Beyond
3-D & Electronic Printing

Nanomaterials-based Manufacturing Platform for Printed Sensors, Electronics, Energy and Material Applications

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NSF Nanoscale Science and Engineering center for High-rate Nanomanufacturing

www.nano.neu.edu

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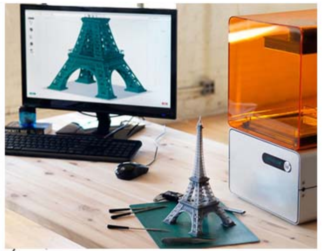
What is the status and the future of 3-D and Printed Electronics?

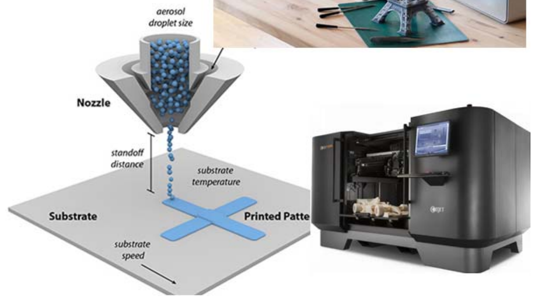
➢ Printed electronics methods are being used to manufacture OFETs, OLEDs, ICs and OPVCs.

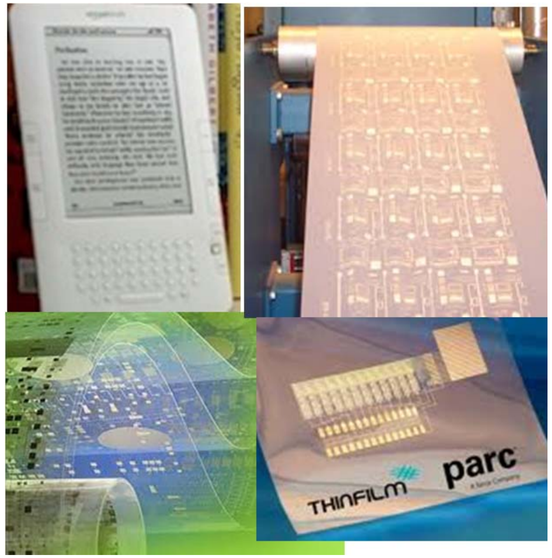
➢ The modern 3D printer and printed electronics uses inkjet printer utilizing an ink that could contain a polymer or particles suspended in a solution.

➢ Inkjets are very slow, so patterns requiring higher resolution and/or large areas take a very long time.

➢ inkjets offer lower throughput of around 100 m^2/h and lower resolution. If we use a very fast inkjet printer (1 m/s) to print 1 micron lines (current resolution is 30 micron) over 1mx1m, it will take 12 days to print.







How could printed electronics compete with current semiconductor manufacturing in performance and scale and lower the cost by by two orders of magnitude?

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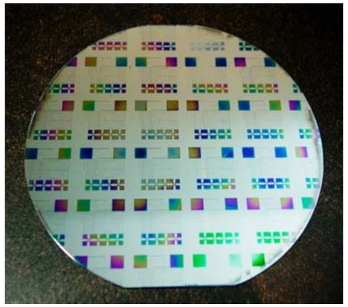
How can we accomplish High-rate Nanoscale Printing?



- Leveraging the printing processes developed at CHN could lead to the development of a printing system that's like offset printing, where you have a big plate, you ink it, and one hit, you're done.
- Only here, the ink is made of nanoparticles, nanotubes, polymers or other nanoelements that are attracted to the printing template using directed assembly.
- This novel approach will be accomplished by integrating multiple directed assembly processes, printing and semiconductor manufacturing.

This novel approach offers 1000 times faster printing with a 1000 times higher resolution.

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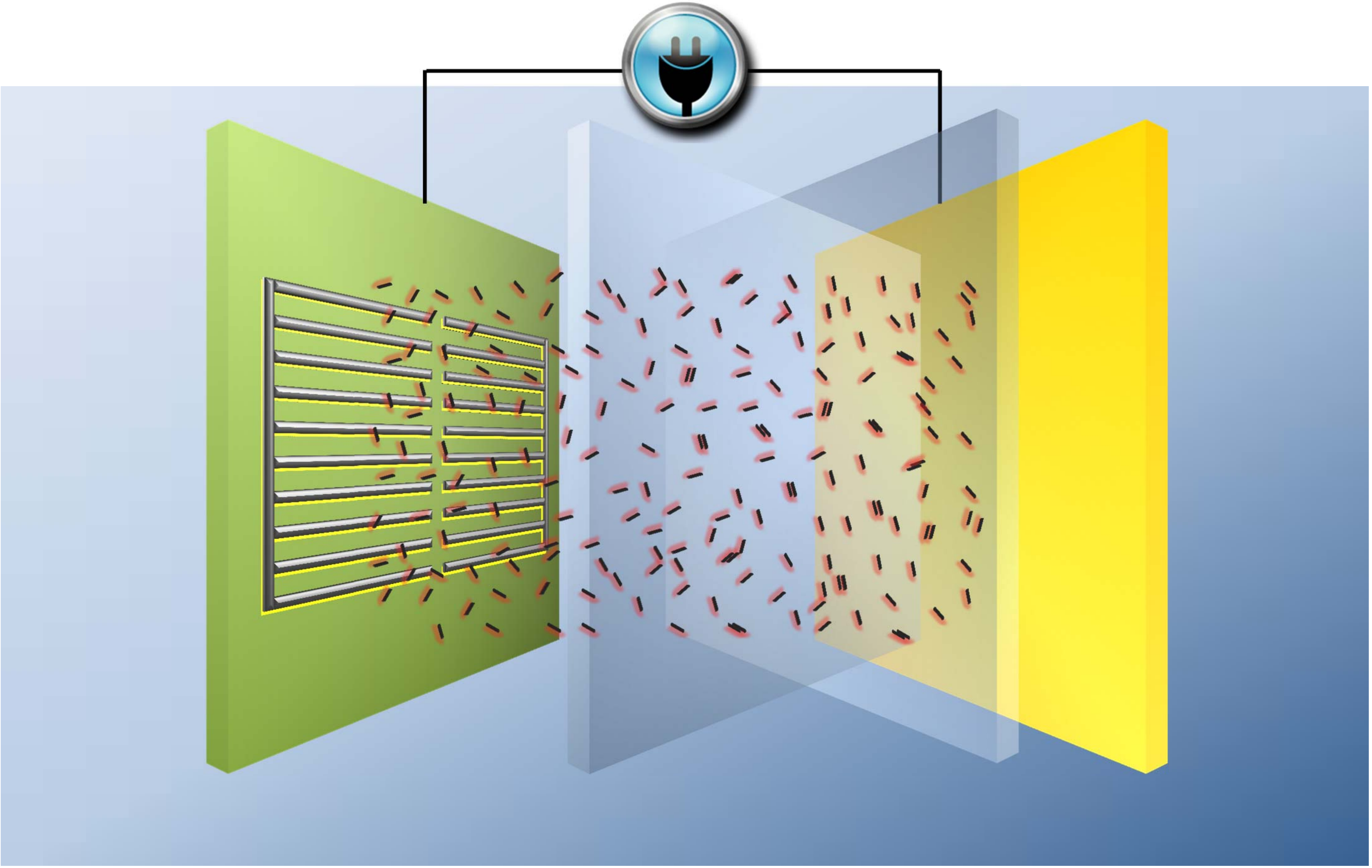
Introducing a New Manufacturing Technology for
Beyond 3-D & Electronic Printing

- Additive and parallel
- Scalable high throughput (much faster than 3-D printing)
- Printing down to 20nm
- Room temperature and pressure
- Prints 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



CHN Team Strength and Capability

NEU: Directed assembly, MEMS, fabrication, contamination control

Semiconductor & MEMs fab
- 7,000 ft² class 10 and 100 cleanrooms

UML: High volume polymer processing and assembly

UNH: Synthesis, self-assembly

Plastics processing labs
- **20,000 ft² +**

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A unique partnership

MSU: Molecular Modeling

Synthetic labs
- **10,000 ft² +**

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

Strong Industrial Partnerships

varian
CORNING
TEXTRON
Ticona ENGINEERING POLYMERS
kuraray
Schlumberger
TERADYNE
BAE SYSTEMS
tsi
zyvex
AEC
VELCRO
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

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

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Leverage

- Over the past 8 years, CHN has obtained over $51 million
- CHN has received a $2 million grant to promote commercialization.
- Funding from Industry is over $7.5 million

Development of IP Protfolio

- Over the past 8 years, CHN has filed more than 75 patents (20 awarded).

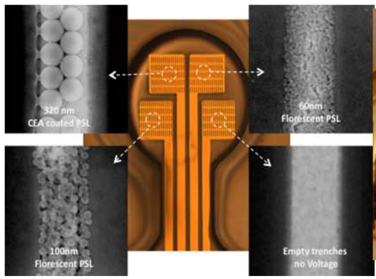
Spin-offs

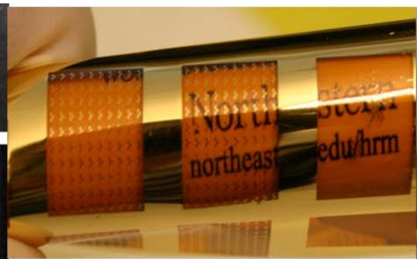
- launched Innovacene and BIOLOM by CHN professors and graduate students.

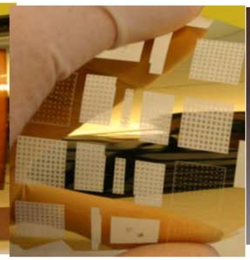
Investment in People

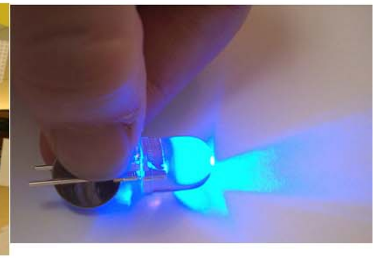
- Hired more than 24 young professors that boosted CHN capability in nanomanufacturing.

The Kostas Center

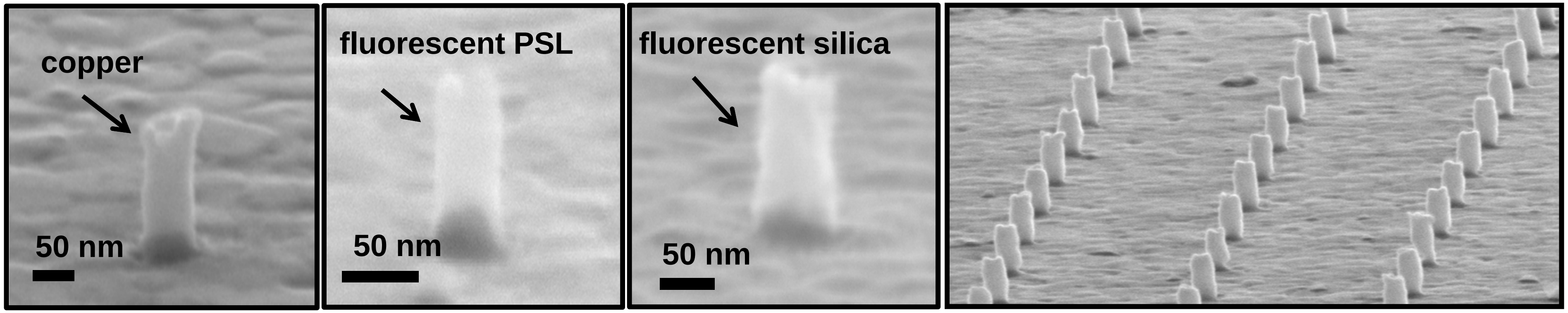




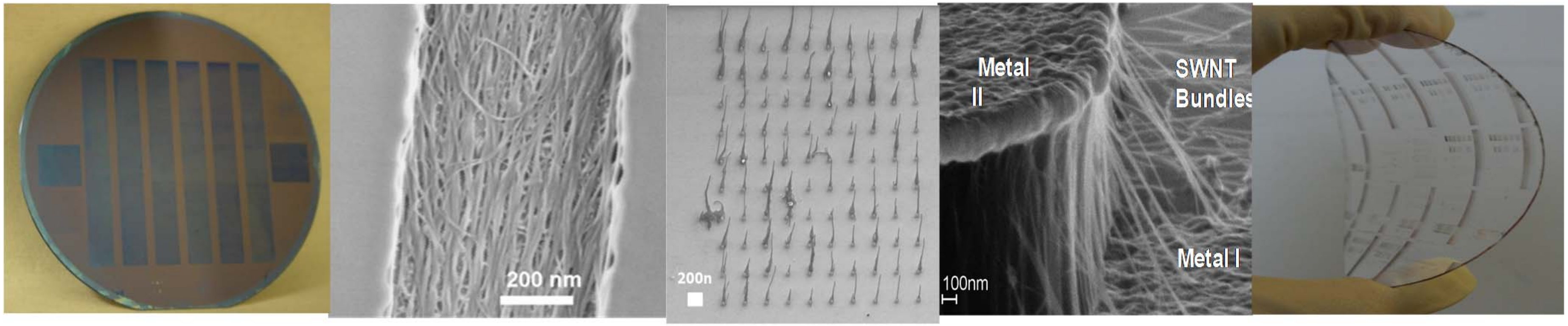




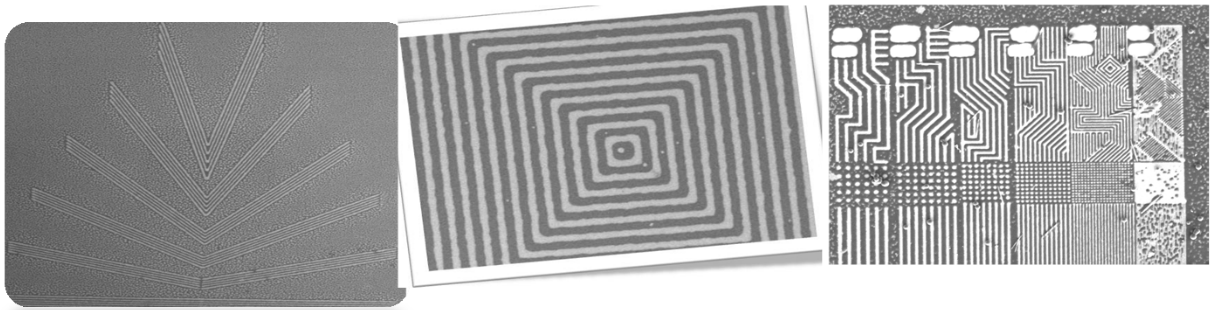
What Structures Can This Technology Make?

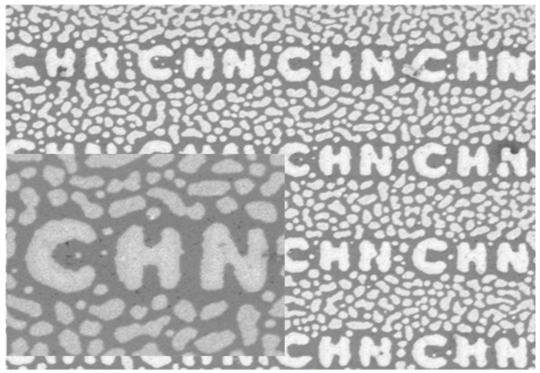


Rapid, multi-scales assembly of nanoparticles



Rapid, multi-scales assembly of Carbon Nanotubes



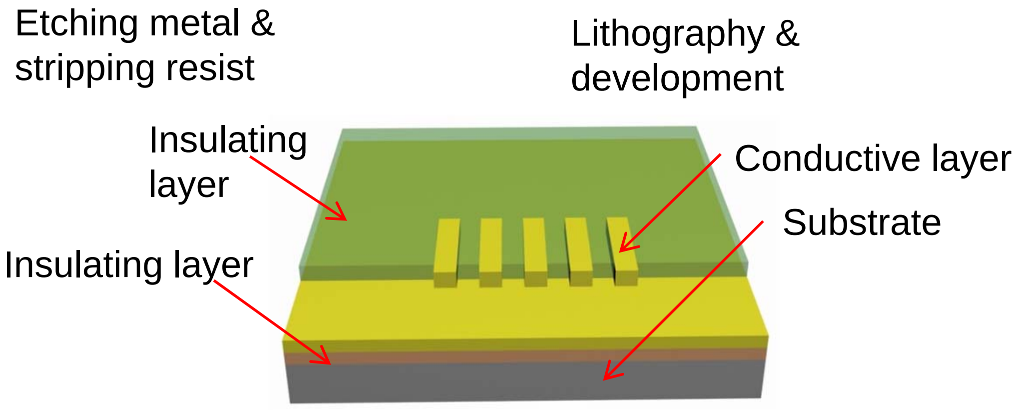


Rapid, multi-scales assembly of polymers

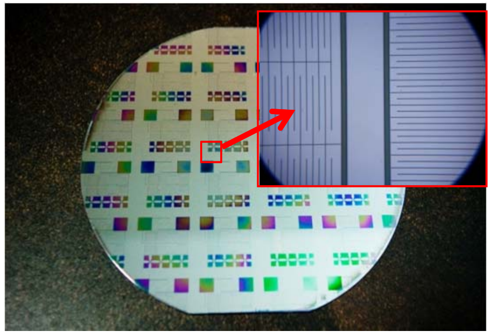
CHN Toolbox
Bridging research to applications

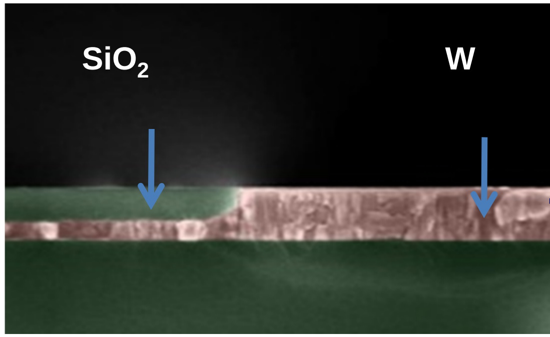
Templates	Nanoelements	Assembly Processes	Transfer Processes	Substrates	Applications
Microwires template	Nanoparticles	Electrophoretic 2-D and 3-D	Direct transfer (no functionalization)	Silicon	SWNT switch for memory devices
Nanowires templates	Carbon nanotubes (SWNTs and MWNTs)	Chemical Functionalization	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	***Fullerenes***	***Convective***	***Switchable functionalization***		Photovoltaics
Flexible Damascene Template	***Acenes***	***Convective interfacial***			SWNT Chem Sensors

Damascene Templates for Assembly and Transfer

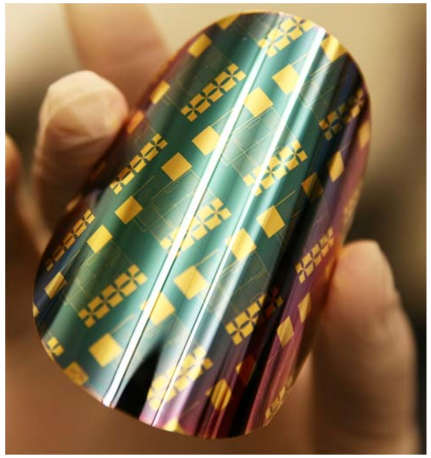


Cross section of damascene template

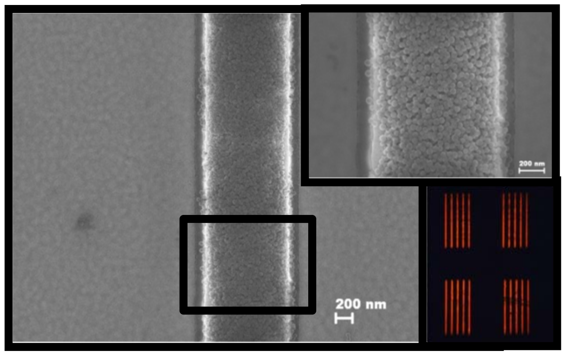


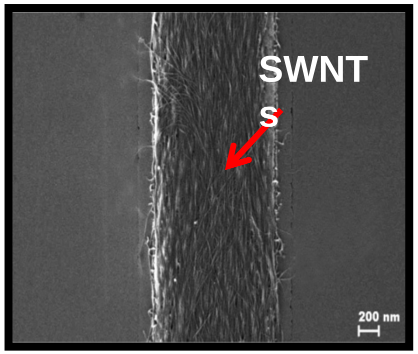


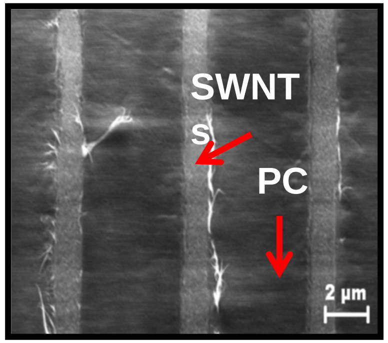
Silicon-based Hard Templates

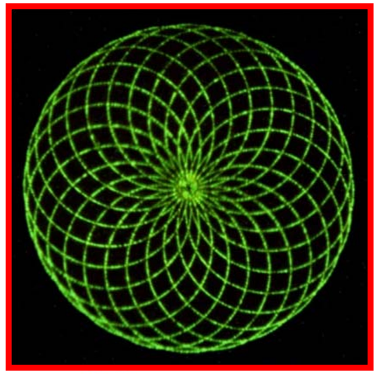


Flexible Templates for Roll-to-Roll Manufacturing



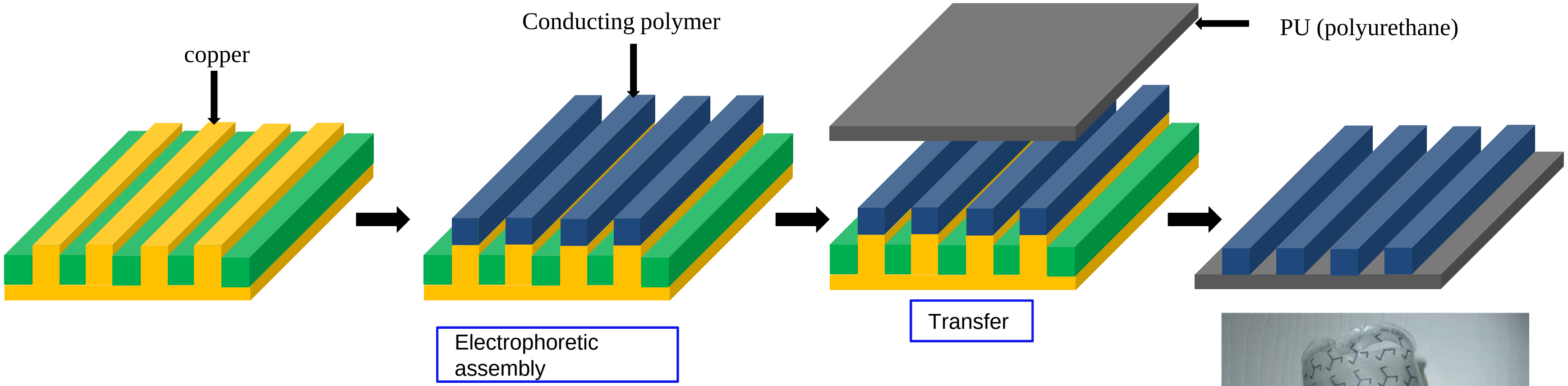


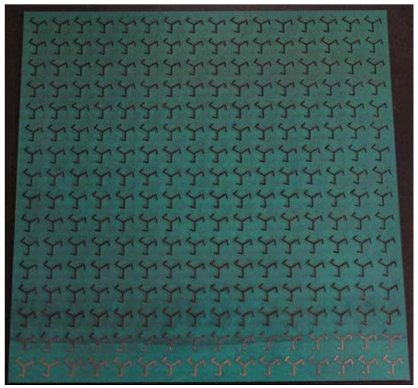


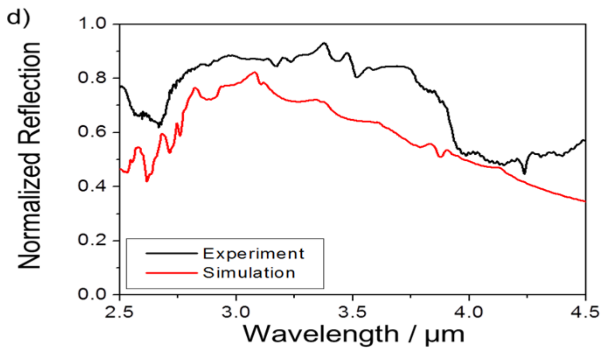


Fabrication of Chiral Metamaterial (mm Scale features)

Electrophoretic Assembly and Transfer



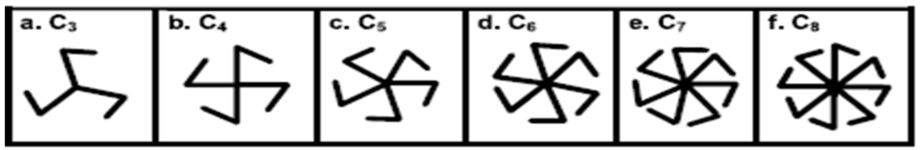




Mid-infrared

Microwave

Modeling provides designs and dimensions



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

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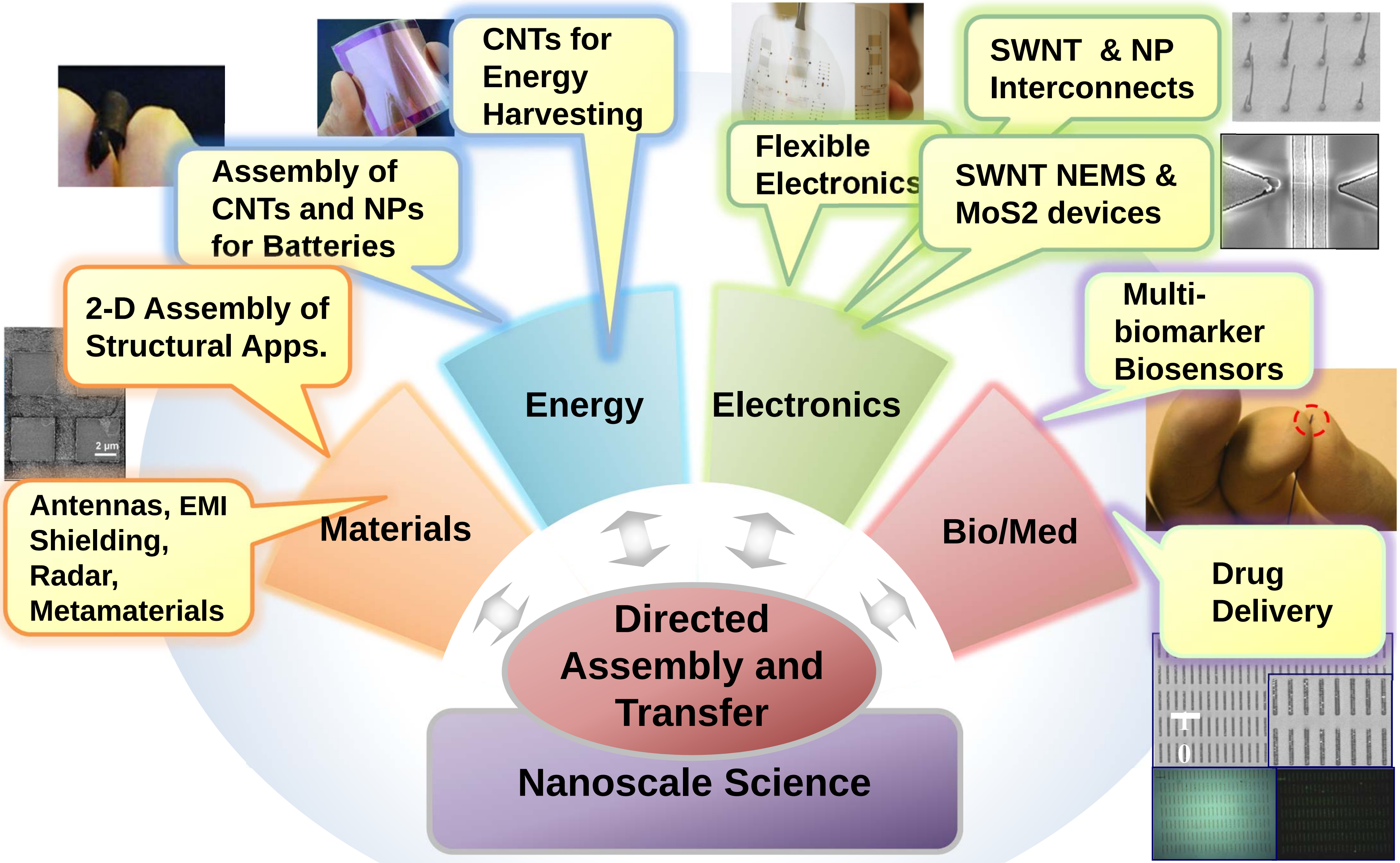
What Applications Could This Technology Make?



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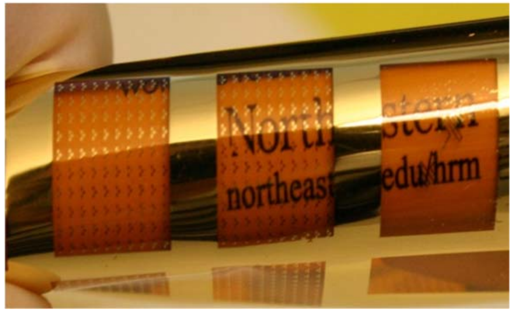
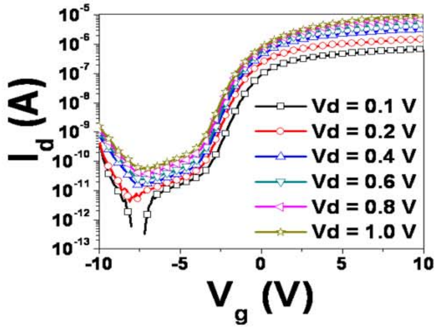
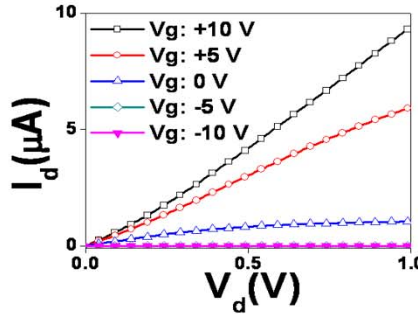
Nanoelectronics

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

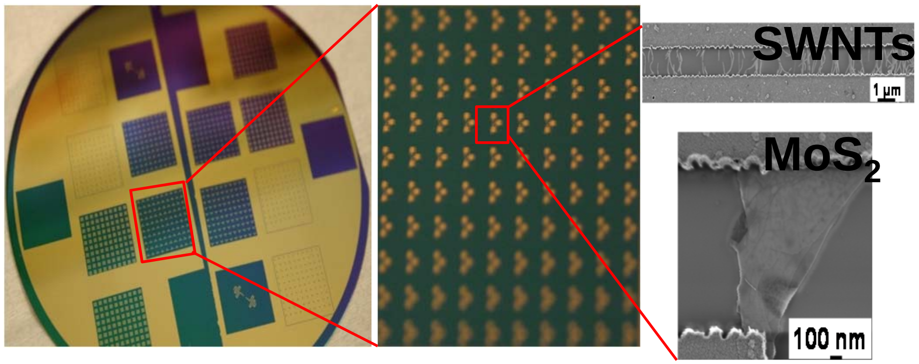
Nanotechnology, *Vol. 22, (2012).*

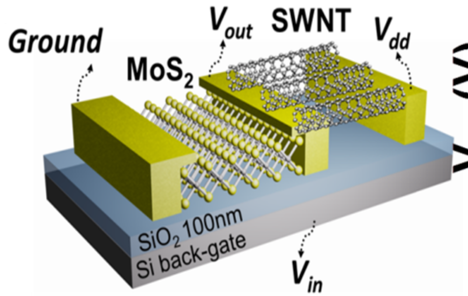


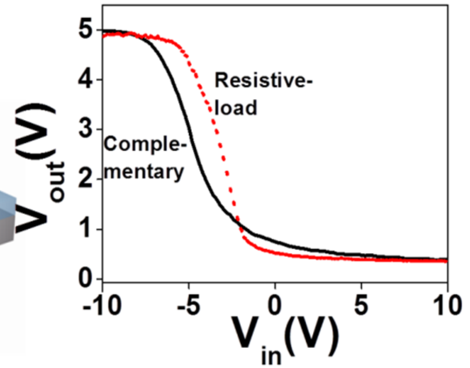




- **Heterogeneous SWNTs and MoS_2 complimentary invertors through assembly**



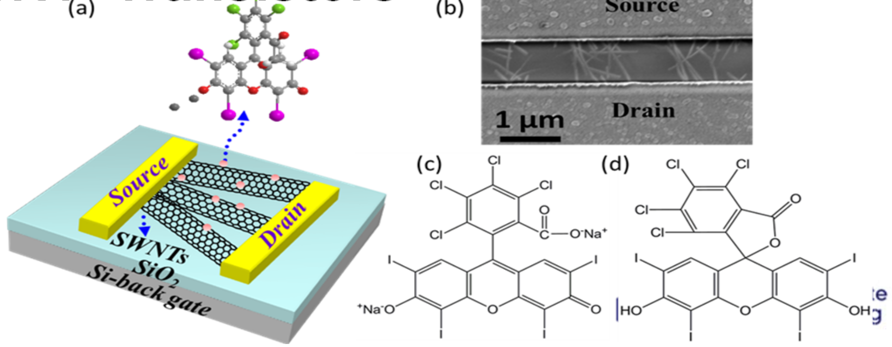




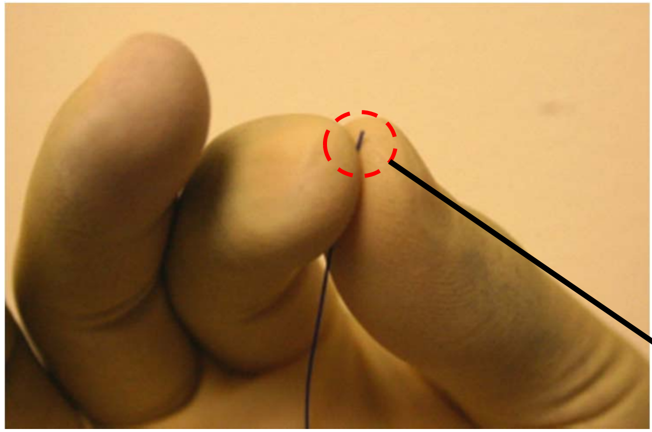
Nanotechnology, *Vol. 23, (2012)*

- **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



In vivo Nano Biosensor



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

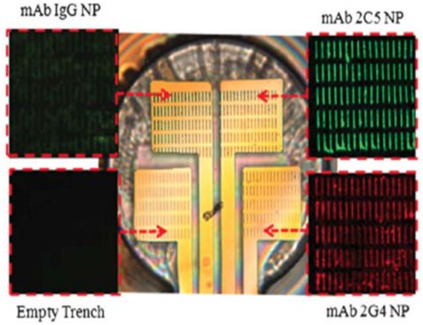
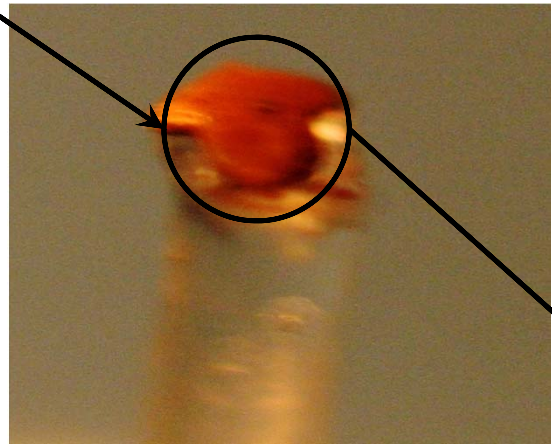
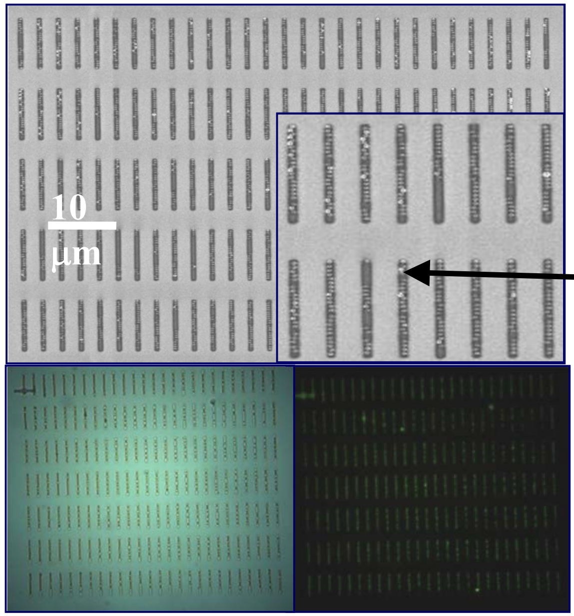


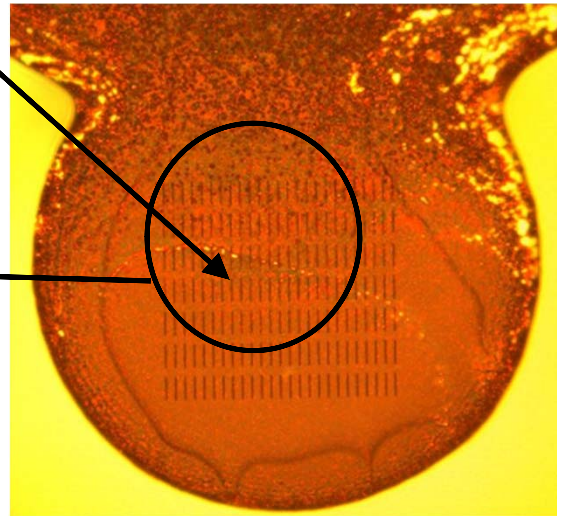
Image of the *in-vivo* biosensor (0.1 mm x 0.1 mm) after animal testing

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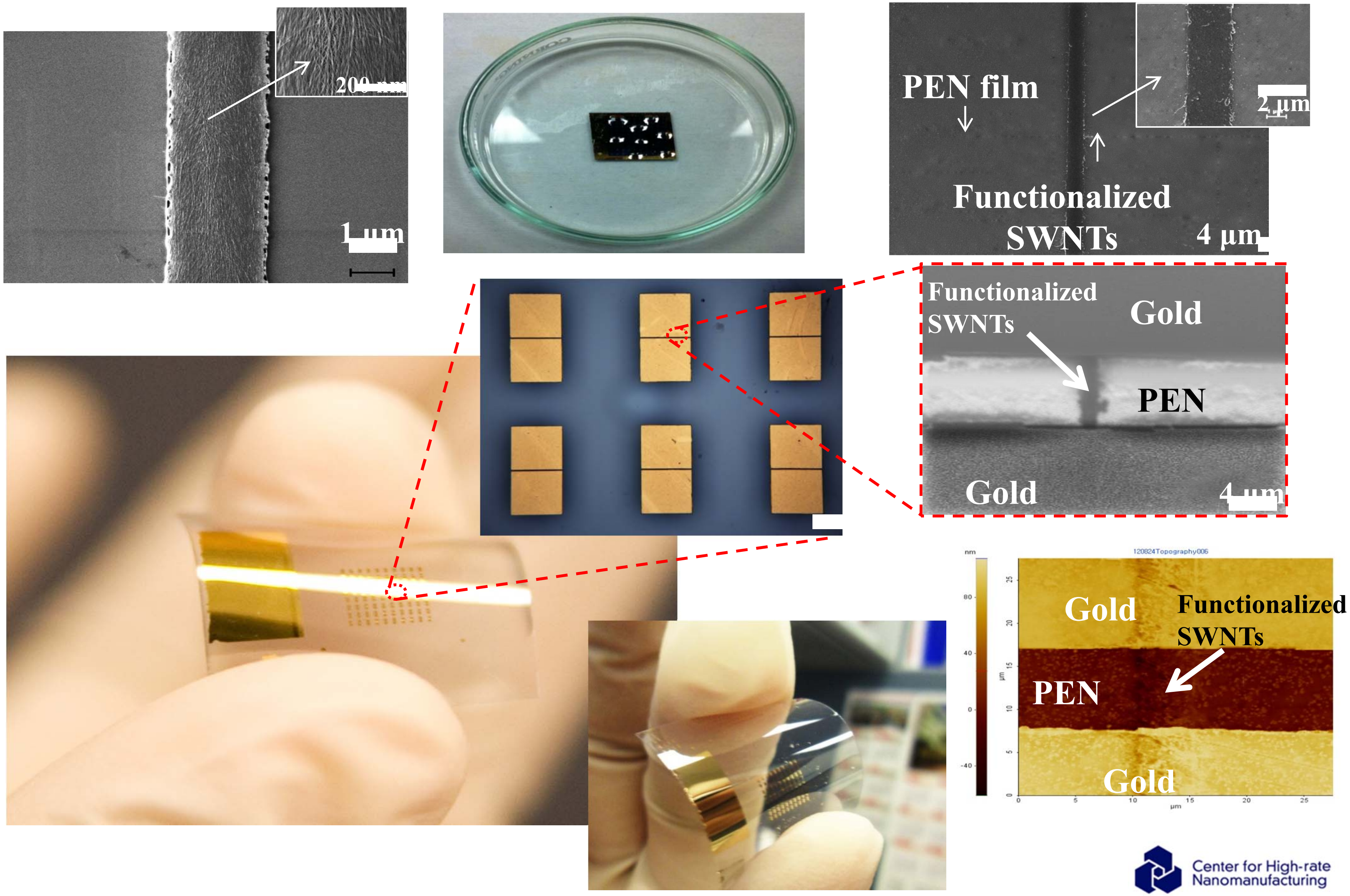
Biosensor for Physiological Monitoring of D-glucose/L-lactate/urea



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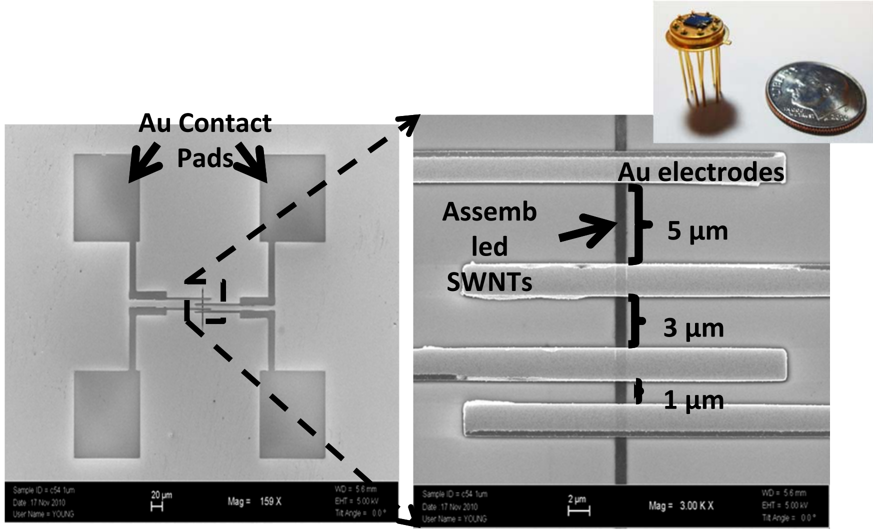
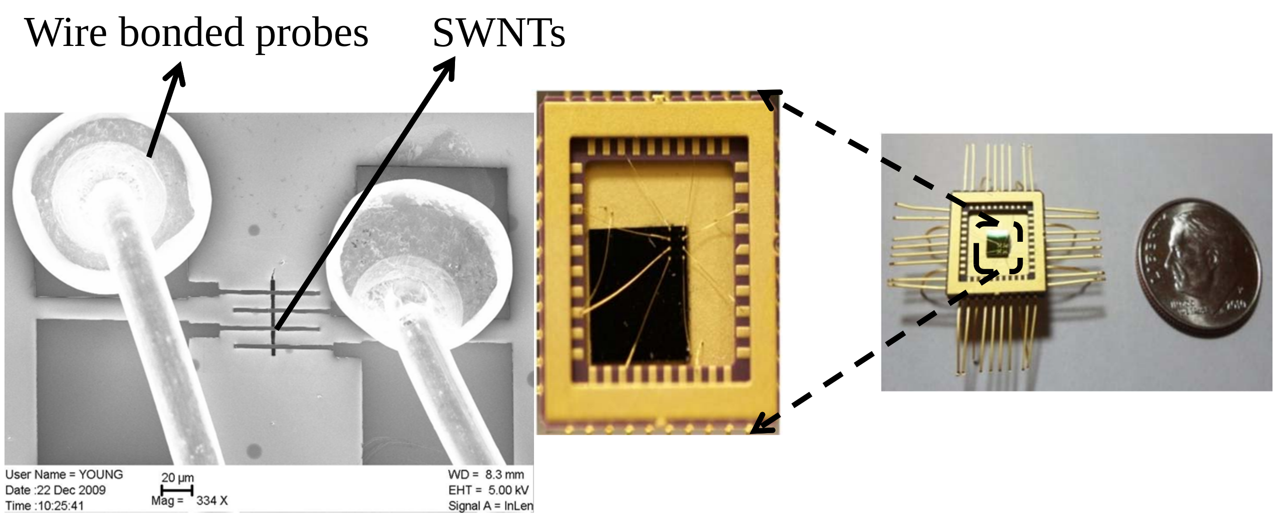
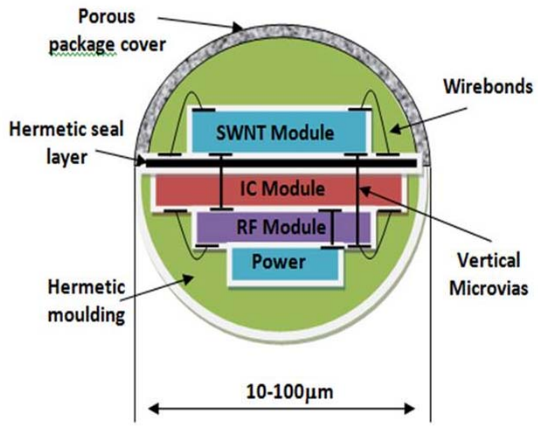
Chemical and Bio Sensors

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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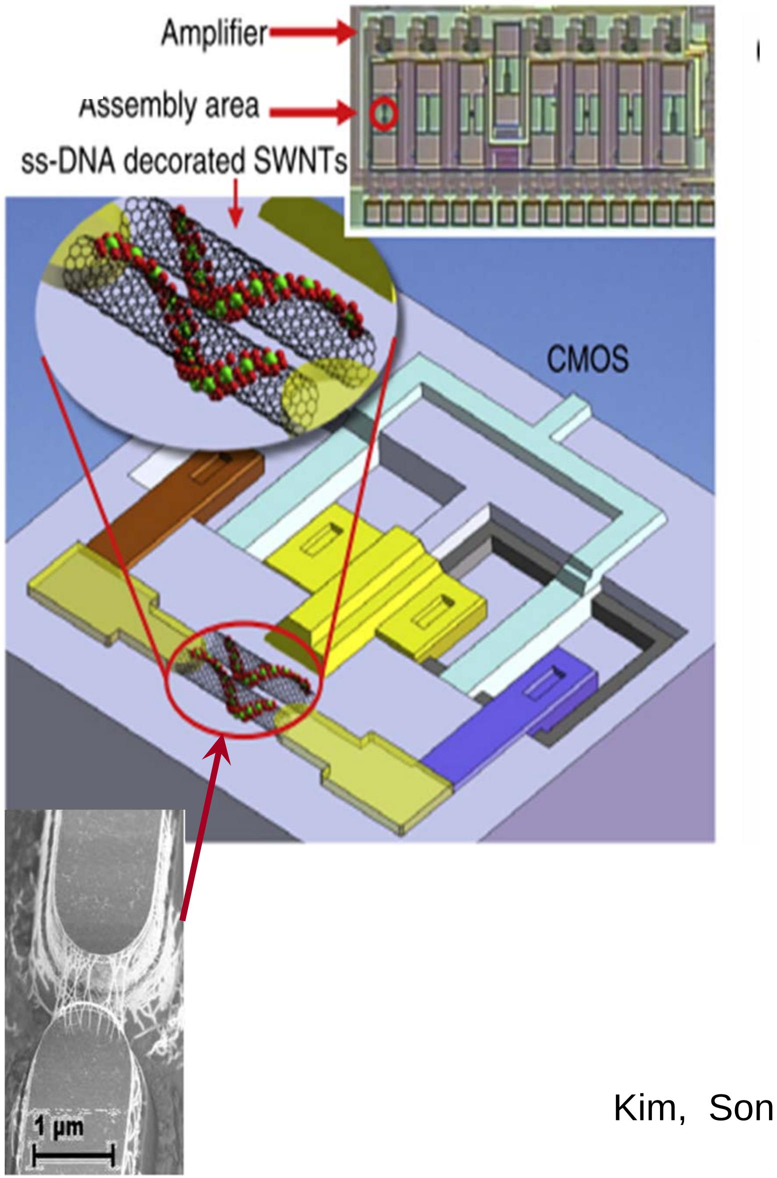
Monolithic Chemical Sensors



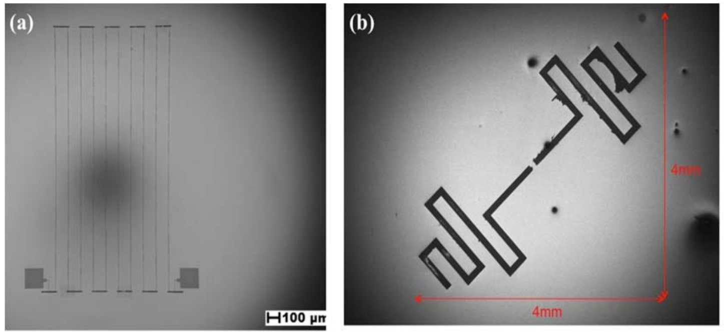
- ➢ **The SWNTs integration on CMOS circuitry demonstrates a step towards realizing integrating nanomaterials on current semiconductor devices.**
- ➢ **SWNTs were assembled onto CMOS circuitry via a low voltage dielectrophoretic (DEP) process.**
- ➢ **The the gas sensor was enhanced (up to ~300% and ~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)***

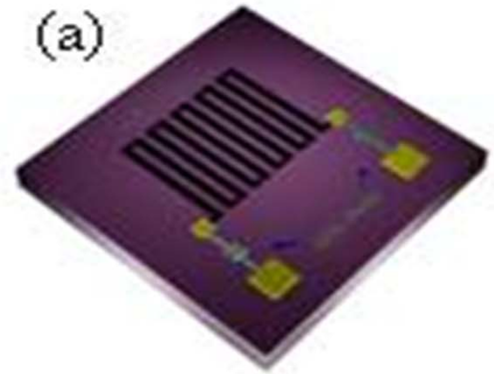
Energy Harvesting

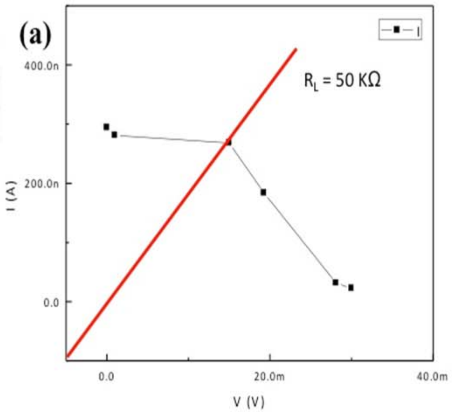
SWNT based infrared energy harvesting device

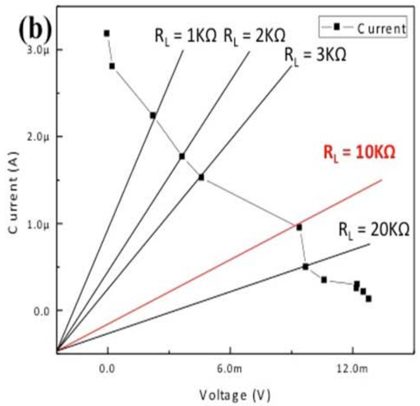


- Developed rectifying SWNT antennas having the potential for absorption of far and mid-Infra red incident light.
- Developed both Zig-Zag and linear designs.
- Rectifying circuit consists of commercially available MIM diodes operating in the W band.
- Harvesting energy wherever there is temperature difference of >5 degrees

CNT Infrared Energy Harvester







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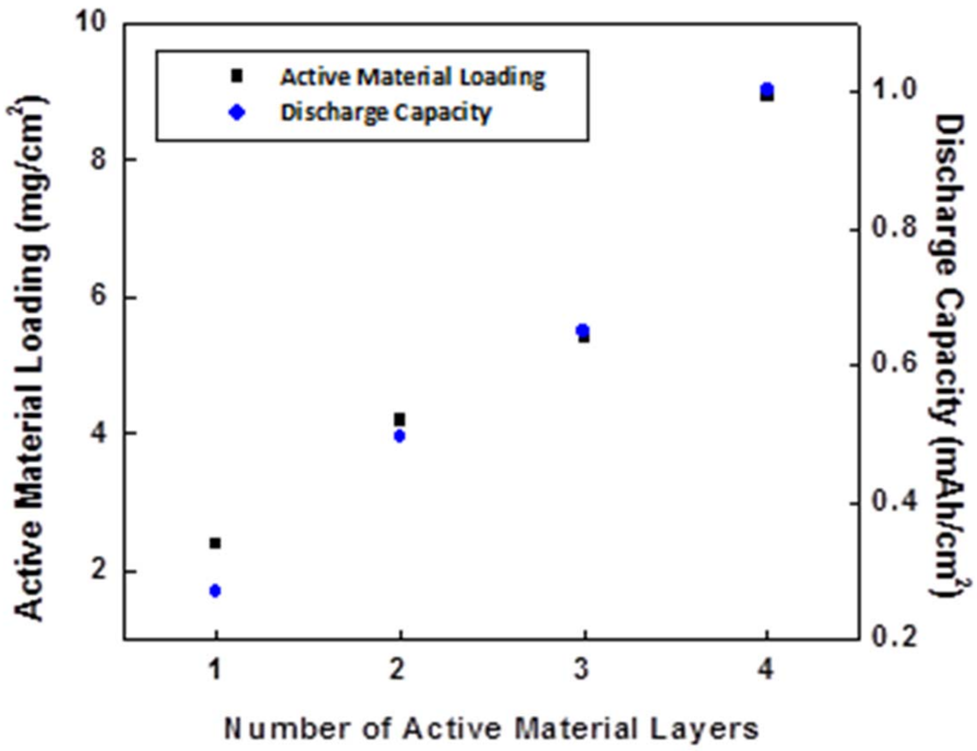
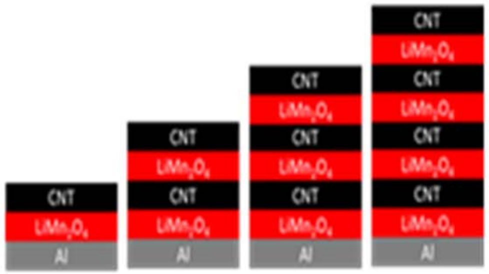
CNT Battery Discharge Capacity





	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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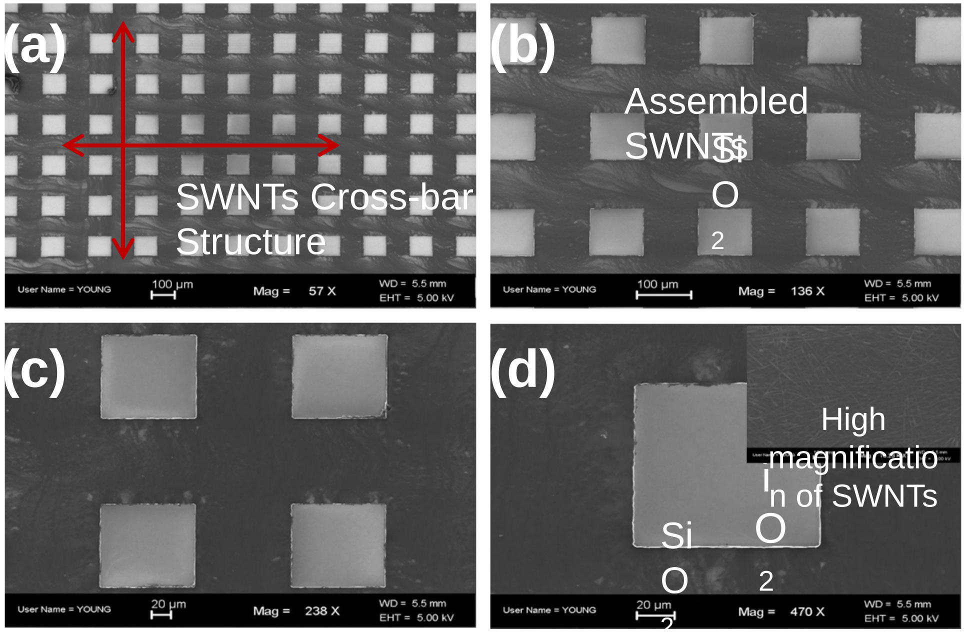
EMI Shielding

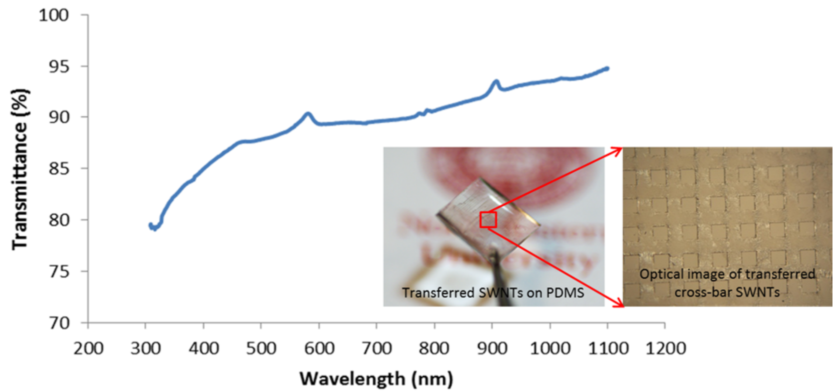
Transparent SWNTs
Cross-bar structure

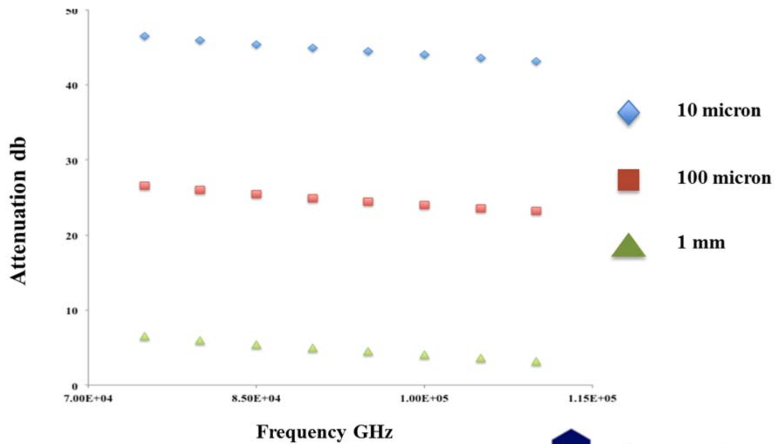
Need:

- ➢ Very high shielding effect over a defined range
- ➢ Cost effective
- ➢ Operational over wide temperature ranges
- ➢ Optical transparent



SEM Images of Cross-bar Structure of aligned carbon nanotubes





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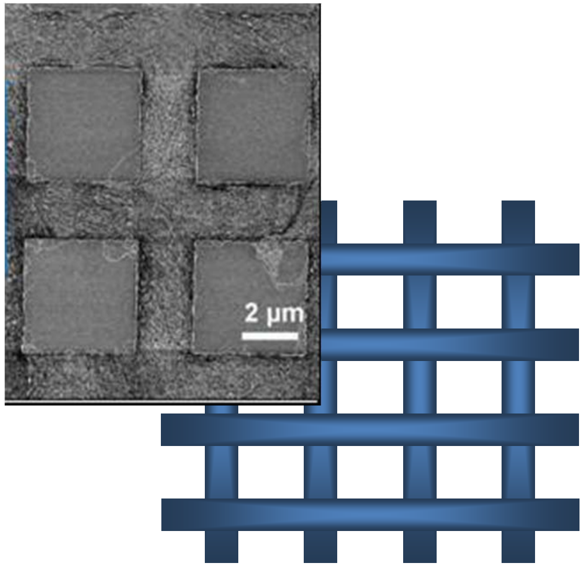
Performance comparison for EMI shielding



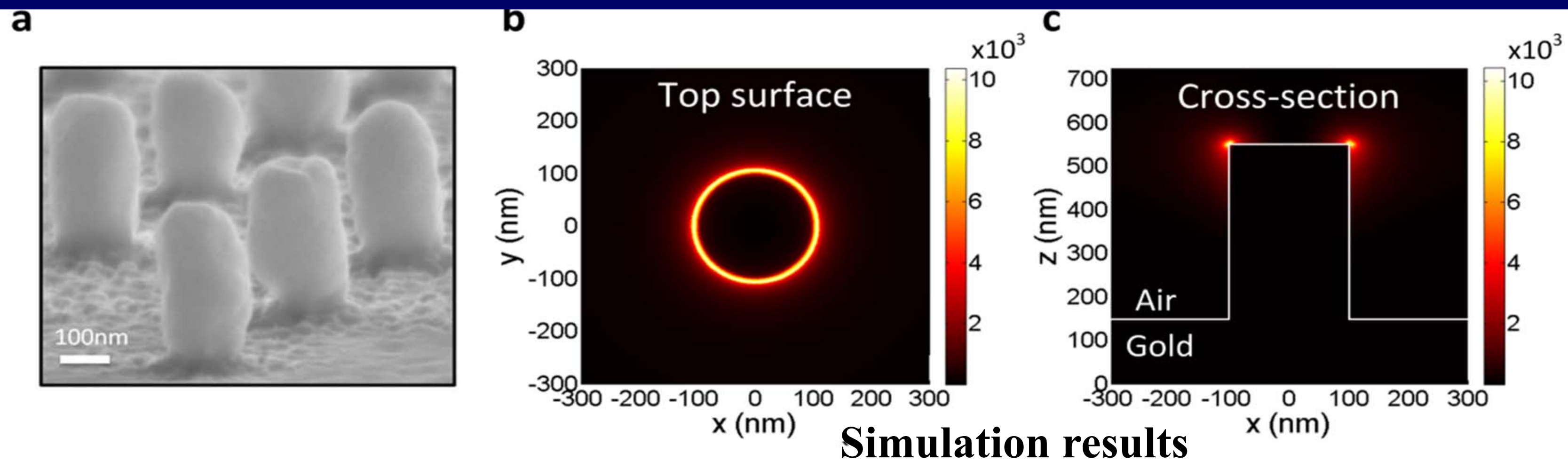
Mesh linewidth	= 1μ
Mesh period	= 10μ
Mesh height	= 20nm
Mesh length	= 2m
Mesh Width	= 2m
Optical trans	= 90.3

Frequency	RF Attenuation (dB)
1 MHz	1.38E+02
10 MHz	1.18E+02
100 MHz	9.82E+01
1GHz	7.80E+01
10 GHz	5.82E+01
100 GHz	3.80E+01
1 THz	1.80E+01

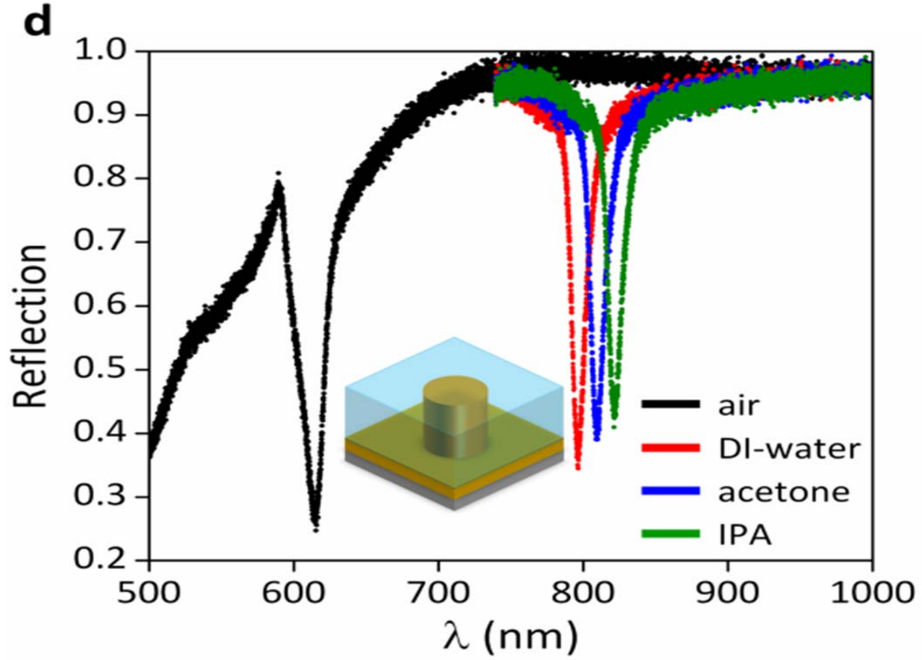
Material	Density(kg/m³)	Mass (kg)	Bulk Resistivity(Ωcm)	RF Attenuation (dB)
Al	2.70E+03	4.32E-05	2.70E-08	42.96
Cu	8.92E+03	1.43E-04	1.67E-08	47.11
Au	1.93E+04	3.09E-04	2.20E-08	44.73
Fe	7.87E+03	1.26E-04	9.70E-08	32.01
Ti	4.51E+03	7.21E-05	4.20E-07	19.98
W	1.93E+04	3.08E-04	5.60E-08	36.69
SWNT*	1.33E+03	2.13E-05	1.67E-11	107.07

*Philip G. Collins and Phaedon Avouris, 62 Scientific American December 2000

Plasmonic Enhancement – Adaptive Camouflage



Simulation results



Experimental result

- **Enhancement defined by various geometries**
- **Very good absorption in the visible (red) and near infrared regime**
- **Can be used as a camouflage**

Appl. Phys. Lett. 98, (2011)

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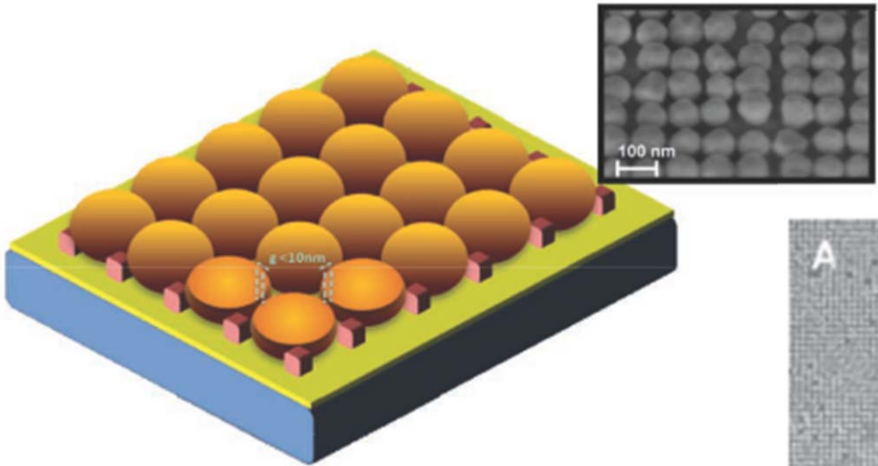
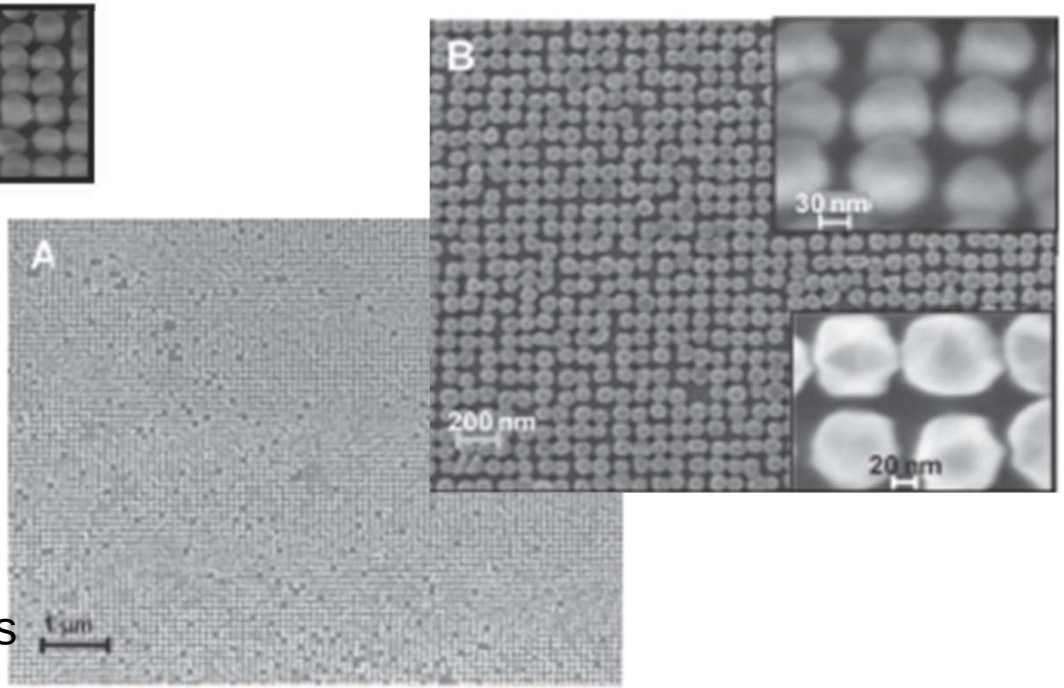
SERS Sensors





- ➢ Employs directed assembly technique
- ➢ Can be scaled to very large areas (cm^2)
- ➢ Control of ~8 -10 nm gap between assembled particle
- ➢ Assembly time can be reduced to order of secs
- ➢ SERS enhancement factors of 10^7

Applications

- ➢ Chemical sensors; Bio sensors
- ➢ Energy solar conversion
- ➢ Spacers
- ➢ Local field amplifiers

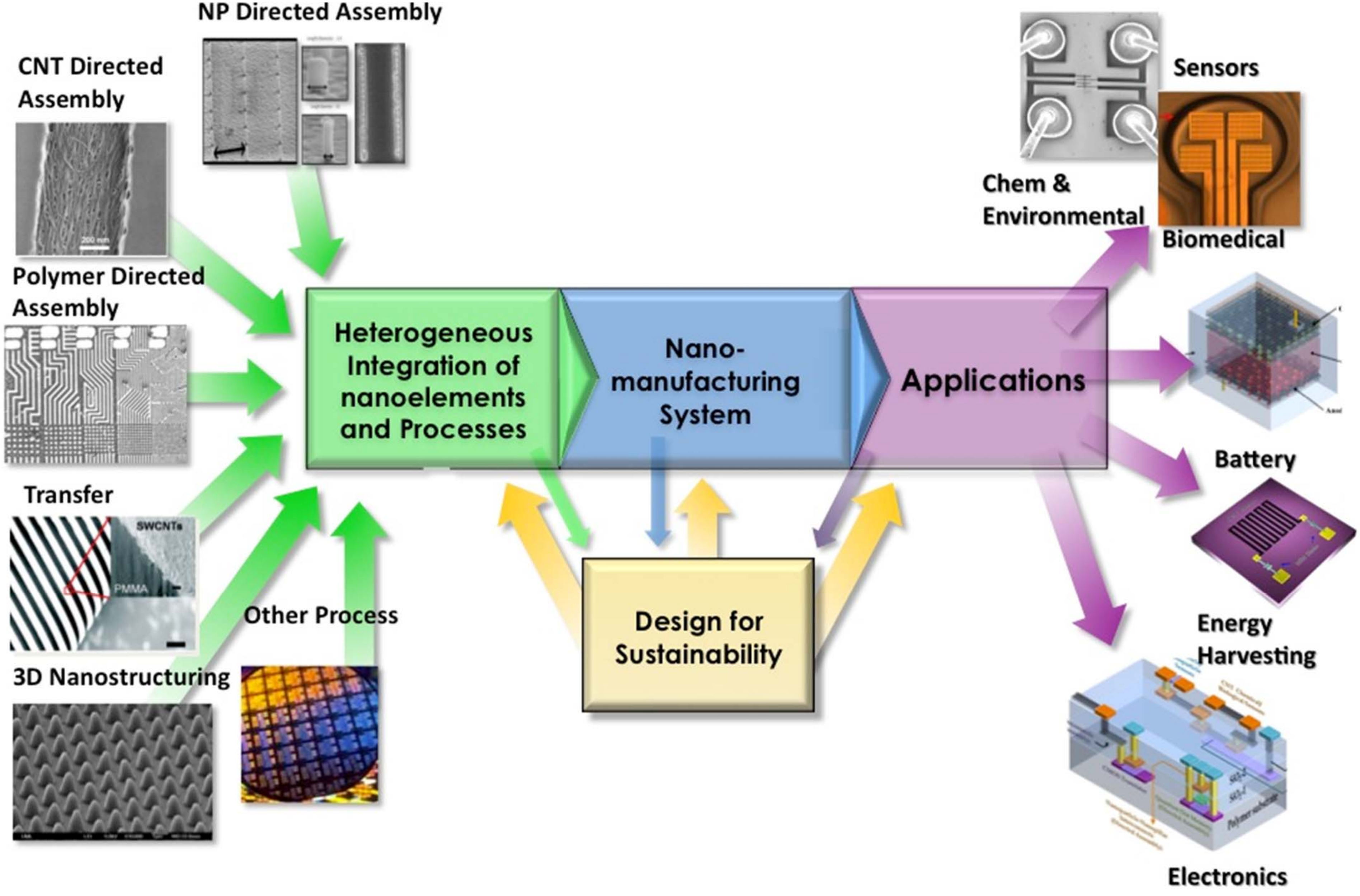
Liberman, Yilmaz, Busnaina, et. al., ***Advanced Materials 2010***

Industry Supported Applications

- **CHN emerging applications roadmap led to increased industrial sponsorship**
  - **Chemical sensors**
  - **Energy storage and harvesting**
  - **Photovoltaics**
  - **Nonvolatile memory**
  - **EMI shielding**
  - **Metamaterials**
  - **Biosensor**
  - **SWNT composites**

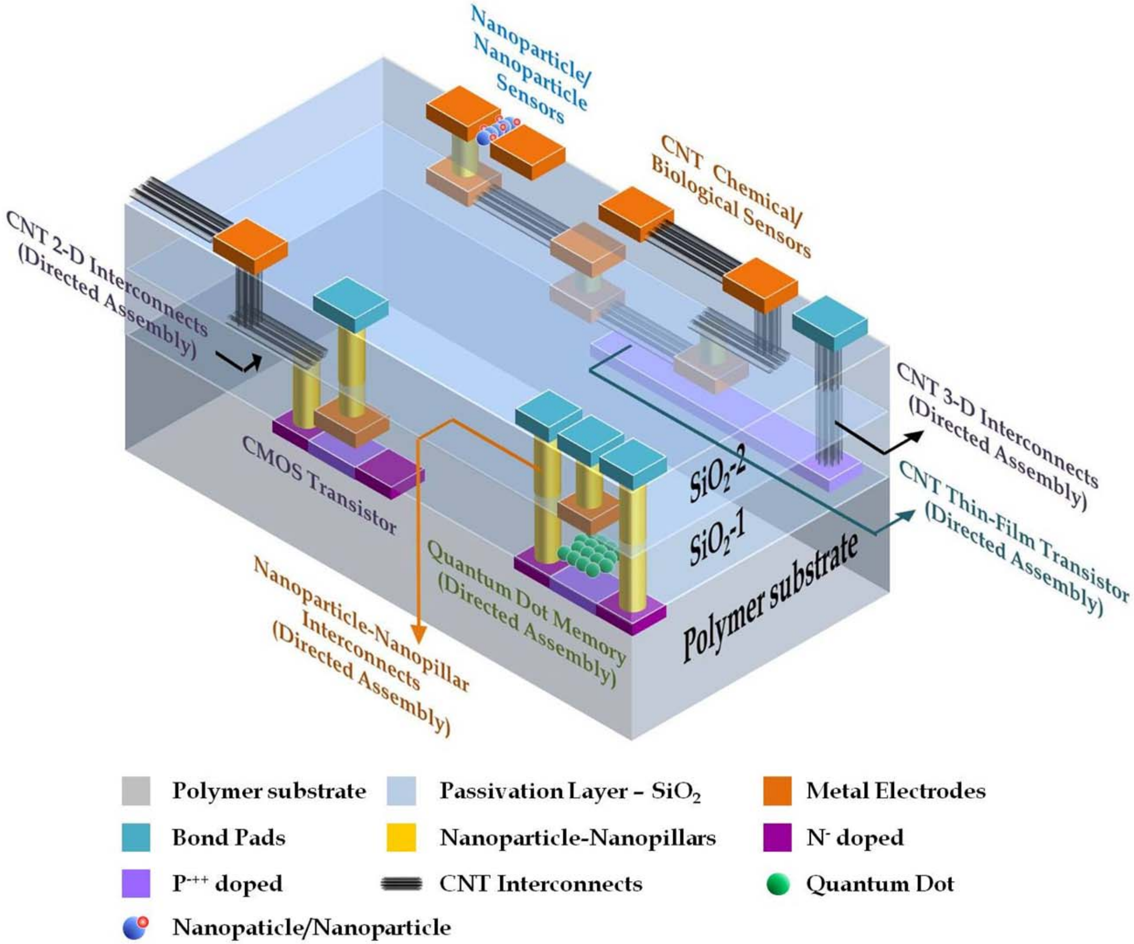
AEC
LOCKHEED MARTIN We never forget who we're working for®
NOVATIO ENGINEERING, INC
KONARKA®
EMC²
CHASM TECHNOLOGIES BRIDGING THE GAP
TEXTRON
NanoTechLabs
SWeNT SouthWest NanoTechnologies
Raytheon
W. M. KECK FOUNDATION
VELCRO®

Rethinking Manufacturing



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

- This technology is a great enabler and equalizer
- A nanofactory could be built for under $50 million, a small fraction of today's cost
- Nanotechnology accessible to millions of innovators and entrepreneurs
- Unleash a wave of creativity



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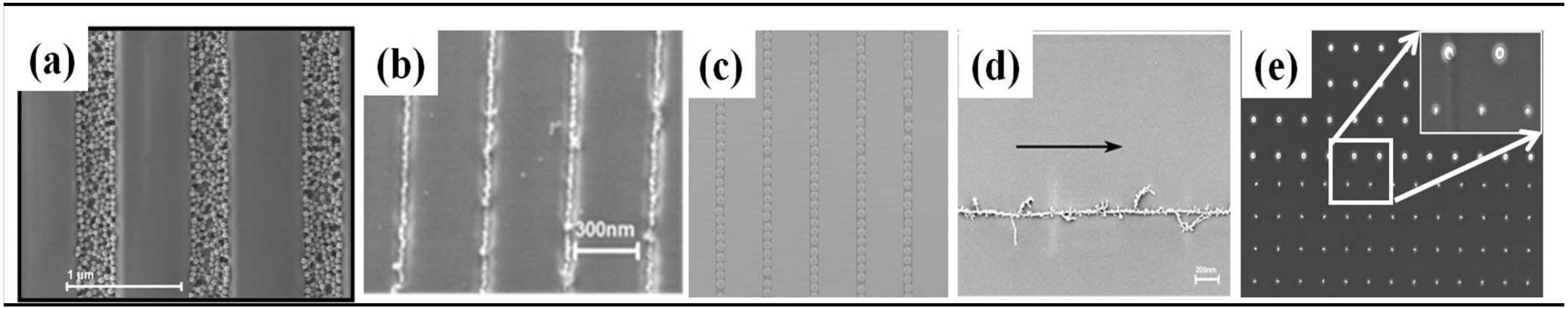
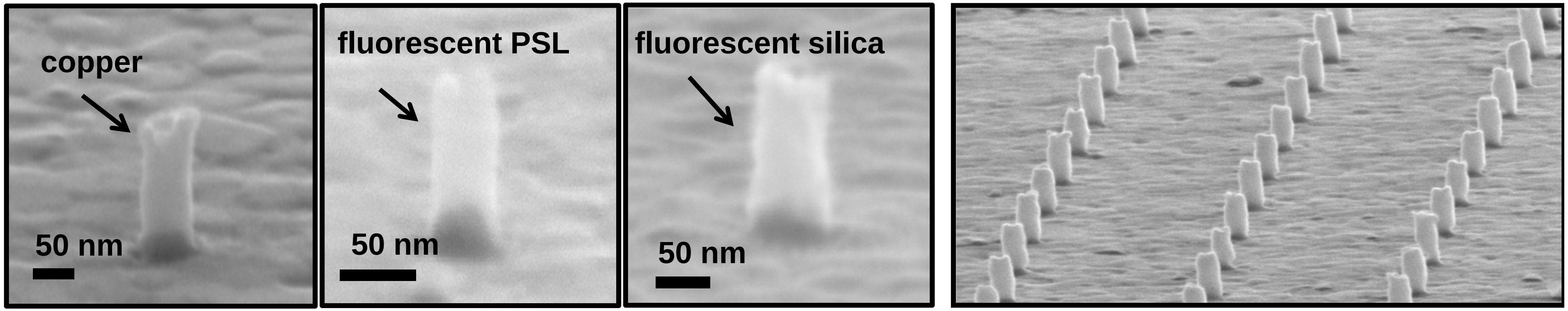
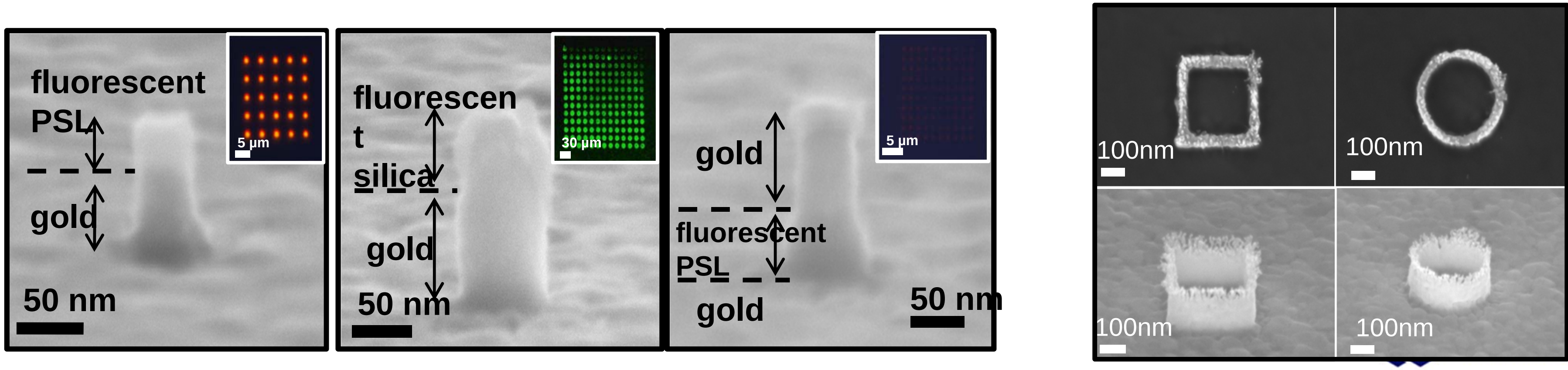
Questions and Discussion?

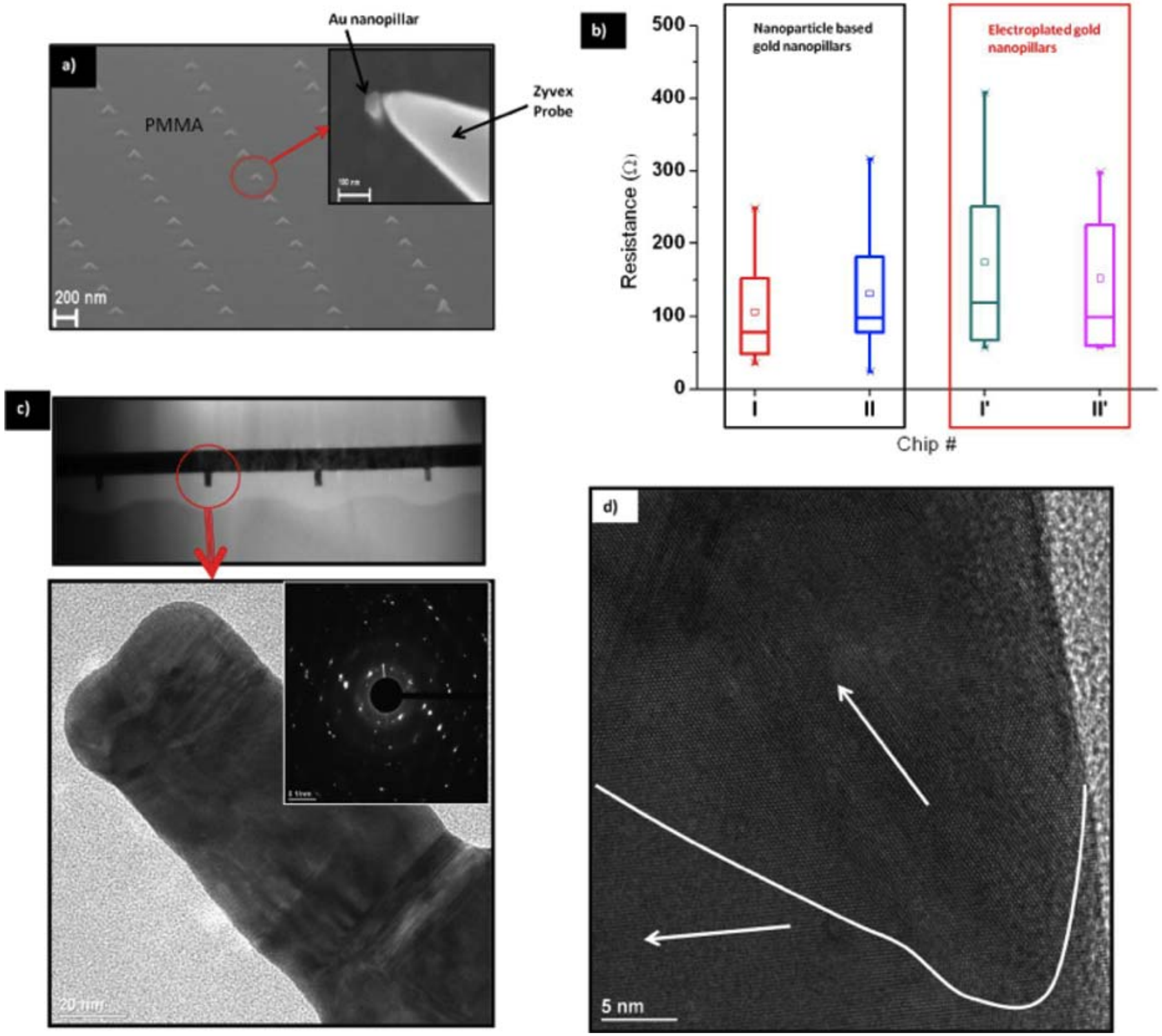
Assembly of Nanoparticles



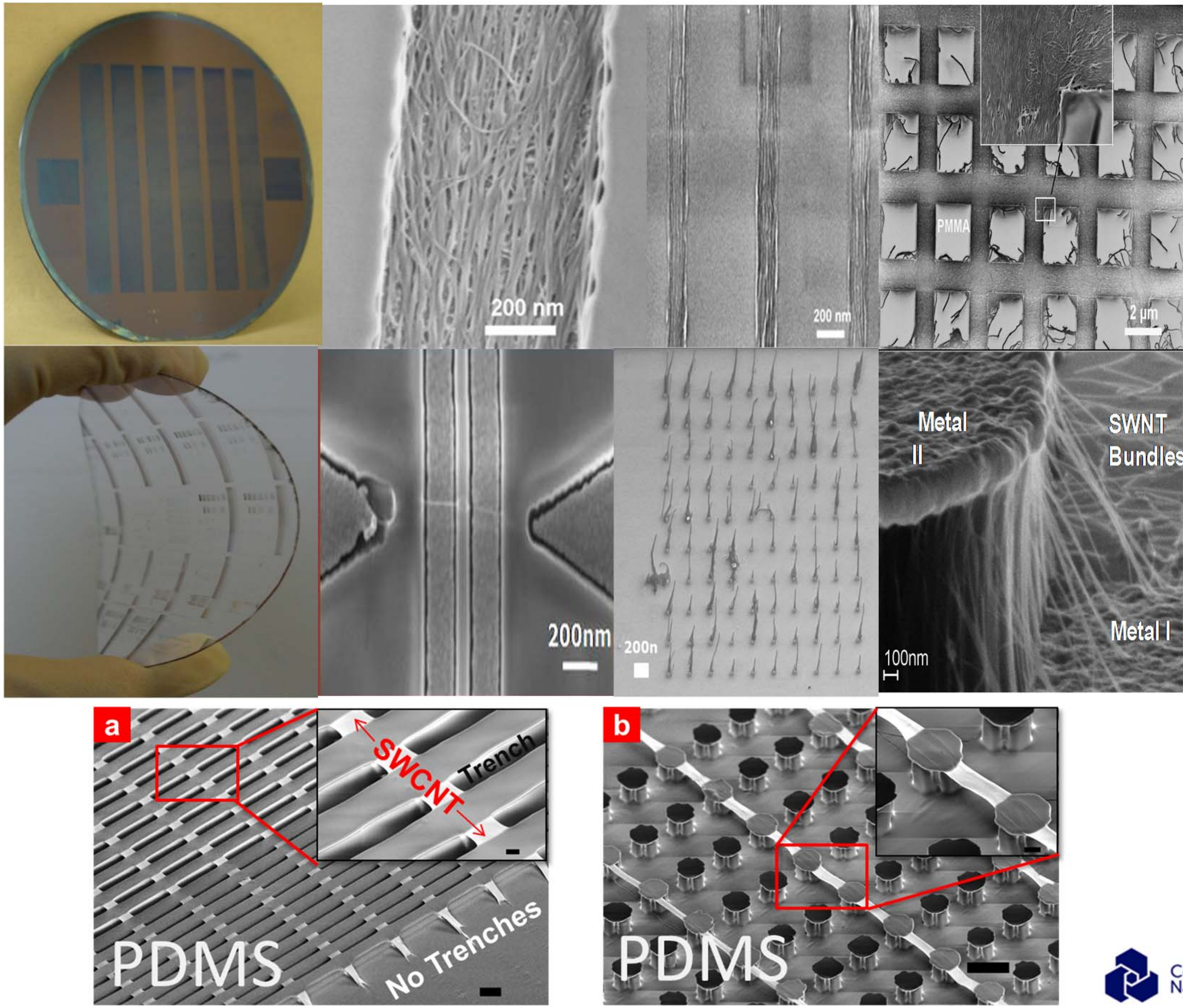




Nanopillars made from Conducting, Semiconducting and/or Insulating Materials



Assembly of Carbon Nanotubes



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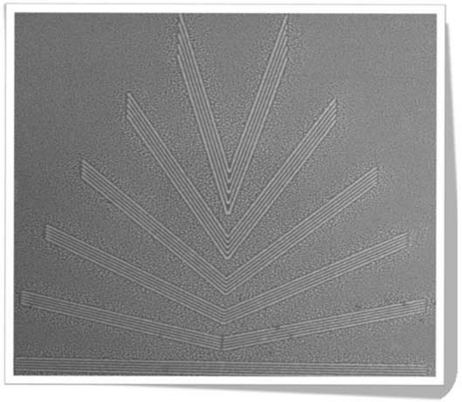
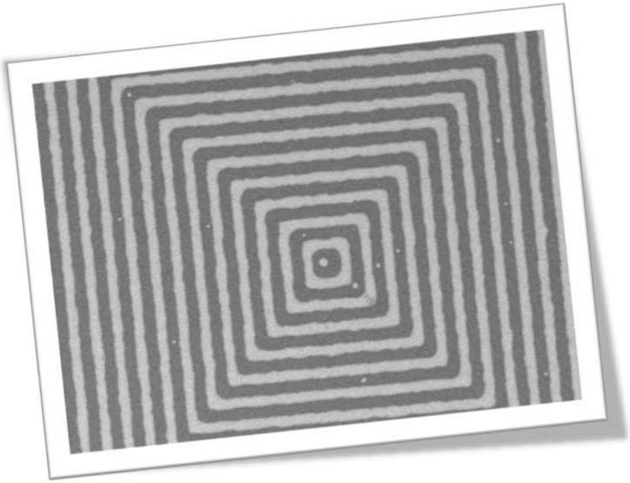
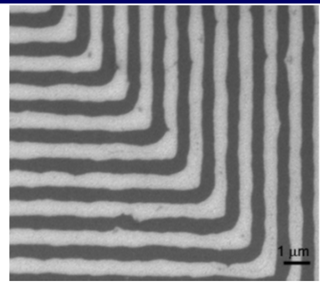
Nanomanufacturing

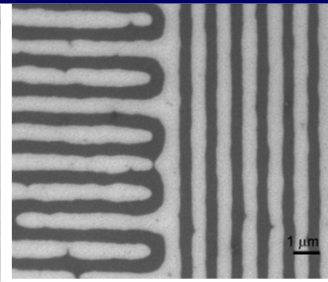
Assembly of Heterogeneous Polymers



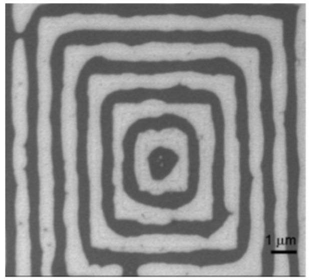




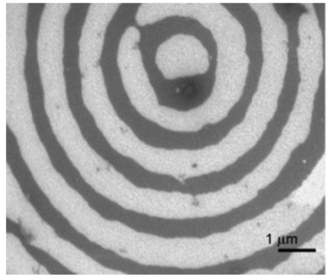
90° bends



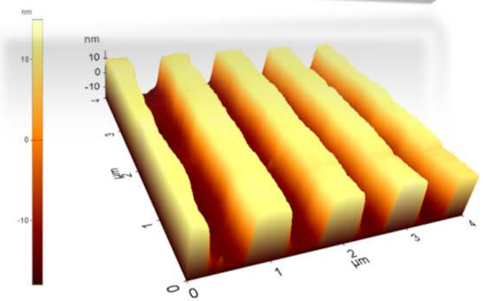
T-junctions



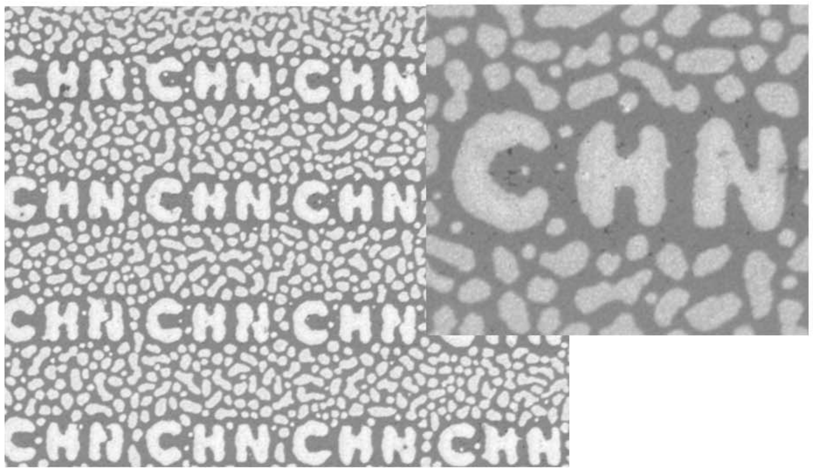
Square arrays

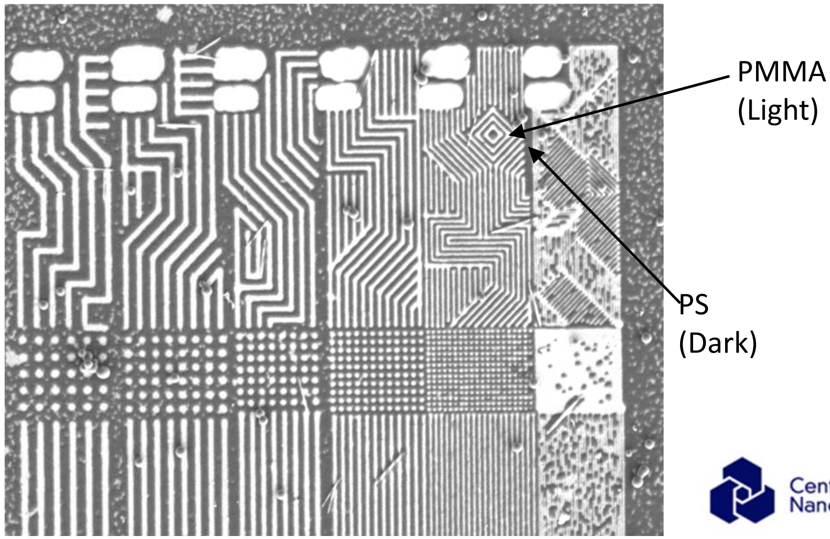


Circle arrays



Multiple polymer systems, Rapid Assembly, multi-scales





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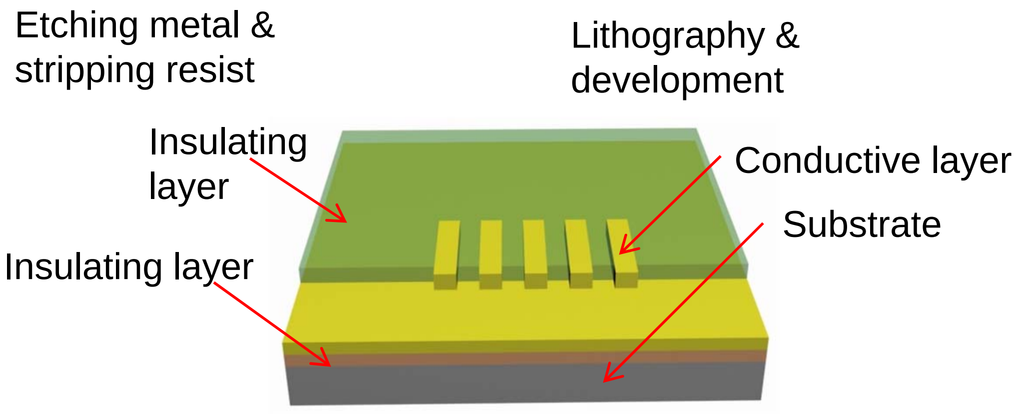
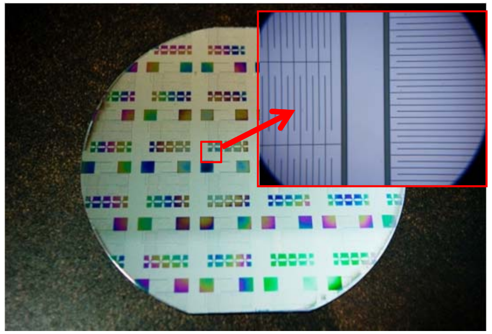
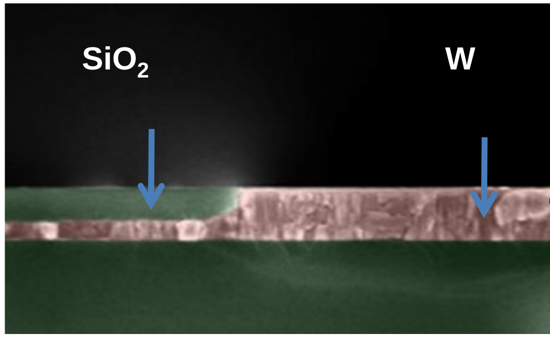
Damascene Templates for Assembly and Transfer

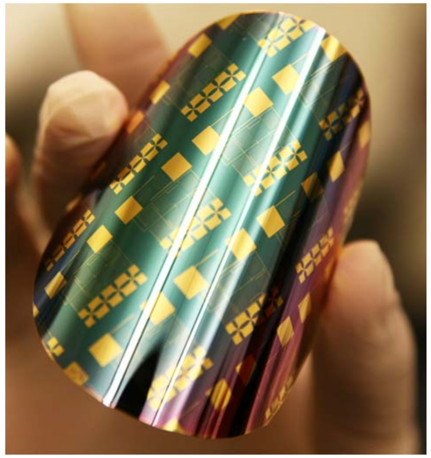


Cross section of damascene template

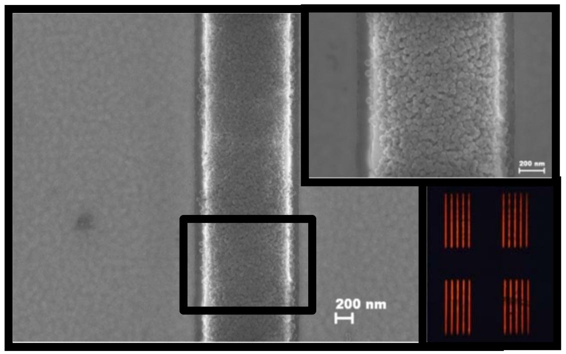


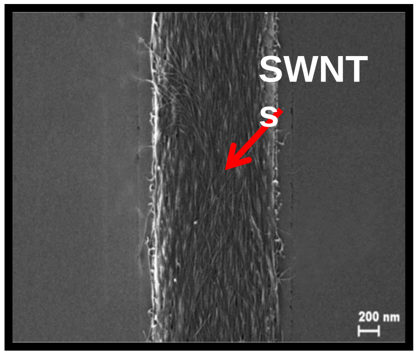


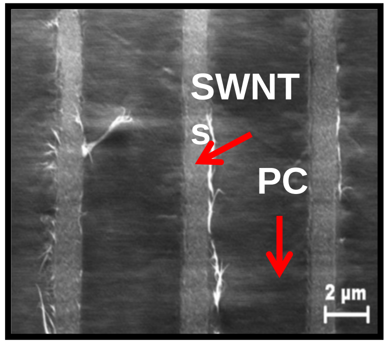
Silicon-based Hard Templates

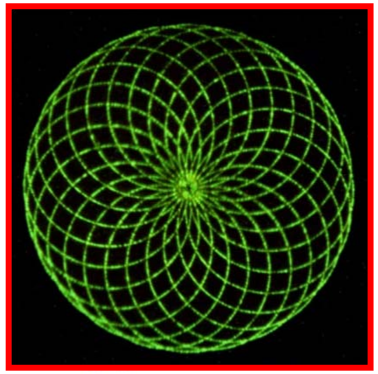


Flexible Templates for Roll-to-Roll Manufacturing

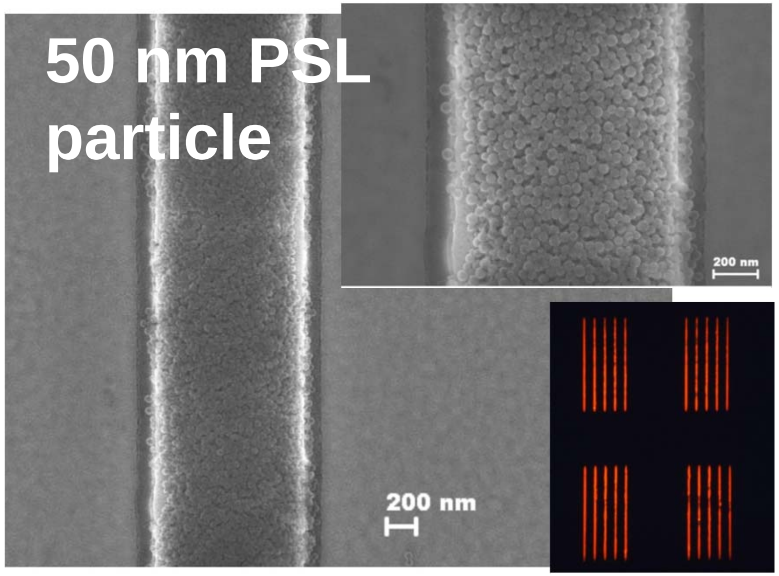


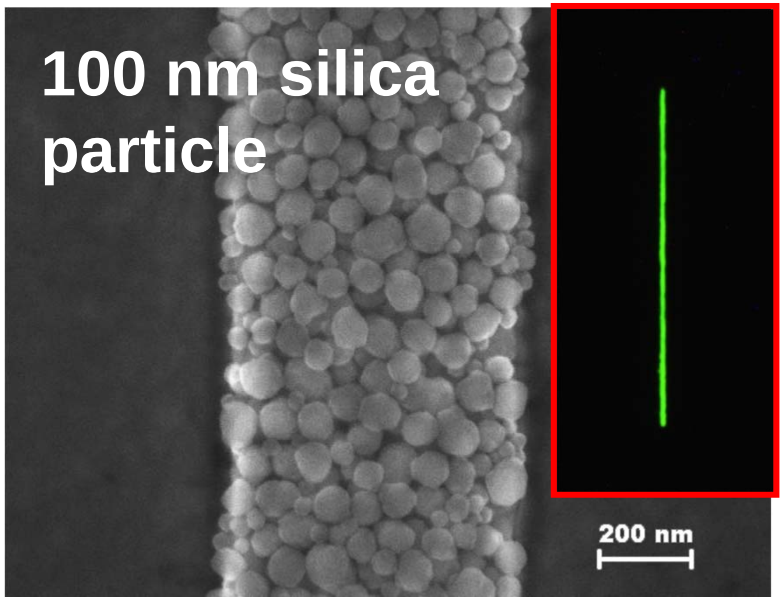


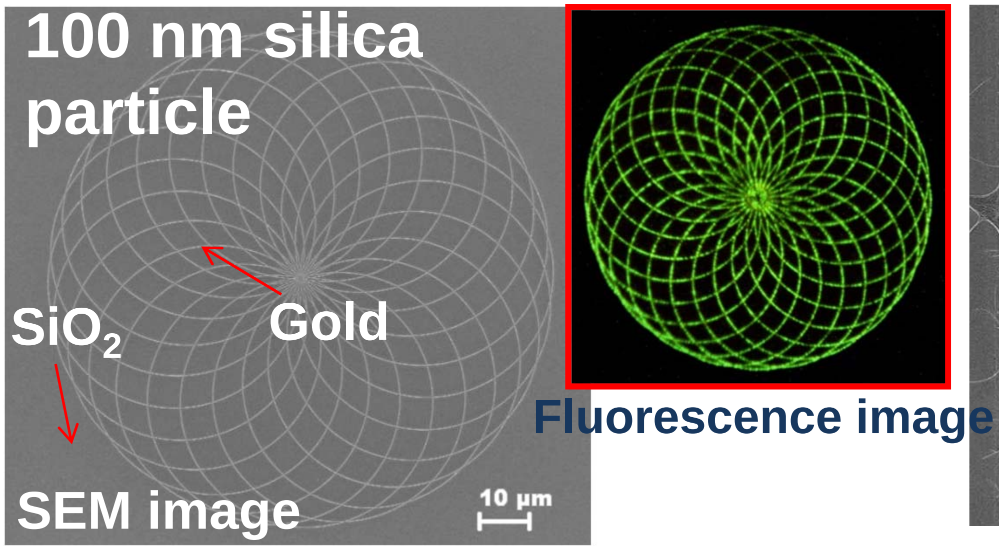


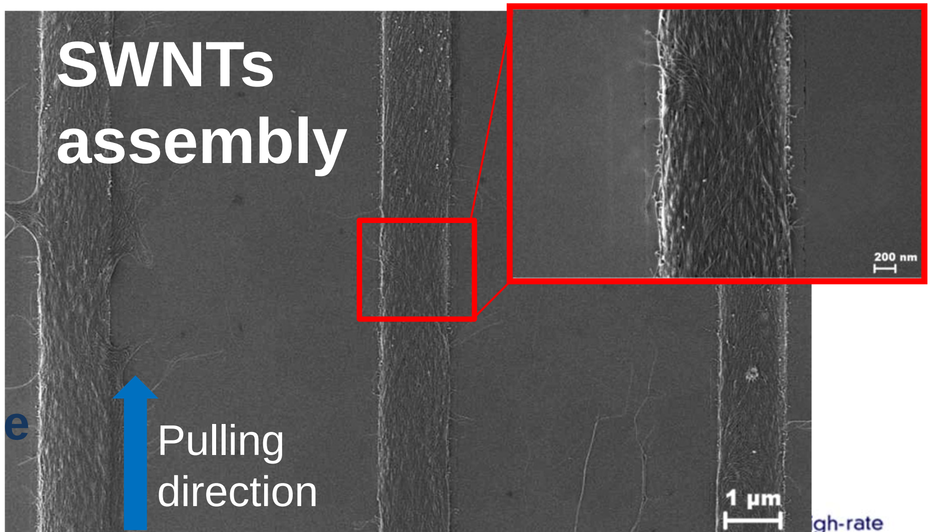


Nanoelements Assembly on Functionalized Damascene Templates



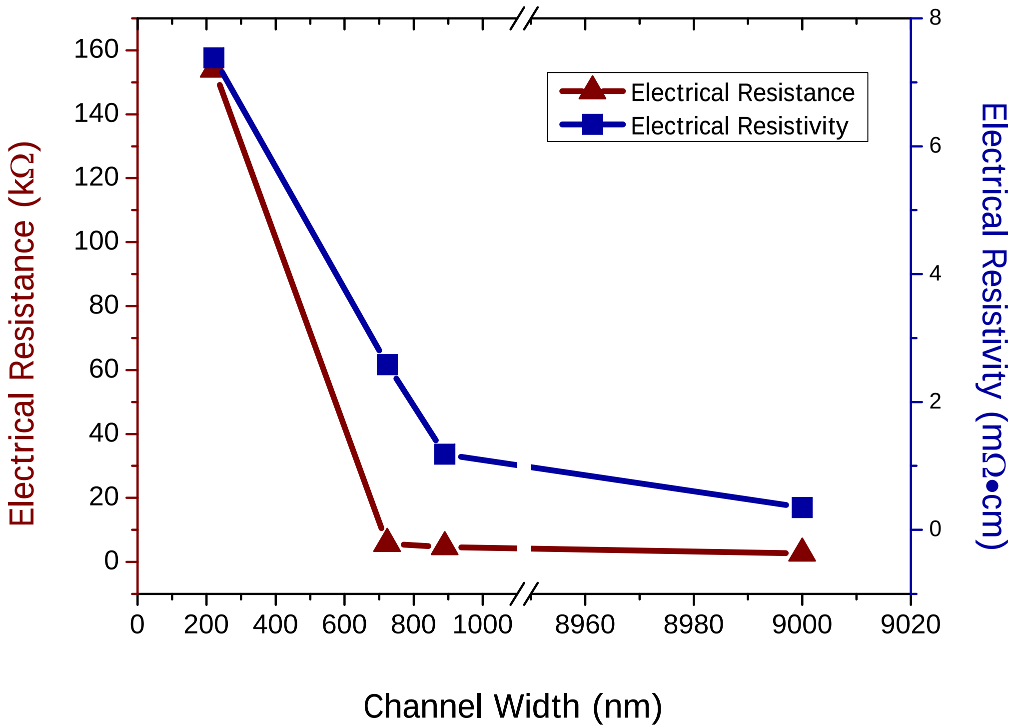


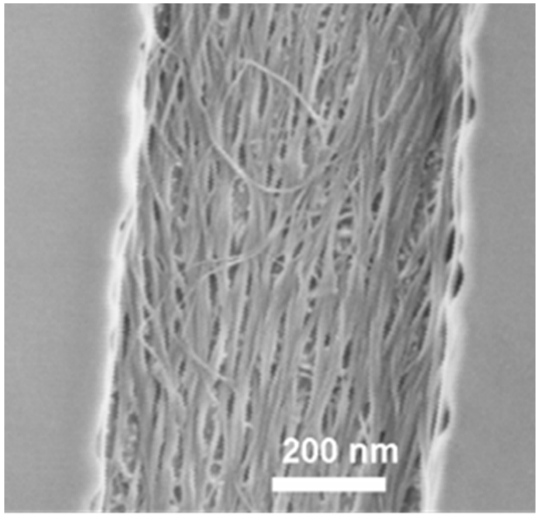


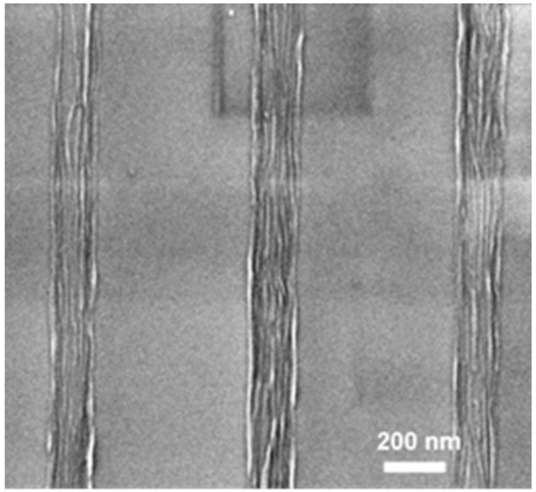


Electrical Properties of Highly Organized SWCNT Networks

Two-terminal I-V Properties







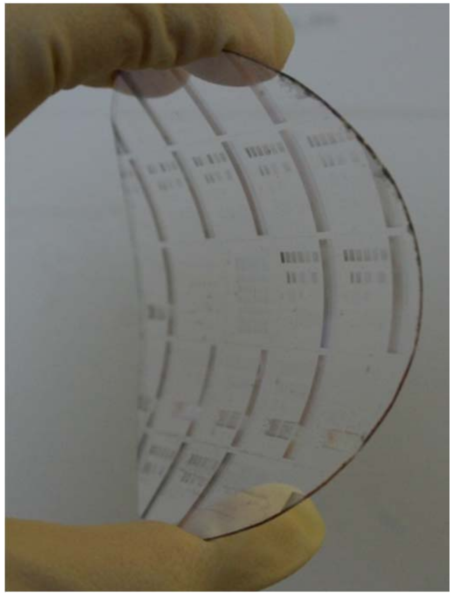
- Alignment gives the network semiconducting behavior

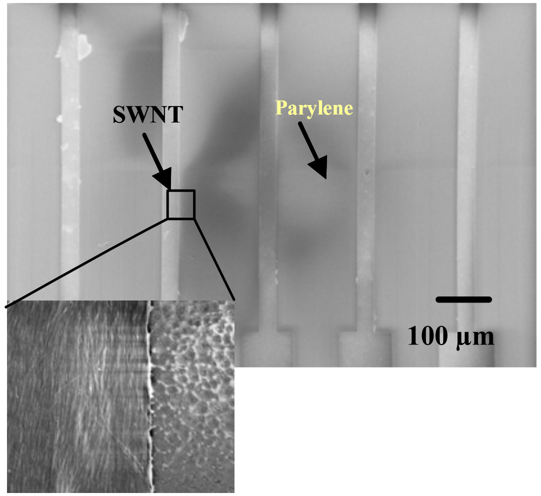
Somu, Jung, Busnaina, et. al., ***ACS Nano, 4, 4142-4148 (2010)***

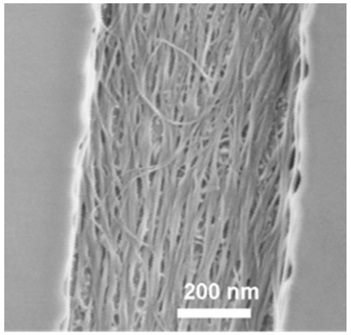
Center for High-rate Nanomanufacturing

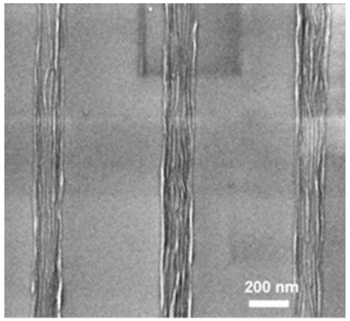
Assembly on various substrates

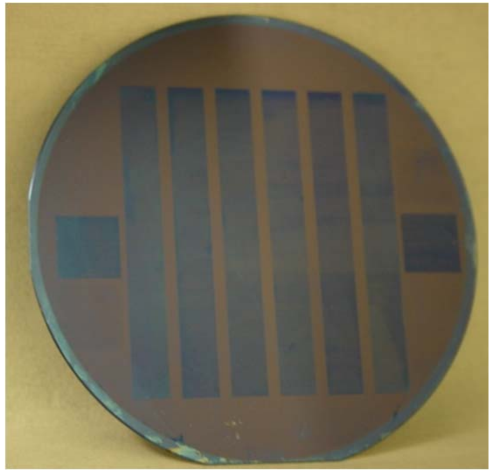
- Large scale assembly on polymer and silicon substrates
  - Enables assembly of lines over large areas (i.e., centimeters)











Aligned CNTs on parylene, polycarbonate, polystyrene or Si wafers

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, (2009)**
Somu, S., Wang, H., Kim, y., Jaberansari, L., Hahm, Mg, Li, B., Kim, T., Xiong, X., Jung, Yj, Upmanyu, M. and Busnaina, A., **ACS Nano, 4, (2010)**

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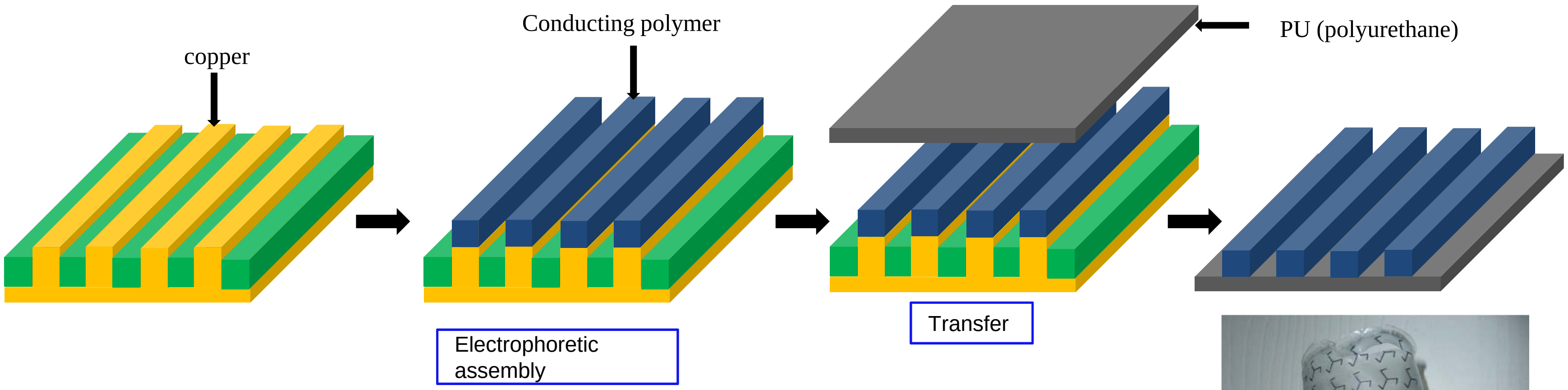
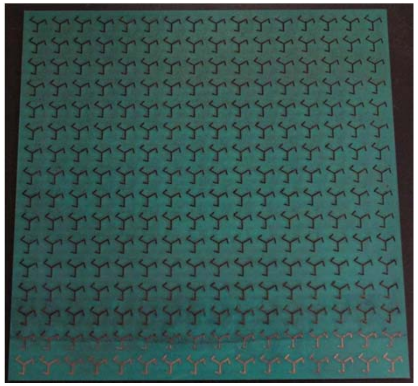
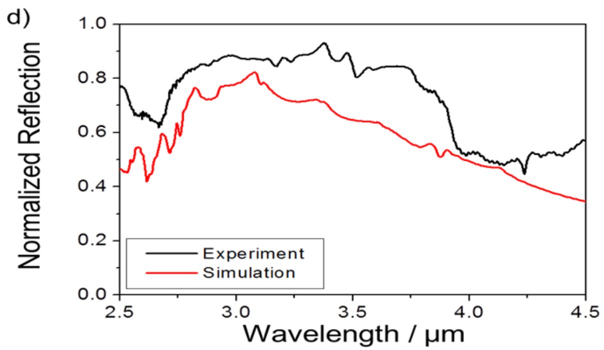
Fabrication of Chiral Metamaterial (mm Scale features)

Electrophoretic Assembly and Transfer



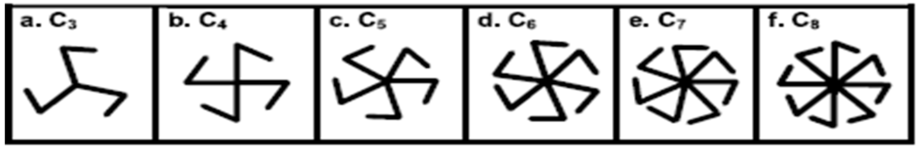




Mid-infrared

Microwave

Modeling provides designs and dimensions

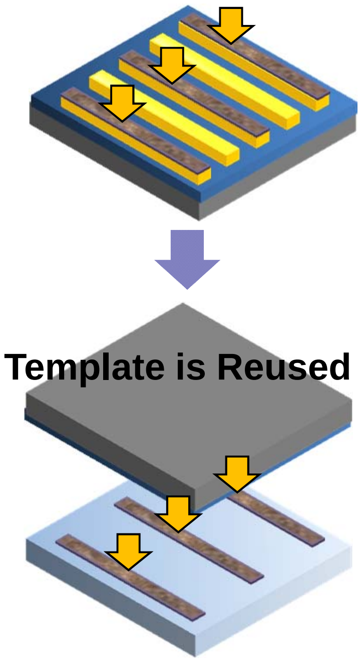


N Wongkasem et al, J. Opt. A: Pure Appl. Opt. **11 (2009) 074011**

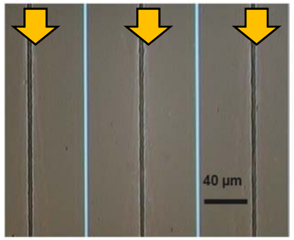
Center for High-rate Nanomanufacturing

High-rate Transfer (< 1 min)

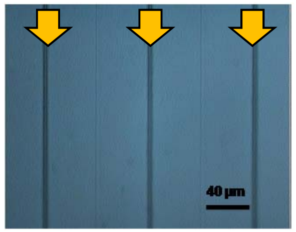
Transfer of conductive polymer wires



Assembled polymer

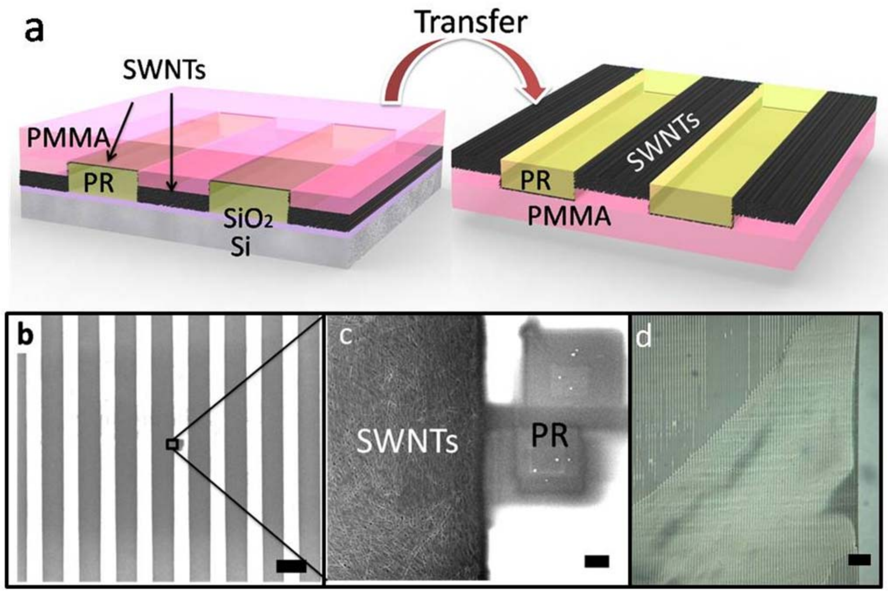


Transfer to polyurethane



Template after transfer

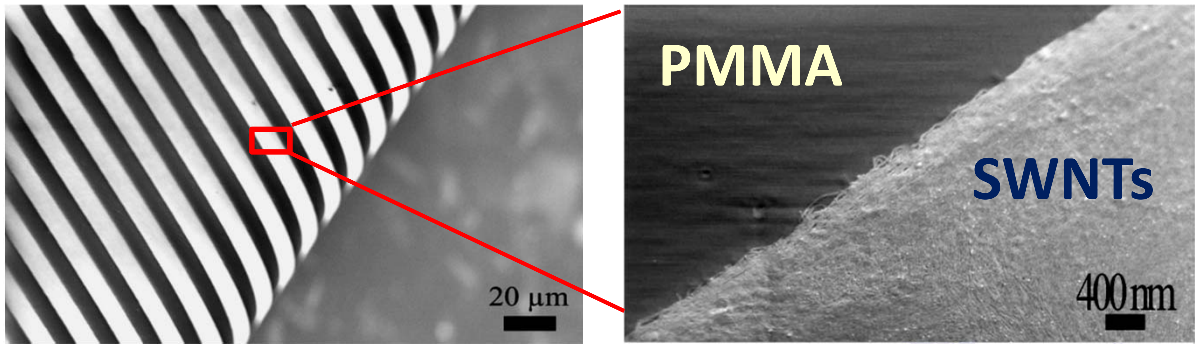
J. of Macromolecular Rapid Comm, 2006



Bo Li, A. Busnaina, M. Upmanyu, Y. Jung,
Advanced Functional Materials, 2011

Transfer of assembled SWNT Wires

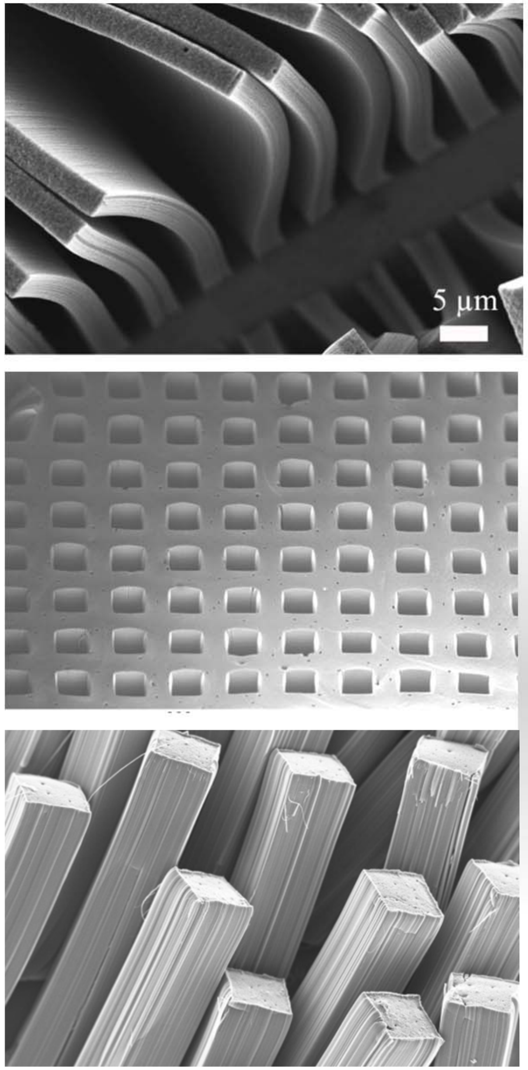
ACS Nano, 2011

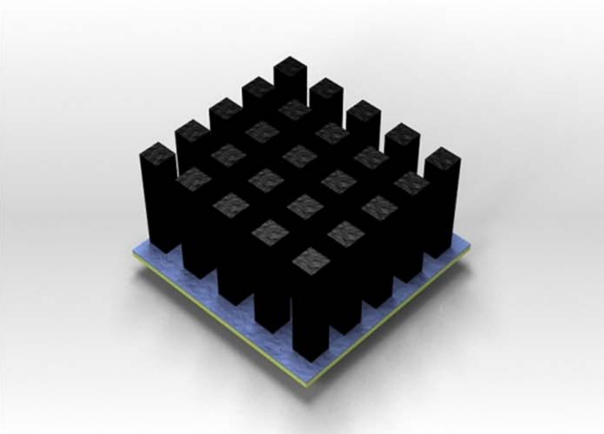


Nanomanufacturing

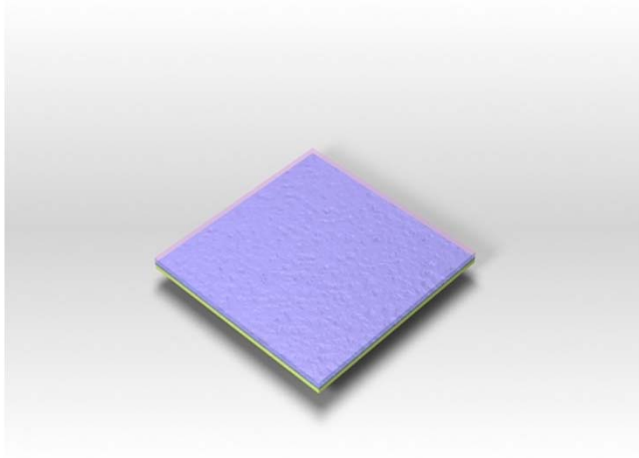
Transfer of Vertically Aligned (3D) SWNTs on Polymer Substrates

M. Hahm, Bo Li and Y. Jung, Submitted

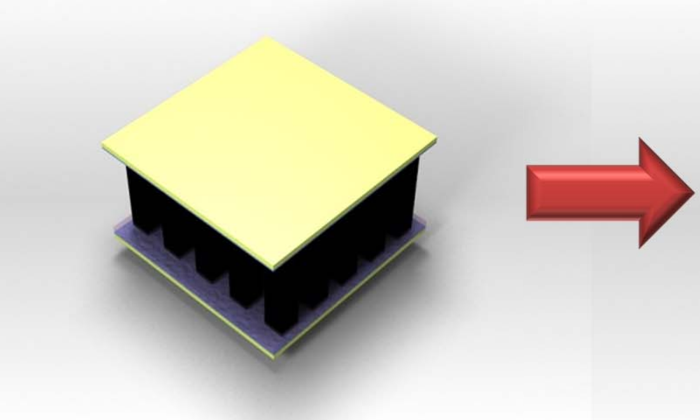




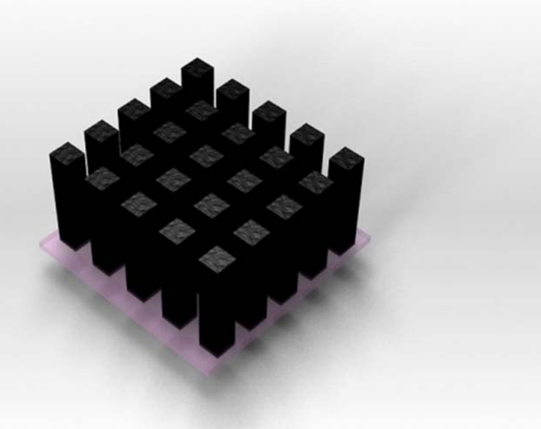
1. SWCNTs Growth on SiO_2 Chip



2. Spin Coating PDMS on SiO_2 Chip



3. Curing Polymer



4. Removing SiO_2 Chips

Reconfigurable Nanomanufacturing

Center for High-rate Nanomanufacturing

Process Flow for Nanoparticle-based Biosensors

Templates	Nanoelements	Assembly Processes	Transfer Processes	Substrates	Applications
Microwires template	Nanoparticles	Electrophoretic	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	Reel-to-reel transfer		SWNT Batteries
Damascene Templates	Fullerenes	Convective	Switchable functionalization		Photovoltaics
Flexible Damascene Template	Acenes	Convective interfacial			SWNT Chem Sensors

Center for High-rate Nanomanufacturing

CHN Directed Assembly Toolbox

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

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

Center for High-rate Nanomanufacturing

Leverage

- Over the past 8 years, CHN has obtained over $51 million in (NU share is > 70%)
- At Northeastern, over the past 4 years alone, CHN has attracting over $16 million.
- CHN has received a $2 million grant the State to promote commercialization.

Development of IP Protfolio

- Over the past 8 years, CHN has filed more than 75 patents (20 awarded).

Spin-offs

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

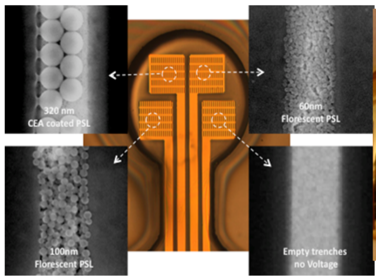
Investment in People

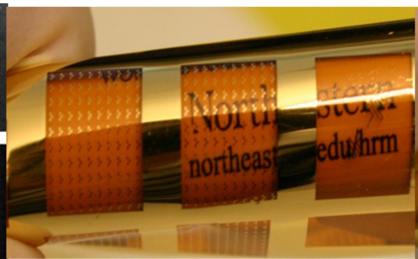
- Hired 9 top young professors that boosted NU capability in nanomanufacturing.

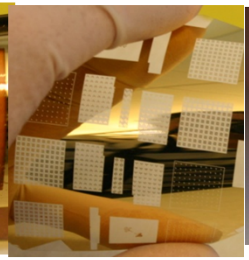
Future plans

- Applying with industry partners for a nanomanufacturing ERC (> 35$ million)
- Applying with industry partners for an Adv. manufacturing Institute (> 150$ million)

The Kostas Center

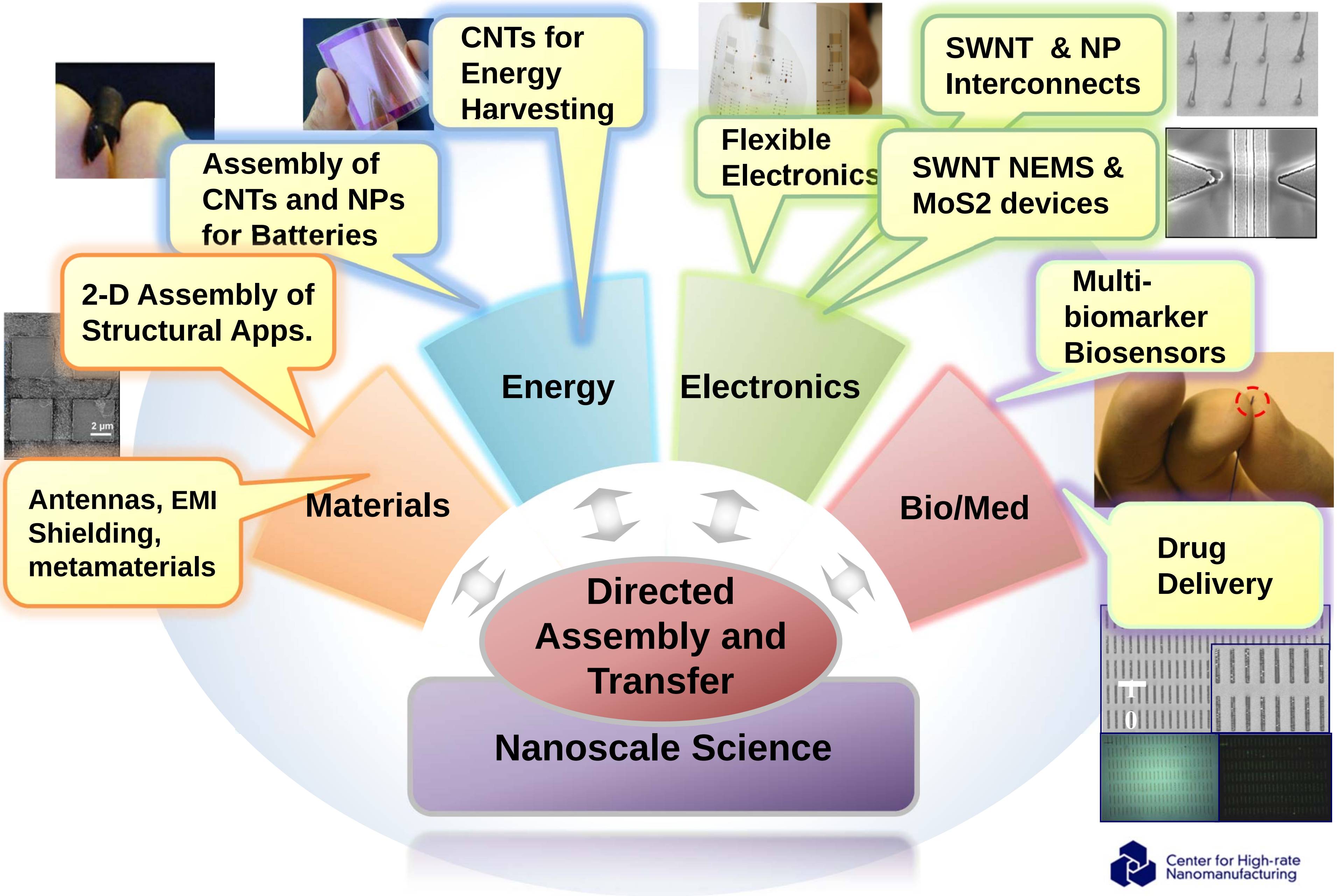






Center for High-rate Nanomanufacturing

Nanomanufacturing Applications Roadmap



Center for High-rate Nanomanufacturing

Strong Industrial Partnerships

varian
CORNING
TEXTRON
Ticona ENGINEERING POLYMERS
kuraray
Schlumberger
TERADYNE
tsi
zyvex
TIAX
VELCRO
BAE SYSTEMS
nanocomp TECHNOLOGIES, INC.
AEC
QinetiQ North America
Foster-Miller
PI
ENVIRON
Veeco
DRAPER LABORATORY
Raytheon
AMBERWAVE
Nypro
MOTOROLA intelligence everywhere
intel
brewer science
NANTERO
EMC²
Microfluidics
BASF The Chemical Company
CABOT
KONARKA technologies
IBM
LOCKHEED MARTIN We never forget who we're working for
SOLOPOWER
Kodak
GE
A Division of the Massachusetts Technology Collaborative

Over 30 Companies

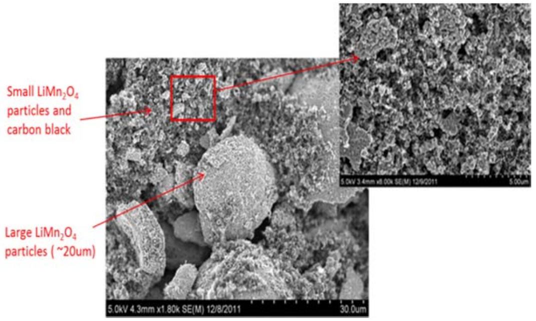
Center for High-rate Nanomanufacturing

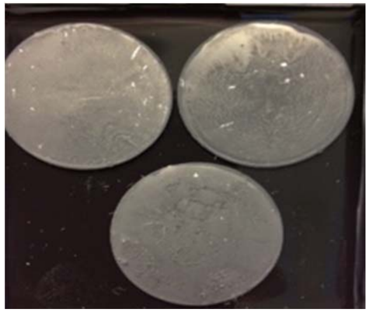
Industry Supported Applications

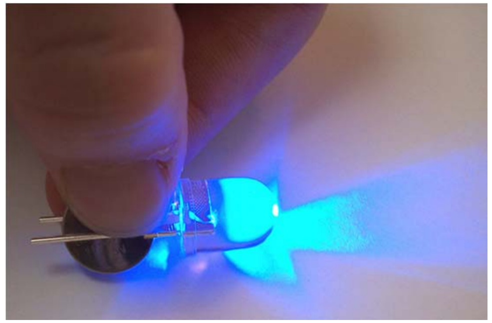
- **CHN emerging applications roadmap led to increased industrial sponsorship**
  - **Chemical sensors**
  - **Energy storage and harvesting**
  - **Photovoltaics**
  - **Nonvolatile memory**
  - **EMI shielding**
  - **Metamaterials**
  - **Biosensor**
  - **SWNT composites**

CHN Applications

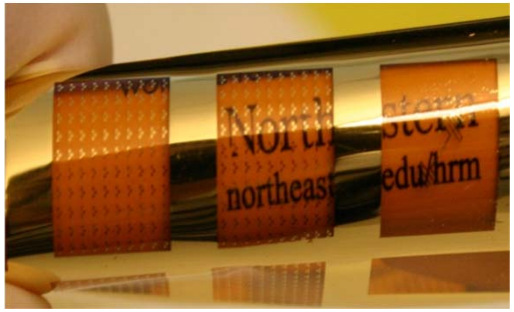
- **Layered Carbon Nanotube architecture for high power density Li-ion battery**

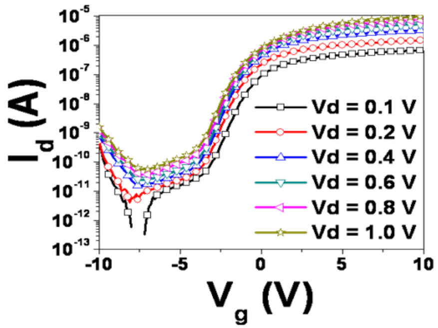


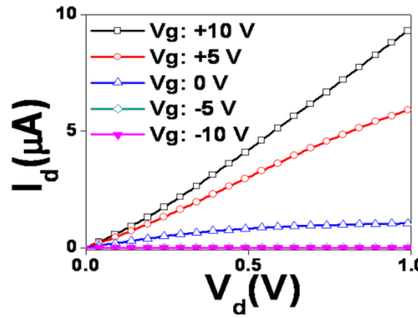




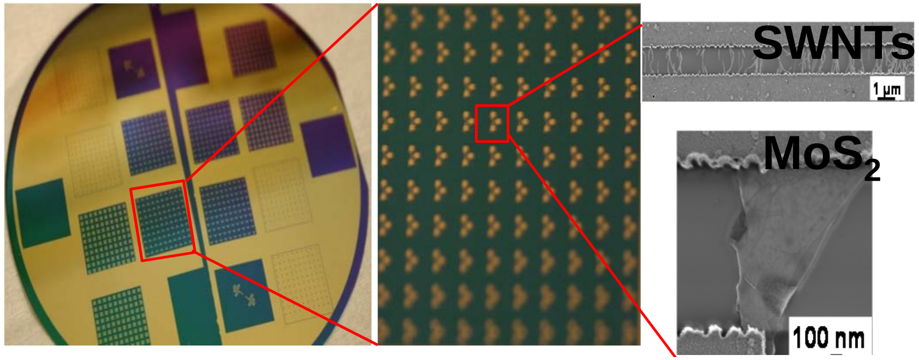
- **Flexible transparent n-type MoS_2 transistors**

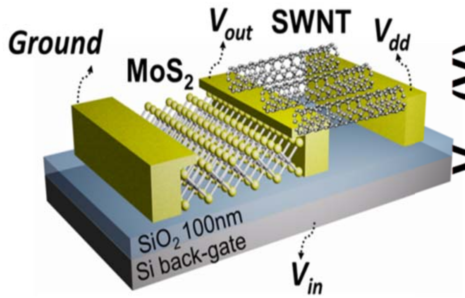


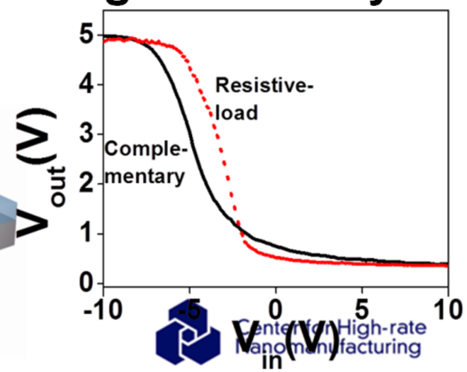




- **Heterogeneous SWNTs and MoS_2 complimentary invertors through assembly**







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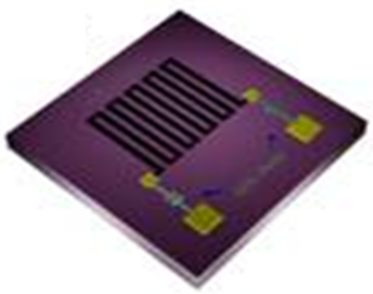
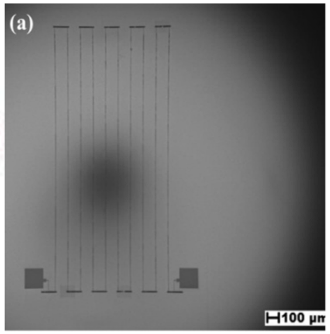
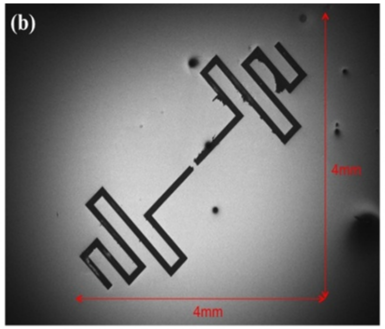
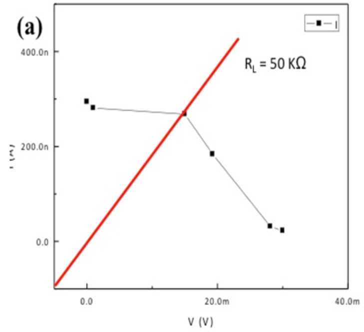
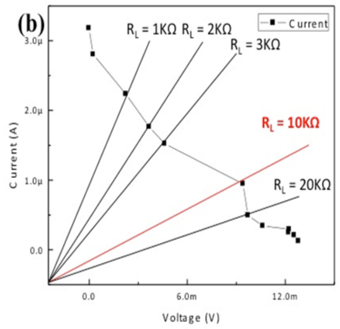
CHN Applications

- **Carbon Nanotube Infra red energy harvester**

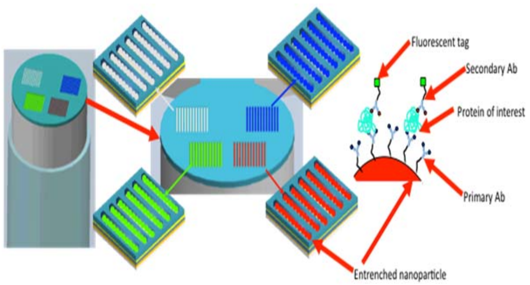



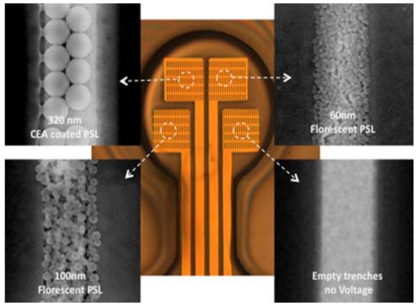


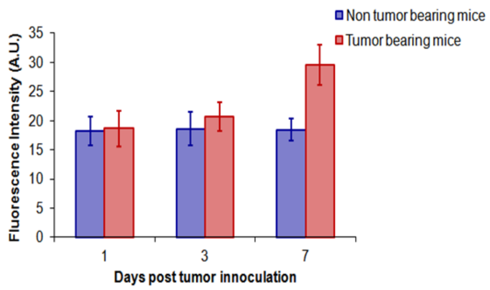




- **Highly sensitive Biosensors**





- **Functionalized Carbon Nanotube enzymatic Glucose sensors**