Center For High-rate Nanomanufacturing

Year 9 Review

Director: Ahmed Busnaina, NEU

Deputy Director: Joey Mead, UML, Associate Directors: Carol Barry, UML; Glen Miller, UNH; Jacqueline Isaacs, NEU

Rethinking Manufacturing

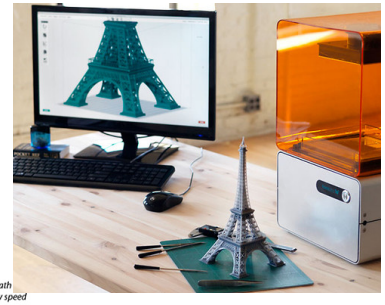
- Manufacturing is the process of adding or removing materials by means of a large-scale industrial operation, which can take place at macro, micro or nano scales.

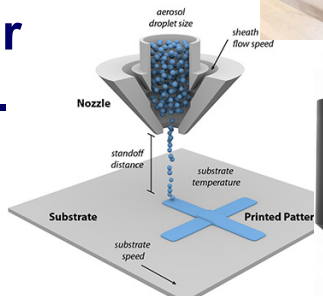
- Macro-manufacturing involves cutting, coating, shaping, welding and assembly of various parts.

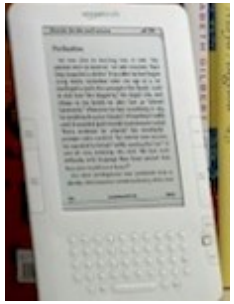
- Current micro and nanoscale manufacturing involves deposition (thin film using chemical or physical processes), etching, polishing, assembly, packaging, and wire bonding.

3D and Electronic Printing

- The modern 3D printer is a specialized ink jet printer that uses special ink that could contain a polymer, particles, or suspended in a solution.
- It prints line by line, so products requiring higher resolution and/or large areas take a very long time.
  - A fast ink jet printer printing 1 micron lines (current resolution is 30 micron) at 1 m/s speed over an area of $1m^2$ will take 12 days.
- There is a need for high-rate and nanoscale manufacturing







Nanomanufacturing using high-rate directed assembly involves adding materials selectively such that no material removal is needed, thereby both reducing waste and the number of required processes.

Center for High-rate Nanomanufacturing

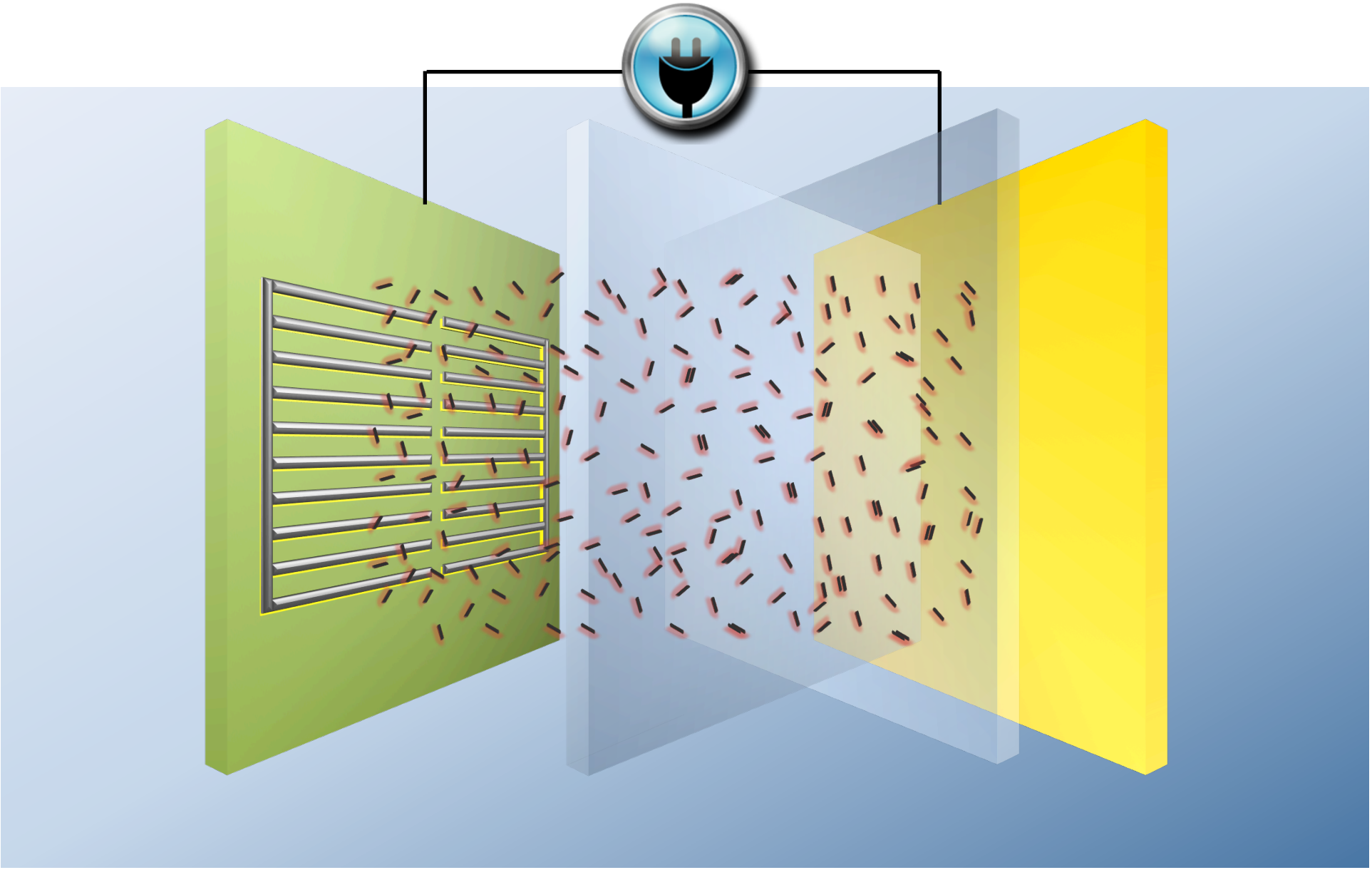
Our Goals

1. Understand the fundamentals of synthesis and control at the nanoscale to enable high-rate/high-volume bottom-up, precise directed assembly of nanoelements
2. Translate the nanoscale science into practical applications in energy, bio/medical, electronics and materials.
3. Develop responsible manufacturing by understanding and managing potential risks of nanotechnology
4. Educate the current and emerging nanomanufacturing workforce.

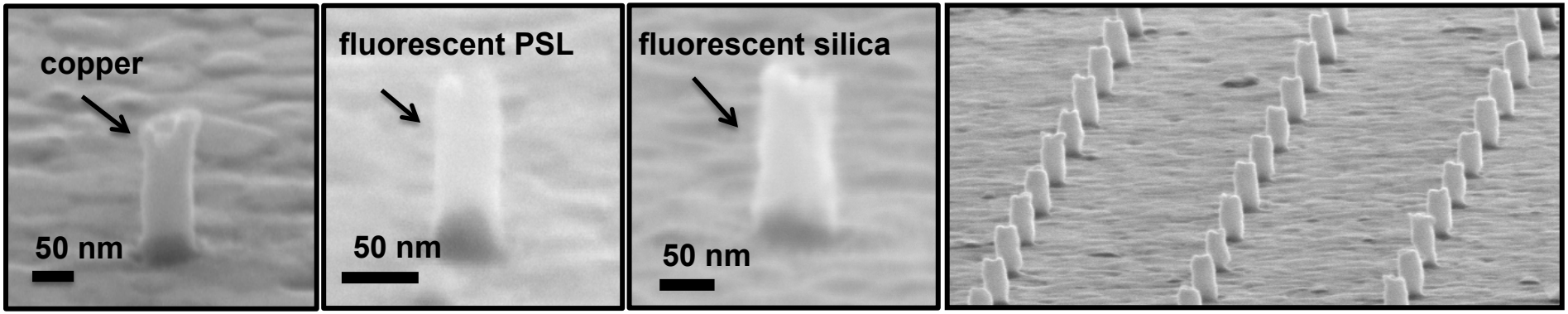
Introducing a Directed Assembly Based Nanomanufacturing

- Additive and parallel
- Scalable high throughput (much faster than 3-D printing)
- Manufacture down to 20nm
- Room temperature and pressure
- Manufactures structures on flexible or hard substrates
- Multi-scale; can print nano, micro and macro structures on the same layer
- Little use of chemicals (uses mostly water)
- Material independent
- Very low energy consumption
- Very low capital investment (equipment)

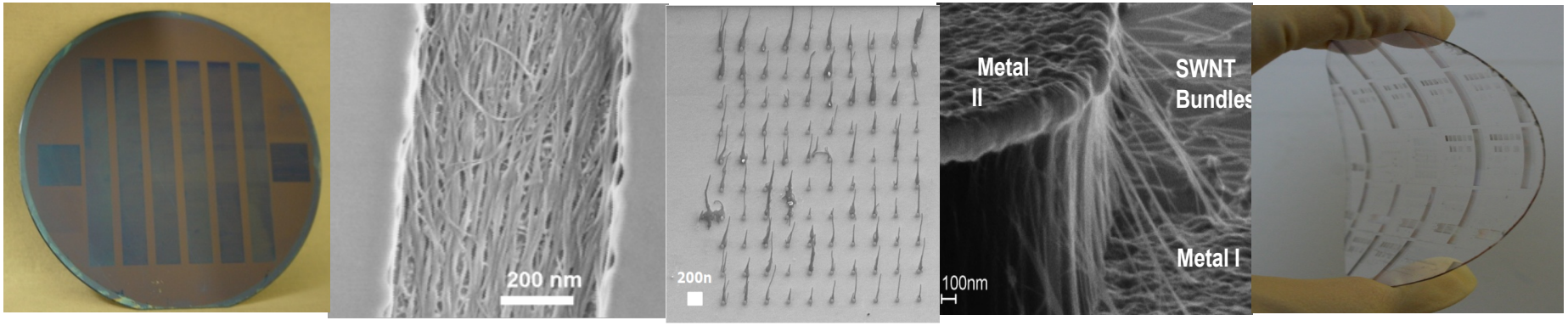
How does it work?
Directed Assembly and Transfer



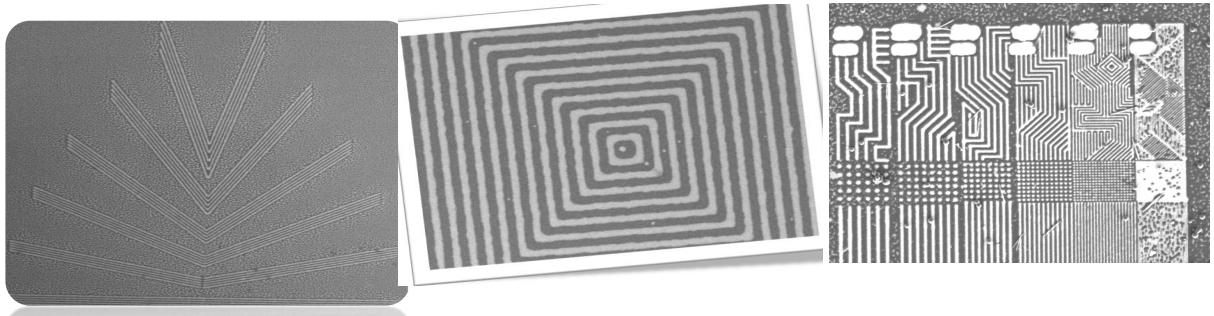
What Structures Can This Technology Make?

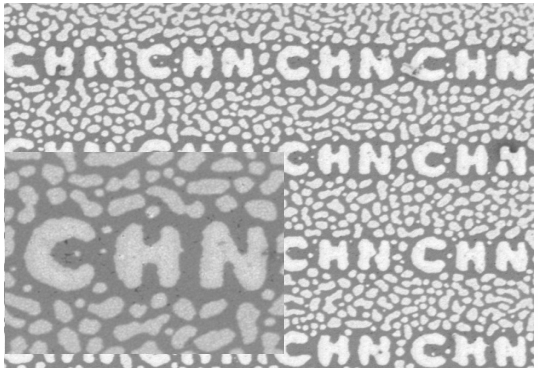


Rapid, multi-scales assembly of nanoparticles



Rapid, multi-scales assembly of Carbon Nanotubes





Rapid, multi-scales assembly of polymers

What are the Critical Barriers to Nanomanufacturing?

- **Barrier 1: How can we assemble and connect different nano-scale elements?**
  - Identified the various mechanisms of directed assembly nanoscale structures and what variables govern the directed assembly process.

- **Barrier 2: How can we scale-up assembly processes in a continuous or high rate manner?**
  - Identified many interfacial behavior and forces required to assemble and transfer nanoelements at high rates and over large areas.

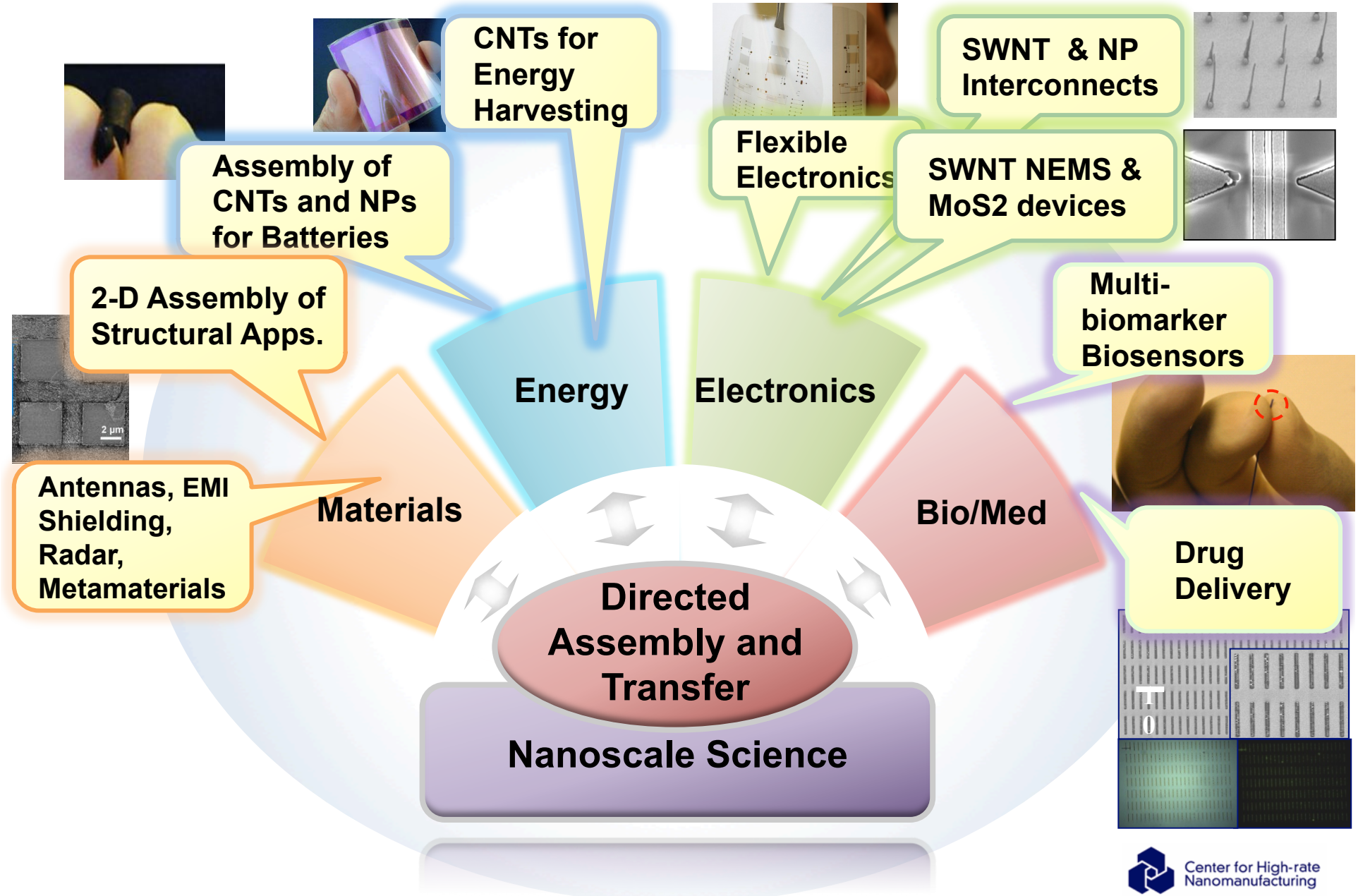
- **Barrier 3: How can we translate technology into useful applications and increase process reliability and throughput ?**
  - Many variables (such as humidity, pH, voltage, etc.) that govern reliability were identified and investigated.

- **Barrier 4: How can we ensure nanomanufacturing processes and products remain safe for workers, consumers and the environment?**
  - Developed best practices for screening and handling nanomaterials and is exploring the life cycle of nano-enabled products.

CHN Toolbox
Bridging research to applications

Templates	Nanoelements	Assembly Processes	Transfer Processes	Substrates	Applications
Microwires template	Nanoparticles	Electrophoretic 2-D and 3-D	Direct transfer (no functionalization)	Silicon	SWNT switch for memory devices
Nanowires templates	Carbon nanotubes (SWNTs and MWNTs)	Chemical Functionalization	Direct transfer with chemical functionalization	Polymer	Polymer-based Biosensors
Nanotrench template	Conductive polymers (PANi)	Electrophoretic and chemical functionalization	No transfer needed	Metal	Nanoparticle-based Biosensors
Template-free	Polymer blends	Dielectrophoretic 2-D and 3-D	Reel-to-reel transfer		SWNT Batteries
Damascene Template		***Convective***			Photovoltaics
Flexible Damascene Template		***Convective interfacial***			SWNT Chem Sensors

What Applications Could This Technology Make?



Center for High-rate Nanomanufacturing

CHN Team Strength and Capability

NEU: Directed assembly, MEMS, fabrication, contamination control

Semiconductor & MEMs fab

- 7,000 ft^2 class 10 and 100 cleanrooms

UML: High volume polymer processing and assembly

UNH: Synthesis, self-assembly

Center for High-rate Nanomanufacturing

A unique partnership

Plastics processing labs

- **20,000 ft^2 +**

MSU: Molecular Modeling

Synthetic labs

- **10,000 ft^2 +**

Institution	Faculty	Post-docs	Graduate	Undergrad.	Total
NEU	17	6	31	8	62
UML	14	6	27	13	60
UNH	7	7	15	10	39
MSU	1	1	0	0	2
TOTAL	39	20	73	23	163

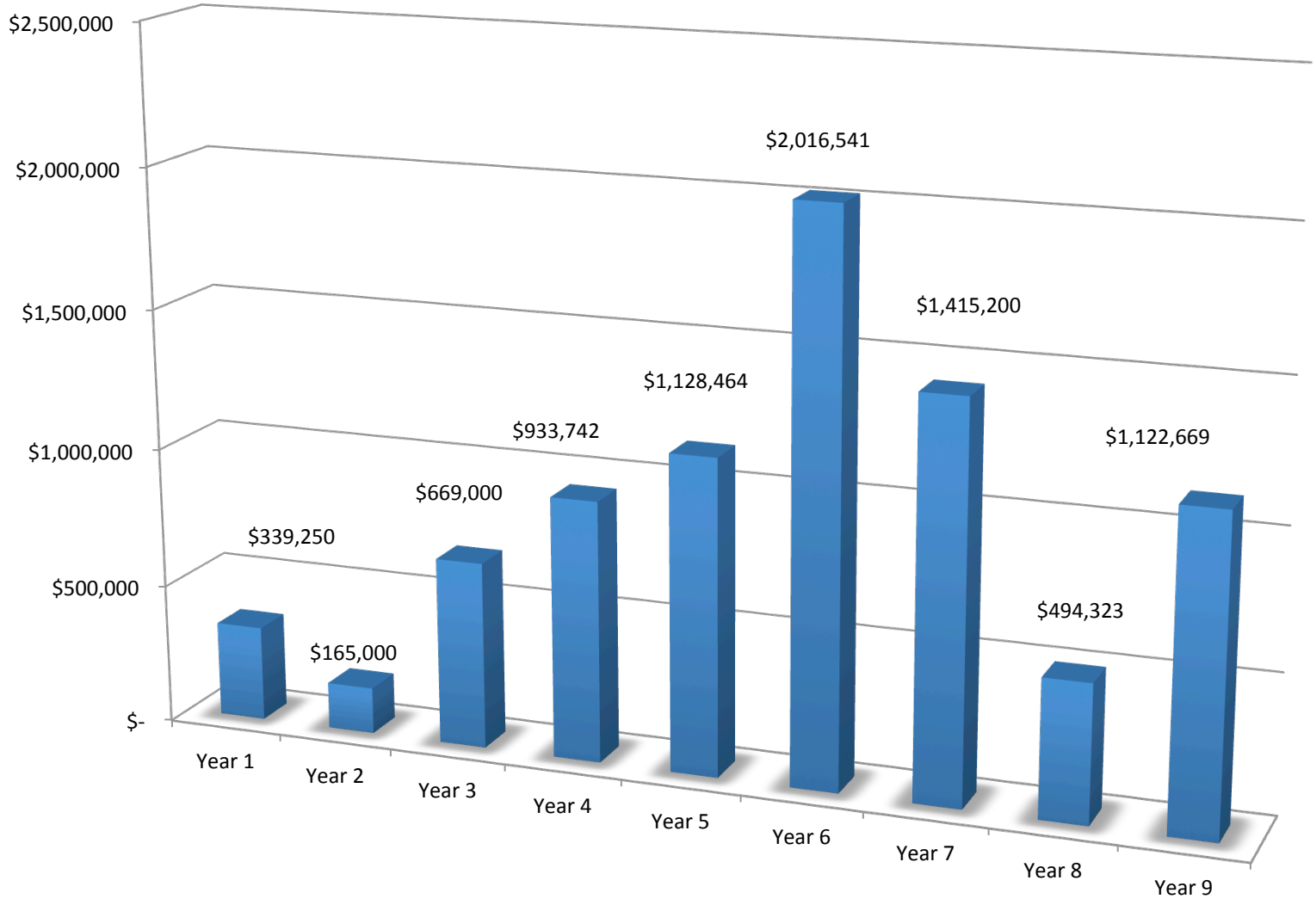
Industrial Partnerships

varian
CORNING
TEXTRON
Ticona ENGINEERING POLYMERS
kuraray
Schlumberger
TERADYNE
tsi
zyvex
AEC
VELCRO
BAE SYSTEMS
QinetiQ North America
Foster-Miller
Raytheon
ENVIRON
Veeco
DRAPER LABORATORY
nanocomp TECHNOLOGIES, INC.
intel.
brewer science
Nypro
MOTOROLA intelligence everywhere
NANTERO
Microfluidics
BASF The Chemical Company
EMC²
CABOT
IBM
LOCKHEED MARTIN We never forget who we're working for
SOLOPOWER
Kodak
GE
A DIVISION OF THE MASSACHUSETTS TECHNOLOGY COLLABORATIVE

Over 30 companies

Center for High-rate Nanomanufacturing

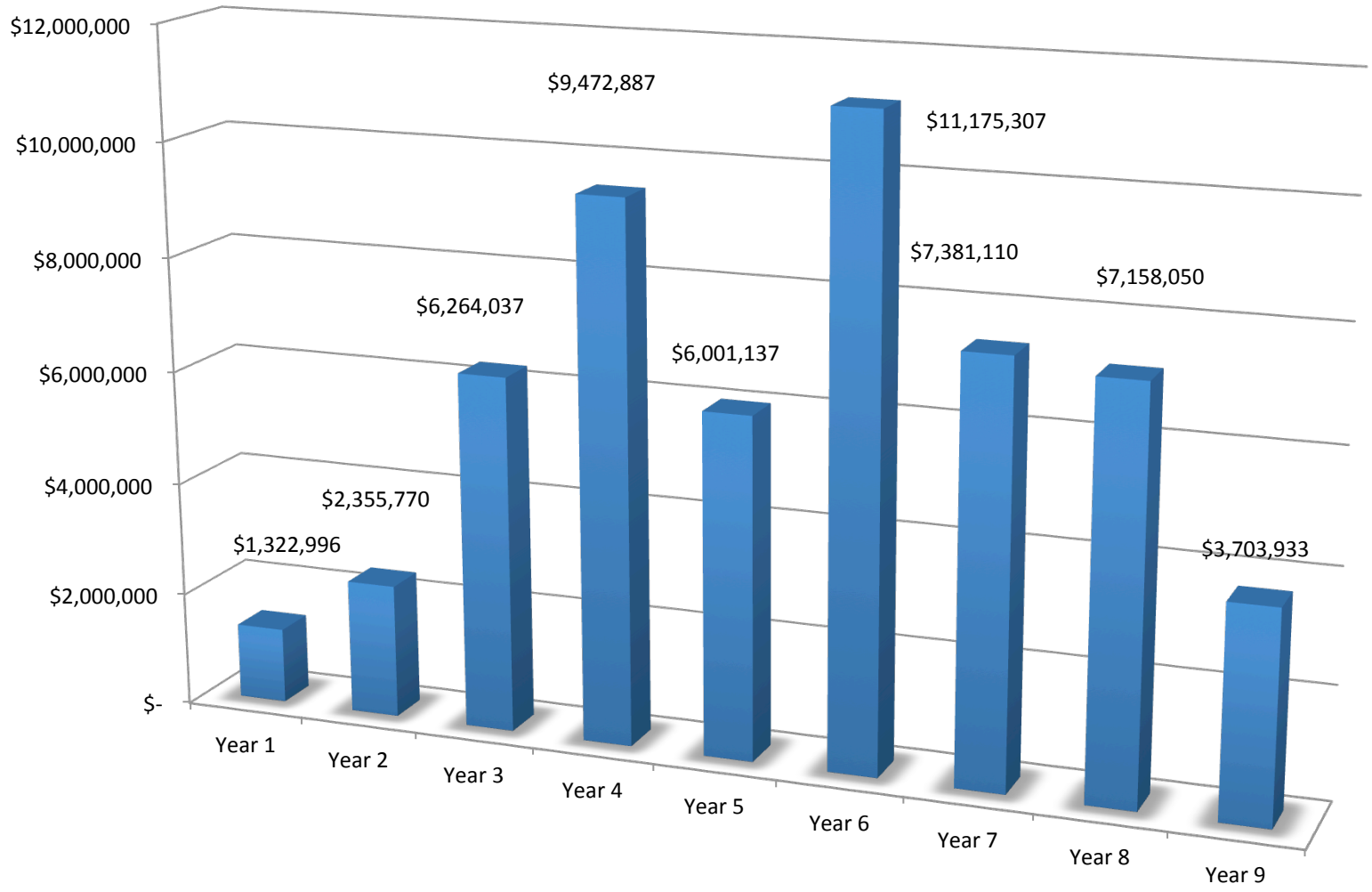
Industrial Funding



Total for years 1-9: $8,284,000

Center for High-rate Nanomanufacturing

Total Leverage



Total for years 1-9: $54,834,000

Center for High-rate Nanomanufacturing

Path to $ustainability

1. Membership Fees for Collaborative Center

- **The Center will be supported by a membership fee. In return, each company gets access to the Center technology and IP.**

Category	Fees	IAB member	IP @ Northeastern	Matching funds	Technology Process Workshop
Strategic	$50K Cash	Yes	3 process patents at no charge for 3 years; 1 - device patent at 60% off best royalty rates for 3 years.	None	2 days' active consulting on process technology implementation.
Corporate	$30K Cash Or $18K Cash	Yes	1 or 2 process patents at no charge for 3 years; 1 - device patent at 20% or 40% off.	None	1 day active consulting on process technology implementation.
Associate	$6K Cash	Yes	90 days (Option at additional cost)	Yes; up to $10K*	None

Center for High-rate Nanomanufacturing

Path to $ustainability

2. Center with Special Allocation Rates

- **The CHN can charge industrial partners, as well as other organizations, a small fee that's added to the direct cost of contracts to cover the operational costs of the center*.**
- **Northeastern University has agreed to this, and Northeastern and UMass-Lowell have agreed to support center basis staff after the end of the NSF funding.**
- **Example: MIT allows them to add "allocation charges" to external contracts, which cover a portion of the administrative and support salaries and some of the non-salary expenses incurred for the overall administration and management of the lab or center.**

Path to $ustainability

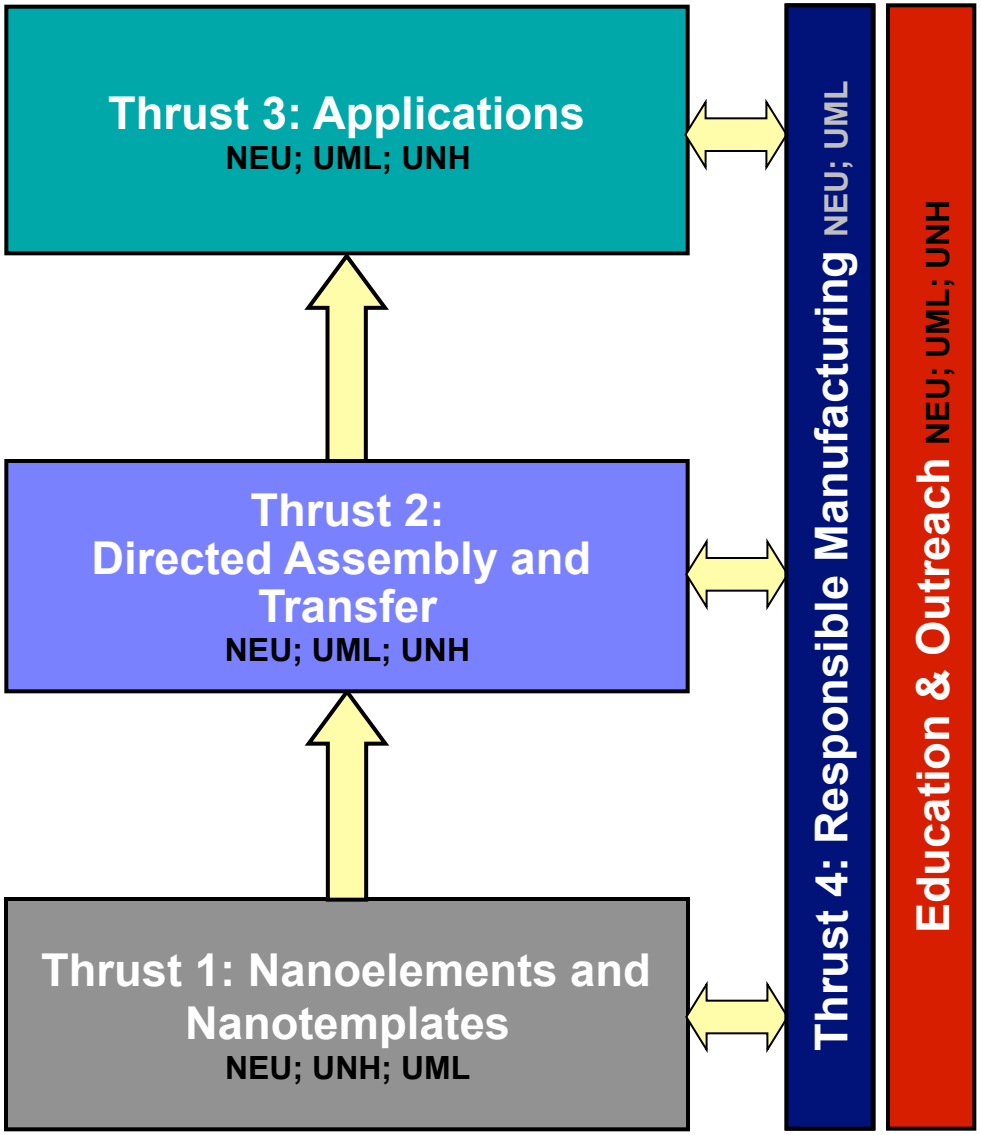
3. Grants and contracts

- **The CHN and the three main university partners (NEU, UNH & UMass-Lowell) are generating funds by securing grants from federal and state agencies, foundations and other grant-giving entities. These grants may be for research, commercialization activities, or other activities.**

4. Tutorial and Shortcourses

- **The CHN can generate funds by organizing tutorials and short courses that provide training of interest to industrial partners. This will generate some funds, but will not provide sufficient funds to maintain full CHN operations.**
- **Example: Onsite Trainings offered by NEU**

CHN Path to Nanomanufacturing



Center for High-rate Nanomanufacturing

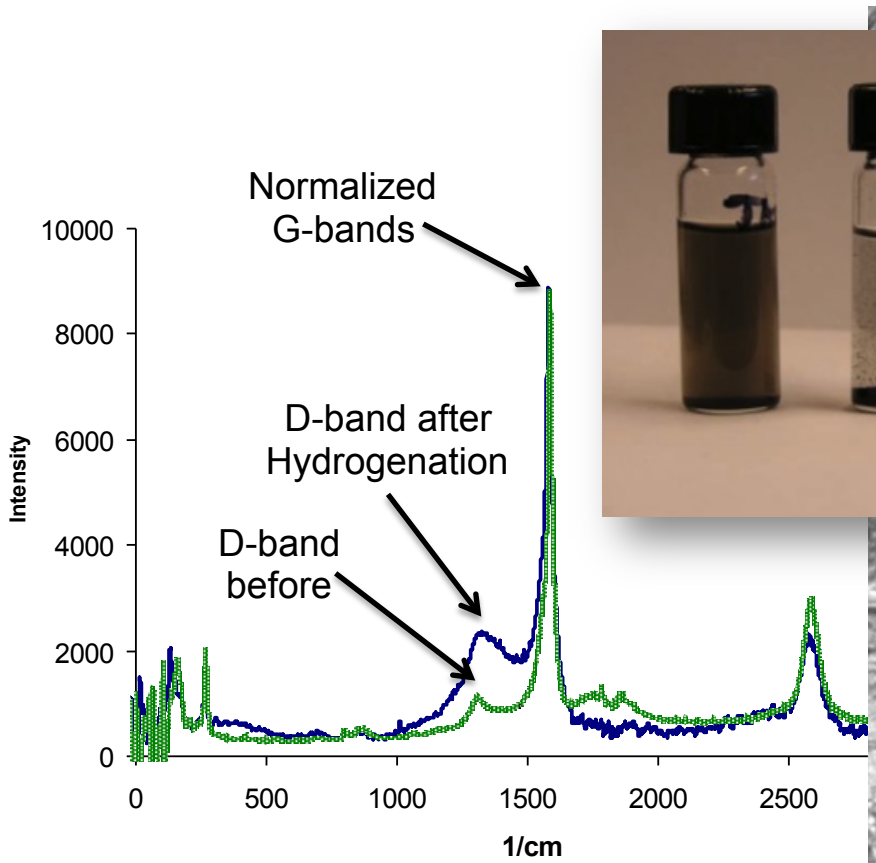
THRUST 1

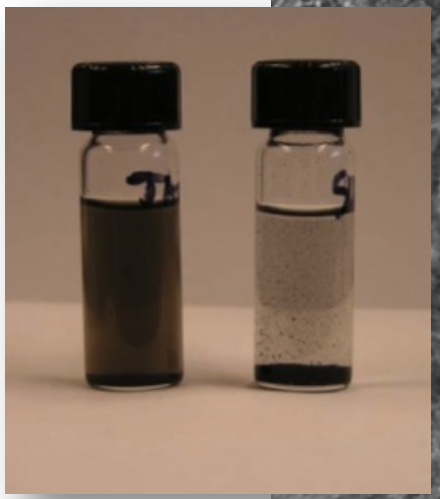
Nanoelements and Nanotemplates

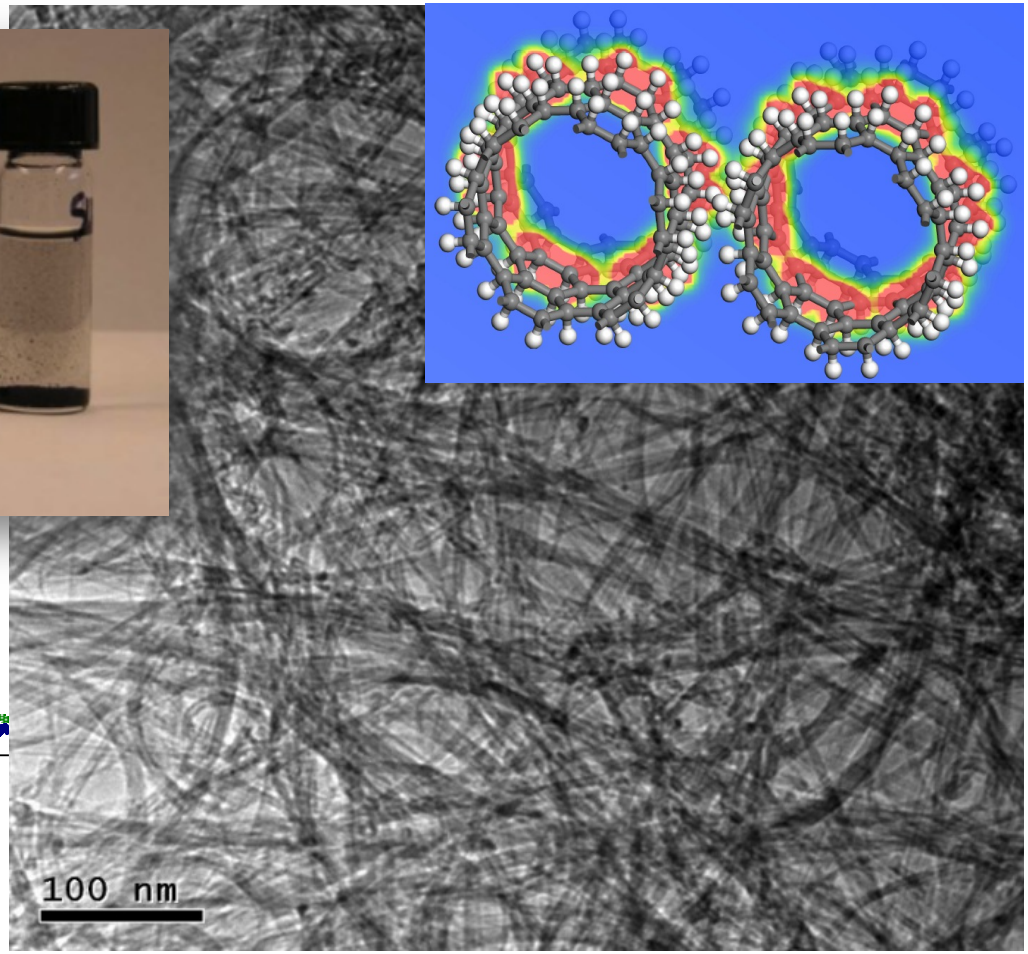
Goals for Thrust 1: Nanoelements & Nanotemplates

1. Design, synthesize and characterize nanoelements (nanobuilding blocks) with desired properties for targeted CHN applications and testbeds
2. Design and fabricate nanotemplates for high-rate/high-volume directed assembly of nanoelements

Highly Dispersed, Hydrogenated SWNTs

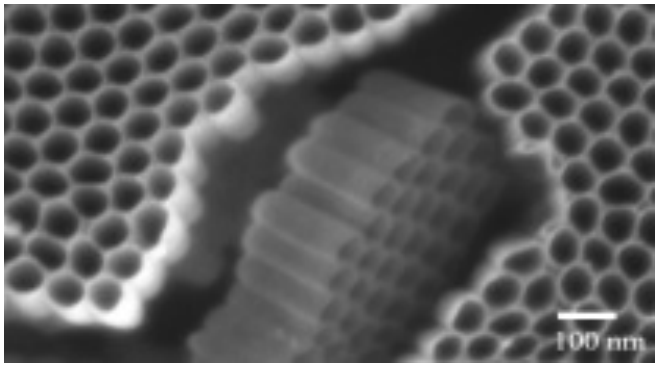


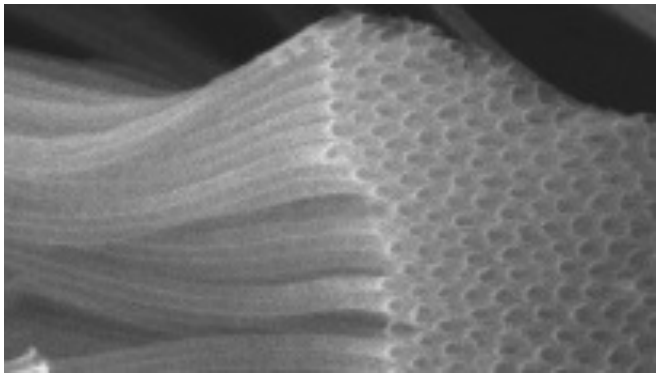


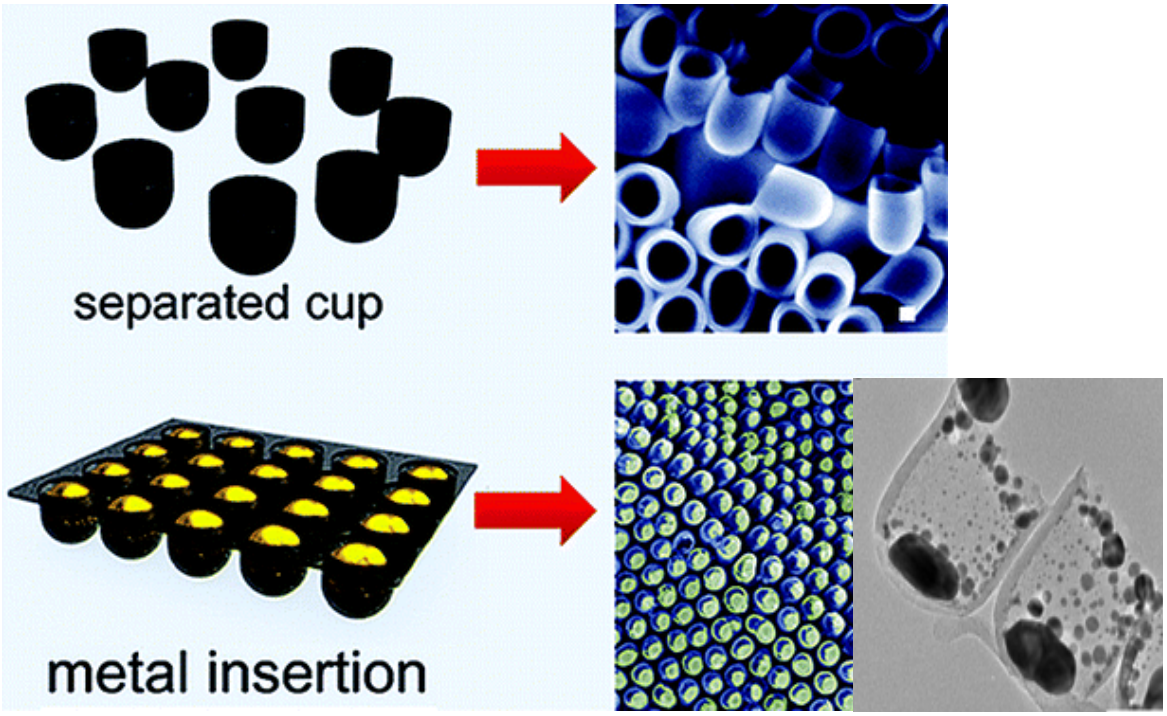


Miller, G. P.; Kintigh, J.; Kim, E.; Weck, P. F.; Berber, S.; Tomanek, D., "**Hydrogenation of Single-Wall Carbon Nanotubes Using Polyamine Reagents: Combined Experimental and Theoretical Study**," *J. Amer. Chem. Soc.*, **2008**, *130*, 2296-2303.

Nano-cups & Nano-rings with Adjustable L/D Ratios

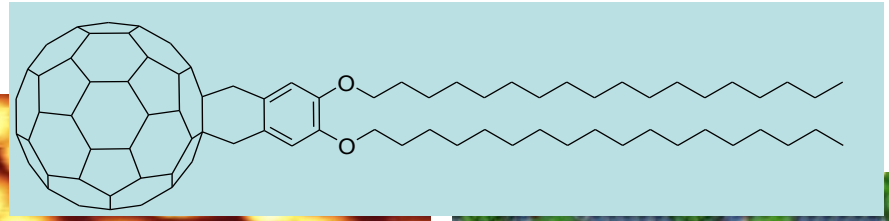


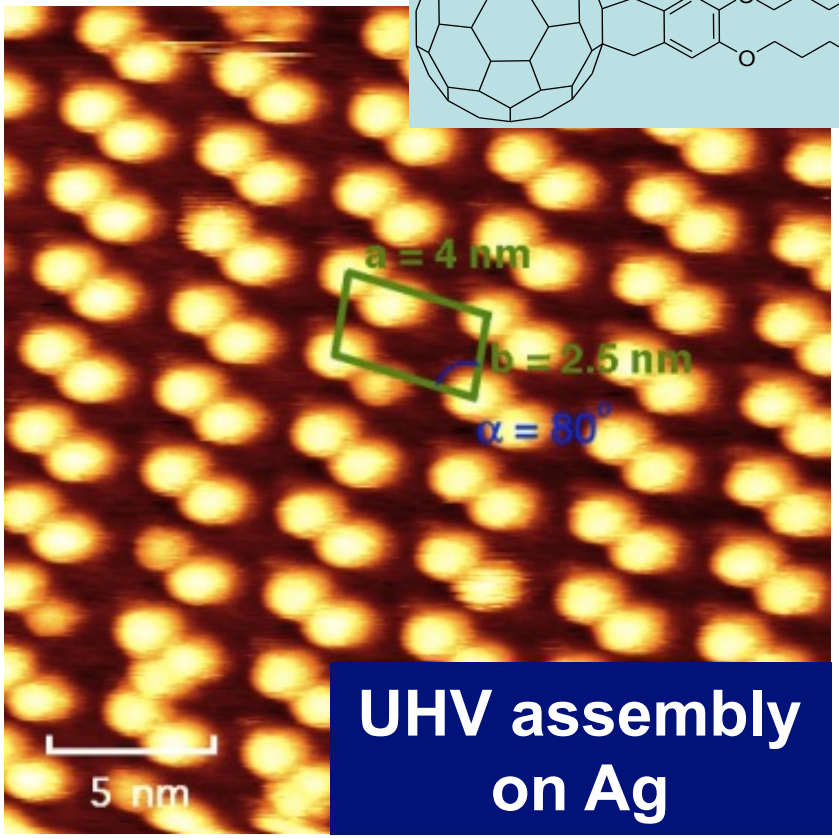




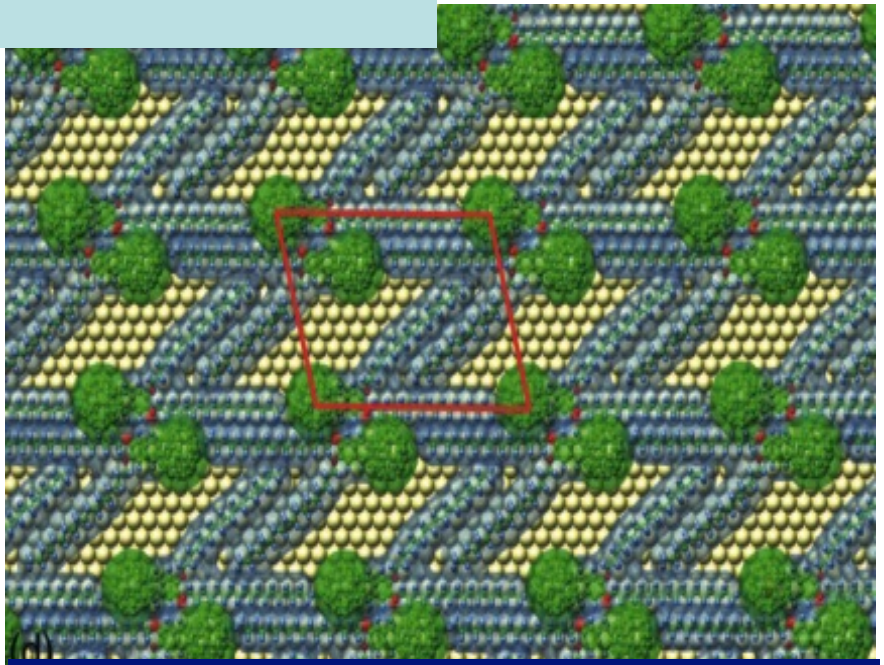
Hyunkyung Chun, Myung Gwan Hahm, Yoshikazu Homma, Rebecca Meritz, Koji Kuramochi, Latika Menon, Lijie Ci , Pulickel M. Ajayan and Yung Joon Jung,, "**Engineering Low-Aspect Ratio Carbon Nanostructures: Nanocups, Nanorings, and Nanocontainers**," *ACS Nano* , **2009**, *3* (5), 1274–1278.

Assembly of Functionalized Fullerenes





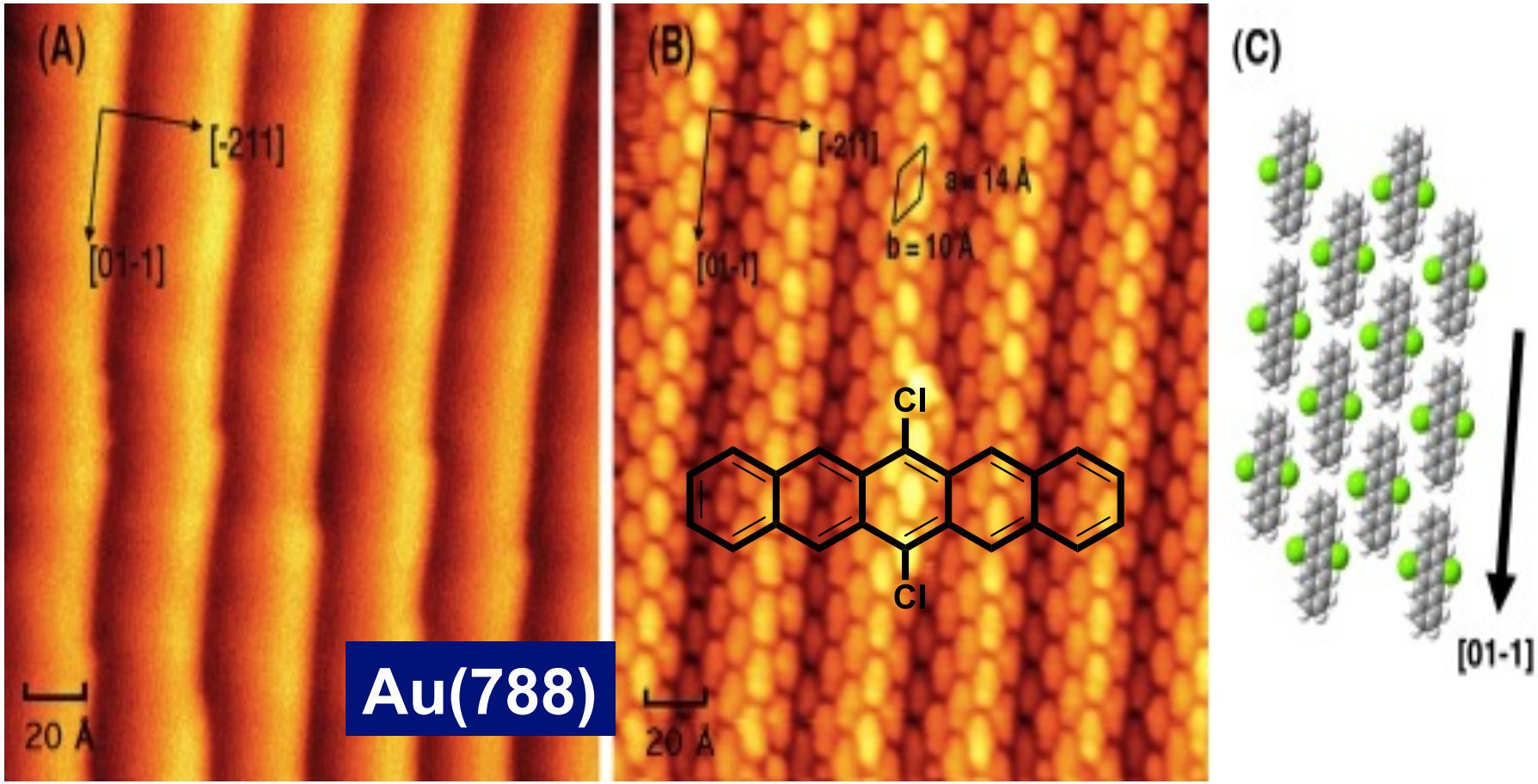
UHV assembly on Ag



DFT Model: 4 nm Pitch

Diaconescu, B.; Yang, T.; Berber, S.; Jazdzyk, M.; Miller, G. P.; Tománek, D.; Pohl, K., "**Molecular self-assembly of funtionalized fullerenes on a metal surface**," *Phys. Rev. Lett.*, **2009**, *102*, 056102-1 - 056102-4

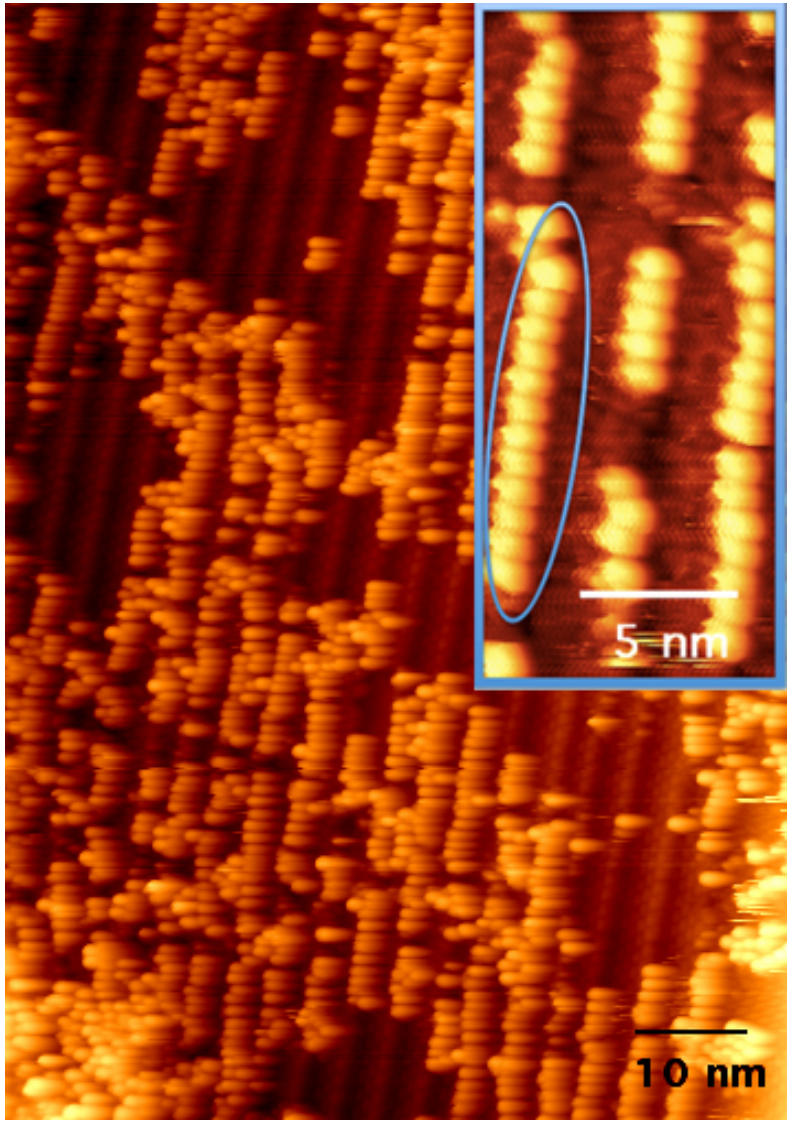
Dichloropentacene Assembly on Au(788) Controlled by Substrate Morphology



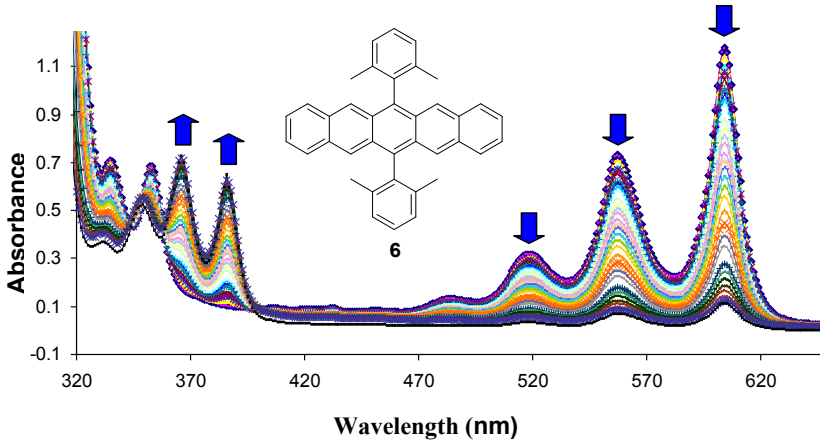
Wang, J.; Kaur, I.; Diaconescu, B.; Tang, J.-M.; Miller, G. P., Pohl, K. "**Highly Ordered Assembly of Single-Domain Dichloropentacene over Large Areas on Vicinal Gold Surfaces**," *ACS Nano*, **2011**, *5*, 1792-97.

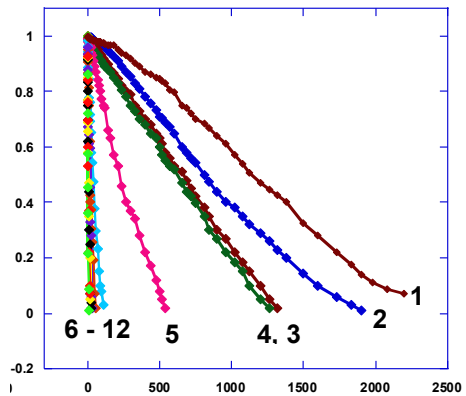
Multi-Layer Assembly: Fullerene SAM on Dichloropentacene on Au

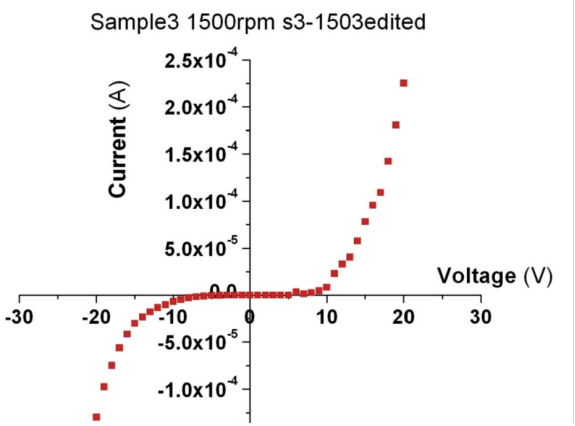
- Fullerene assemble onto step edges of DCP/Au
- "Single-chains" and "double chains" observed
- Model Bi-layer Organic Photovoltaic Device

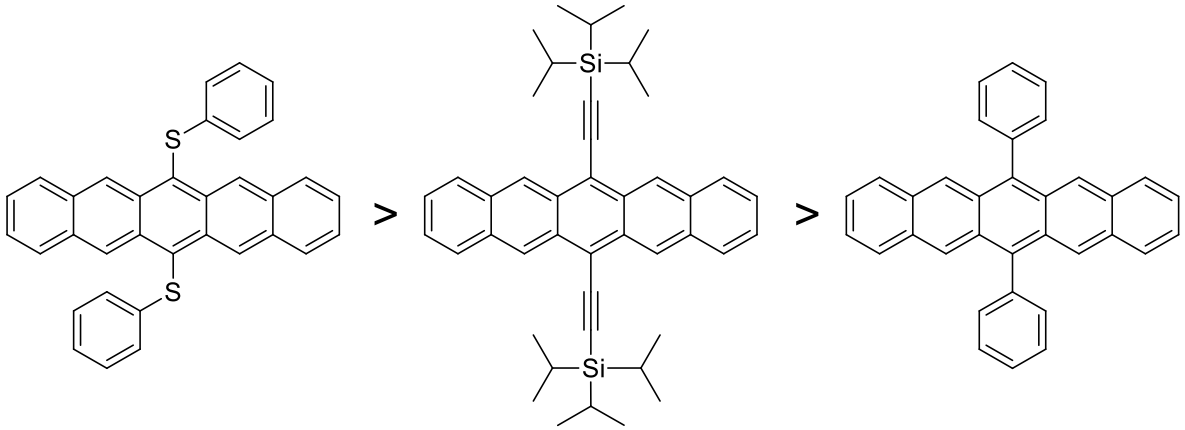


Substituent Effect Study Identifies Robust, Photooxidatively Resistant Acenes







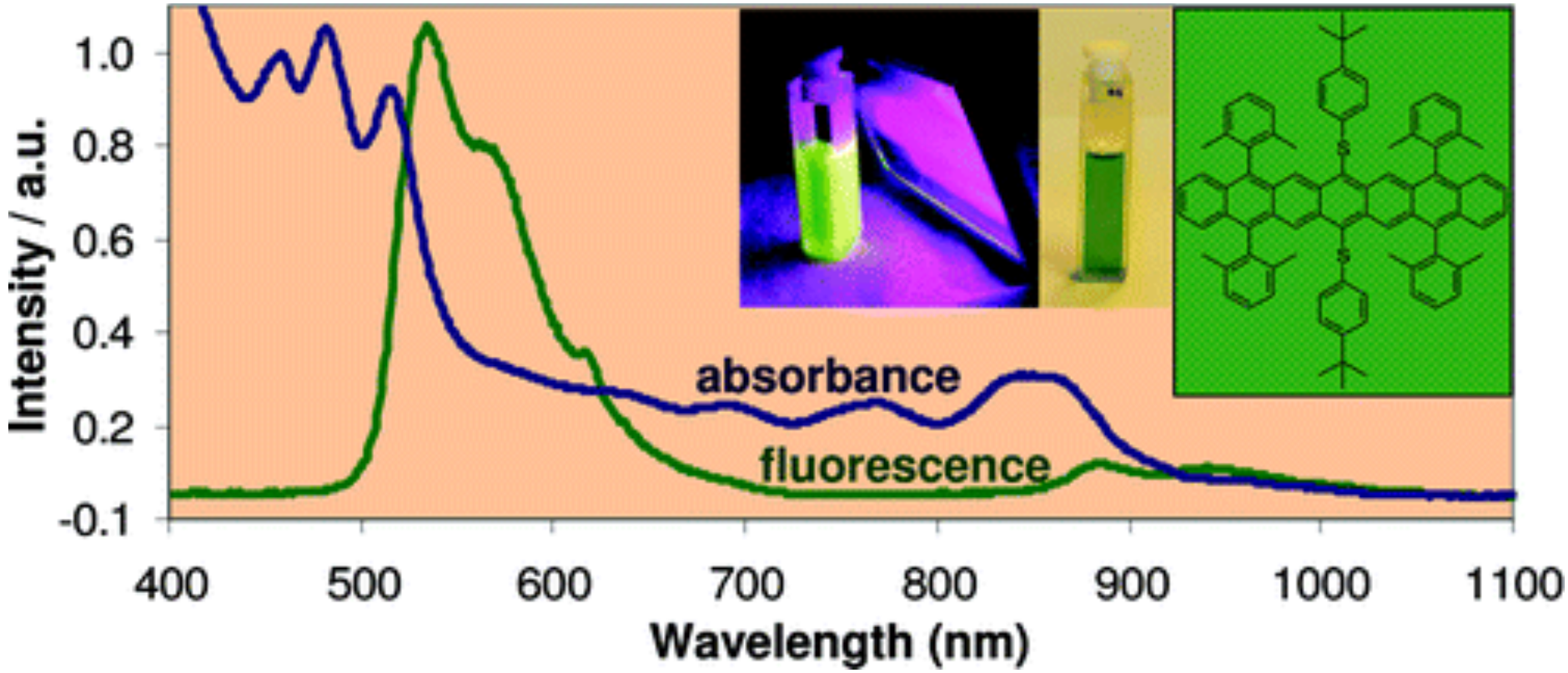


Applications

- Transistors
- OPVs
- OLEDs

Kaur, I., Jia, W., Kopreski, R., Selvarasah, S., Dokmeci, M. R., McGruer, N. and Miller, G. P., "**Substituent Effects in Pentacenes: Gaining Control Over HOMO-LUMO Gaps and Photooxidative Resistances**," *J. Am. Chem. Soc.*, **2008**, *130*, 16274–16286

A Photooxidatively Resistant Heptacene

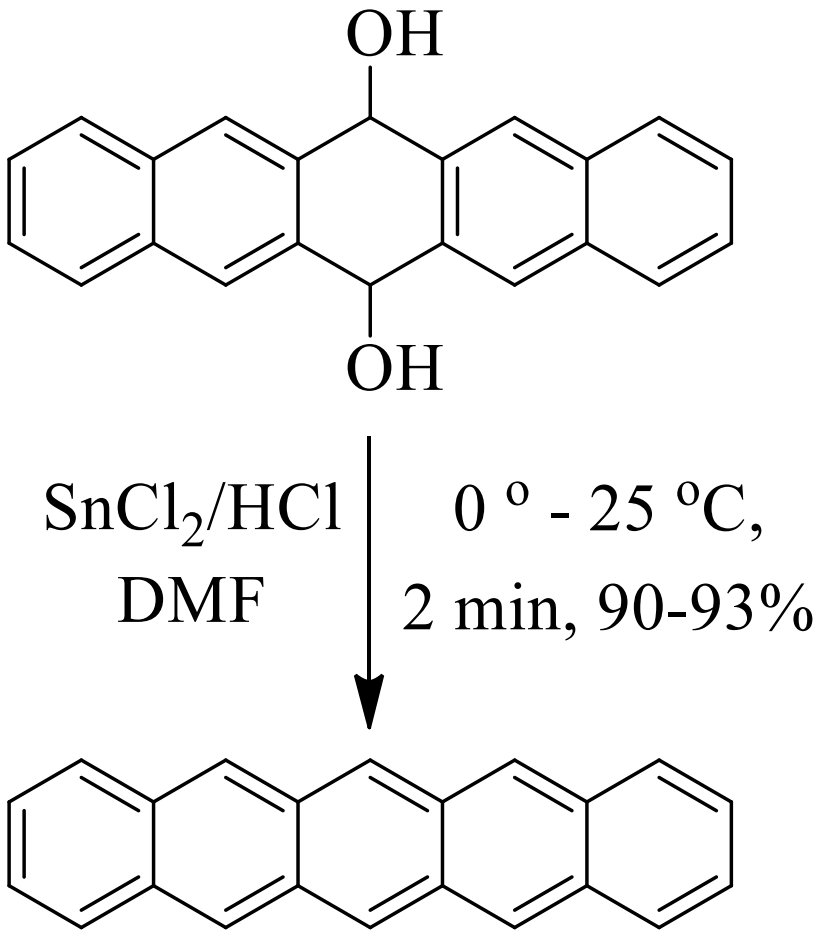


Smaller Band Gaps Realized with Larger Acenes

Kaur, I.; Stein, N.; Kopreski, R. P.; Miller, G. P., "**Exploiting substituent effects for the synthesis of a photooxidatively resistent heptacene derivative**," *J. Am. Chem. Soc.*, **2009**, *131*, 3424–3425.

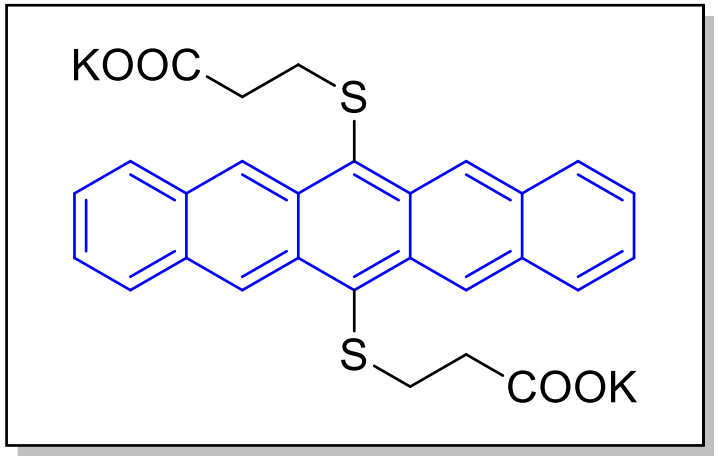
Pentacene Made Easy by CHN

- simple, fast, high yielding synthesis developed
- scalable to large masses
- low temperature method
- simple work-up
- equal or superior quality as expensive, high-purity commercial samples



Pramanik, C.; Miller, G. P.,
"**Pentacene Made Easy**," *Molecules*, **2012**, *17*, 4625-33.

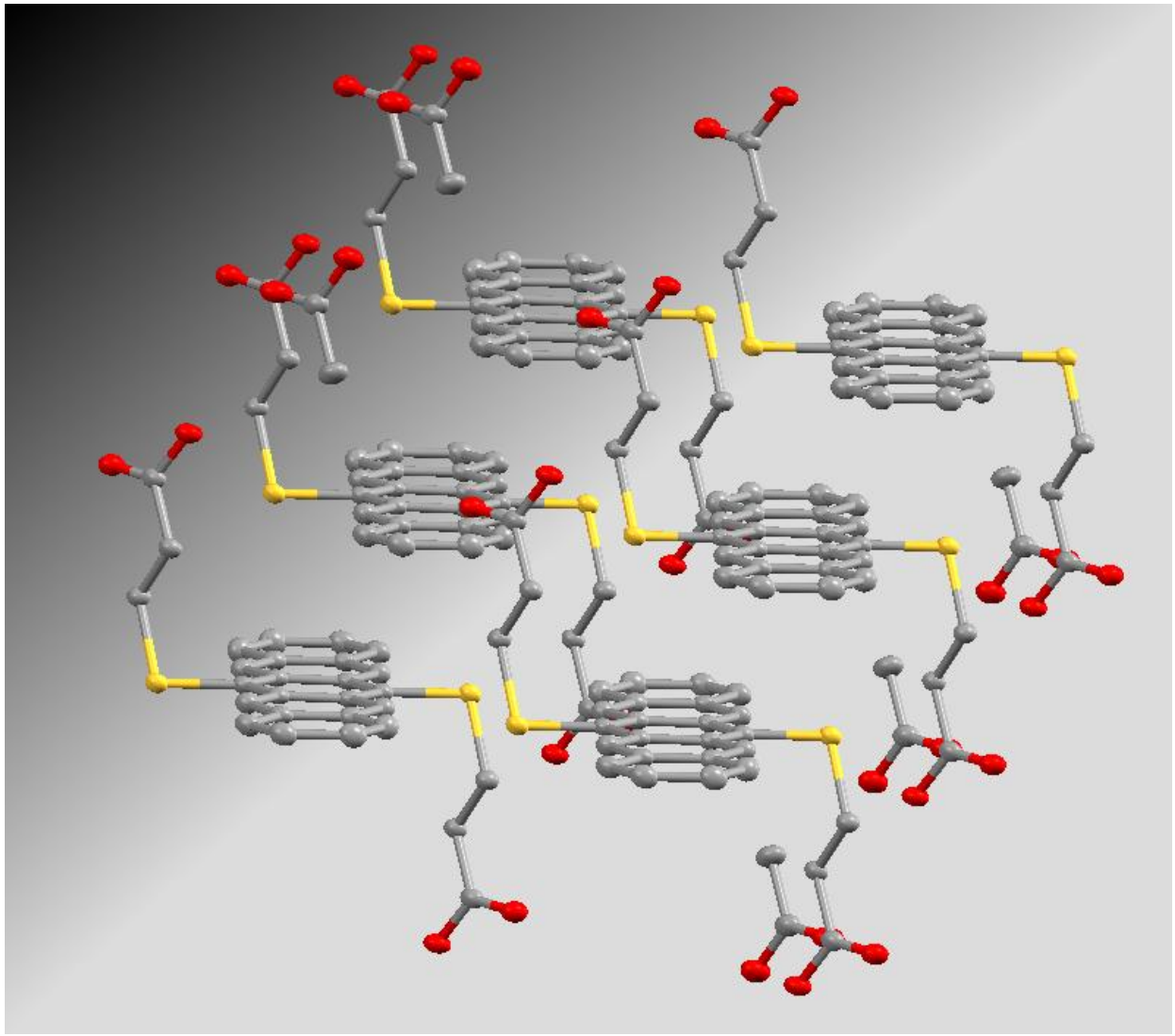
The 1st Water Soluble Pentacene



WSP: New opportunities for thin-film processing and device architectures

Pramanik, C.; Li, Y.; Singh, A.; Lin, W.; Hodgson, J. L.; Briggs, J. B.; Ellis, S., Muller, P.; McGruer, N. E.; Miller, G. P., "**Water Soluble Pentacene**," *J. Mater. Chem. C.*, **2013**, *1*, 2193-2201.

WSP: Readily Crystallizes in π-stacking Motif



HOMO-LUMO gap ~ 1.90-1.97 eV

$t_{1/2}$ in H_2O ~ 4 days

$t_{1/2}$ in solid state indefinite

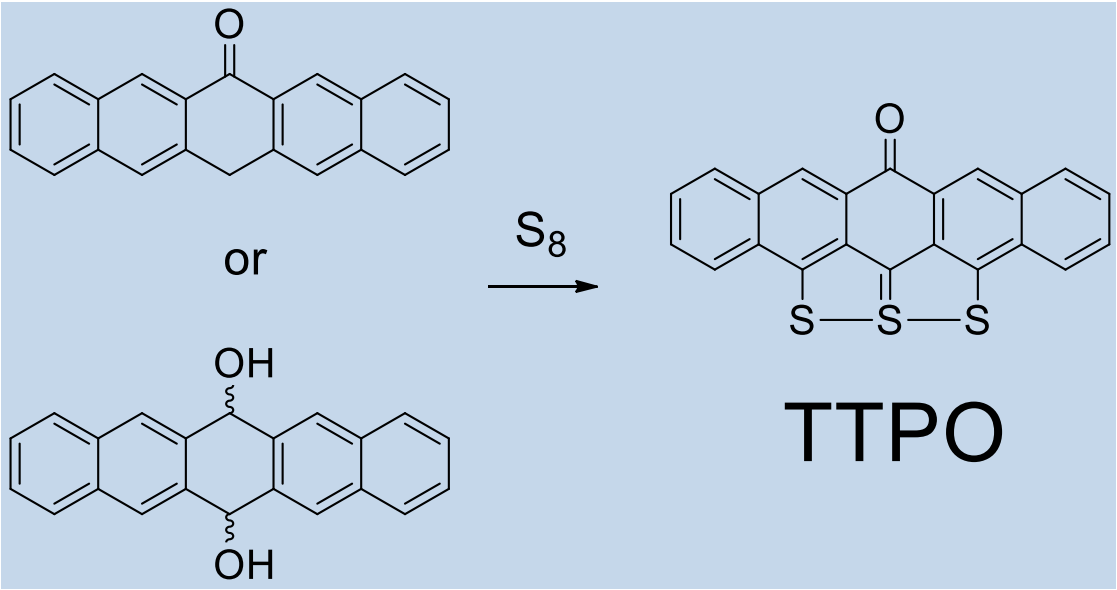
WSP aqueous "ink" formulated

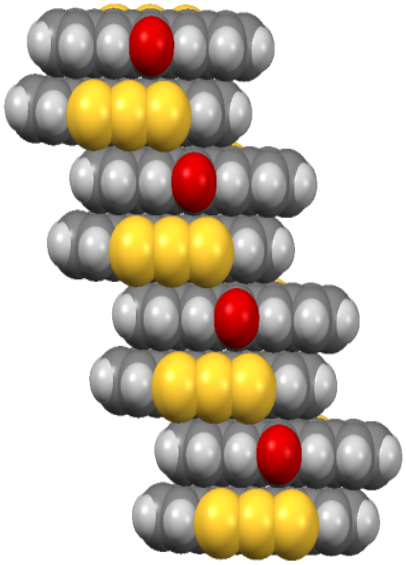
Ink-jet printing demonstrated

TF switches, OPVs and OLEDs under investigation

TTPO: a robust, high-temperature organic semiconductor

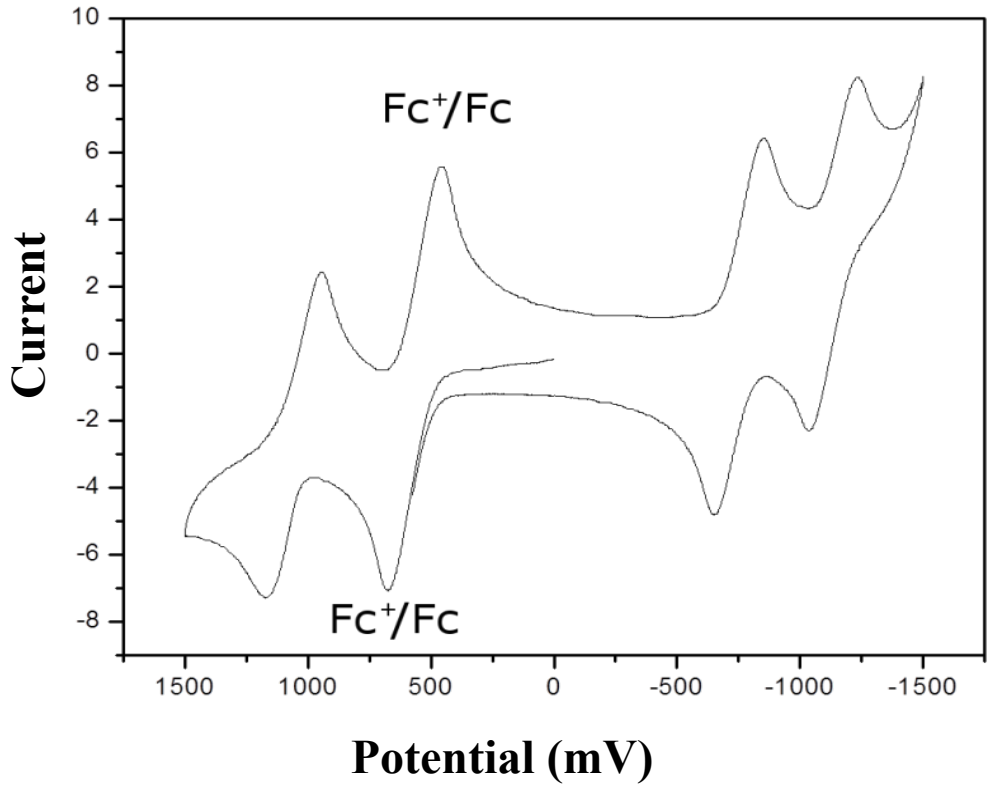
Simple Synthesis, Solution Processable, Columnar X-tals

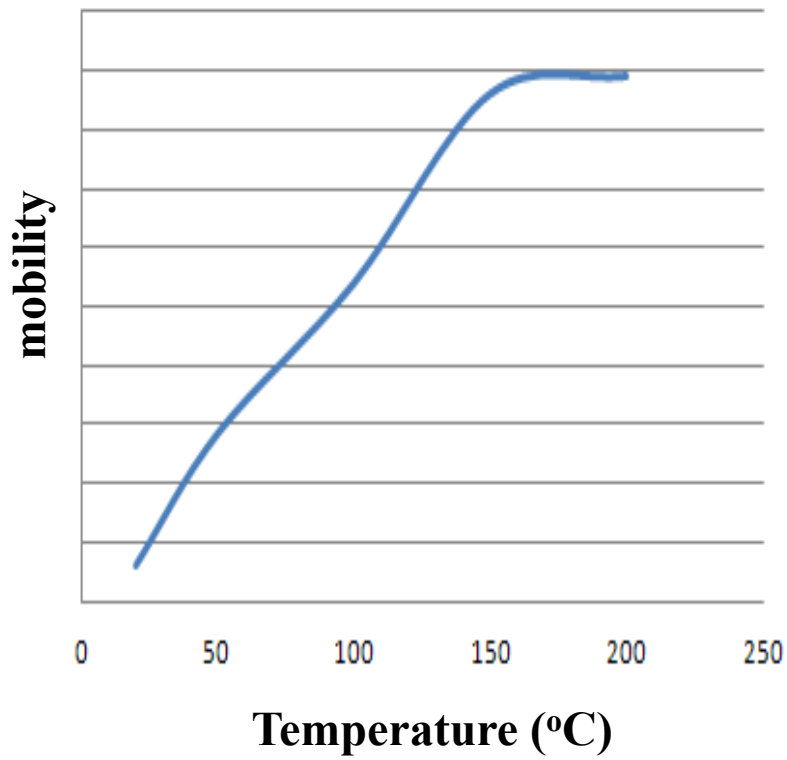




- Melts in air at 386-388 ^{o}C without decomposition – rare for organic semiconductors
- Indefinitely stable against photodegradation – very rare

TTPO: properties well suited for high temperature applications



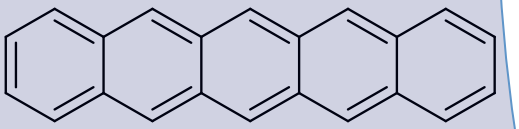


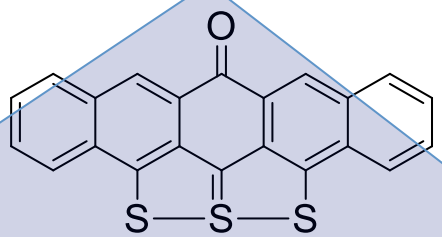
Miller, G. P. and Kintigh, J.

US Patent 8,389,744 B1 March 5, 2013

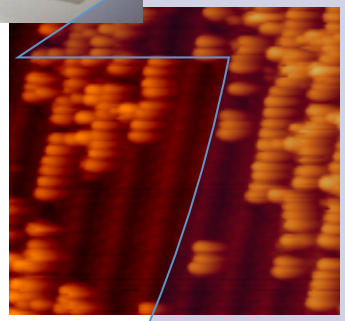
New Nanoelement Building Blocks for Targeted Applications

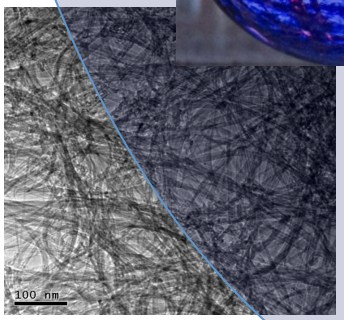
Pentacene Made Easy

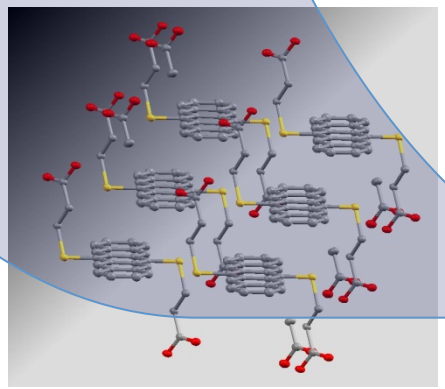




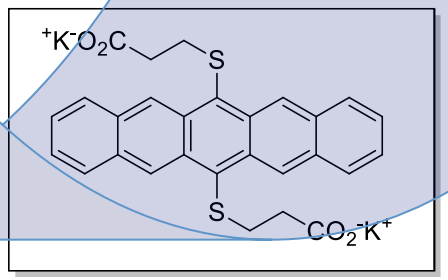
TTPO

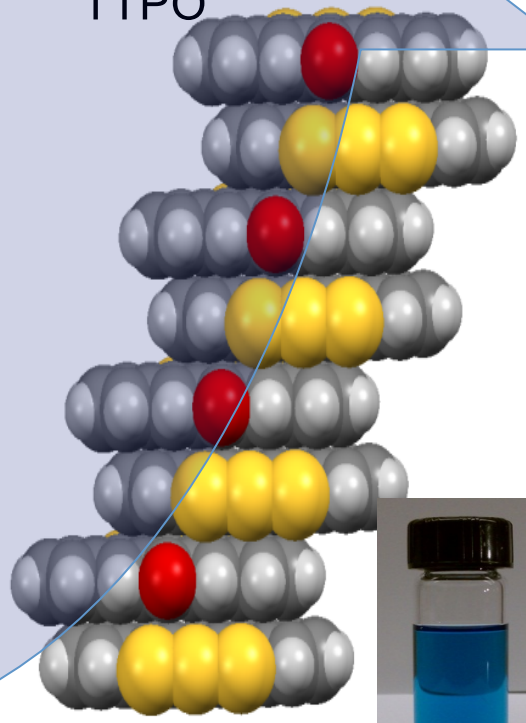






Water Soluble Pentacene





THRUST 2

Directed Assembly

and

Transfer

Center for High-rate Nanomanufacturing

CHN Directed Assembly Toolbox

Process	Speed	Scalability	Nanoelement property	Mechanism	Demonstrated assembly of
Convective	Slow	No	Surface Functionalization	Convection	Nanoparticles
Convective interfacial	Fast	Yes	Surface functionalization and surface tension	Convection and interfacial force	Nanoparticles
Chemical functionalization/ fluidic	Fast/ slow	Yes	Functionalization	Chemistry	Nanoparticles, CNTs, polymers
Electrophoretic and chemical functionalization	Fast	Yes	Charge and surface functionalization	Electrophoresis and surface energy	Nanoparticles, CNTs, polymers
Electrophoretic assembly	Fast	Yes	Charge	Electrophoresis	Nanoparticles, CNTs, polymers
Dielectrophoretic	Fast	Yes/No	Dielectric constant	Dielectrophoresis	Nanoparticles, CNTs, polymers

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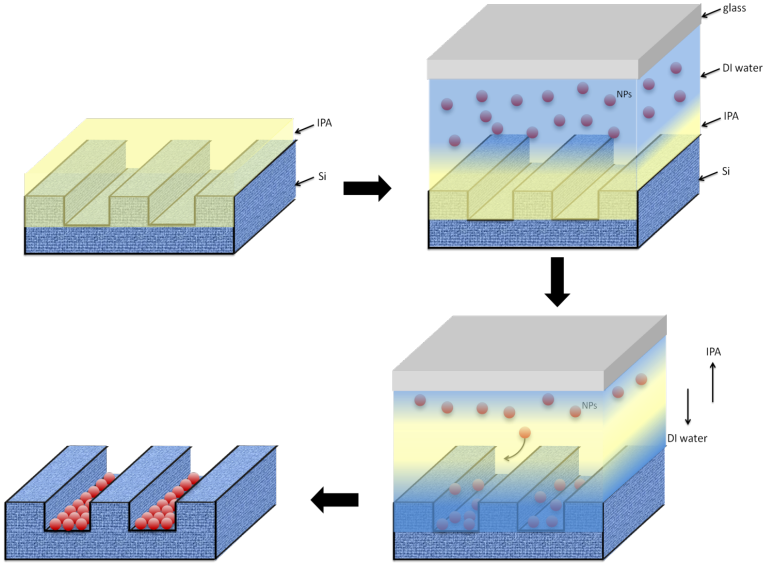
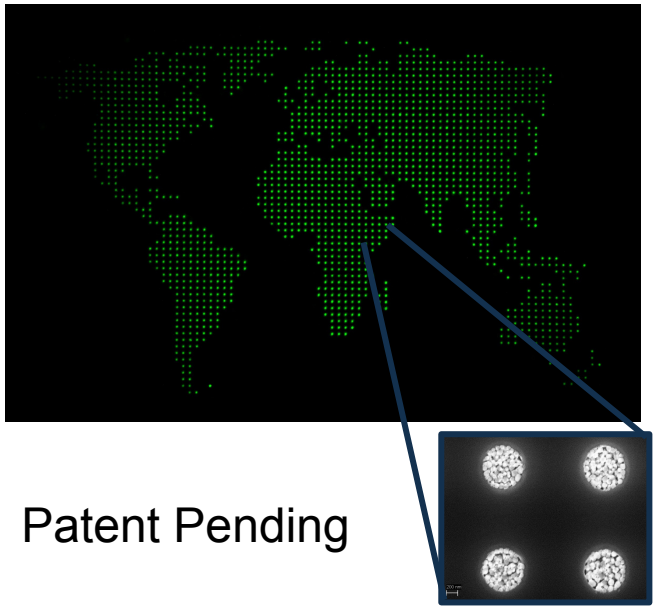
Interfacial Convective Assembly of Nanoparticles – New Process





Patent Pending

- Increases speed compared to convective assembly by use of a more volatile organic solvent
- Assembly of 100 nm silica NPs inside the world map by interfacial convective assembly

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CHN Directed Assembly Toolbox

Process	Speed	Scalability	Nanoelement property	Mechanism	Demonstrated assembly of
Convective	Slow	No	Surface Functionalization	Convection	Nanoparticles
Convective interfacial	Fast	Yes	Surface functionalization and surface tension	Convection and interfacial force	Nanoparticles
Chemical functionalization/ fluidic	Fast/ slow	Yes	Functionalization	Chemistry	Nanoparticles, CNTs, polymers
Electrophoretic and chemical functionalization	Fast	Yes	Charge and surface functionalization	Electrophoresis and surface energy	Nanoparticles, CNTs, polymers
Electrophoretic assembly	Fast	Yes	Charge	Electrophoresis	Nanoparticles, CNTs, polymers
Dielectrophoretic	Fast	Yes/No	Dielectric constant	Dielectrophoresis	Nanoparticles, CNTs, polymers

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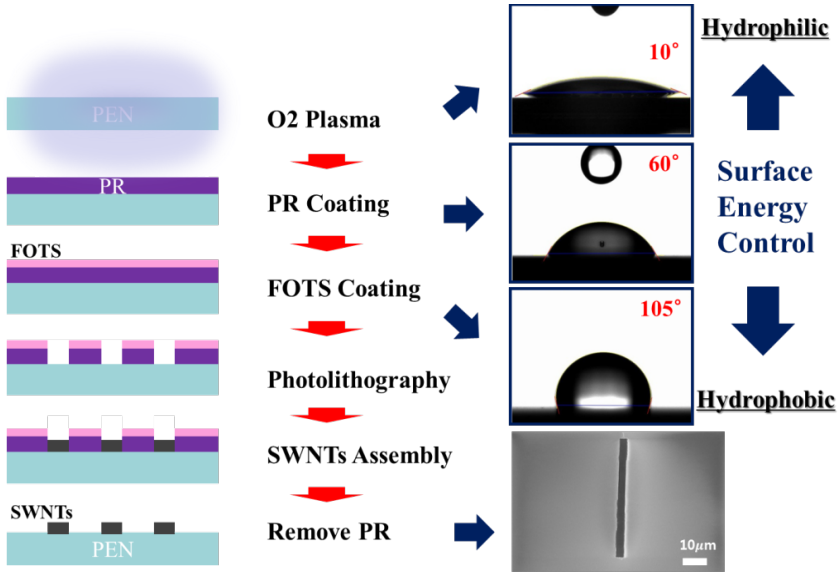
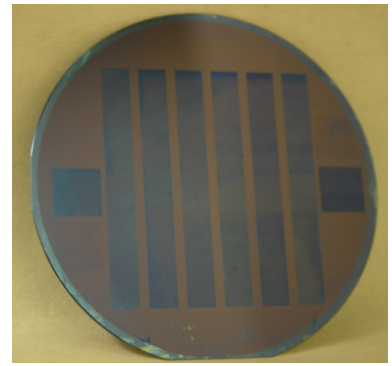
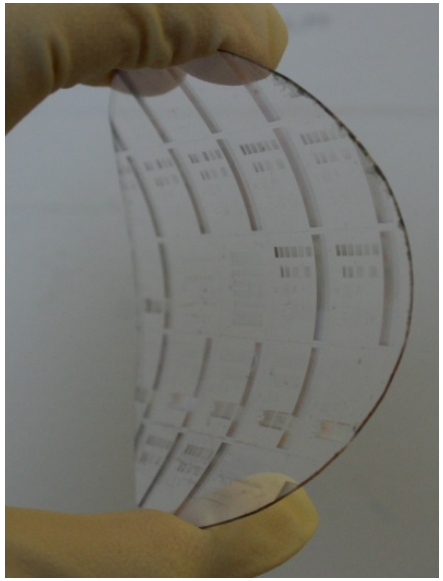
Template Guided Chemical/Fluidic Assembly

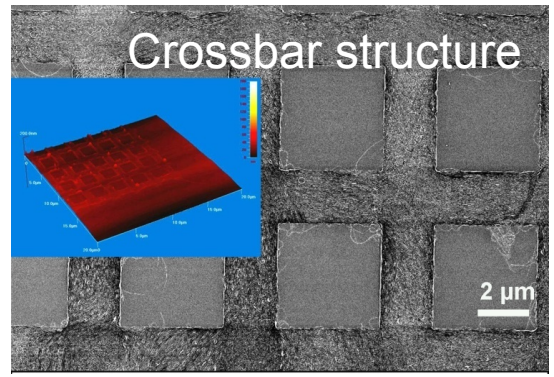
- Assembly of CNTs over large areas on templates with different surface energies
  - Hydrophobic and hydrophilic regions assist fluidic assembly





Large scale assembly on polymer substrates



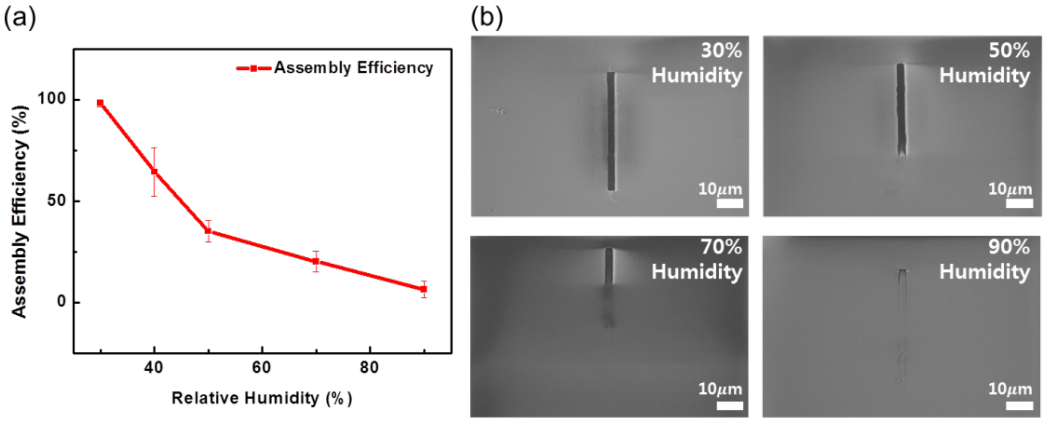


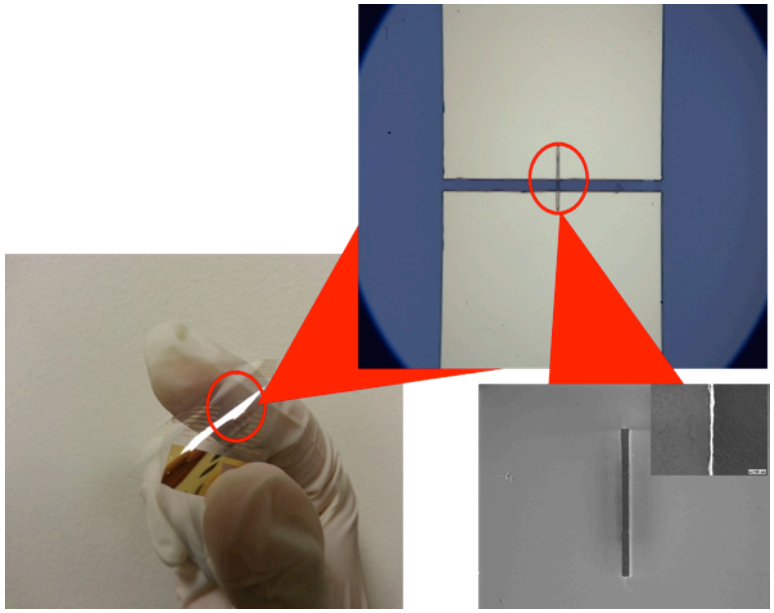
Xiong, X, Jaberabsari, L, Hahm, M G, Busnaina, A, and Jung, Y, J, *Small*, 3(12) 2006 (2007).

Jaber-Ansari, L, Hahm, M G, Somu, S, Echegoyen Sanz, Y, Busnaina, A, and Jung, Y J, *J. Am. Chem. Soc.*, 131 (2), pp 804 (2009).
Jaberasani, L., Somu, S. Hahm, M G, Busnaina, A, and Jung, Y J, *Appl. Phys. A.*, 5194 (2009).

Xiong, X., Chen, C.-L., Ryan, P., Busnaina, A. A., Jung, Y. J. and Dokmeci, M. R., *Nanotechnology*, 20, pp. 295302-308, July 2009.

Large Scale SWNTs Assembly on Plastic Substrate using Template-guided Fluidic Process





- **Large-scale SWNTs assembly process on flexible substrate based on surface modification process and humidity control.**

- **Application to large scale SWNTs-based flexible device fabrication, such as biosensor for D-glucose detection (see Thrust 3)**

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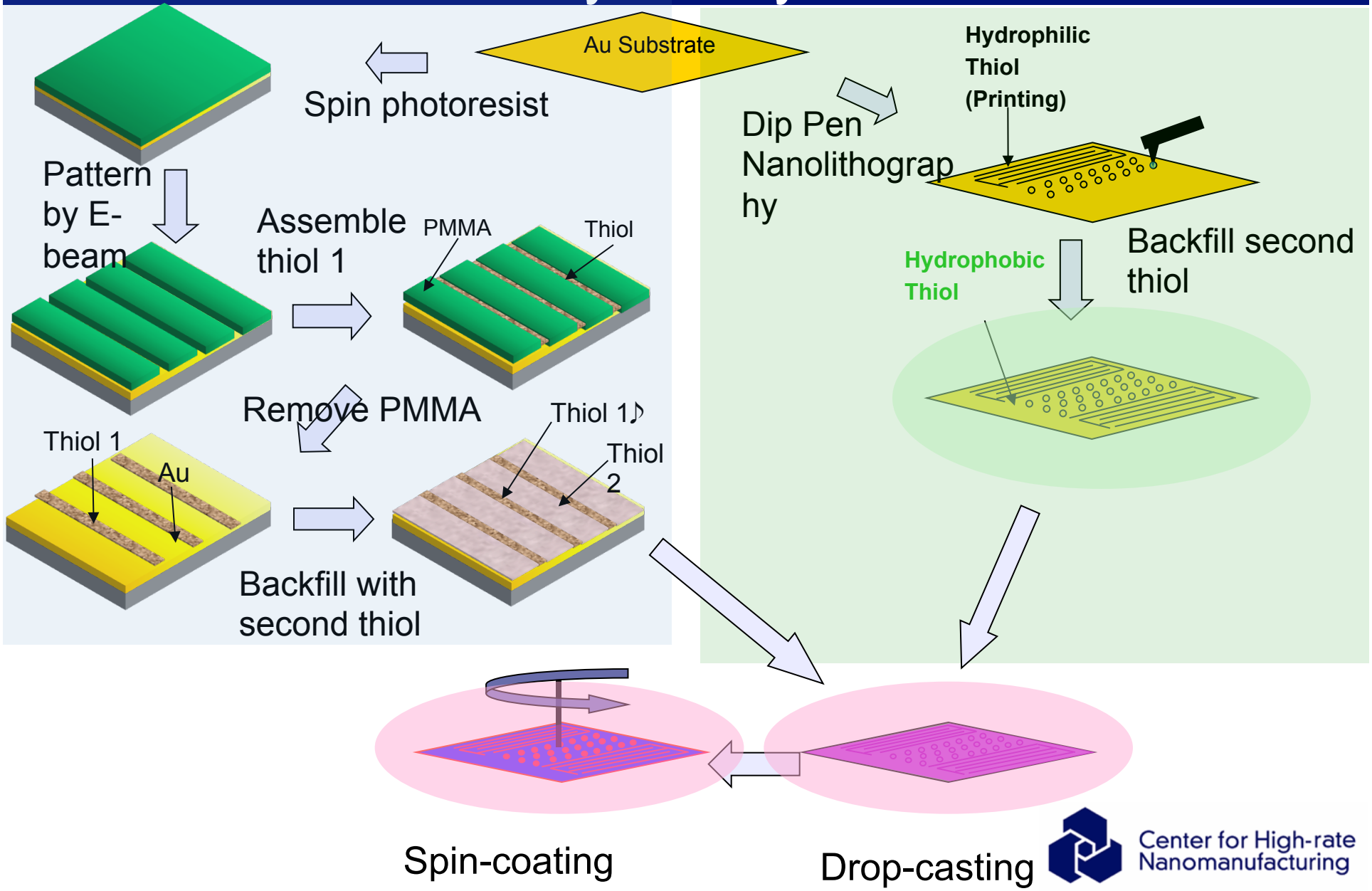
Chemically Functionalized Templates for Assembly of Polymer Blends



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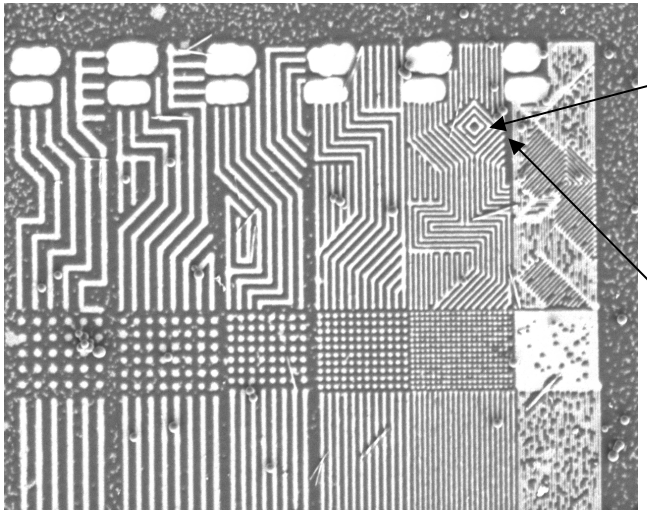
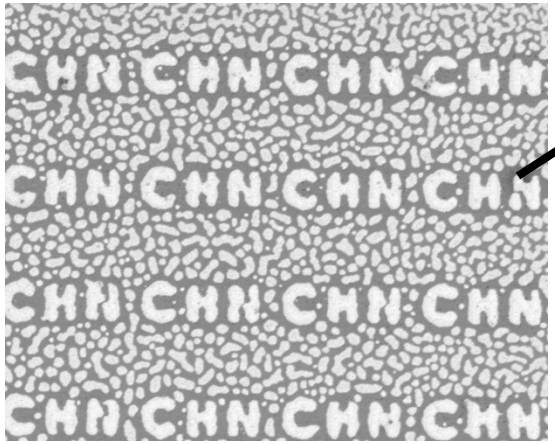
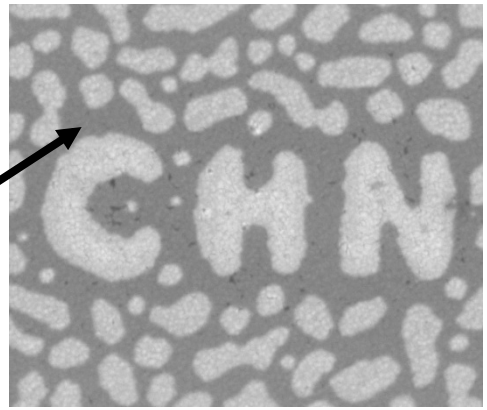
Multi-scale Patterned Polymer Blends

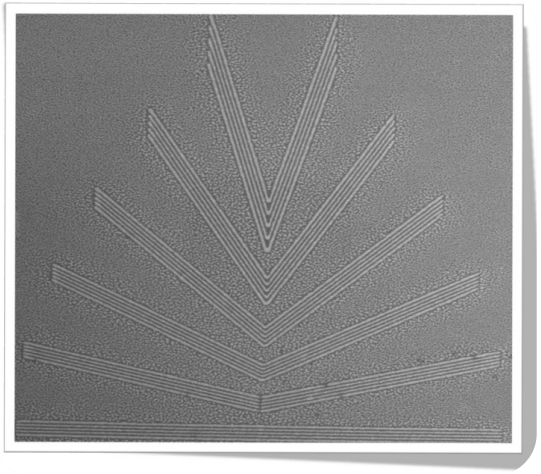
- Chemically functionalized templates assemble PS/ PMMA polymer blends into non-uniform geometries.
- Polymer domains were patterned from 300 nm down to 100 nm on *the same template*.

PS/PMMA (50/50 ratio)









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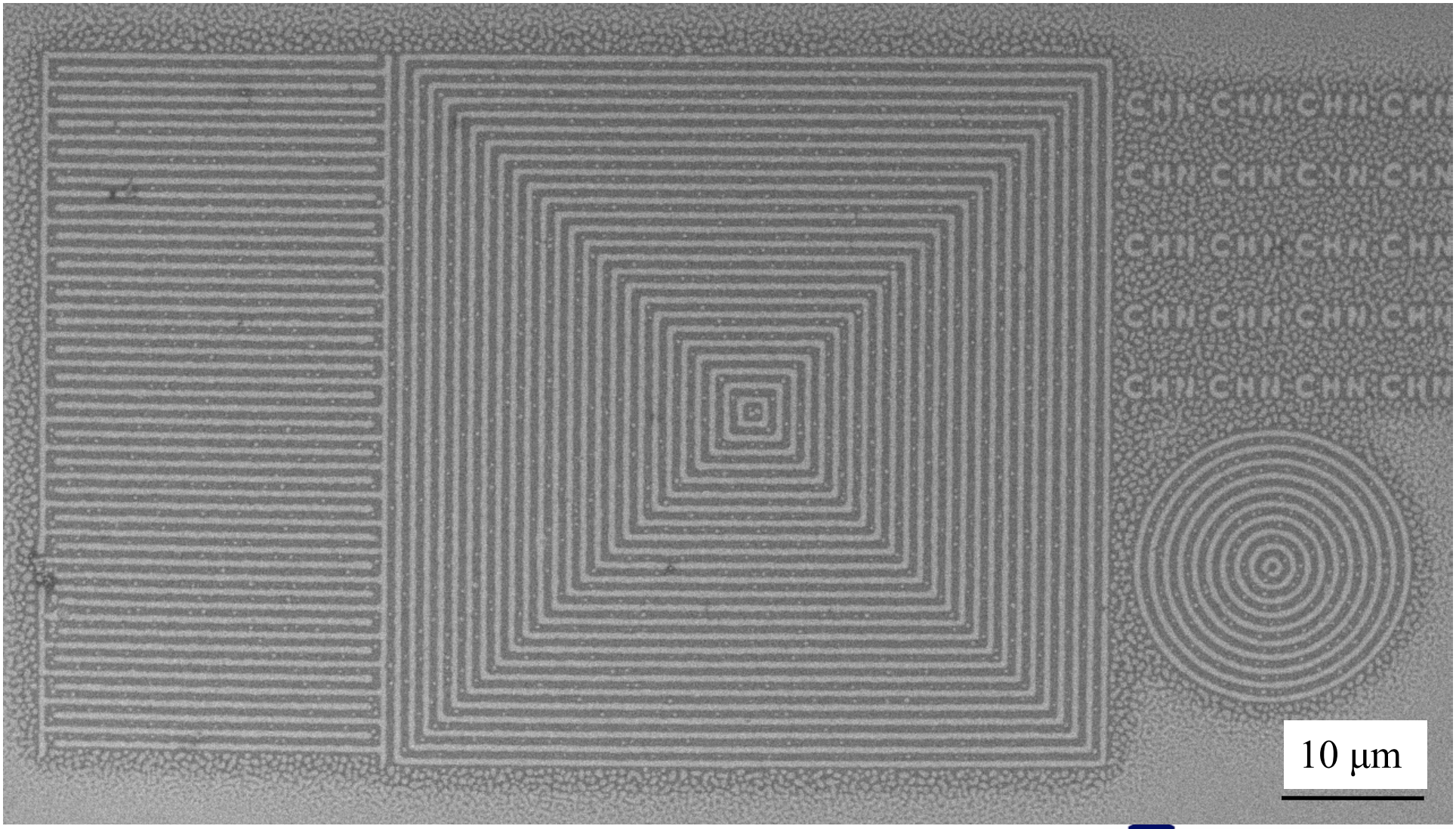
Large Scale Arbitrary Geometries



L Fang, M. Wei, Y. Shang, D. Kazmer, C. Barry, & J. Mead, *Langmuir*, 28(27), 10238–10245 (2012).

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CHN Directed Assembly Toolbox

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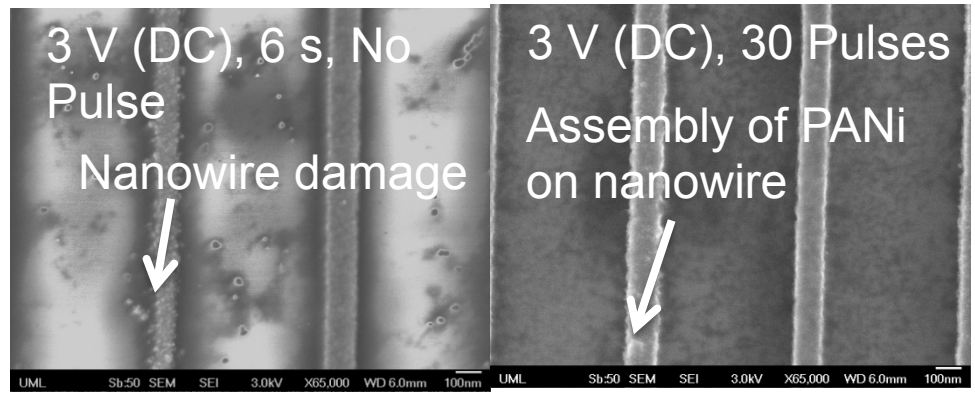
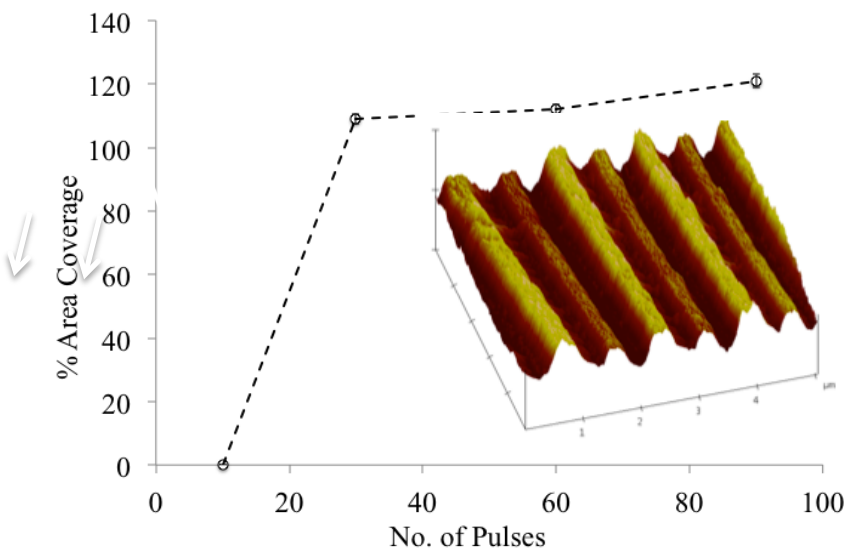
Pulsed Electrophoresis: Durability at Nanoscale

- Reduces cycle time
- Reduces heat build up
- Allows higher voltages to be used
- Damage to the nanowire templates eliminated

A. Kumar, D. Kazmer, C. Barry, J. Mead
Nanotechnology 23 (2012).



Assembly of PANi at Nanowire templates



Pulsed electrophoresis provides control on area coverage with no bridging

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Damascene Templates for Assembly and Transfer

Etching metal & stripping resist

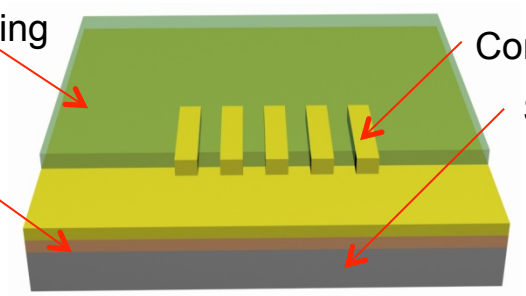
Lithography & development

Insulating layer

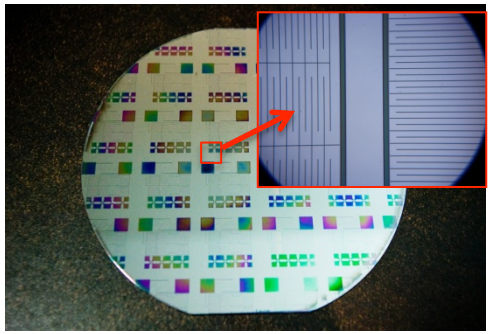
Conductive layer

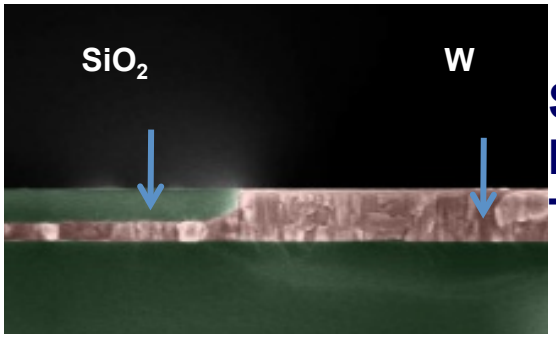
Substrate

Insulating layer



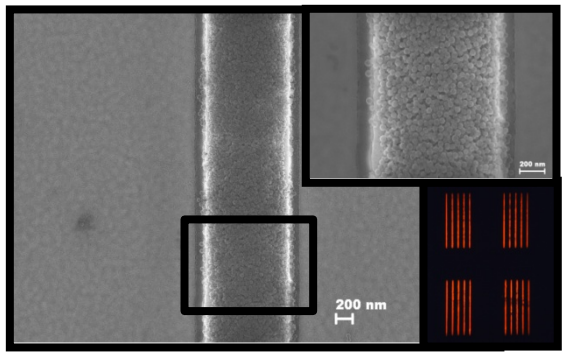
Cross section of damascene template

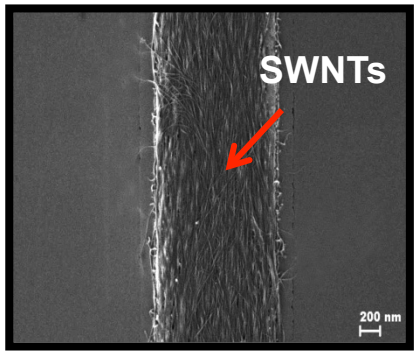


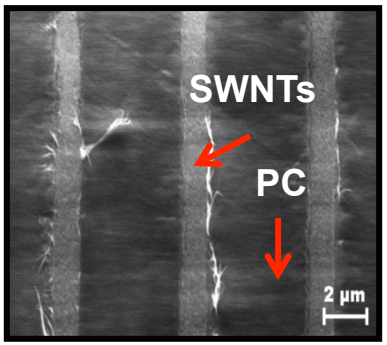


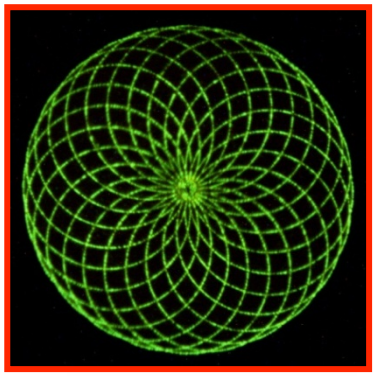
Silicon-based Hard Templates

Flexible Templates for Roll-to-Roll Manufacturing

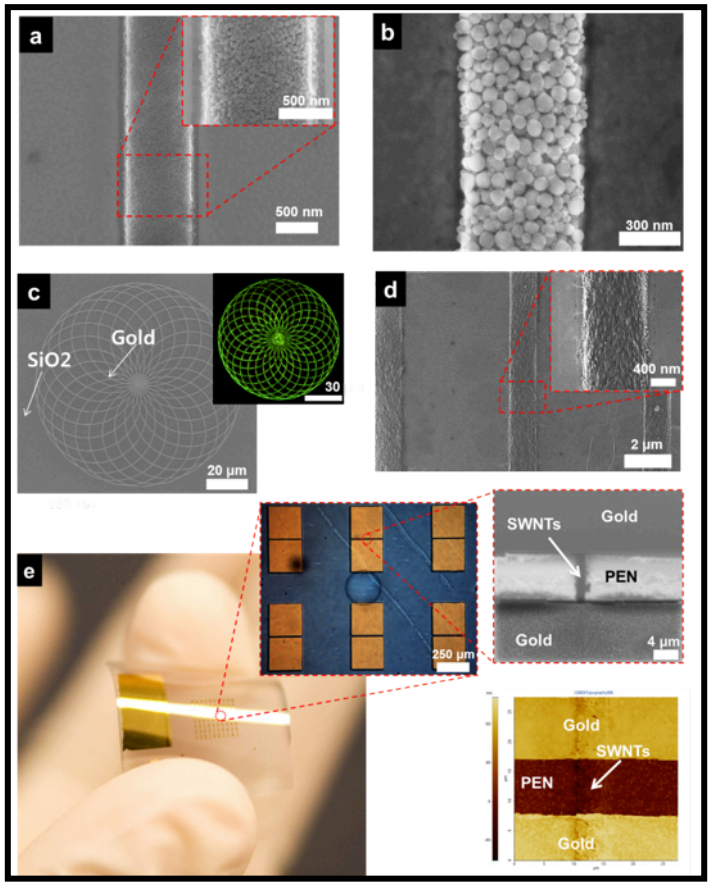








Directed Assembly and Transfer Using Damascene Templates



a-d) nanoparticle and SWNTs assembly
e) flexible device with SWNTs

- **Uniformly assembly of polymer, silica, Au, Cu, W nanoparticles and SWNTs on the template.**
- **100 % transfer yield of SWNTs onto flexible substrate**
- **Template can be reused more than few thousand times.**
- **Template functionalization can be reused more than 100 times.**
- **Flexible template for roll to roll system.**

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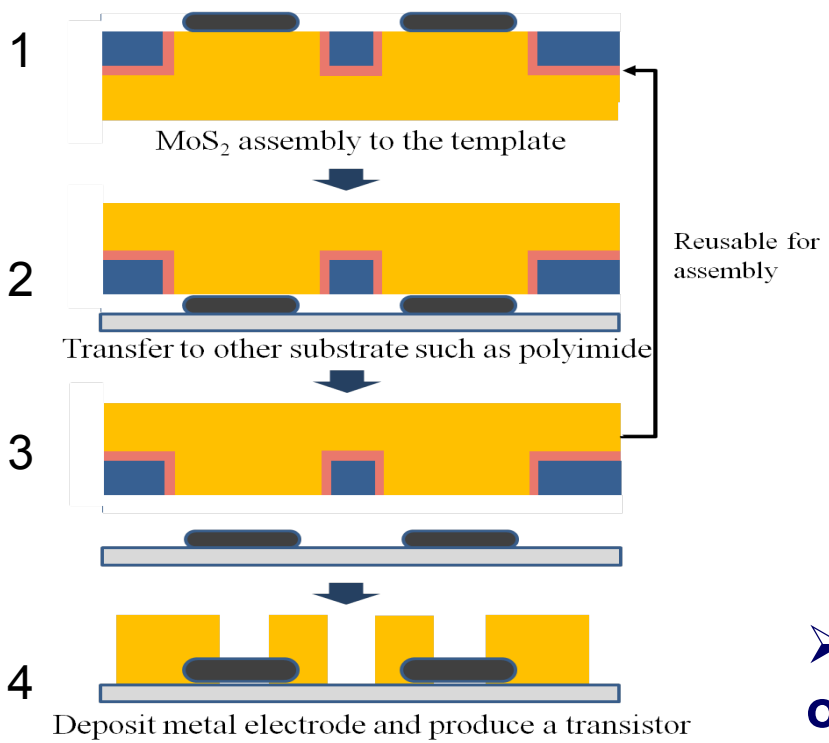
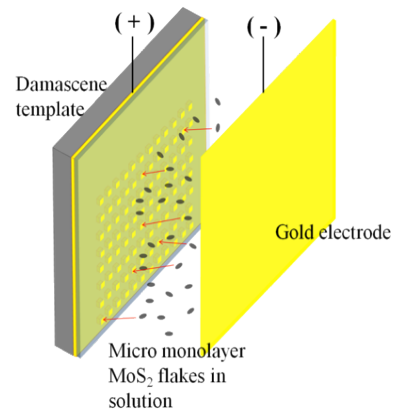
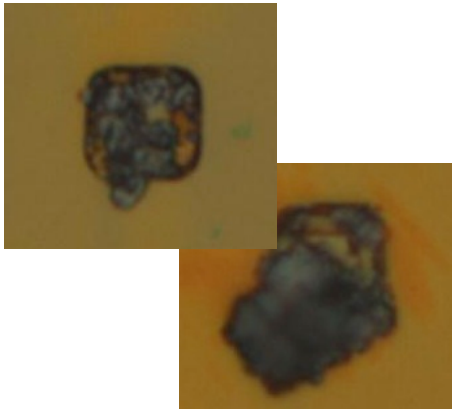
Electrophoretic Assembly of MoS_2 Micro-flakes using Damascene Template



Schematic of a transistor fabrication using the assembly and transfer process.





Schematic of electrophoretic assembly and assembled MoS_2.

- **Chip-scale electrophoretic assembly of MoS_2 flakes using a damascene template**
- **Damascene template can assemble a wide array of materials**

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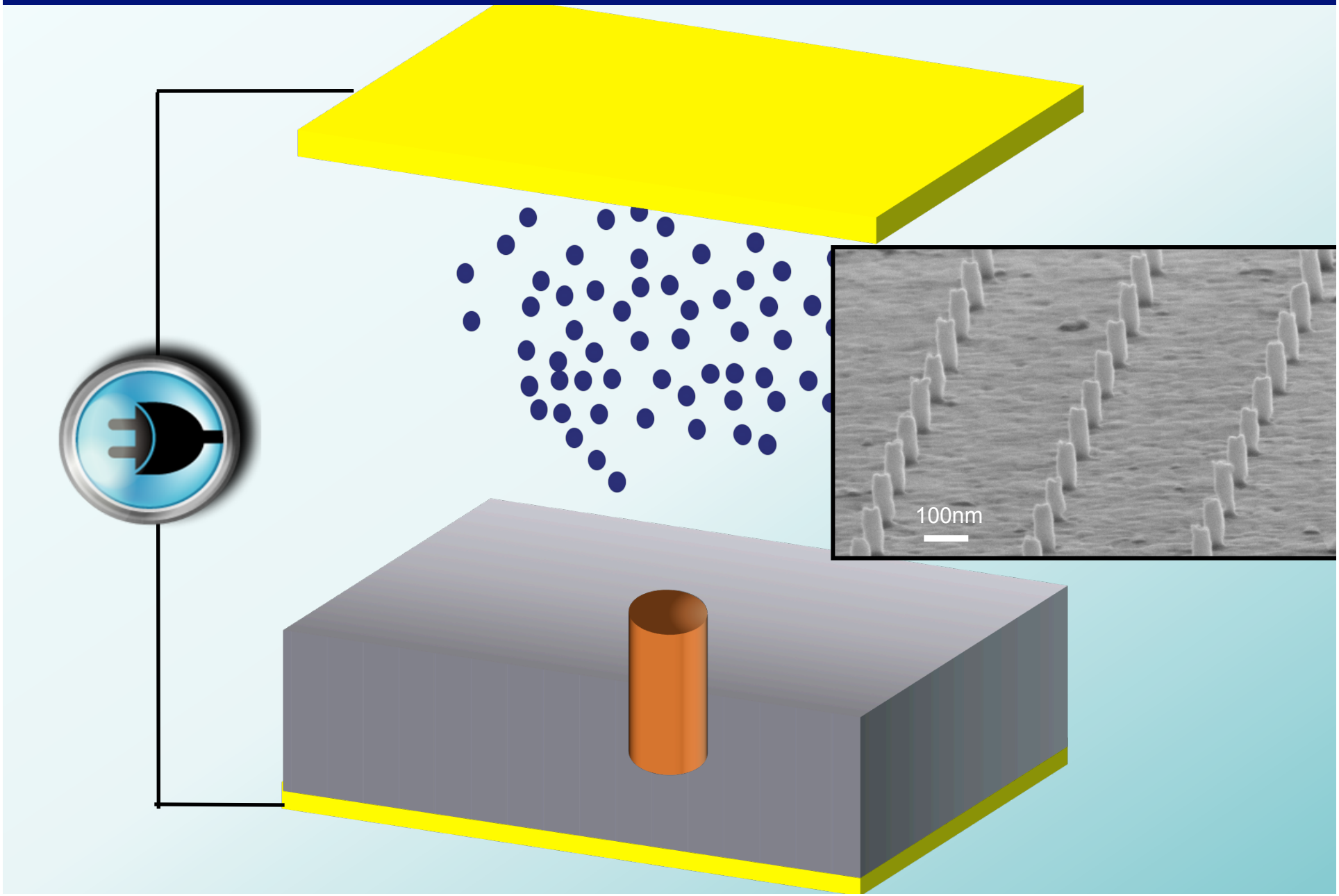
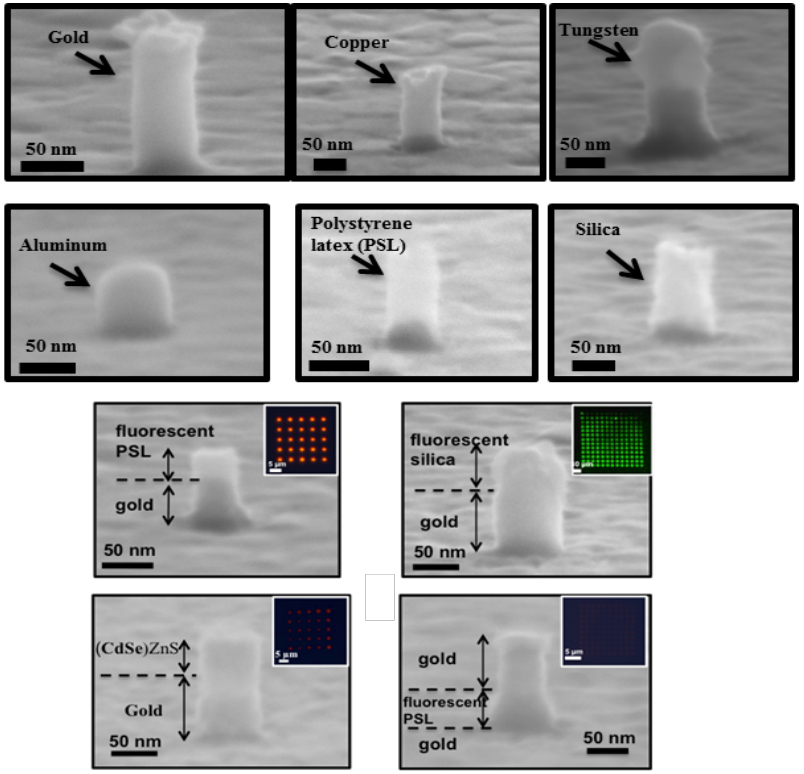
Fabrication of 3-D Nanostructures Using Directed Assembly

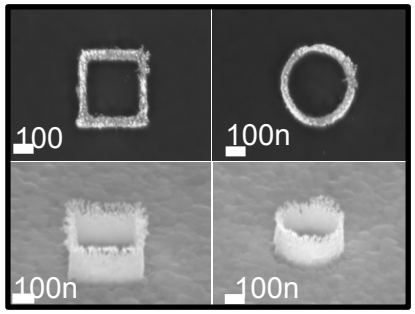


Manufacturing Homogenous and Hybrid 3-D Nanostructures using Directed Assembly of Nanoparticles



Fabrication of various types homogenous and hybrid nanopillars through directed assembly of nanoparticles.

- Water-based, room-temperature and pressure process using nanoparticles (NPs) for fabricating 3-D nanostructures.
- Fabricated nanopillars, nanoboxes and nanorings from Au, W, Cu, PSL, Si, SiO2, and their hybrid derivatives as small as 25 nm.
- Successfully harvested nanostructures from the substrate.



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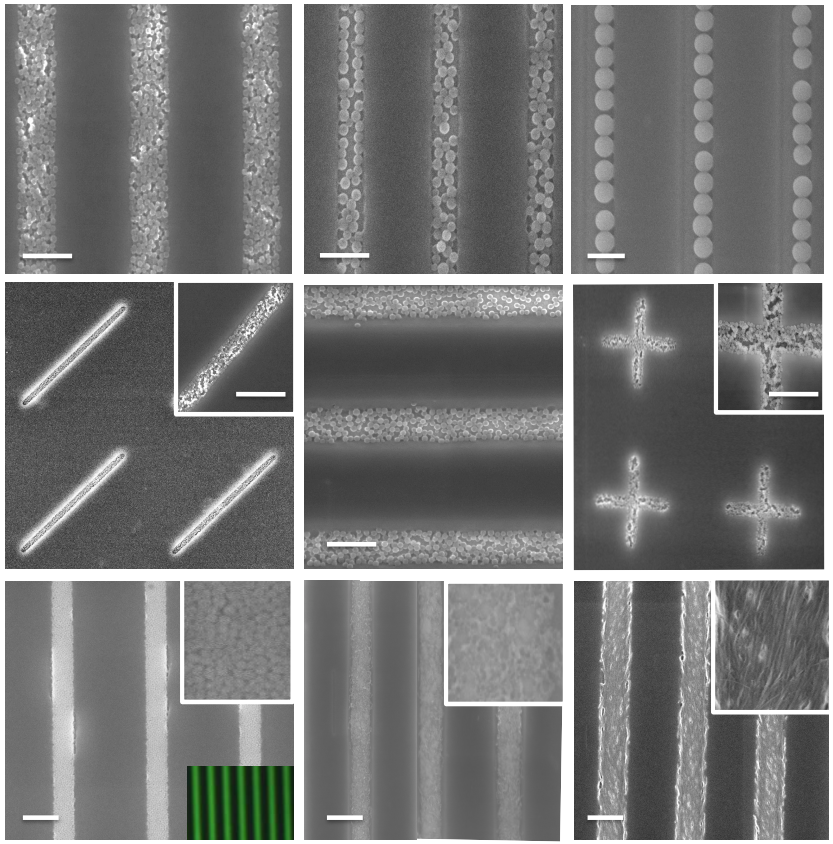
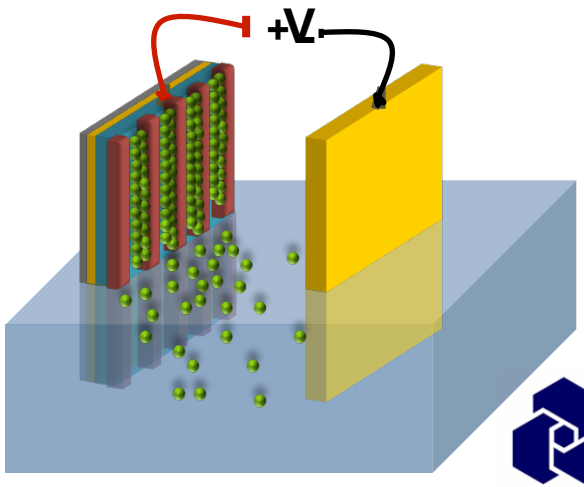
High-rate Electrofluidic Directed Assembly of Nanoelements on Insulating Surfaces



Assembly Capabilities of Electrofluidic Directed Assembly

- **Electrophoretic directed assembly on insulating substrates.**
- **Nanoparticles of multiple sizes (50nm, 100nm and 200nm) assembled into patterns at various angles to pulling direction.**
- **Silica particles, quantum dots and single-walled carbon nanotubes were successfully assembled.**



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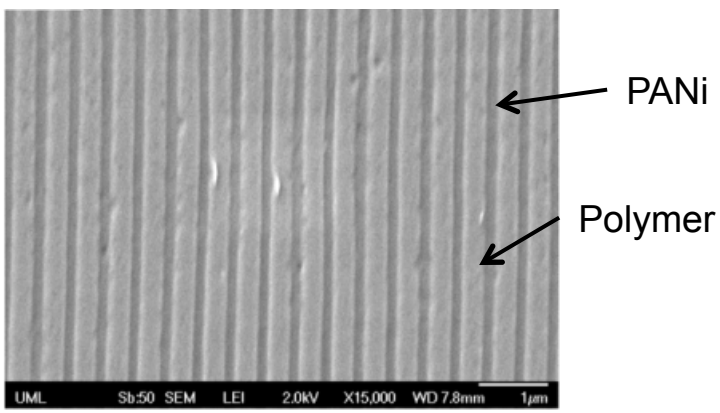
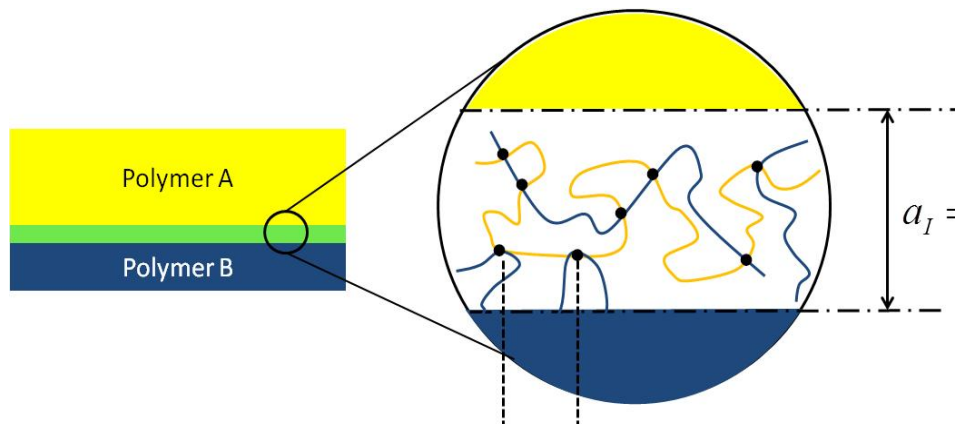
Mechanism of Transfer Process to Polymer Substrates

Transfer expected when interfacial adhesion between assembled polymer and substrate polymer > assembled polymer and assembly substrate (gold).

Adhesion between immiscible polymers related to interphase thickness (a_I), and inversely proportional to solubility parameter difference (δ_1 - δ_2) [1,2,3]





1. Creton, C.; Kramer, E. J.; Brown, H. R.; Hui, C. Y., *Adv Polym Sci* 156 (2001), 53–136
2. Zhang, J, Lodge, T. P., Macosko, C.W., *J. of Polymer Science: Part B: Polymer Physics*, Vol. 47, (2009) 2313–2319
3. Cole, P. J.; Cook, R. F.; Macosko, C. W., *Macromolecules* 36, (2003) 2808–2815

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Mechanism of Transfer Process to Polymer Substrates

Polymer	L_e (nm)	δ ($MPa^{1/2}$)	Interphase Thickness	Transfer result
PANi		22.2		
PU	4.01	22.9	4.42+11	Transferred
PET	4.00	22.0	1.56E+12	Transferred
NBR	5.47	21.0	1.39E+11	Transferred
PMMA	6.70	18.7	3.17E+10	Non-transfer
SEBS	6.07	16.0	2.18E+10	Non-transfer
Polyisoprene	4.74	17.5	3.87E+10	Non-transfer
PS	7.65	18.7	2.43E+10	Non- transfer

Need strong interphase for efficient transfer

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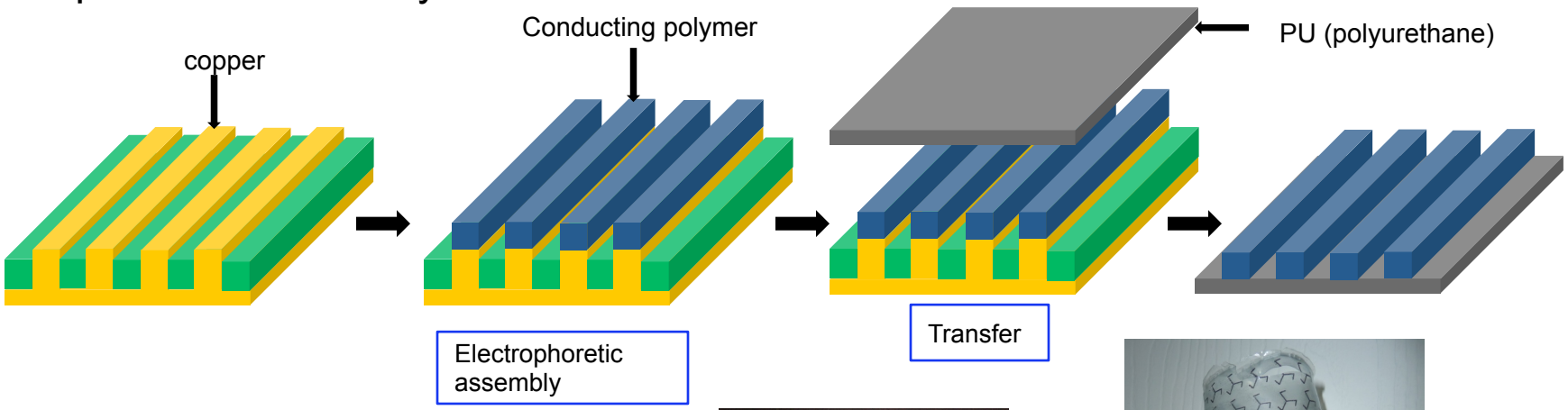
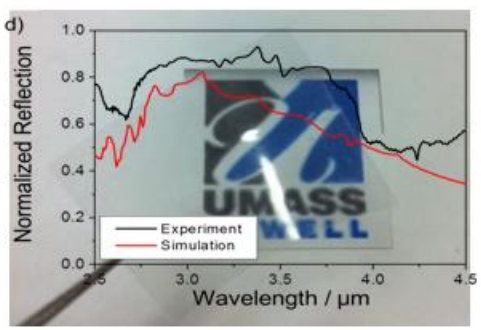
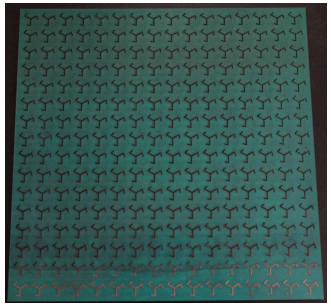
Fabrication of Chiral Metamaterial

Electrophoretic Assembly and Transfer



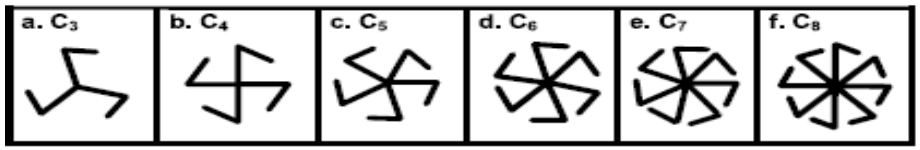


Mid-infrared



microwave

Modeling provides designs and dimensions



N Wongkasem et al, J. Opt. A: Pure Appl. Opt. **11 (2009) 074011**

L. Fang, M.Wei, N. Wongkasem, H. Jaradat, A. Mokhlis, J. Shen, A. Akyurtlu, K. Marx, C. Barry, & J. Mead, *Microelectronic Engineering* 107 (2013) 42–49

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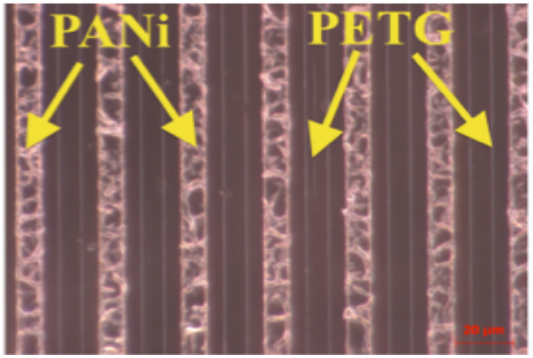
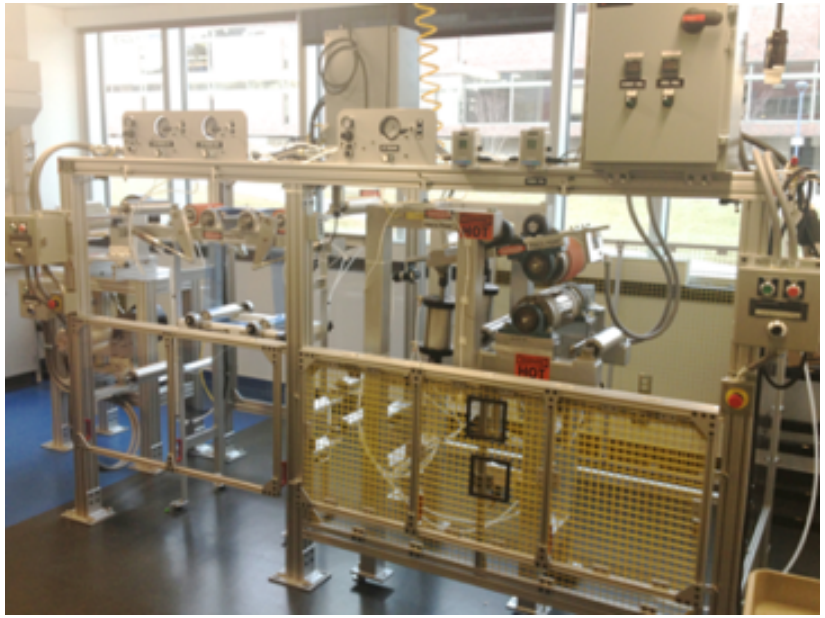
Assembly of Nanoelements and Transfer to Polymer Using the Roll to Roll Process



- Roll to roll process for directed assembly of a conducting polymer and transfer to polymer sheets.
- Assembly by pulsed electrophoresis
- Pre-patterned polymer transferred to a polymeric substrate. Critical parameters for the transfer process were surface energy, temperature, and belt speed.
- New prototype scale machine recently designed and installed.



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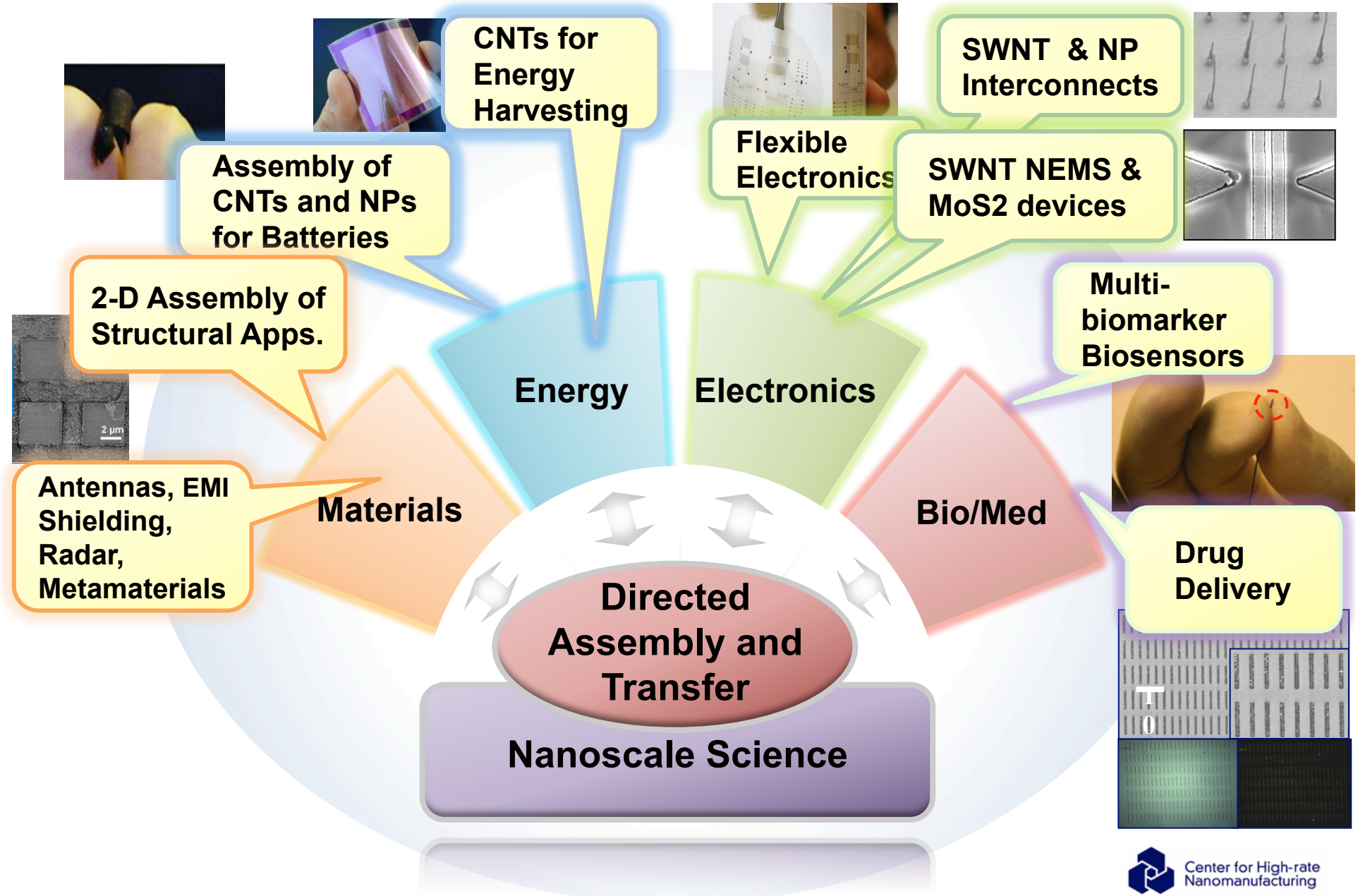
THRUST 3

Applications

What Could This Technology Make?



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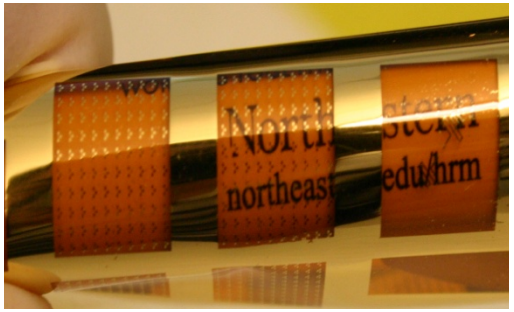
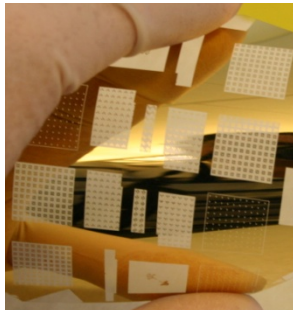
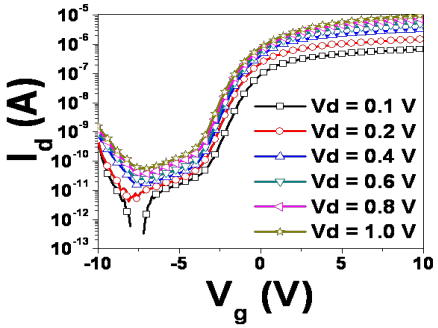
Nanoelectronics

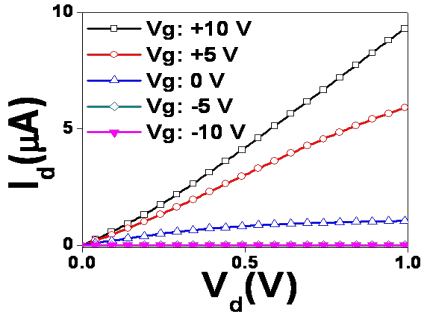
- **Flexible transparent n-type MoS_2 transistors**

Nanotechnology, Vol. 22, (2012).

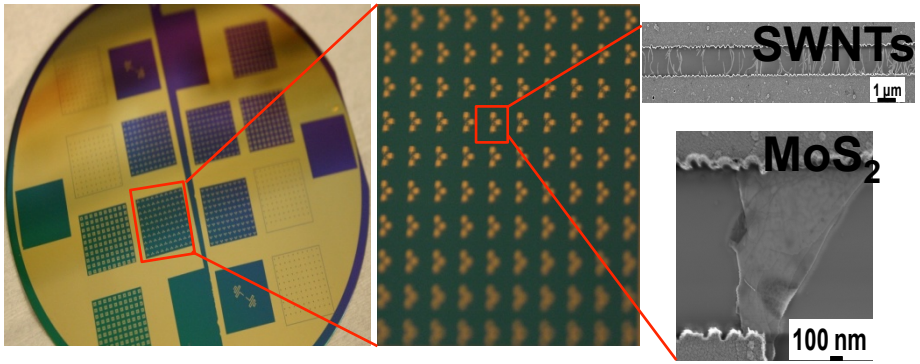


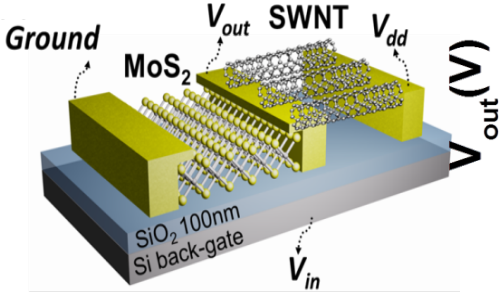


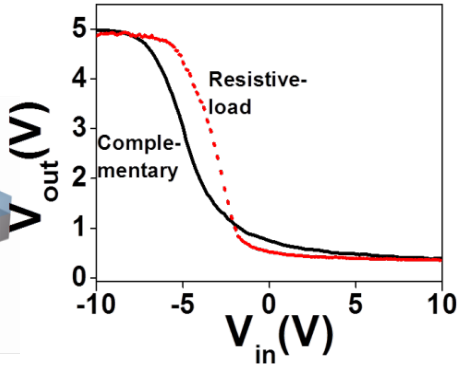




- **Heterogeneous SWNTs and MoS_2 complimentary invertors through assembly**



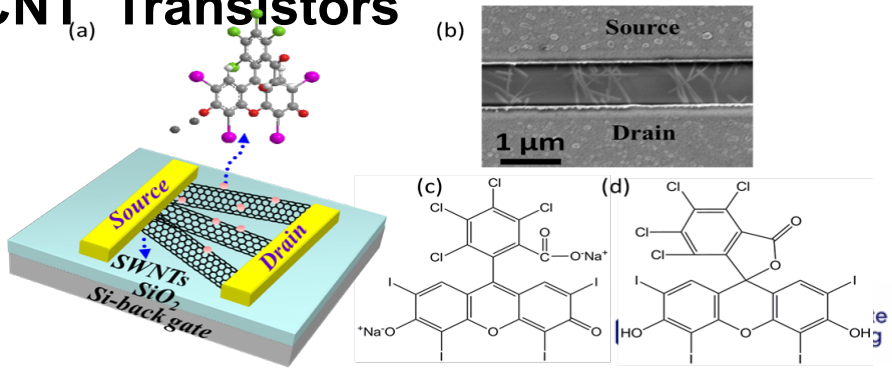




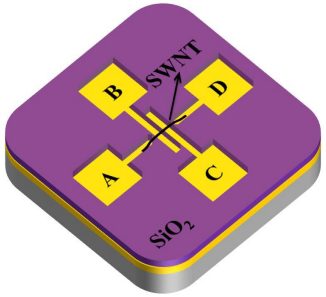
Nanotechnology, Vol. 23, (2012)

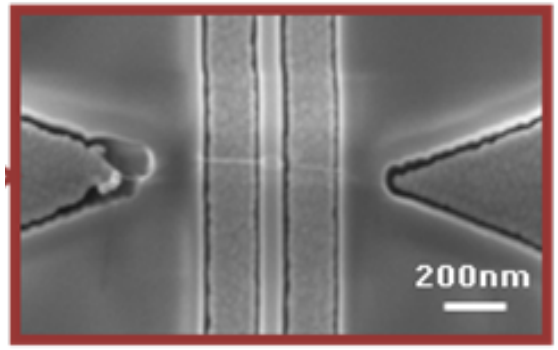
- **Rose Bengal Molecular Doping of CNT Transistors**

  - RB-Na doping shifts the threshold voltage of CNTFETs up to ~6V, lower the sub-threshold swing for 4 times, and increase the effective field-effect mobility



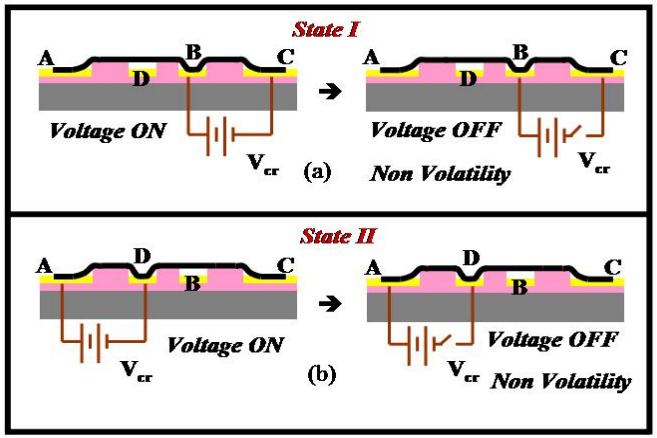
Carbon Nanotube NEMS Switch





Applications

- Memory element
- Logic gates
- Latches; Registries
- Analog devices
- Operational Amplifiers
- Sensors



Schematic of states I and II.

- Nano electromechanical Switch
- Non-voaltile
- Bistable Latch
- Position –Alternative state variable
- Novel State Variable Based Logic
- Fabrication employs field assisted directed assembly technique & a single mask process
- CMOS compatible

Characteristics:

- Read write erase time ~ns
- Read write erase power ~ 100nW
- Infinite sub-threshold slope
- Zero leakage current
- Performance increases with scaling down

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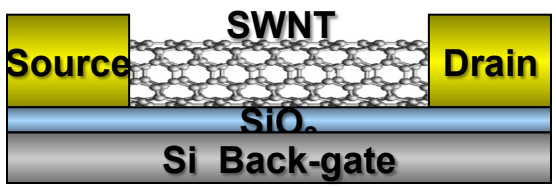
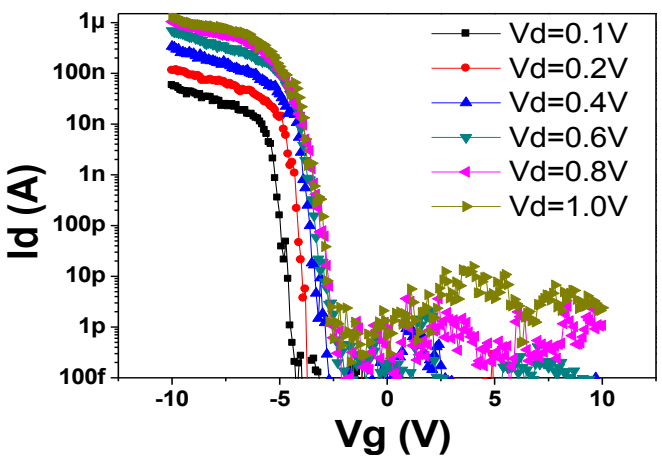
Carbon Nanotube FET

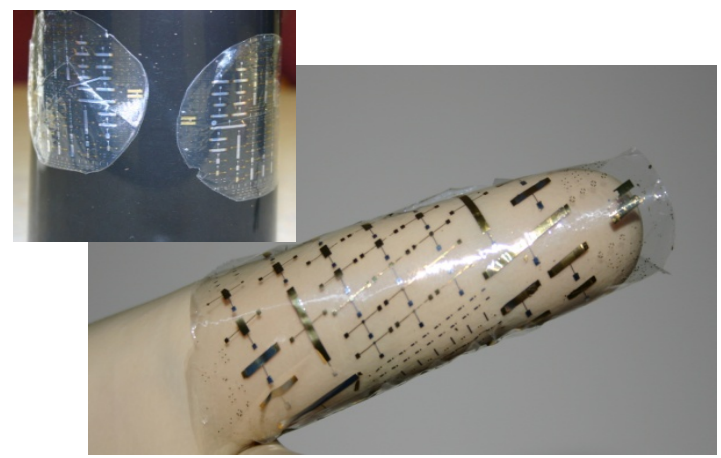
Employs Field Assisted Directed Assembly Technique





Typical p-type behavior, i.e., transistors turn under negative bias.

- The devices show a high $I_{on/off} > 10^5$
- Low off current ~ pA
- Sub-threshold swing of ~ 250 mV/dec,



Applications

High Speed binary transistors ;
Logic gates; Analog devices;
Power amplifiers; Sensors, etc.

Selvarasah, Li, Busnaina, and Dokmeci, ***Appl. Phys. Lett. 97, 1 2010.***

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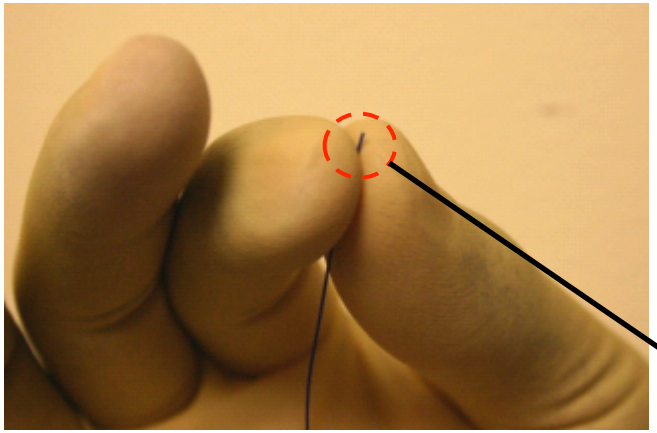
In vivo Nano Biosensor



- ✓ Multiple-biomarker detection
- ✓ High sensitivity
- ✓ Low cost
- ✓ Low sample volume
- ✓ In-vitro and In-vivo testing

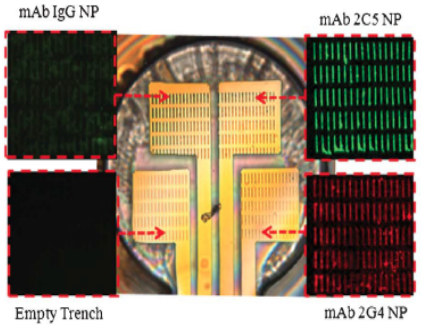
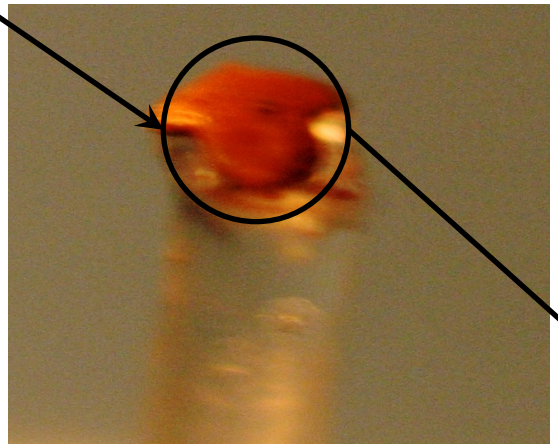
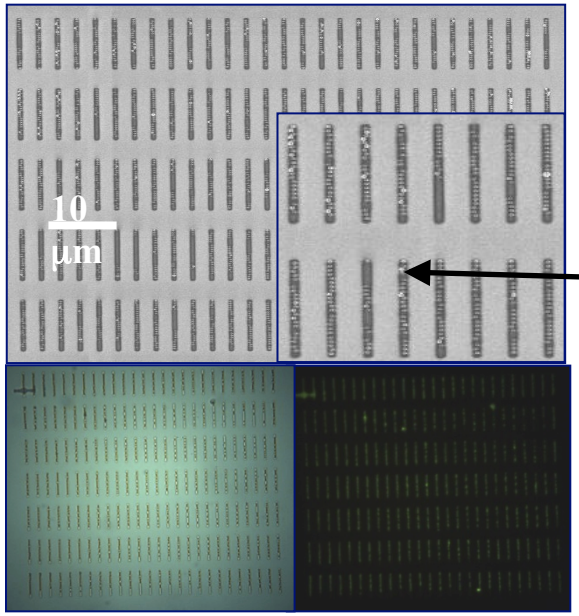
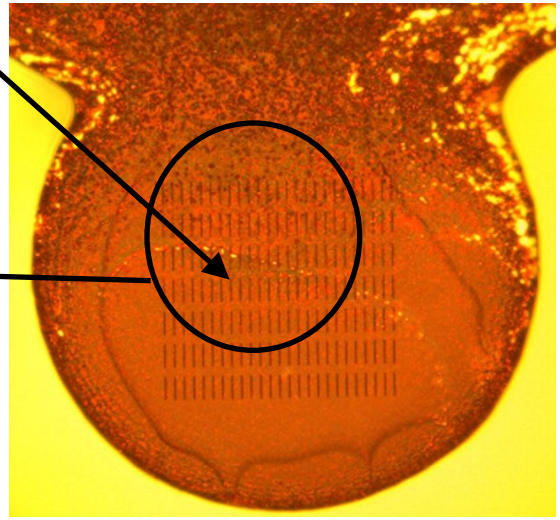


Image of the *in-vivo* biosensor (0.1 mm x 0.1 mm) after animal testing



Langmuir, 27, 2011
Lab on a Chip Journal, 2012





Incubated with human plasma spiked with CEA
Detection limit: 15 pg/ml
Current technology detection limit is 3000 pg/ml

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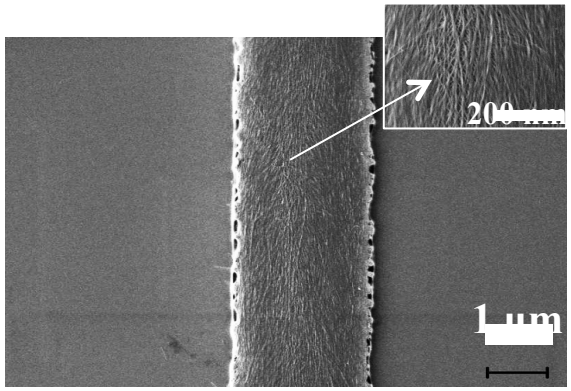
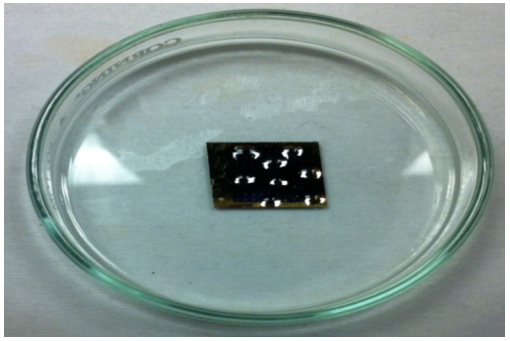
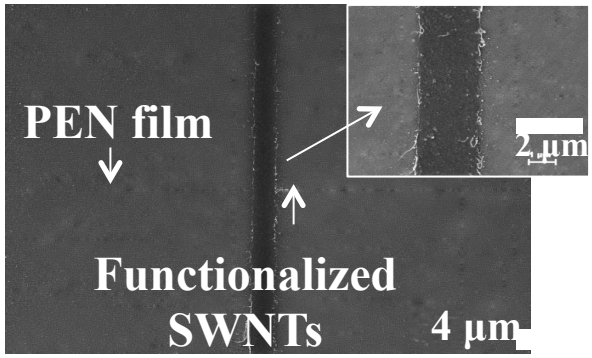
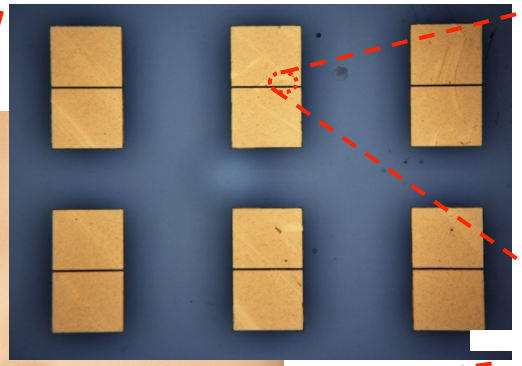
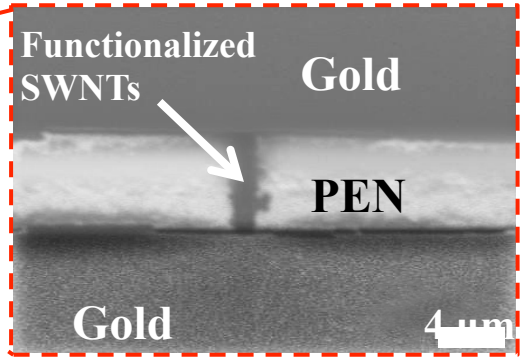
Biosensor for Physiological Monitoring of D-glucose/L-lactate/urea

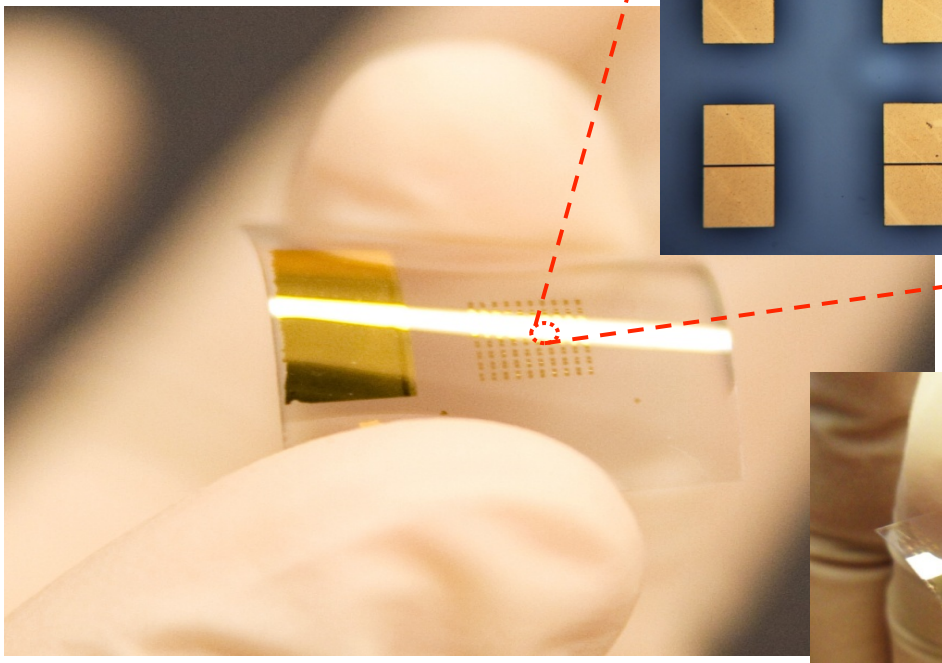


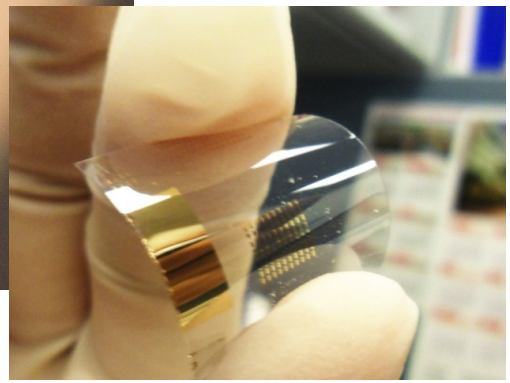


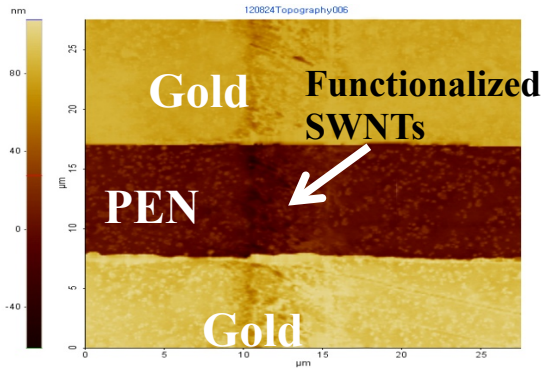












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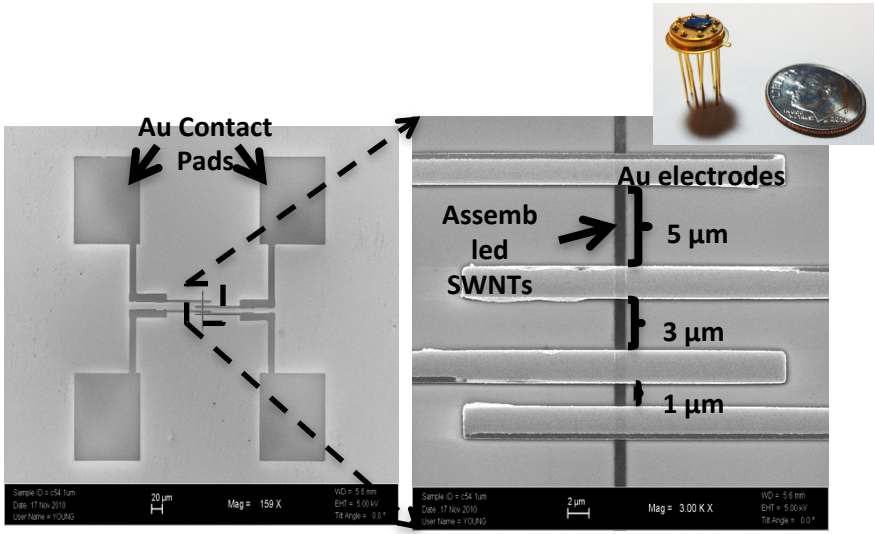
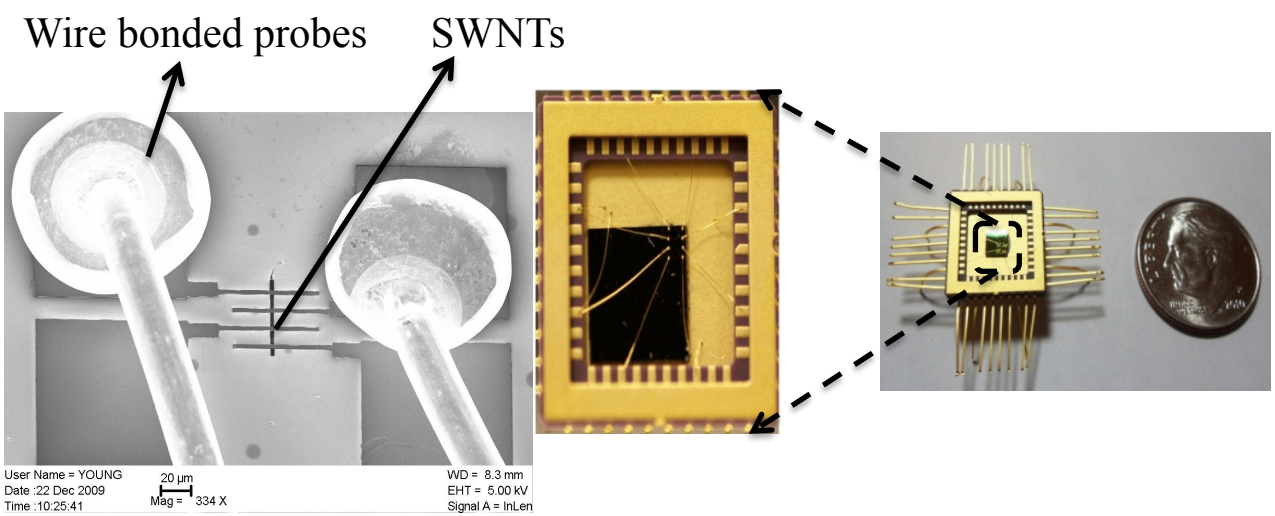
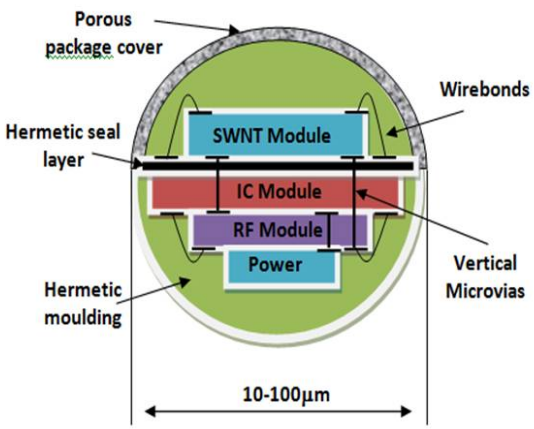
Chemical and Bio Sensors

Functionalized SWNT Chemical sensor



- Developed, fabricated and tested a micro-scale robust semiconducting SWNT based sensor for the detection of H_2S, simple alkanes, thiol, etc.
- Working in harsh environment (200°C; 2500Psi).
- Specific in various environments (N_2, Air, Water vapor, Water, alkanes, etc.)
- Simple inexpensive 2-terminal device
- High sensitivity ~ppm.





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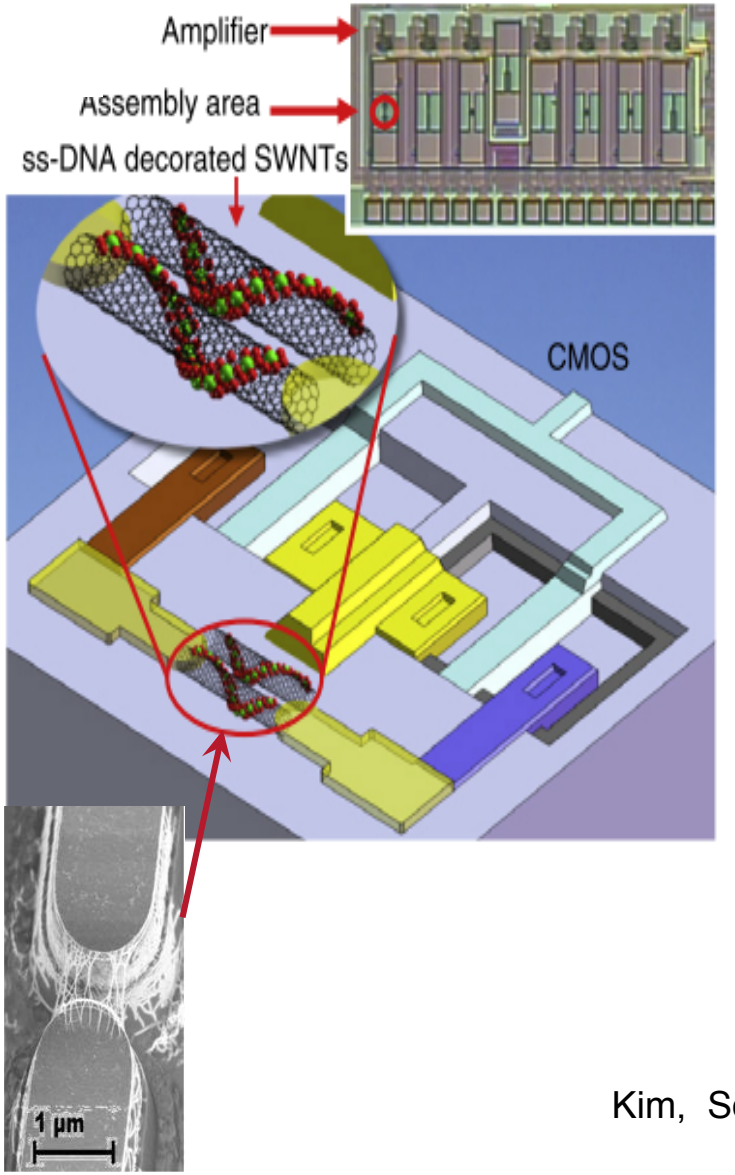
Monolithic Chemical Sensors



- **The SWNTs integration on CMOS circuitry demonstrates a step towards realizing integrating nanomaterials on current semiconductor devices.**
- **SWNTs were assembled onto CMOS circuitry via a low voltage dielectrophoretic (DEP) process.**
- **The the gas sensor was enhanced (up to ~300% and ~250% for methanol vapor and isopropanol alcohol vapor, respectively) compared with bare SWNTs.**

Application

Organic solvent Chemical sensors; Bio sensors

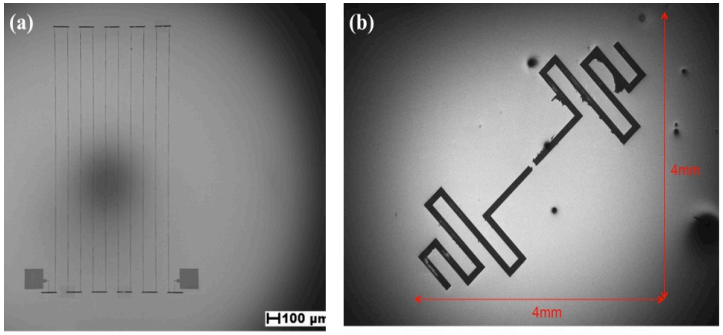
Modifications can lead to organic vapor sensors

Kim, Sonkusale, Busnaina, Dokmeci, et al. ***Nanotechnology, 21 (2010)***

Center for High-rate Nanomanufacturing

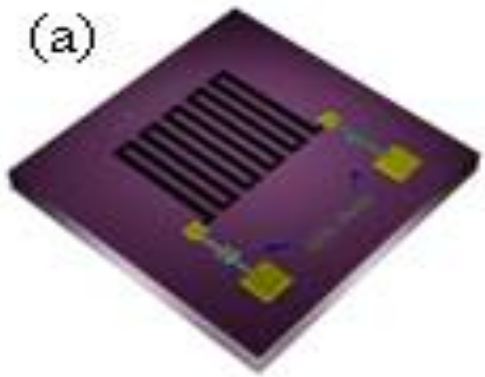
Energy Harvesting

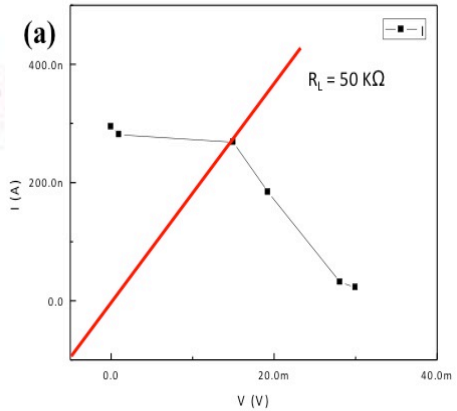
SWNT based infrared energy harvesting device

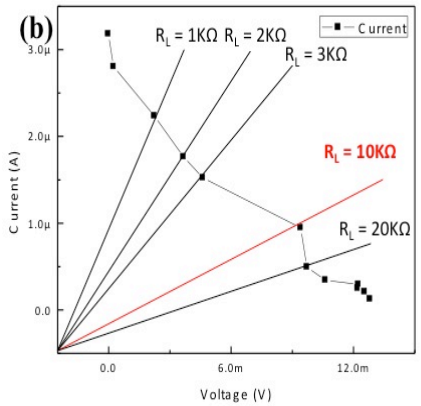


- Developed rectifying SWNT antennas having the potential for absorption of far and mid-Infra red incident light.
- Rectifying circuit consists of commercially available MIM diodes operating in the W band.
- Harvesting energy wherever there is temperature difference of ~ 5° C

CNT Infrared Energy Harvester







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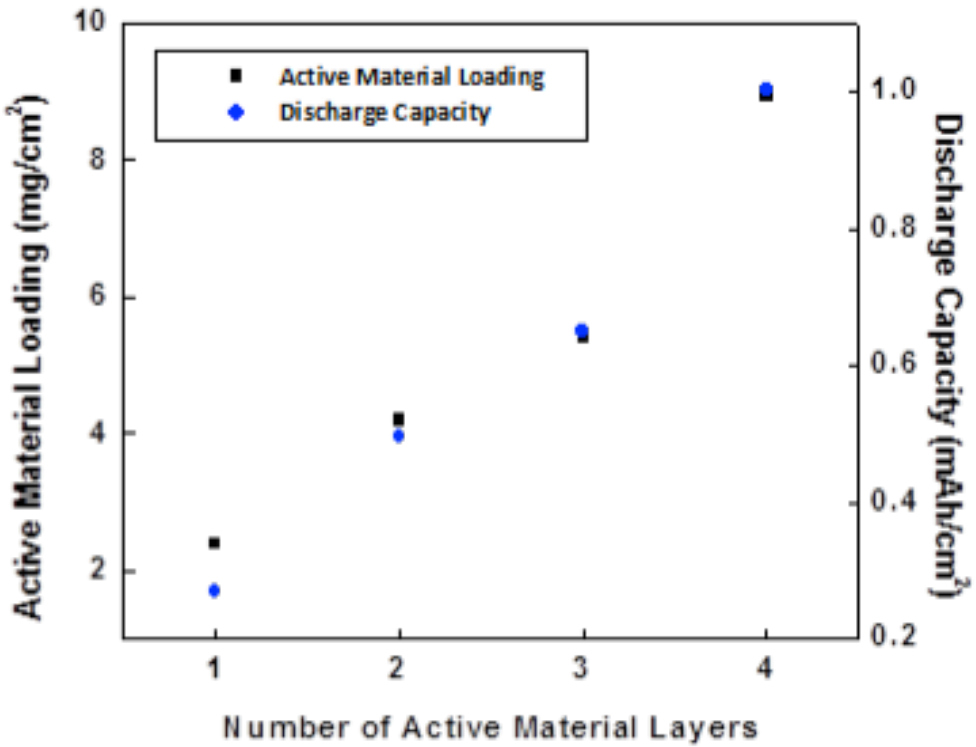
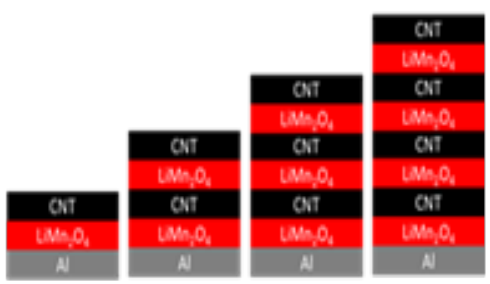
CNT Battery Discharge Capacity



	Anode mAh/g	Cathode mAh/g	Li-ion cell Specific energy Wh/kg	Li-ion cell Energy density Wh/L
Commercial Li-ion Technology	350 (Graphite)	180 (NCA)	250	650
CHN's Work	**2000-3000 (Si)**	**225-250 (LLNMC)**	**350-400**	**800-1000**



- Excellent discharge capacity.
- Discharge capacity is a linear function of number of layers.
- Fabricated coin cells.

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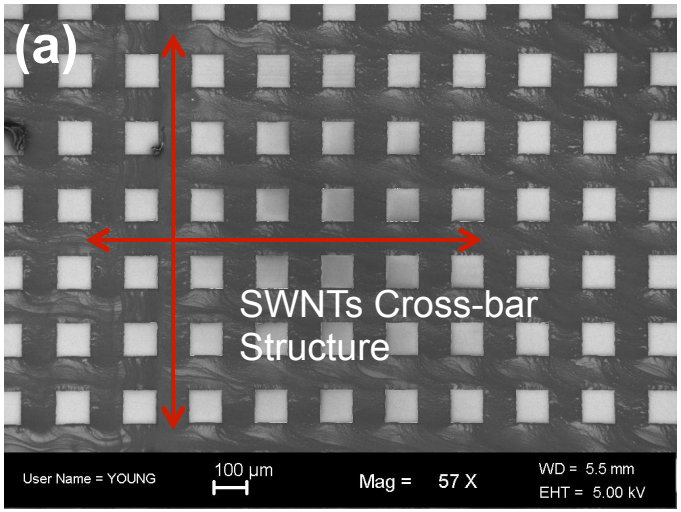
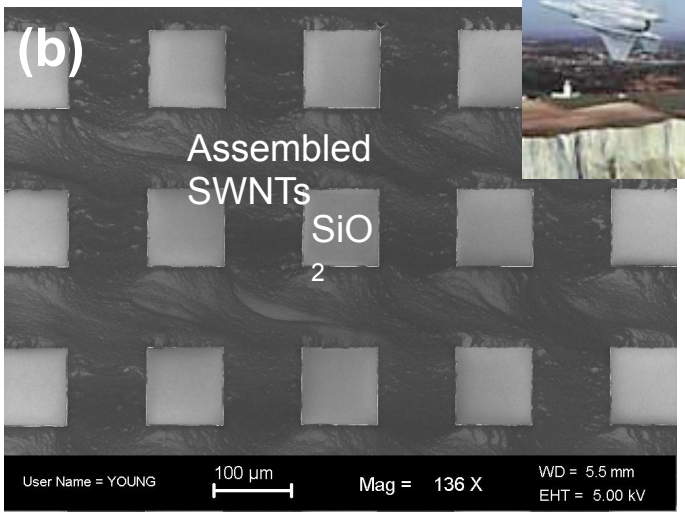
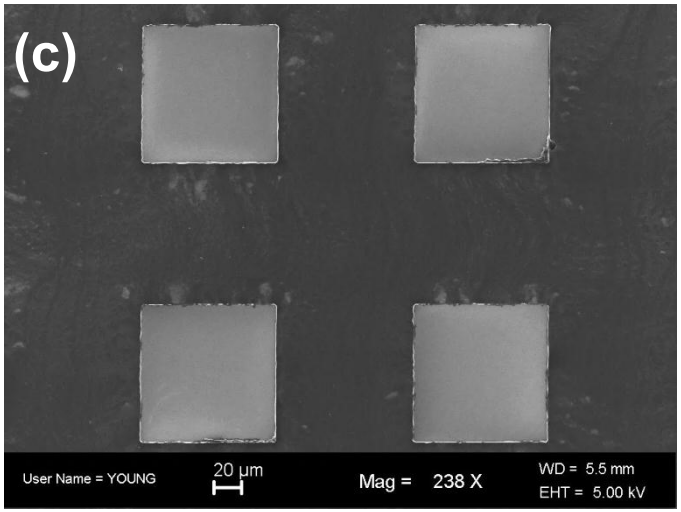
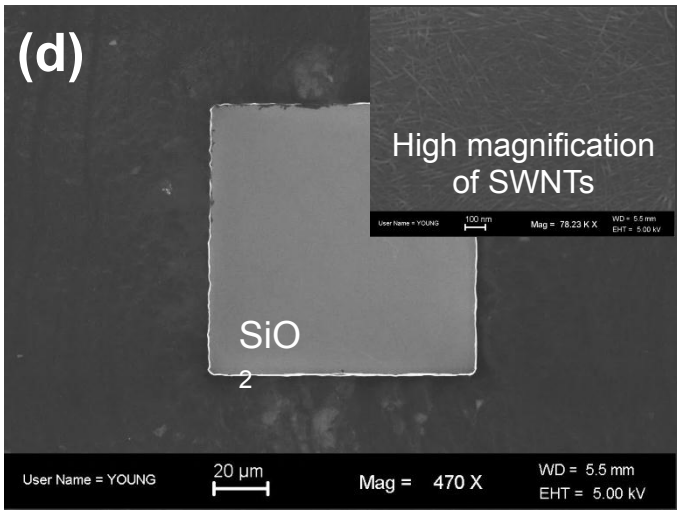
Lightweight Structural Materials for Shielding and Composite Multifunctional Structures

- ***SEM Images of Cross-bar Structure***









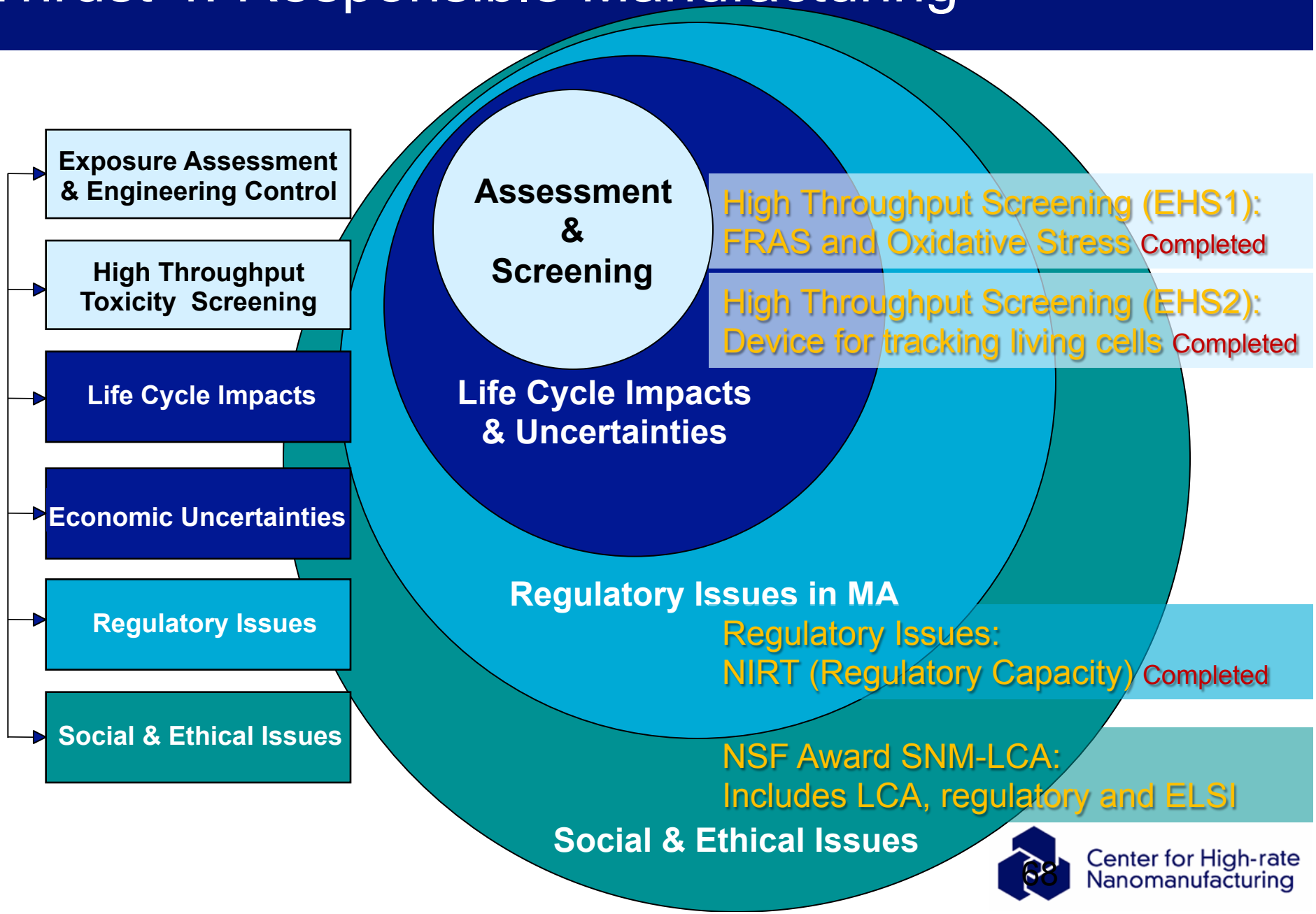
Patterned and aligned carbon nanotubes

Center for High-rate Nanomanufacturing

THRUST 4

Responsible Manufacturing

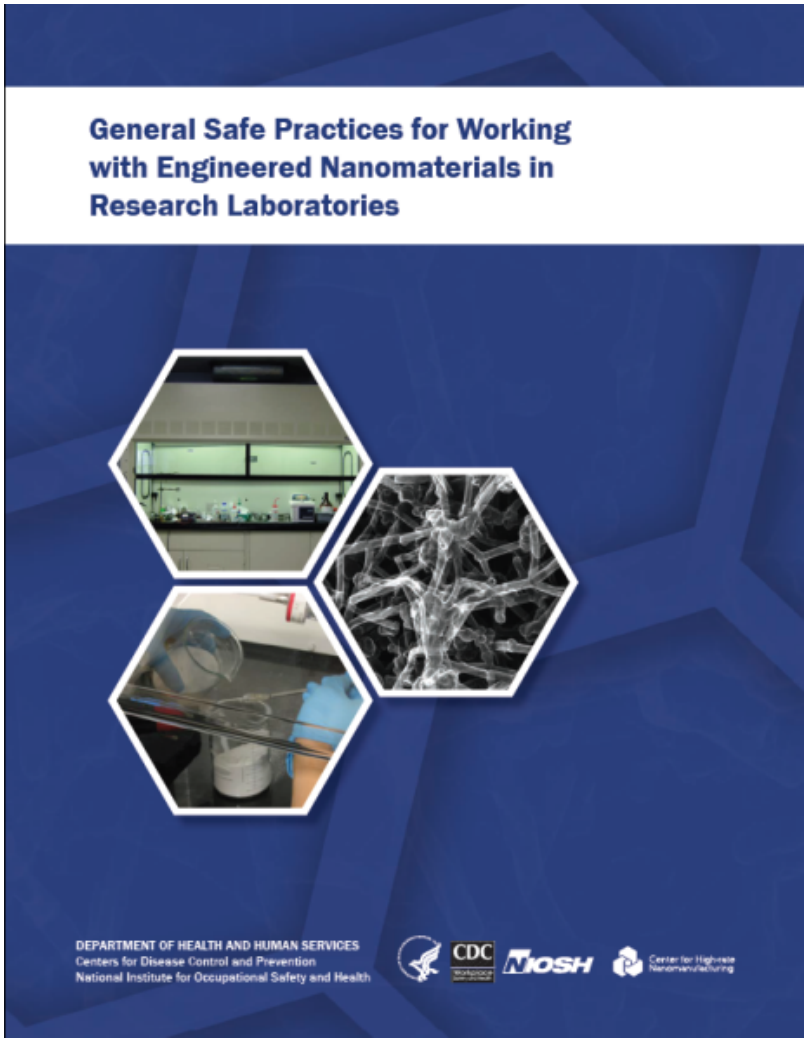
Thrust 4: Responsible Manufacturing



Center for High-rate Nanomanufacturing

Exposure Assessment with NIOSH

- Established MOU between CHN and NIOSH in September 2010
- Led to CHN collaborations with NIOSH team at several academic and industry facilitates
- Published NIOSH/CHN Safe Practices document for ENMs
  - Methodology for risk management and exposure assessment
  - Techniques and guidance for exposure control including local exhaust ventilation and other engineering and administrative controls

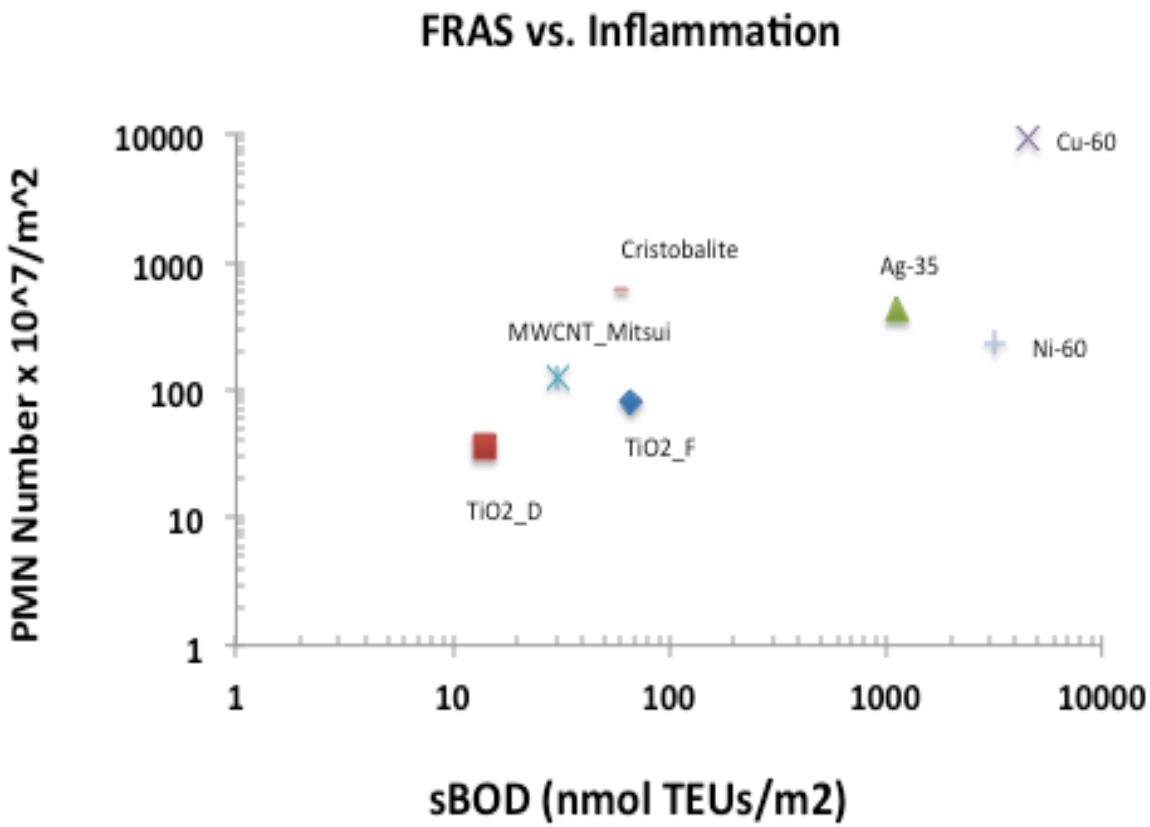


Center for High-rate Nanomanufacturing

Multi-tiered Toxicity Screening of Engineered Nanomaterials: Evaluating Predictive Utility of Oxidative Stress

Work Supported by NSF EHS Supplement 1

- Oxidative stress:
  - fundamental mechanism of toxicity for PM and many ENM
- Acellular assay, Ferric Reducing Ability of Serum (FRAS), developed to evaluate the ability of ENM to exert biological oxidative damage (BOD) in human serum
- Assay used to map BOD in 140 ENMs and to develop a surface activity index



- Serum-based FRAS assay is reasonably predictive of in vivo inflammation in dataset

Bello and Rogers, UML; Isaacs, Carrier, Gu, NEU

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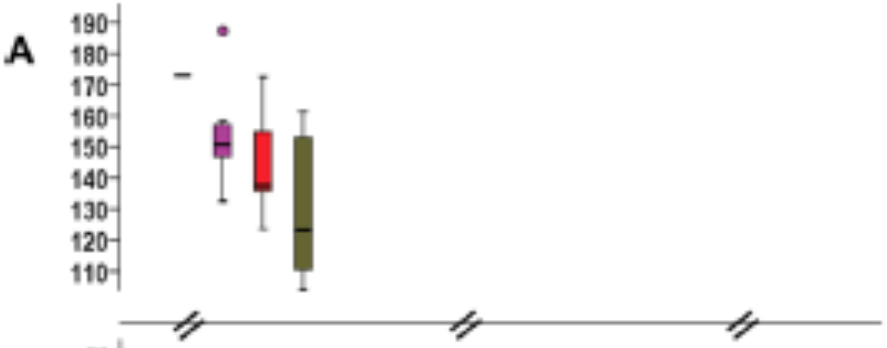
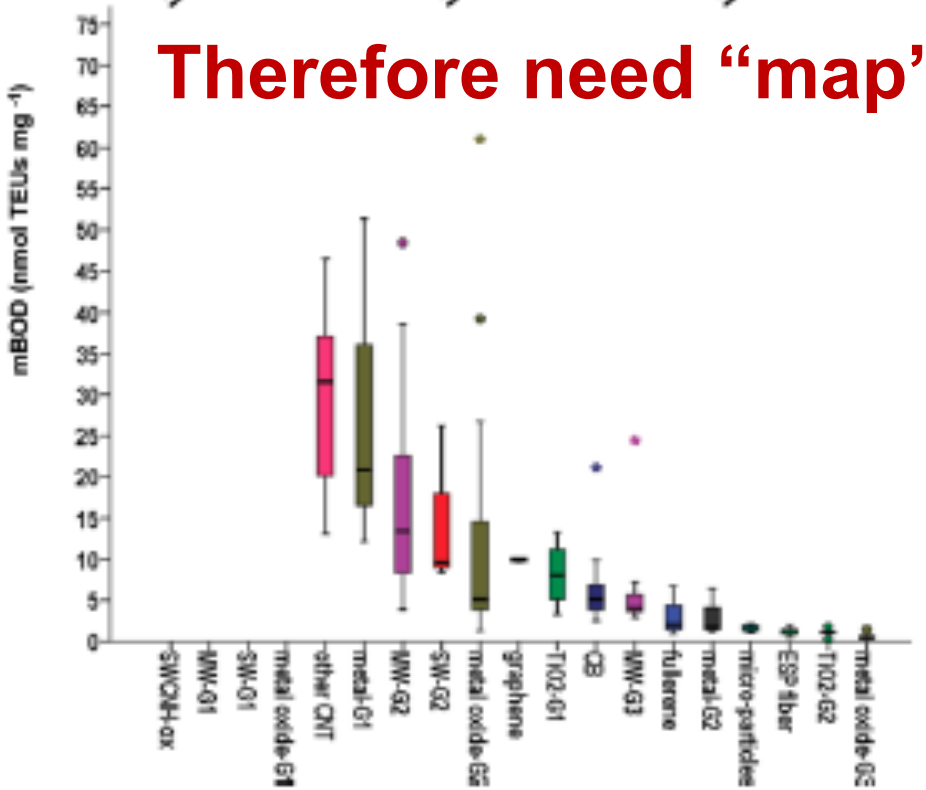
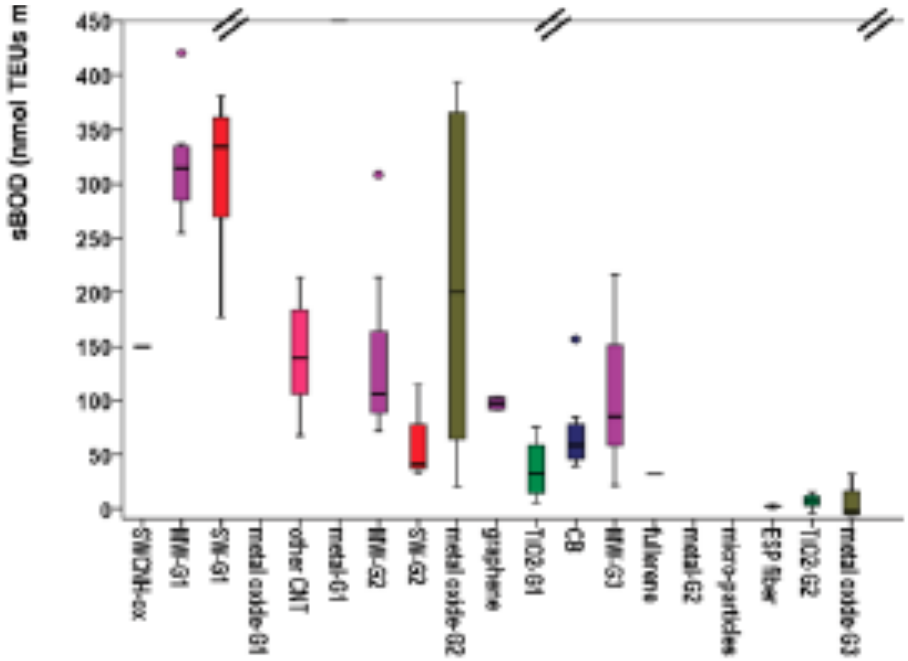
Within- & Among-class Variations in BOD



Therefore need "map" to additional assays





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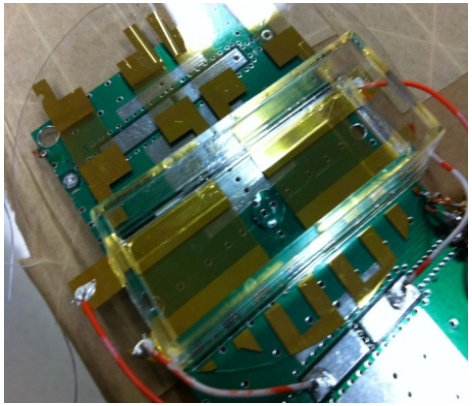
Acoustic Wave Device (AWD) for Detection of ENM Toxicity for Human Cells

Work Supported by NSF EHS Supplement 2

- AWD measures changes in visco-elastic properties of living cells
  - Exposures to toxins result in alterations in cellular substructures
  - Loading changes on a piezoelectric substrate to which the cells are attached
  - Altered oscillation frequency and damping signals result

QCM sensor

- Two devices developed and patented
  - Quartz Crystal Microbalance (QCM): Utilizes bulk acoustic waves for sensing
  - Surface Acoustic Wave sensor (SAW): Utilizes surface waves for sensing



SAW sensor

Braunhut, Marx, Therrien, UML

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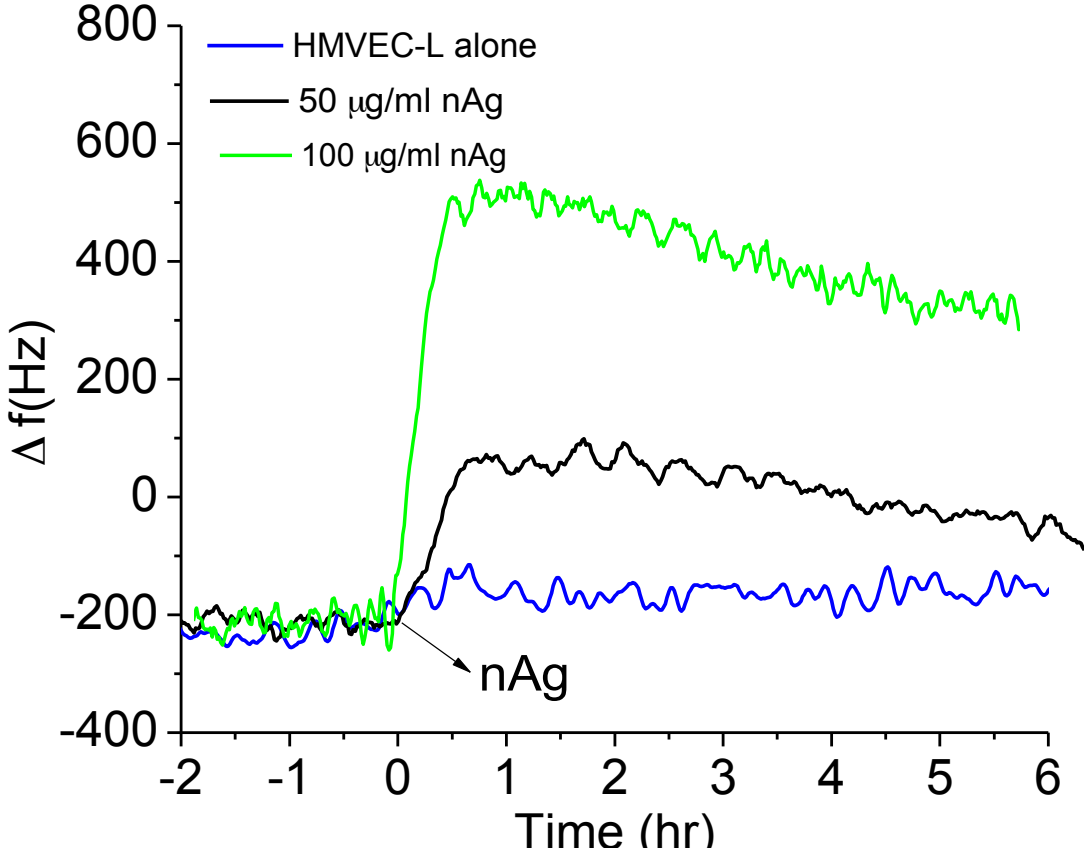
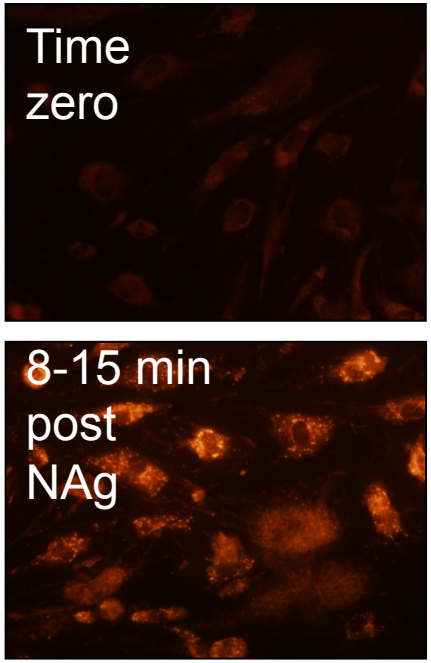
Detecting Toxicity of Nano-Ag and Mechanisms





Human microvascular endothelial cells (HMVEC) were the most sensitive cell of the human lung to toxicity after exposure to nanosilver. Apoptosis at 24-72 hrs was predicted by mitochondrial depolarization 10-15 min after exposure detectable by the biosensor (left panel) and mitotracker labeling (right panels).

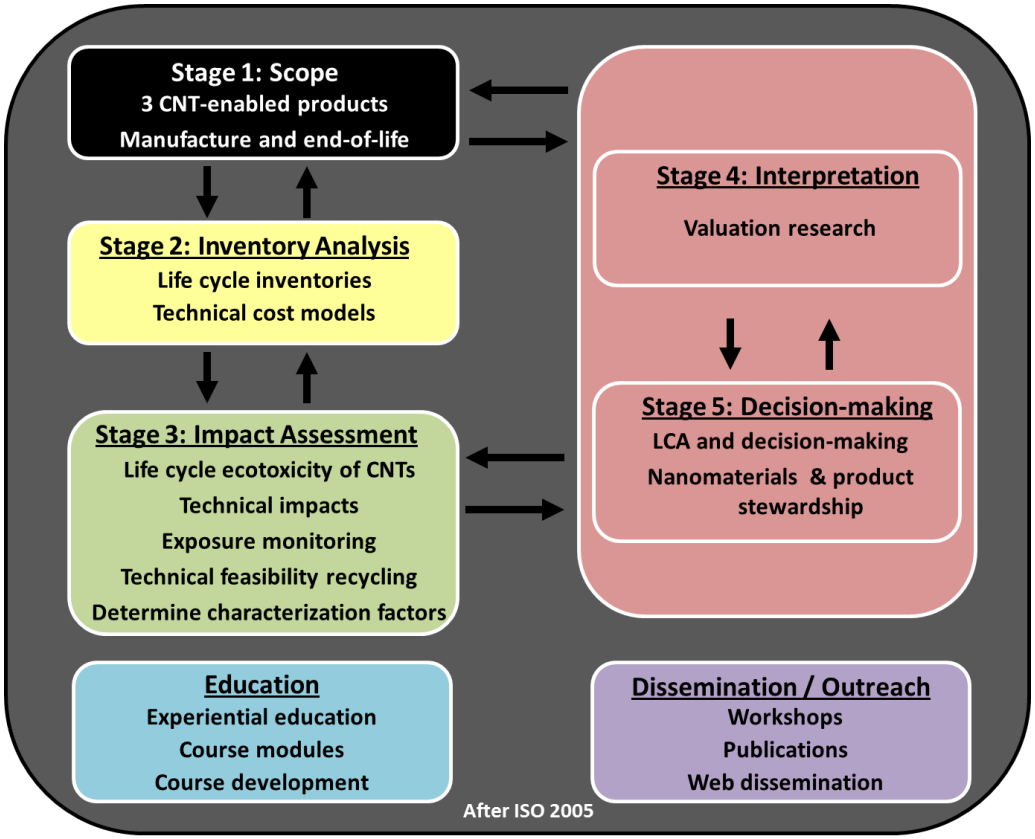
Dewilde, Wang, Zhang, Marx, Therrien, Braunhut, Analytical Biochem. 2013

Center for High-rate Nanomanufacturing

Assessing Emerging Product Life Cycles

Work Supported by NSF SNM-120329

- Addresses ethical, legal, and societal impacts (ELSI) in decision-making for commercialization throughout the life cycle of CNT-enabled products
- Resources and emissions from manufacture, use, and end-of-life (EOL) management, (recycling or other disposal)
- Includes strategies for
  - Exposure prevention
  - Product stewardship
  - Value sensitive design



Isaacs, Eckelman, Sandler, Bosso, Busnaina, NEU;
Mead, Bello, UML; Zimmerman, Yale; Nash, Harvard

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Increased Emphasis on Life Cycle Perspective

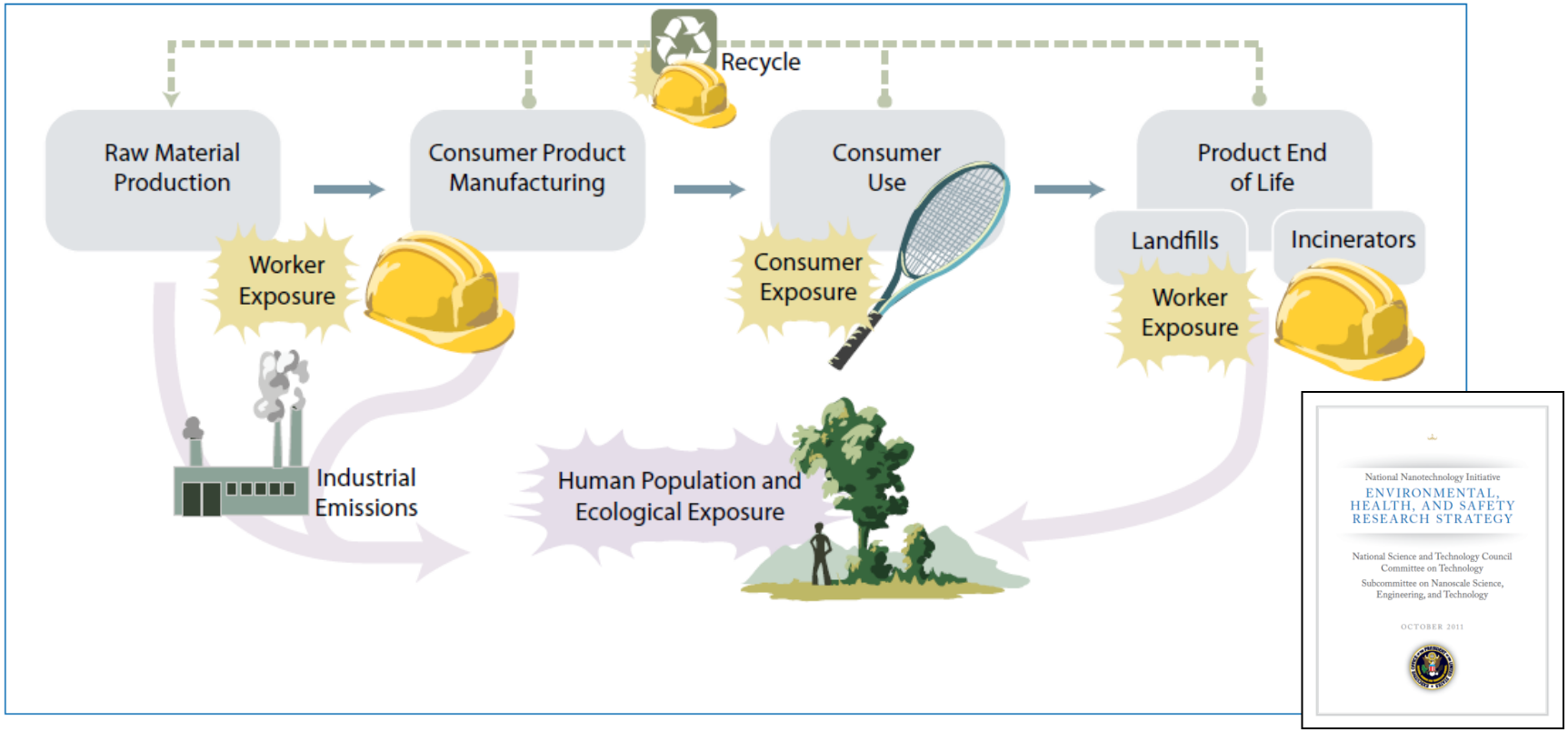

Figure 1-5. The life cycle perspective on risk assessment. Life cycle assessment supports sound product development, responsible nanomanufacturing (scaling up), and protection of public health.

Source: EPA 100/B07/001, February 2007, http://epa.gov/osa. N.R. Fuller of Sayo-Art provided revised image graphics.

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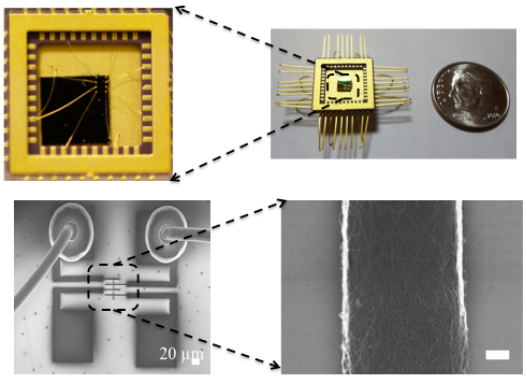
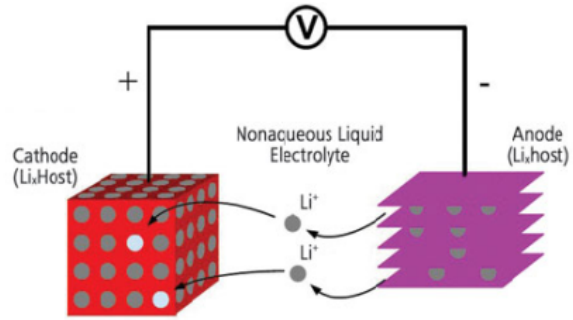
LCAs for Several CNT-Applications

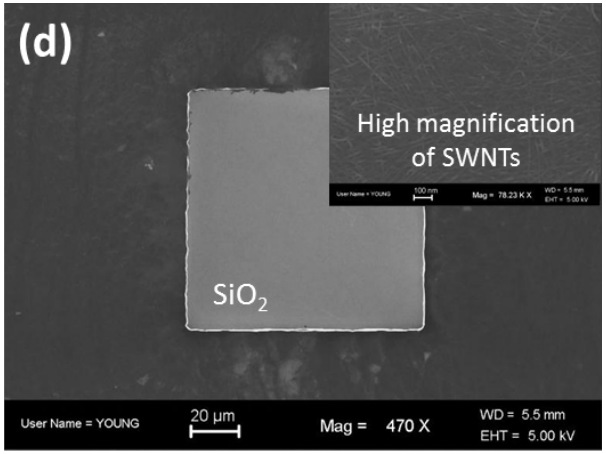
Chemical Sensors



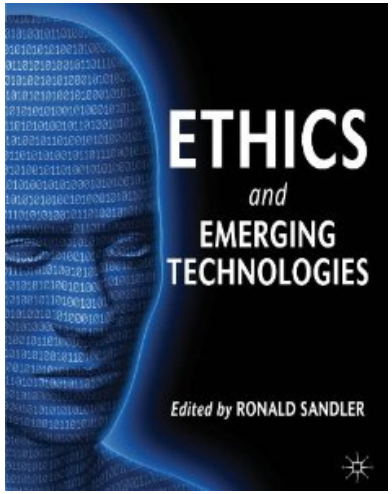
CNT-Li Batteries



EMI Shielding



- CNT loading differs for each
- Uncertainties for life cycle consequences
- Value tradeoffs for societal benefits
- How to avoid exposures, yet reap benefits?



Assessing Exposures during Pre/Post-Process

Recycling of regrind for CNT-composites?

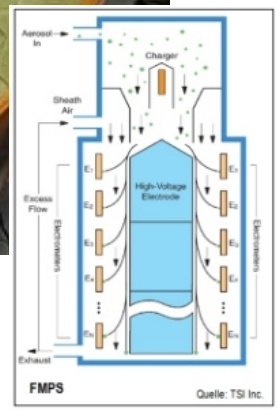
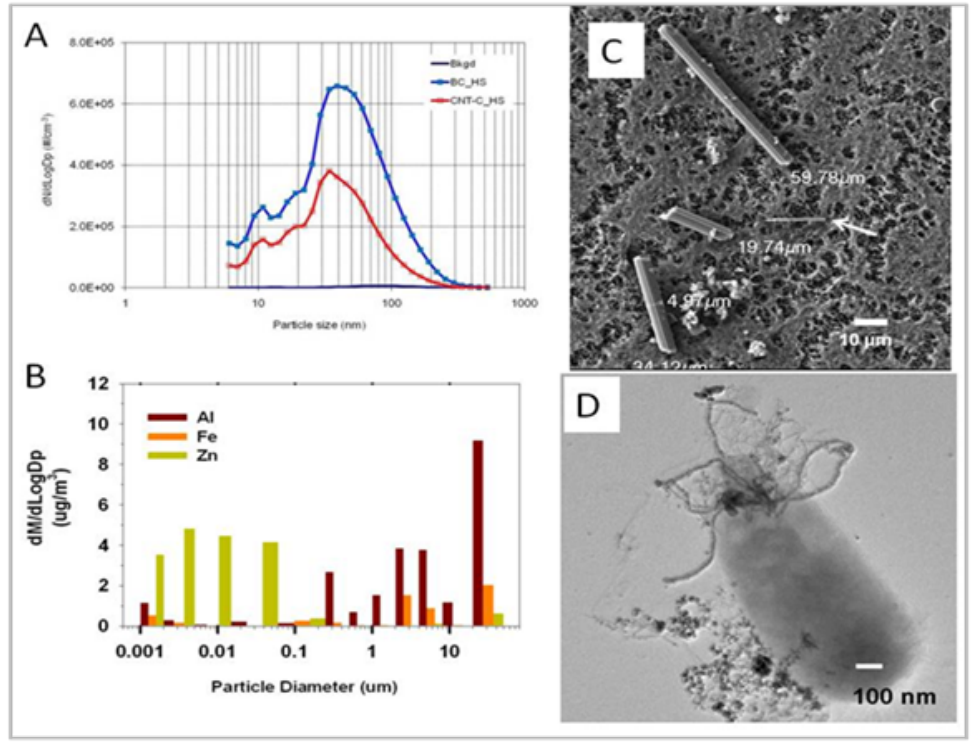


Illustration of solid core drilling:



A- Average breathing zone size distributions by FMPS

B- Mass distribution of airborne signature CNT metals

C- Respirable fibers (SEM/EDAX & personal sampling, 3 fibers/cm^3)

D- Airborne CNT ropes/aggregates

Abrasive cutting of same composites had very different results

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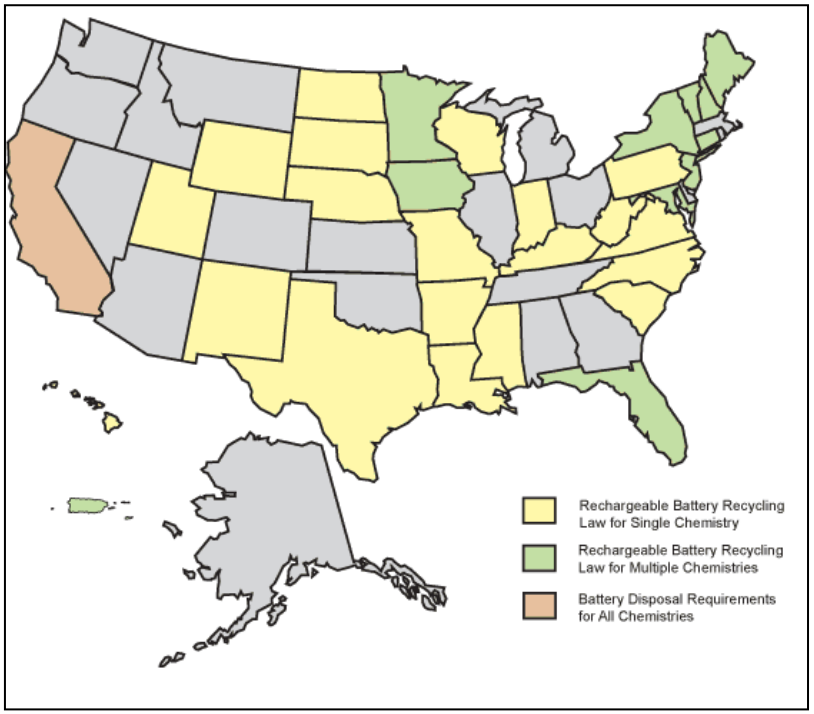
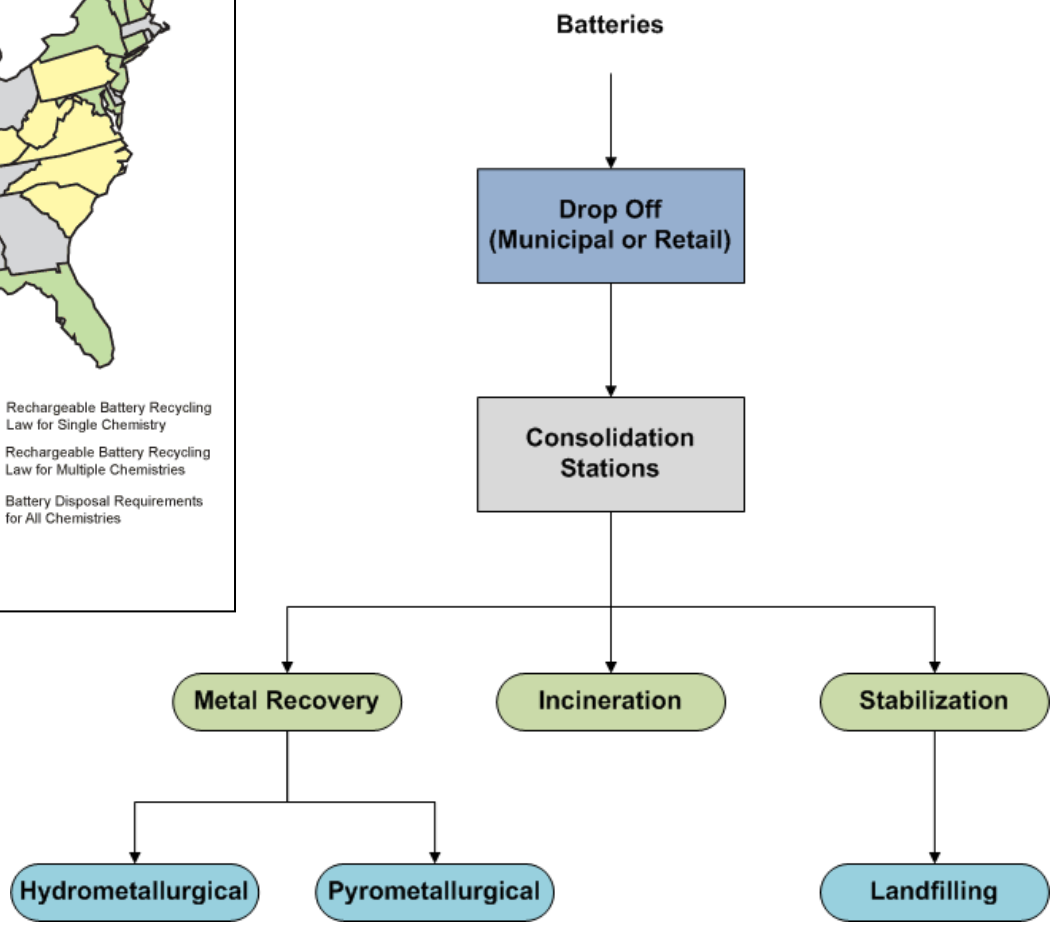
End-of-Life Disposal Scenarios



Consequences for CNT-Li Batteries?



Nash and Bosso, "Extended Producer Responsibility in the United States: Full Speed Ahead? J Industrial Ecology 2013

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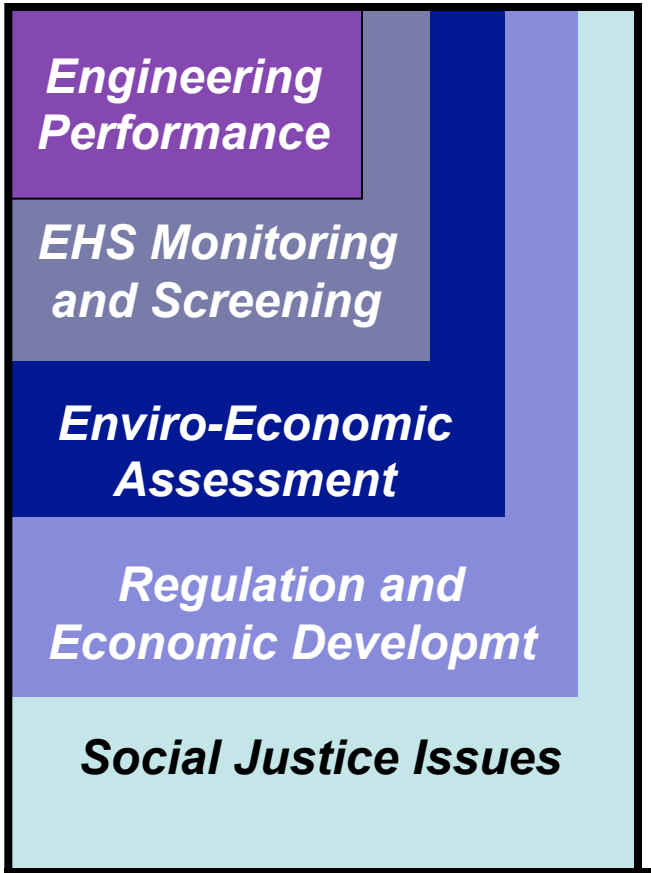
Sustainable Process/Product Development



- Create technological feasibility
- Determine best safety practices and screening methods for nanomaterials
- Evaluate EHS /economic tradeoffs and impact of possible releases
- Promote informed policymaking
- Advocate productive public discourse

Integrated Systems Approach Required for Appropriate and Efficient Commercialization

Center for High-rate Nanomanufacturing

Building the Foundation for the Nano Workforce

Public Lectures	Public Forums	Museum of Science	General Public
Short Courses	Workshops/ Conferences	Special Events	Professionals
Course Offerings	CHN Seminar	Work Experiences	Graduate Students
Course Offerings	REU Program	Work Experiences	UG Students
NU STEP-UP	Seamless Articulation	Middlesex Course	CC Faculty/Students
Geckoman!	Middle School Science Fair	Nanotech Will Travel	K-12 Students
RET Program	Teacher Training	Teacher Conferences	K-12 Teachers

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Programs for K-12 Teachers

Major CHN activities

- K12 Teacher Conference (UNH) - reached 487 teachers
  - Synergies with other CHN activities
- Summer research experiences for 40 teachers
- STEM pipeline activities

Major Program	Y 1-5	Y 6	Y 7	Y 8	Y 9	Total
UNH Teacher Conference	273	43	47	54	70	487
Nanotech Symp, Summer Inst.[1]	312	---	---	---	---	312
RET Programs	34	2	2	2	0	40
Total	619	45	49	56	70	839

[1] Discontinued after Year 2 or 3

Center for High-rate Nanomanufacturing

Programs for K-12 Students

Content for existing K-12 programs

- Building Bridges (NEU)
- Project SMART (UNH)
- Lawrence middle school program (UML)

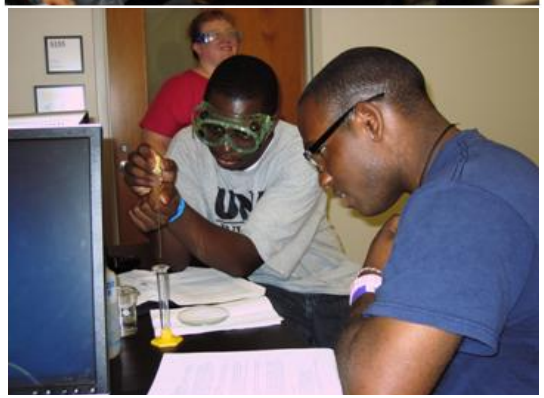
Tours and presentations

- Within Universities
- To K-12 classes and afterschool programs

Key support factors

- NISE Net activities
- *Sharing Science Workshop* (MOS)

Impact: >1900 students per year



Center for High-rate Nanomanufacturing

MA Region IV Middle School Science Fair

CHN organized Region IV Fair (UML)

- Increased participation[1] and improved projects
  - Added four Haverhill public middle schools in 2013

Year	2008	2009	2010	2011	2012	2013
Projects	59	95	123	184	187	197
Students	94	125	189	255	240	258
Schools	9	12	20	26	25	36

2013: W = 52%; URG = 21%; free lunch ~ 33%

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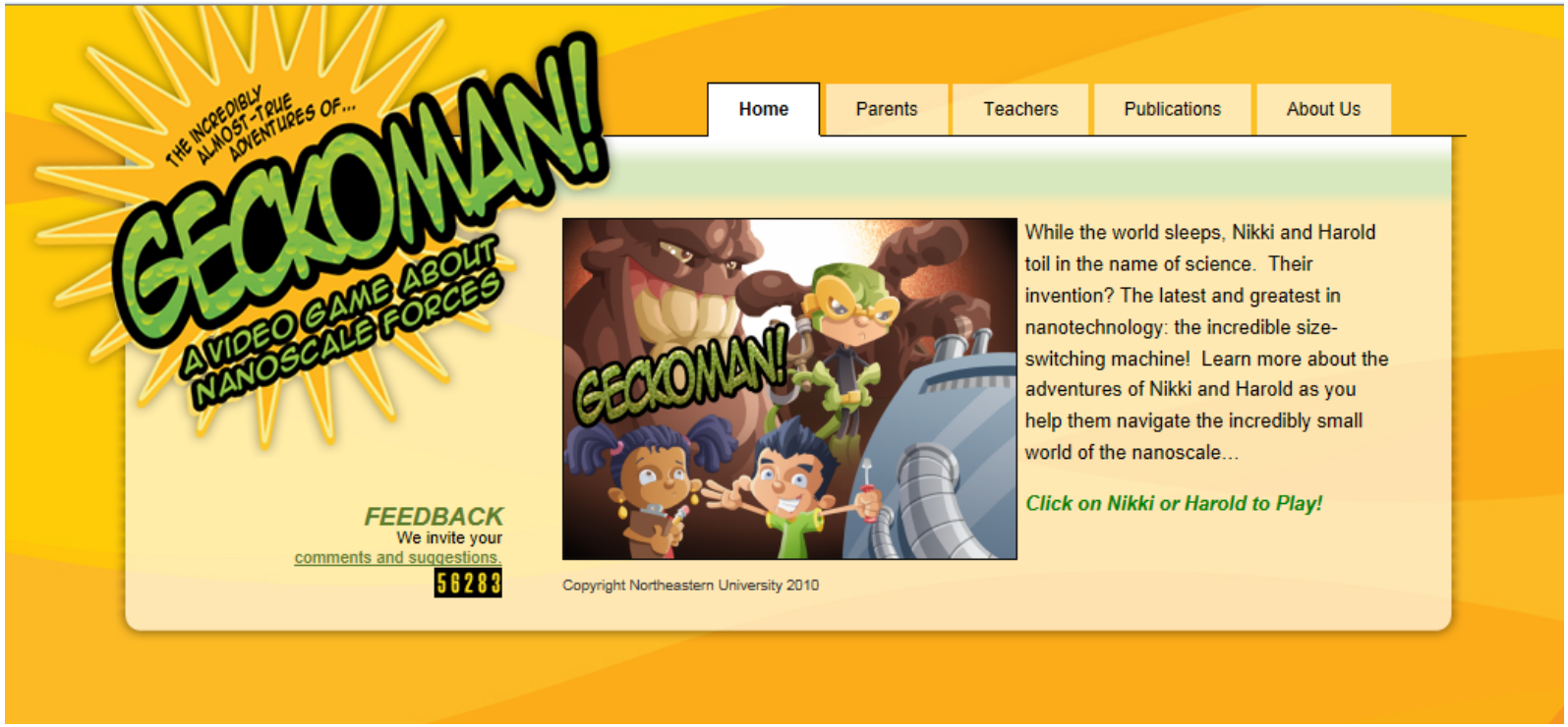
Status of *Geckoman!*

- Recode Flash code to latest software version
  - Allows incorporation of new Spanish audio files
- Expect updated MA science standards to include nanoscale forces… leading to greater utilization
- Submit game and teaching modules to NSDL for review



Center for High-rate Nanomanufacturing

Research Experiences for Undergraduates

10-week summer program

- NEU, UML, and UNH
- Wide range of research topics
- Successful use of graduate student mentors

- 2005-2013: 219 participants
  - Extensive recruiting
  - 2-3 community college students per year

Year	Y1-5	Y6	Y7	Y8	Y9	Total
Participants	114	32	38	22	13	219
Women (%)	36	28	50	54	38	40
URG (%)	24	22	32	32	62	28

2009-2012: "REU Site: Incorporating Ethical Decisions into Nanomanufacturing Research"

Center for High-rate Nanomanufacturing

Research Experiences for Undergraduates

Unique three-university professional development program

- *Science Communication Workshop* (with MOS) [1]

- Value Sensitive Design [2]
  - Framework for societal impacts of research

[1] Disseminated through NISE Net
[2] R. Sandler, "Value Sensitive Design and Nanotechnology, " in Debating Science, D. Scott and B. Francis, eds., Humanity Books/Prometheus Books (2012)

Center for High-rate Nanomanufacturing

Graduate Student Programs

2009-2013 programs

- Nano EHS updates
- *Sharing Science Workshop*
  - Co-developed with MOS
  - Communicating with diverse audiences
- Value Sensitive Design
  - First workshop (2013)
  - Will be incorporated into dissertations
- Graduate Student Council-led events
  - Professional development activities
  - Social events

Dempsey et al., "A Student-Directed Professional Development Program for Doctoral Students Seeking Industry Placement," *120th ASEE Conference and Exposition*, June 23-26, 2013, Atlanta, GA

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Programs for Professionals

- New England International Nanomanufacturing Workshops
- Destination Nano
  - UML, May 2012
  - Scheduled for September 2013
- Industry Day
  - UML, October 2012
  - NEU, February 2013
- Other Outreach
  - Short Courses
  - Presentations to industry groups

Destination Nano with Tsongas

Discussions on Industry Day

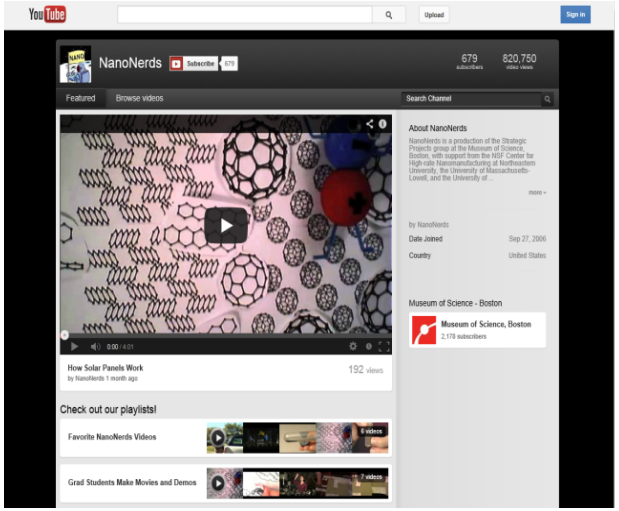
Programs for the General Public

2012-2013 Museum of Science Activities

- 128 live presentations (> 4,700 attendees)
  - QSTORM Quest to See Inside Living Cells
- Hands-on lab activities (4,100 visitors)
- *Amazing Nano Brothers Juggling Show*
  - 5,200 attendees (57,230 in 5 years) in USA
  - Translated and licensed for Polish museum

Presentations by Thate

- 8 podcasts (~5,000 views each)
- YouTube.com on world wide web
  - 780,000 views; 600 subscribers
- Talking Nano DVD set (115)
- *Nanomedicine Explorer* (225)



Web media by Antill

Museum of Science® Boston

Carol Lynn Alpert, Karine Thate, Jeanne Antill

Center for High-rate Nanomanufacturing

Public Outreach

NanoDays (MOS)

- >6,000 attendees in 2012
- 23 CHN grad students in 2012

AAAS Family Science Days

- ~3,700 attendees in 2013

NH TechFest

- ~1,000 attendees in 2012

Center for High-rate Nanomanufacturing

After 9 Years, Substantial Workforce Contributions

- Presentations
- Teacher conferences
- RET research

K-12 Teachers ~100/yr → **K-12 Students > 1900/yr**

- Presentations, lab tours, demonstrations, hands-on activities
- Region IV Science Fair
- Geckoman!

Undergraduates ~25/yr

- REU program
- Other research
- Capstone projects
- Internships and coops

"Researchers" ~ 70/yr

- Courses and certificate
- Safety training
- Sharing Science
- Value Sensitive Design
- Student-led activities

Industry

- Workshops/conferences
- Short courses
- Industry Days

Museum of Science

General Public ~840,000

Live presentations
Hands-on activities
Juggling show
Podcats
YouTube videos
DVDs, etc,
Public outreach by CHN researchers

Wide-reaching Education and Outreach Programs

Center for High-rate Nanomanufacturing

Path Forward
Expanded CHN Toolbox

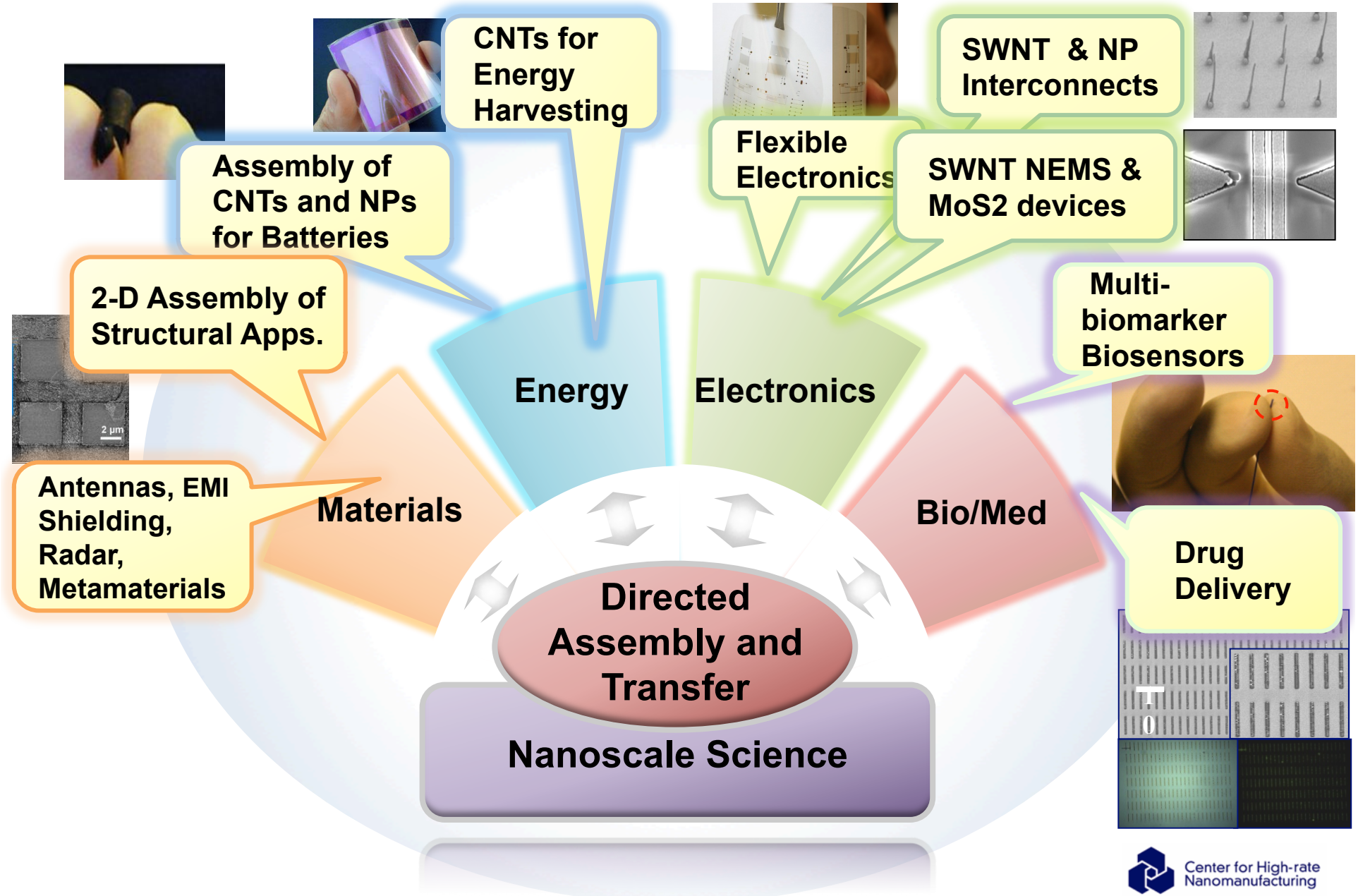
Templates	Nanoelements	Assembly Processes	Transfer Processes	Substrates	Potential Applications
Microwires template	Nanoparticles	Electrophoretic	Direct transfer (no functionalization)	Silicon	SWNT switch for nonvolatile memory devices
Nanowires templates	Carbon nanotubes (SWNTs and MWNTs)	Chemical Functionalization	Direct transfer with chemical functionalization	Polymer	Polymer-based Biosensors
Nanotrench template	Conductive polymers (PANi)	Electrophoretic and chemical functionalization	No transfer needed	Metal	Nanoparticle-based Biosensors
Template-free	Polymer blends	Dielectrophoretic	Reel-to-reel transfer		SWNT Batteries
Damascene template	MoS2	Interfacial Convective assembly	Switchable functionalization		Photovoltaics
Flexible Damascene template	Graphene	3D assembly			EMI Shielding

Center for High-rate Nanomanufacturing

Introducing a Directed Assembly Based Nanomanufacturing

- Additive, scalable, parallel and high throughput
- Manufcaturing down to 20nm
- Room temperature and pressure
- Manufacture structures on flexible or hard substrates
- Multi-scale; can manufacture nano, micro and macro structures on the same layer
- Little use of chemicals (uses mostly water)
- Material independent
- Low energy consumption and low capital investment (equipment)

What Could This Technology Make?



Center for High-rate Nanomanufacturing

NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing (CHN)

Center for High-rate Nanomanufacturing

Leverage

- Over the past 9 years, CHN has obtained $54.8 million
- CHN has received a $8.2 million support from industry in the past 9 years.

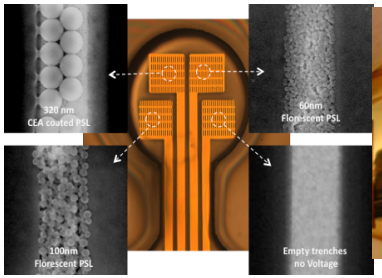
Development of IP Portfolio

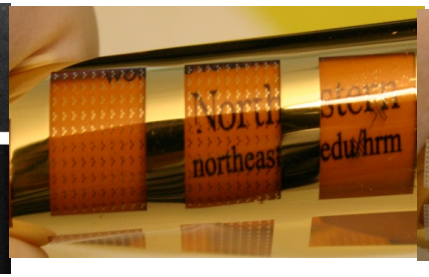
- Over the past 7 years, CHN has filed over 75 patents (9 inter-universities).

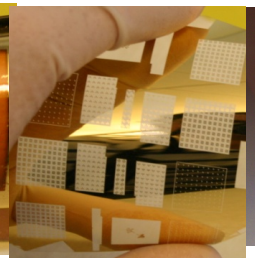
Spin-offs

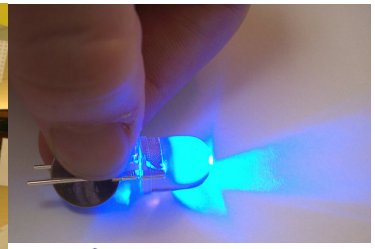
- Launched Innovacene and BIOLOM by CHN professors and graduate students.

The Kostas Center









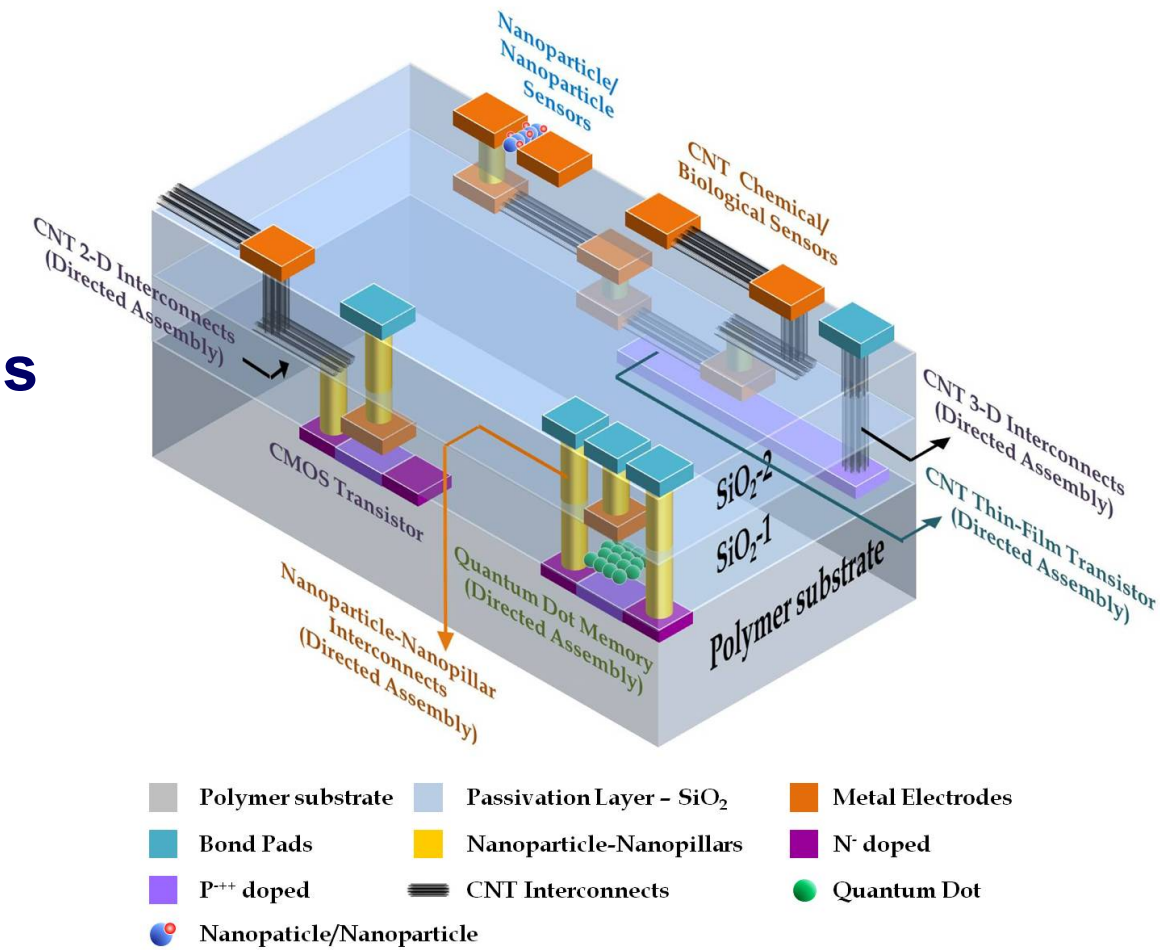
Center for High-rate Nanomanufacturing

Summary

- CHN made and continues to make substantial progress toward bridging the gap between scientific research and commercial products.
- CHN is generating fundamental understanding of nanoscale directed assembly at high-rates.
- CHN has developed a suite of tools and processes to enable high-rate directed assembly.
- Addressed exposure, economic, regulatory and ethical impacts.
- Strong CHN-industry partnerships, funding, and interaction.
- Wide-reaching education and outreach program.

Enabling from Nano to Macro; from Electronics to Medicine; from Energy to Materials

- This technology is a great enabler and equalizer
- Nanotechnology accessible to millions of innovators and entrepreneurs
- Unleash a wave of creativity



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Questions?