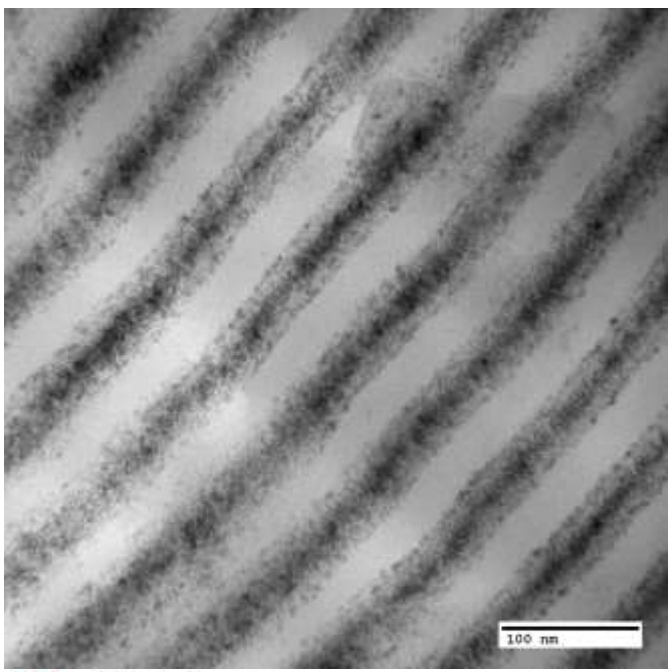
PS-P2VP+FePt+ZrO_2+Additives

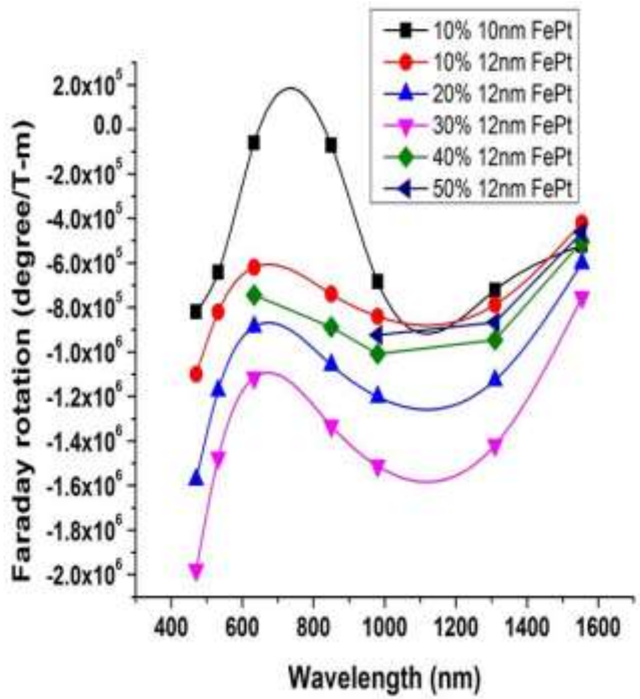


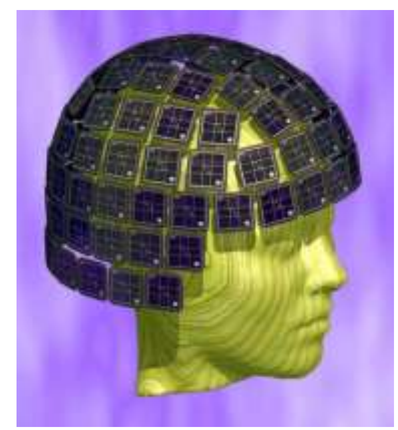


$$\theta = V B d$$









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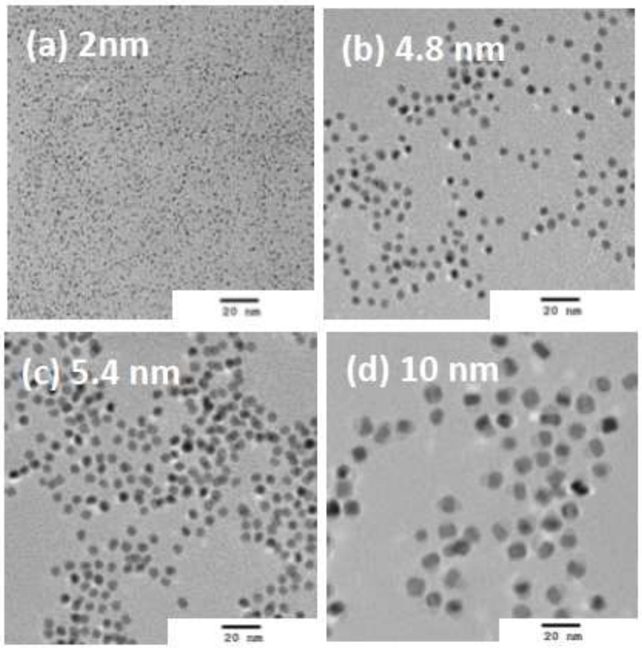
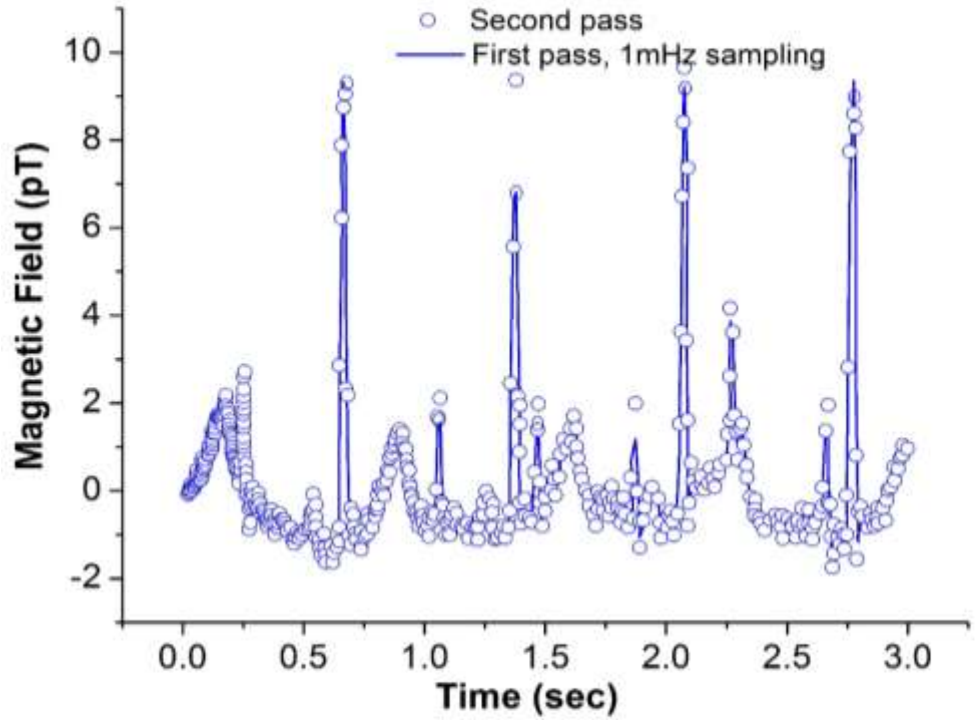
Bob Norwood University of Arizona

Magneto-optic composites for biological field imaging



FePt nanoparticles for magnetic field sensing



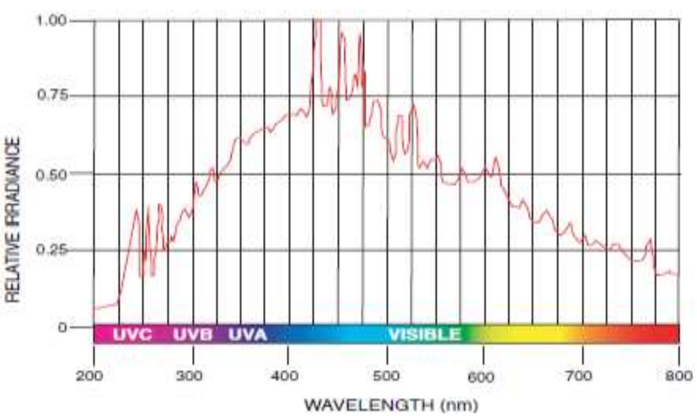
Sensing heartbeats with magneto-optic polymer nanocomposite based sensor

Ultrasensitive (femtotesla) magneto-optic sensors based on polymer nanoparticle composites have potential applications in heart and brain imaging among other areas

College of Optical Sciences
THE UNIVERSITY OF ARIZONA

Scale for UMass Nanocoater

Web Width: 6” Max, Coating Width: 5.75” Max.
Line Speed: 0.008-83 FPM/0.002-25.23 MPM
Slot Die Coating Head: Thickness Range 2-600 ums Wet
Solution Viscosity 10-4,000 Cps
Cored Die for Optional Heating to 95 Deg.C
2 Micro-Gravure Stations: Thickness Range 1-80 um Wet
Solution Viscosity 1-200 Cps
Coating Width 120mm/4.72”
2 Radiant Heat Dryers: Operating Limit 150 C
Positive Nitrogen Purging
4 Flowmeters Adjust Nitrogen
3 Thermocouples X-Web at both oven entrances
and exits monitor Nitrogen temperature
2 In-line Ionizing Anti-static Bars
2 Ultrasonic Sensors/with Steering Rollers for Web Alignment

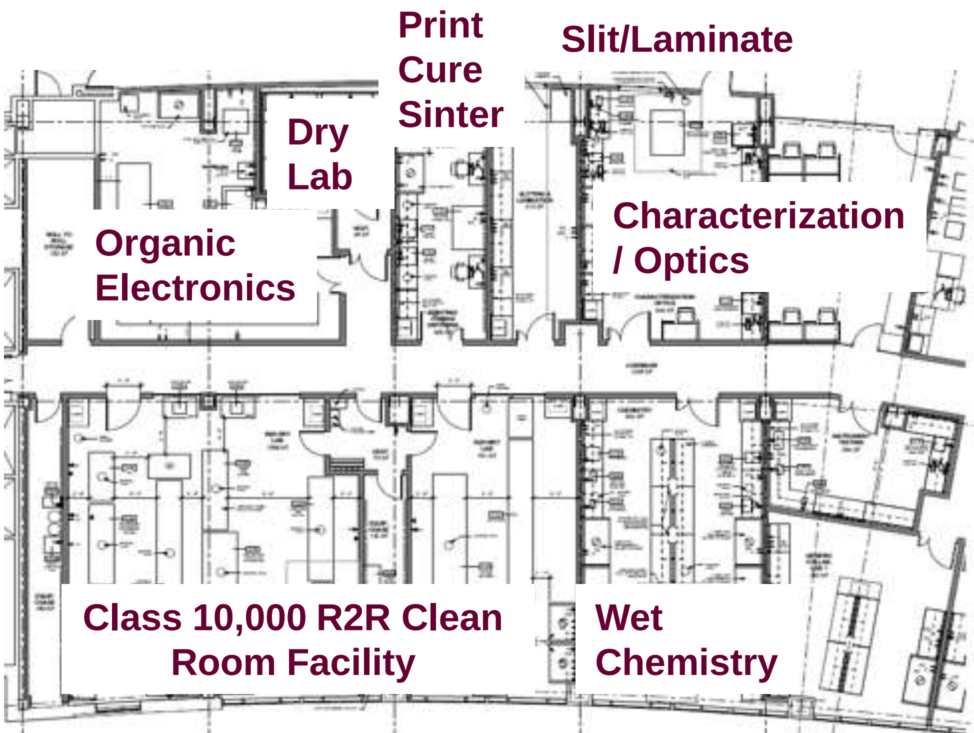


Spectrum of Xenon Pulsed Lamp

UV Cure Capability Added with the addition of the Xenon RC 847 LH 820 System.
Location allows for Pre-heating before the Cure station.
Pulse Energy & Rate: 13J/Pulse @ 100 pps
Lamp Optical Energy at 0.5” = 3.3 W/cm2

What is on the horizon?

APRM: Advanced Print and Roll-to-Roll Manufacturing Demonstration Facility Completion 2Q 2016



- R2R Sputter Deposition – 4 Target System (Choose - Cu, Au, Pd, ITO, Al_2O_3, SiO_2, Ni, Ti)
- R2R Deep Reactive Ion Etching / Ion Beam Milling (CF_4, O_2, SF_6, Ar, CHF_3, He)
- R2R Spatial ALD
- Advanced R2R Coater – Gravure and Slot Die with Controlled Emissions Exhaust
- R2R Inkjet Printing (Xaar) with Xenon Pulse Flash Lamp and NIR Cure (NovaCentrix)
- R2R Alignment Technology with overlay resolution of 1 micron
- Advanced R2R NIL with through master exposure and solvent assisted NIL
- R2R Optical Contact Lithography
- Sheet-Based and R2R Pick and Place
- Secondary processes: slitting/cutting, layer release/transfer, integration/bonding/assembly
- Dry Room
- Optomec Aerosol printing system
- Sheet-based Inkjet and Optical Cure
- Nanonex Batch NIL Tool NX-2608BA
- CHM legacy tools: UV-Assisted Nanoimprint and Nanocoater

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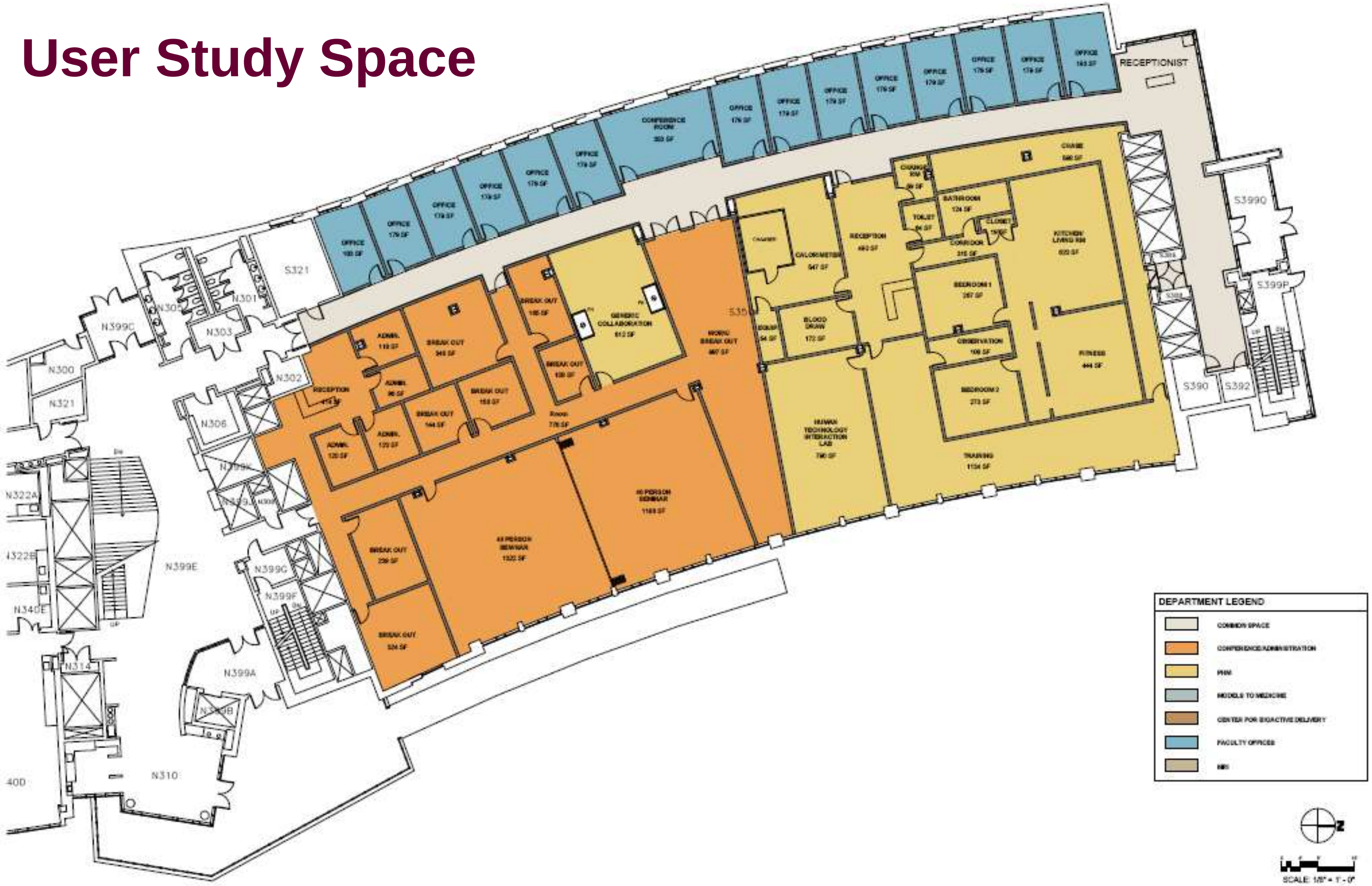
User Study Space



Controlled User Study Space

- Sleep Monitor Space
- Exercise Measurement
- Instrumented Living Space

Investigator Space

- Visiting Scientists' Offices (10)
- Postdoc Double Offices (3)
- Conference Room/Teaching Room (2)
- Graduate Student Cubicle Space

Watkins Research Group and CHM Staff

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University of Massachusetts Amherst

collaborators for this work: A. Briseno, S. Gido, H.H. Winter

Takeaways

- Creation of intelligent devices by R2R is within reach
- R2R processing can reduce energy and resource demands
- Incorporation of self-assembly and additive-driven assembly enables new or advanced functionality, additive processing and lower cost
- R2R UV-Assisted NIL provides high-throughput access to device structures as small as 50 nm and on-roll device patterning
- Highly filled polymer/NP composites are useful active layers for devices and offer solution based alternatives to vacuum processing
- Direct patterning of crystalline metal oxide films on flexible substrates opens up options for printed inorganic devices with high integration densities
- Prototyping tools for R2R Hybrid Materials and R2R NIL accessible through CHM at UMass

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