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

Nanomanufacturing and Integration of Nanoscale Elements and Components Using Directed Assembly and Transfer

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Deputy Director: Joey Mead, UML, Associate Directors: Carol Barry, UML; Nick McGruer, NEU; Glen Miller, UNH; Jacqueline Isaacs, NEU, Group Leader: David Tomanek, MSU

www.nano.neu.edu

Outline

- CHN Overview
- Introduction to Nanomanufacturing
- CHN Nanoscale Manufacturing processes using Directed Assembly
- Applications
  - Individual components
  - Integrated Systems (vision for monolithic systems)
- Summary

CHN Team Synergy and Capabilities

NEU: Directed assembly, MEMS, fabrication, nanoscale contamination control

Semiconductor & MEMs fab

- 7,000 ft^2 class 10 and 100 cleanrooms
- 6 inch completer wafer fab, nanolithography capabilities

UML: High volume polymer processing and assembly

Center for High-Rate Nanomanufacturing

A unique partnership

UNH: Synthesis, self-assembly

Plastics processing labs

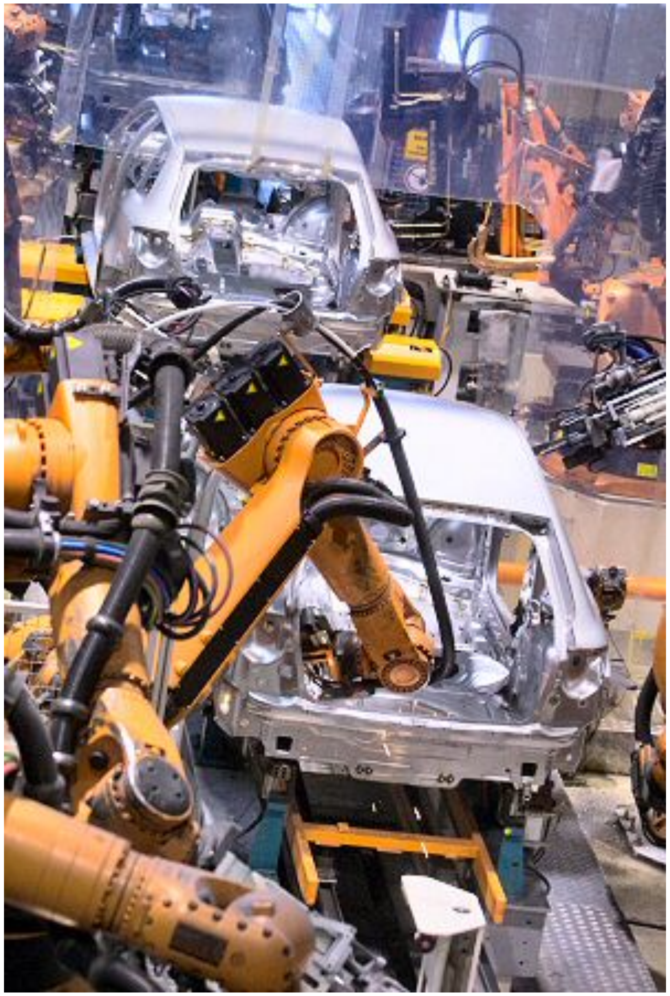
- **20,000 ft^2 +**
- **Compounding and forming equipment**

Fully-equipped synthetic labs

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

Institution	Faculty	Post-docs	Graduate	Undergrad.	Total
NEU	14	8	19	14	50
UML	18	6	35	16	75
UNH	6	5	12	13	36
MSU	1	1	1	0	3
TOTAL	39	20	67	43	169

Macro to Nanomanufacturing

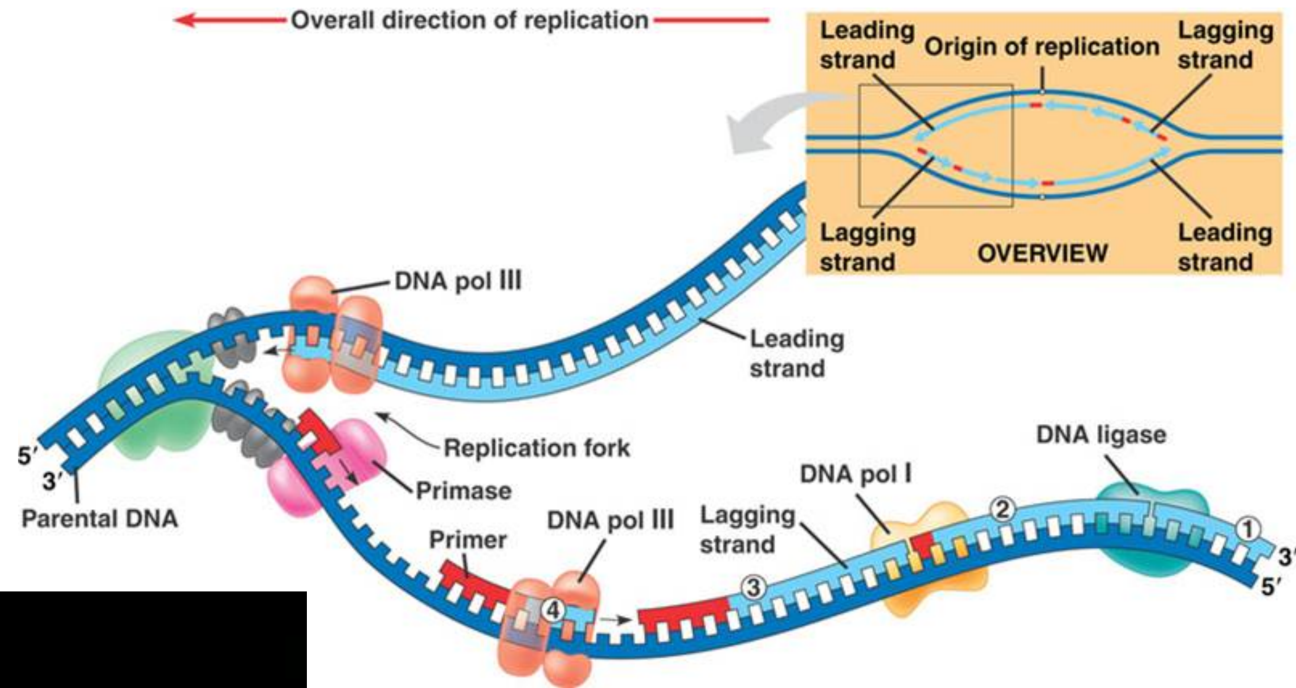


Automotive Manufacturing

Semiconductor Manufacturing

Nanomanufacturing?

A True Nanoscale Factory,
How Does Nature Does it?



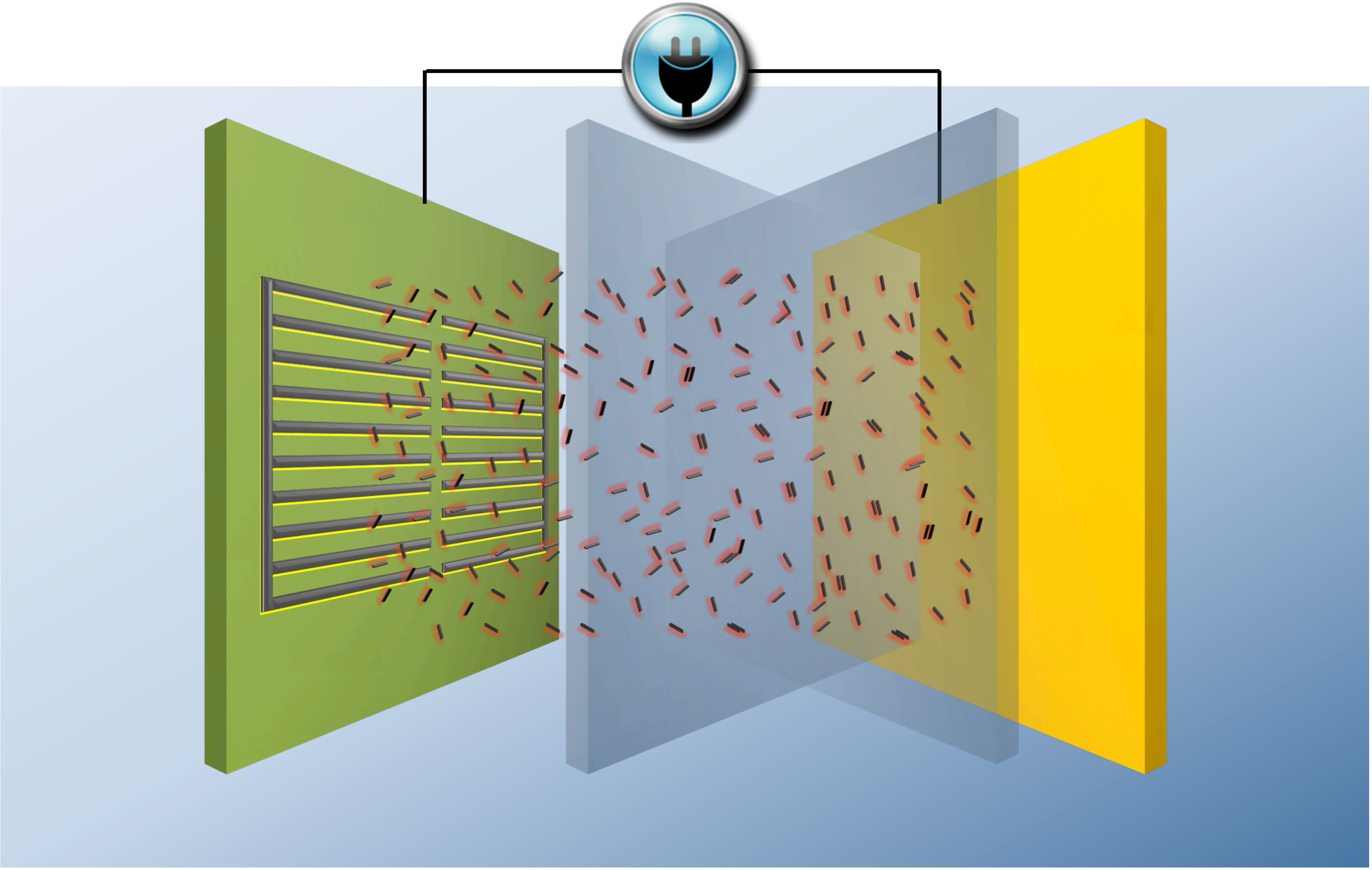
How Can We Do It More Like Nature? Precision, No Waste, etc.

Nature builds from the bottom up, molecule by molecule, cell by cell.

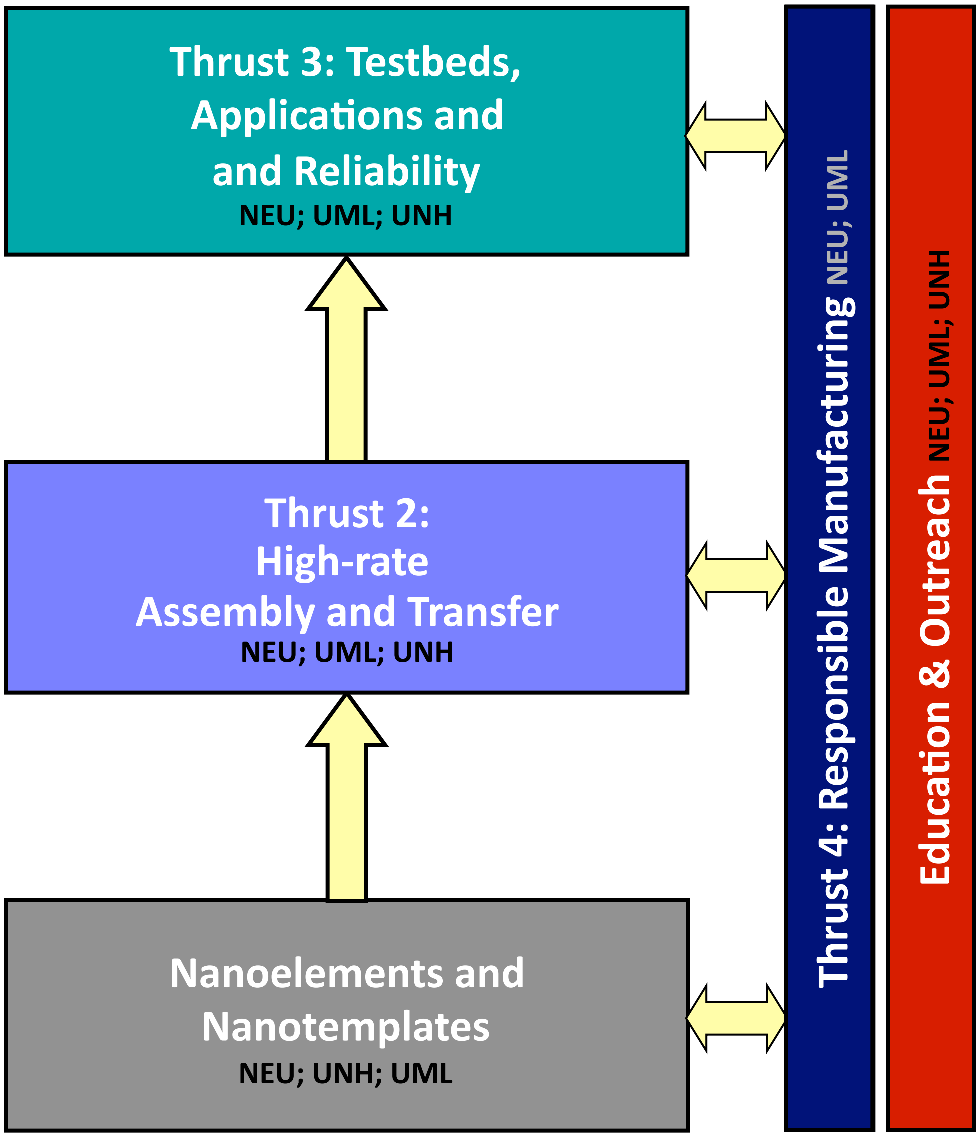
Nanomanufacturing is about building molecule by molecule, particle by particle, nanotube by nanotube, etc.

What is high-rate Nanomanufacturing?

CHN: Directed Assembly and Transfer♪

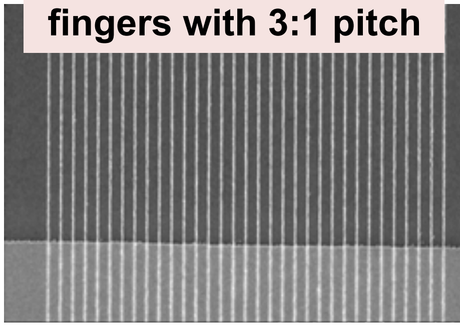


CHN Path to Nanomanufacturing



Thrust 1 Templates for Many Applications

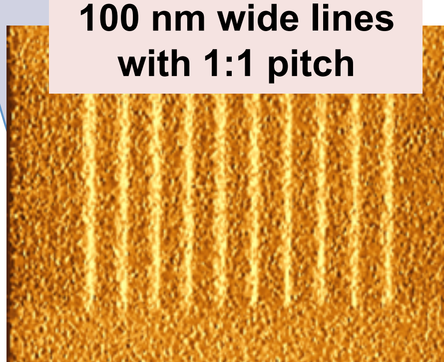
50 nm wide nano-fingers with 3:1 pitch



E-beam nanolithograpy

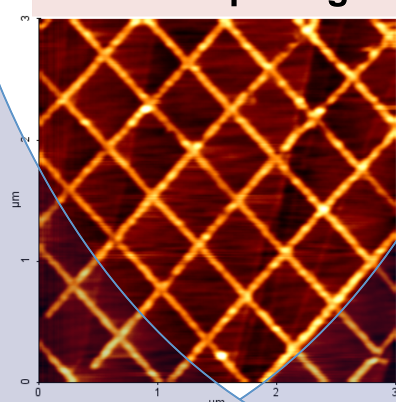
Low RISK

100 nm wide lines with 1:1 pitch



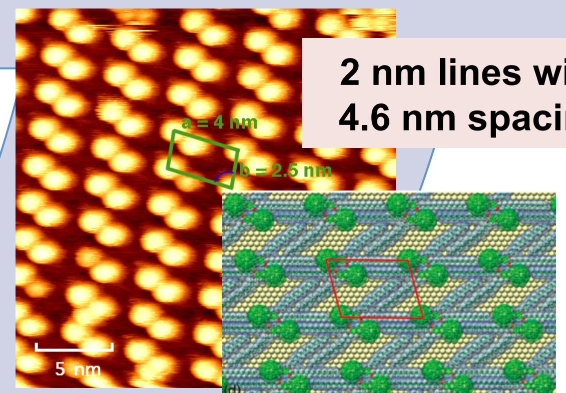
Dip-pen nanolithography

15 nm lines with 50 nm spacing



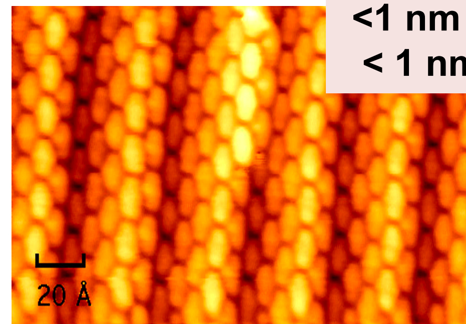
AFM field assisted nanolithography
J. Phy. Chem C111, 10758 (2007)
Nanotechnology, 20, 055303 (2009)

2 nm lines with 4.6 nm spacing



Fullerene Self-Assembly
Phys. Rev. Lett., 102, 056102 (2009)

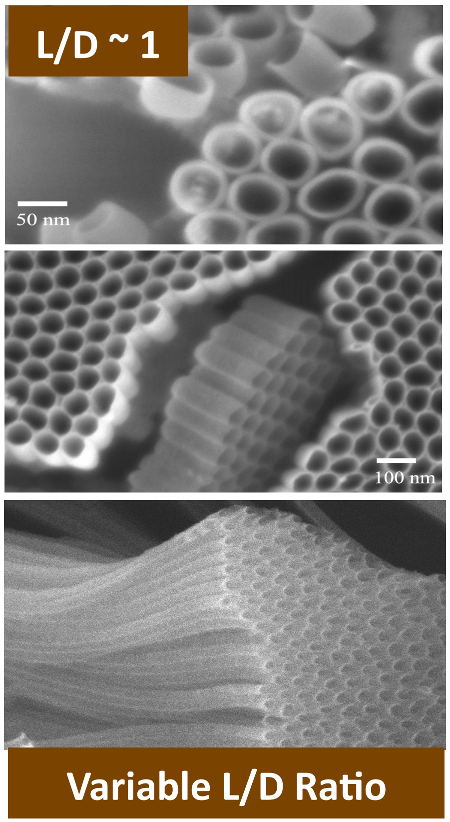
<1 nm rows with < 1 nm spacing

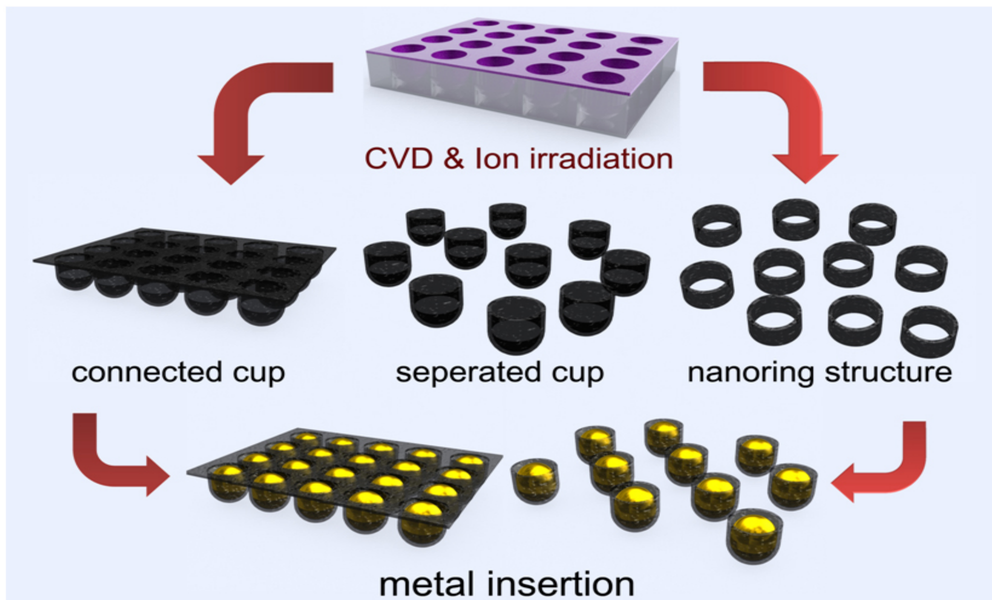


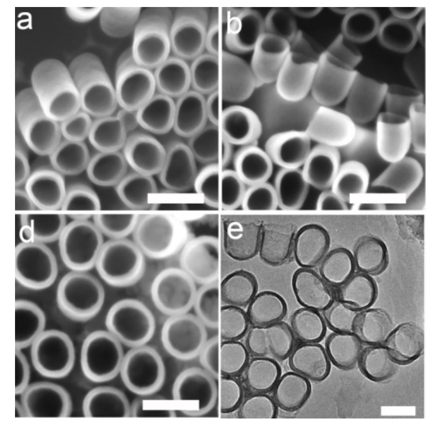
Acene Self-Assembly

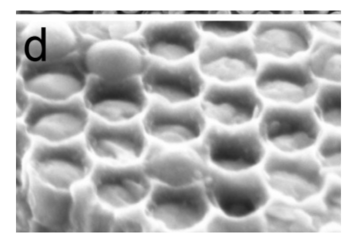
High RISK

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





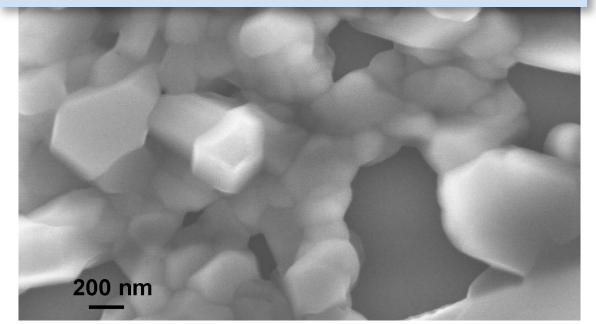




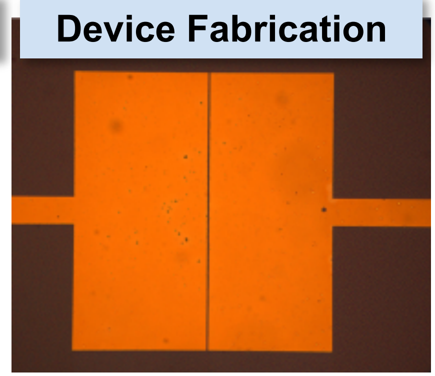
H. Chun, M. G. Hahm, Y. Homma, R. Meritz, K. Kuramochi, L. Menon, L. Ci , P. M. Ajayan, and Y. J. Jung, ***ACS Nano* , 2009**.

Study Carbon Nanoelements in Electronic & Structural Devices

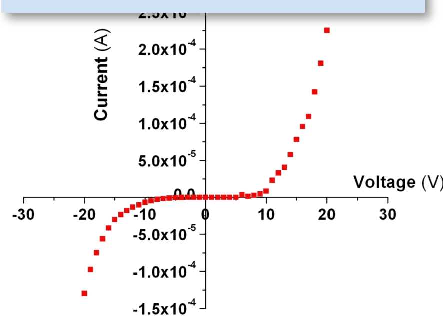
Control thin-film morphologies



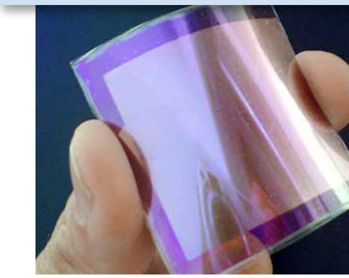
Device Fabrication



I-V Characteristics

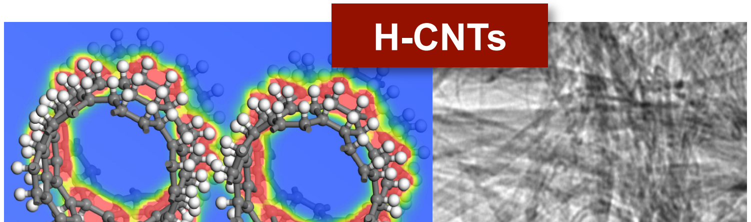


Flexible Substrates



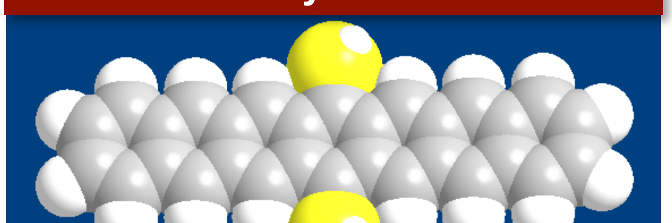
Nanoelements

H-CNTs



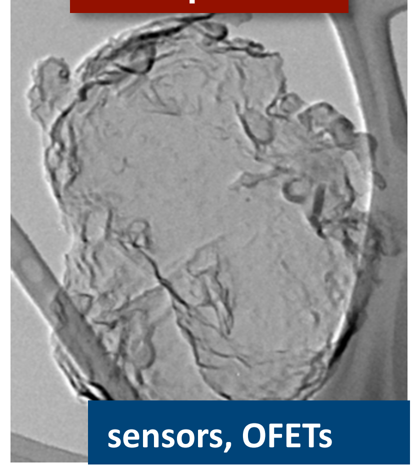
switches, sensors, composites

Photooxidatively Resistent Acenes



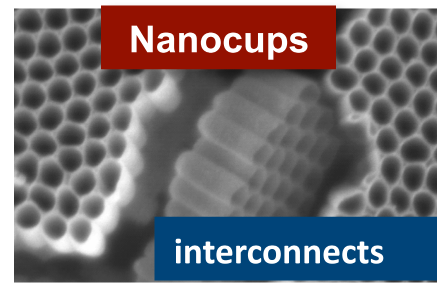
switches, sensors, OFETs

Graphene



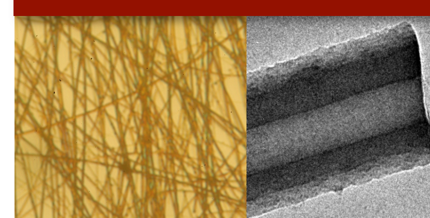
sensors, OFETs

Nanocups



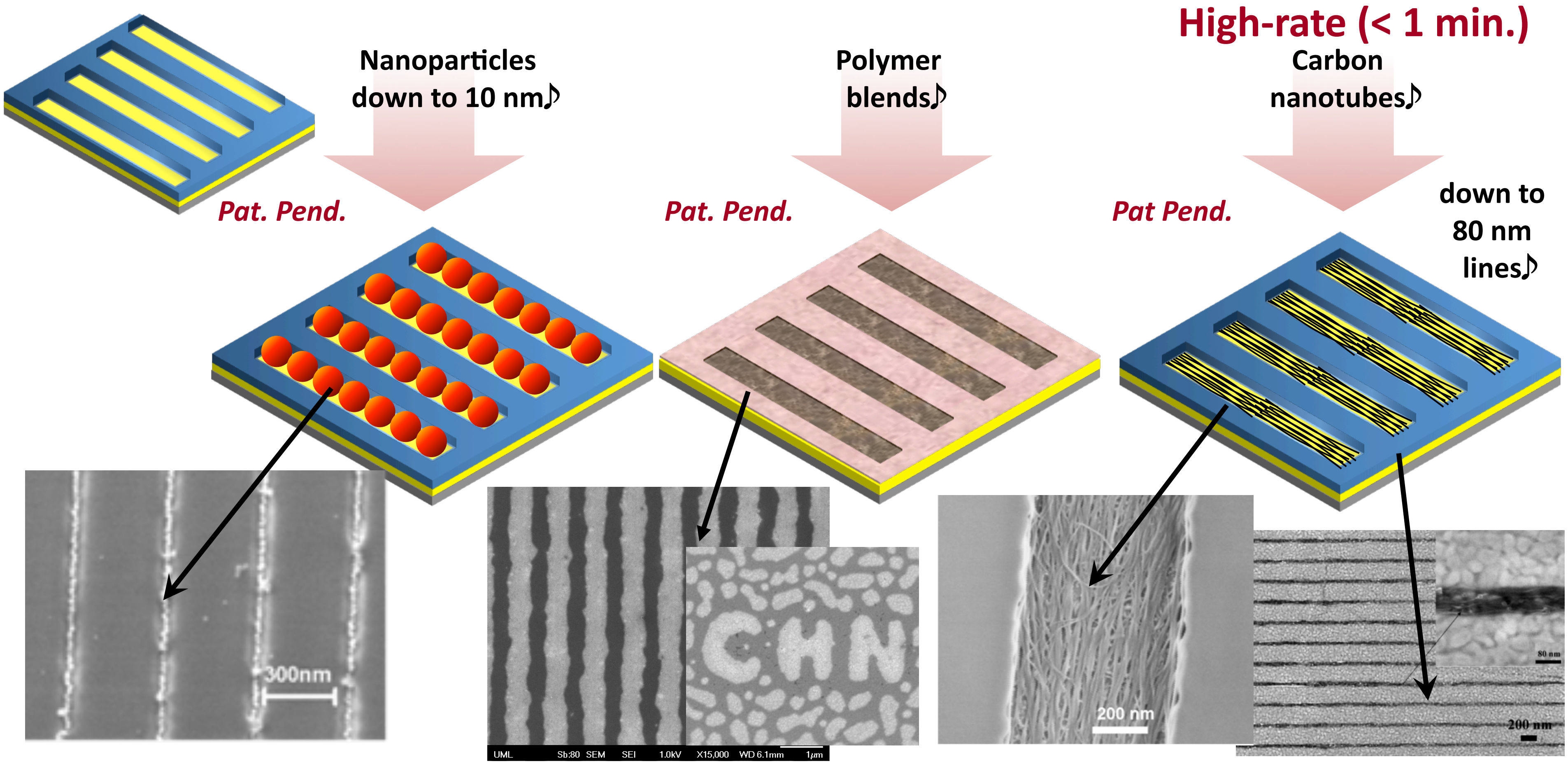
interconnects

Crystalline Fullerene Nanotubes



organic photovoltaics

Nanotrench Template Directed Assembly Using Electrophoresis or Chemical Functionalization

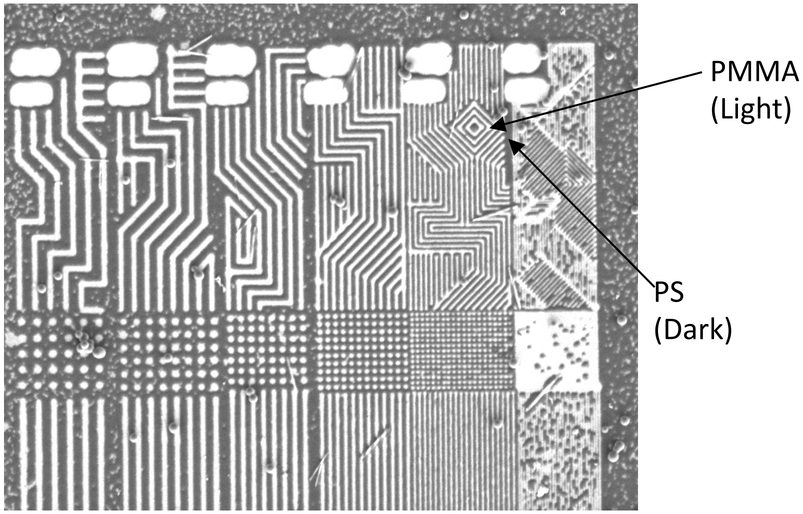


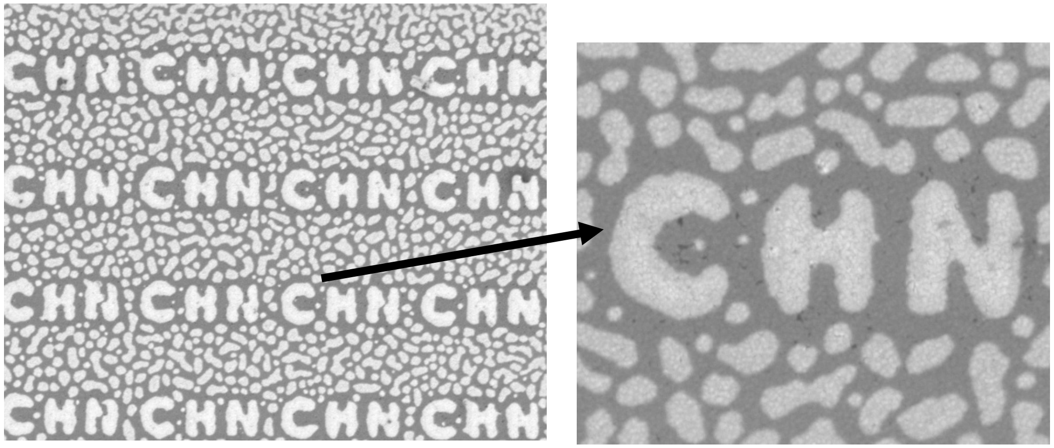
Xiong, X, Busnaina, A, et. Al., ***Appl. Phys. Lett. 2007.***
Wei, M. Liang F., Lee, J. Somu, S., Xiong, X, , Barry, C., Busnaina, A., Mead, J, ***Advanced Materials, 2009***.
Xiong, X, Jaberabsari, L, Hahm, M G, Busnaina, A, and Jung, Y, J, ***Small, 2007.***
Makaram, P, Somu, S, Xiong, X, Busnaina, A, Jung,Y J, and McGruer, N, ***Appl. Phys. Lett., 2007***.

Last Year: 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)

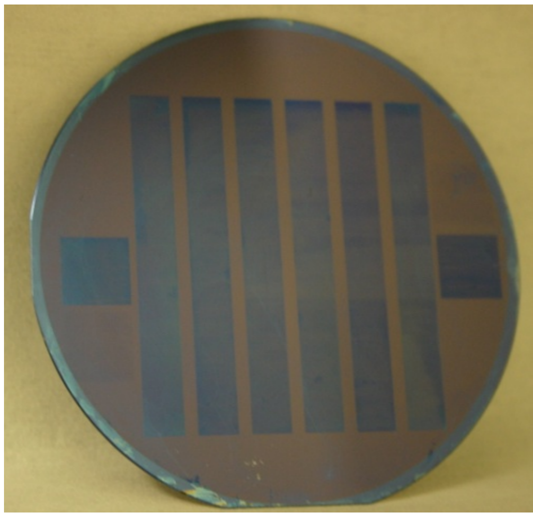


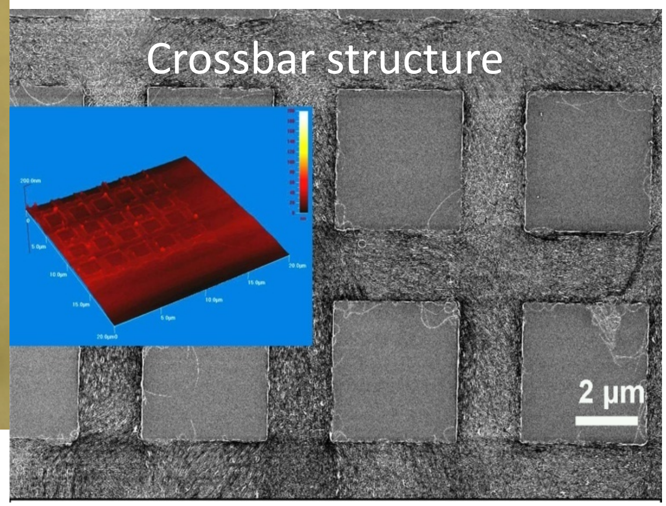


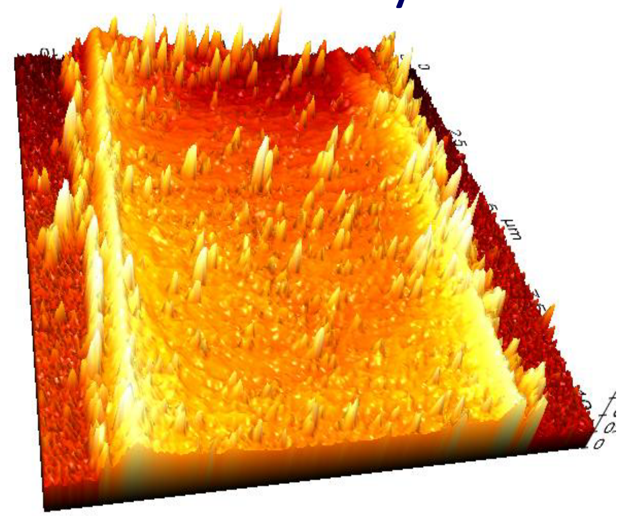
Chiota et al., ***Small,*** **2009 Dec;5(24):2788-91**

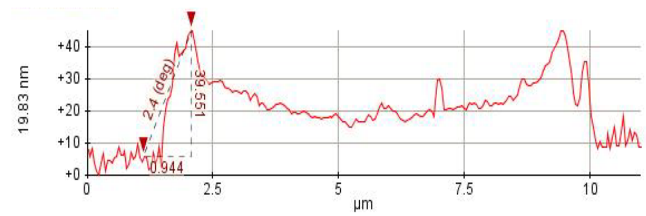
Template Guided Fluidic Assembly of SWNTs

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









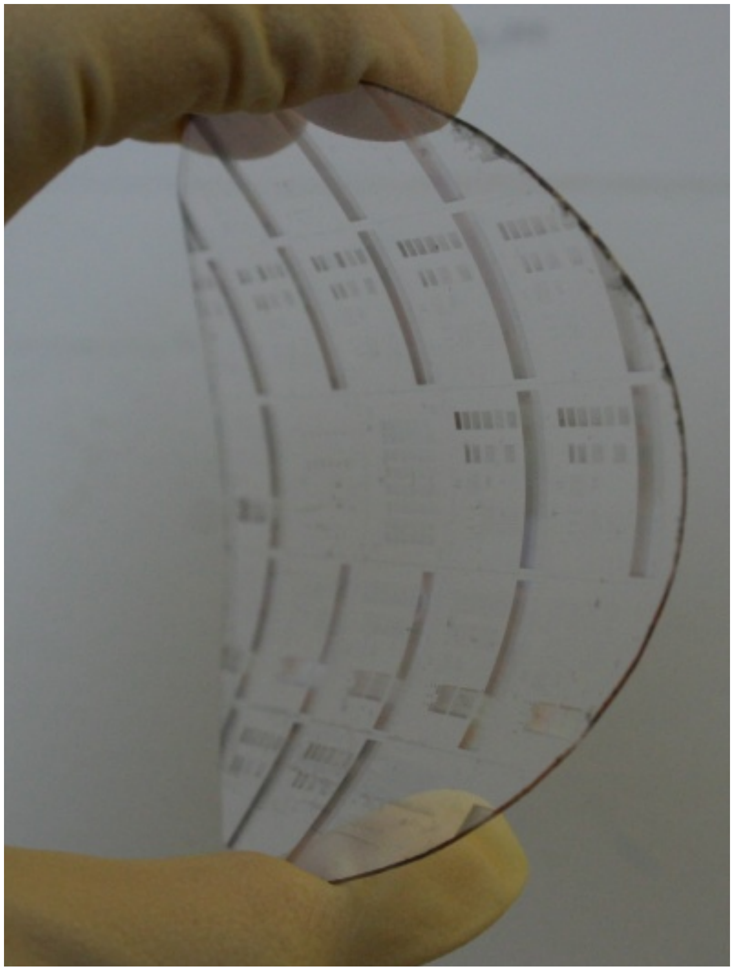
Xiong, X, Jaberabsari, L, Hahm, M G, Busnaina, A, and Jung, Y, J, ***Small*, 3 (12) 2006 (2007)**

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)***

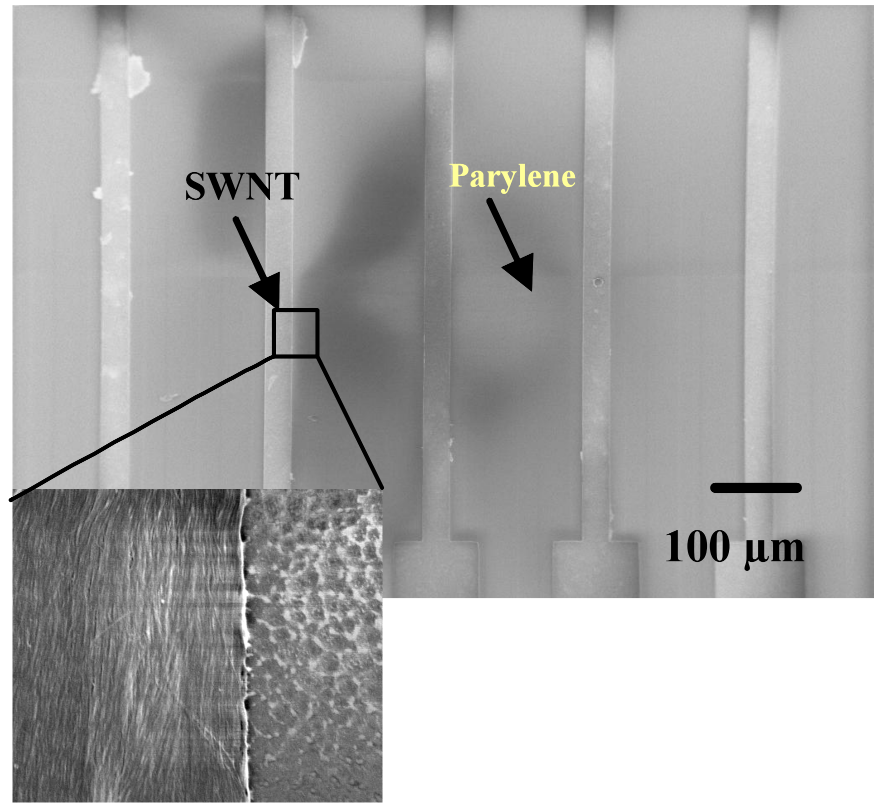
Jaberasani, L., Somu, S. Hahm, M G, Busnaina, A, and Jung, Y J, ***Appl. Phys. A., 5194 (2009)***

Template Guided Fluidic Assembly

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



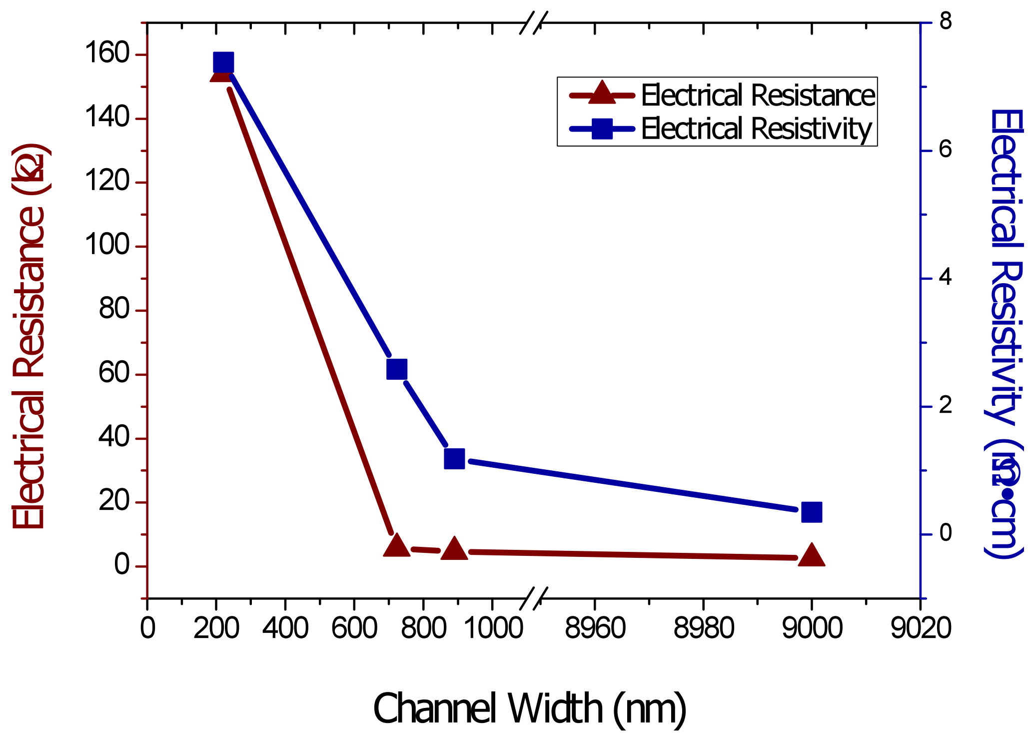
Nanotechnology 2009

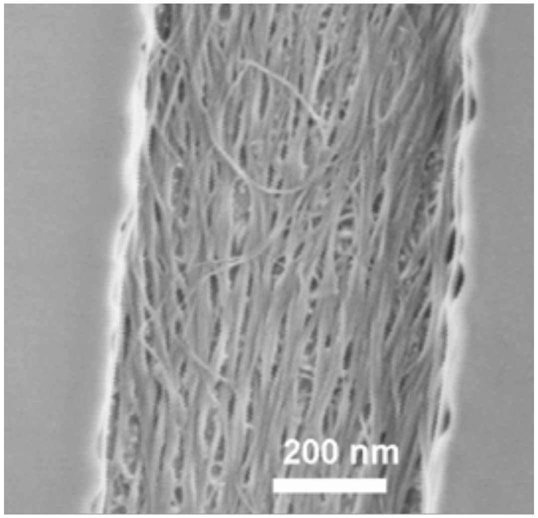


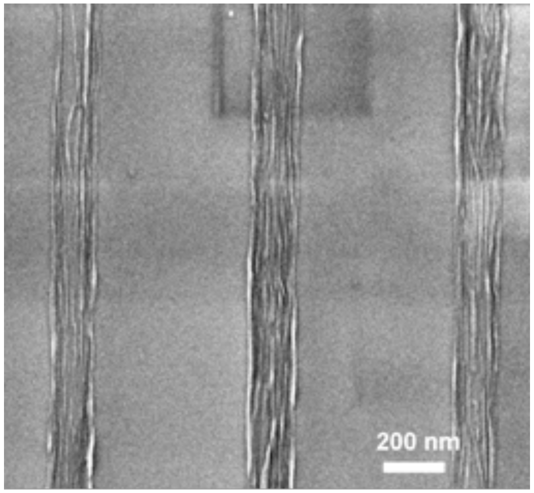
Patterned, aligned CNTs on a parylene, polycarbonate or polystyrene wafers

Electrical Properties of Highly Organized SWCNT Networks as a Function of Trench Width

Two-terminal I-V Properties





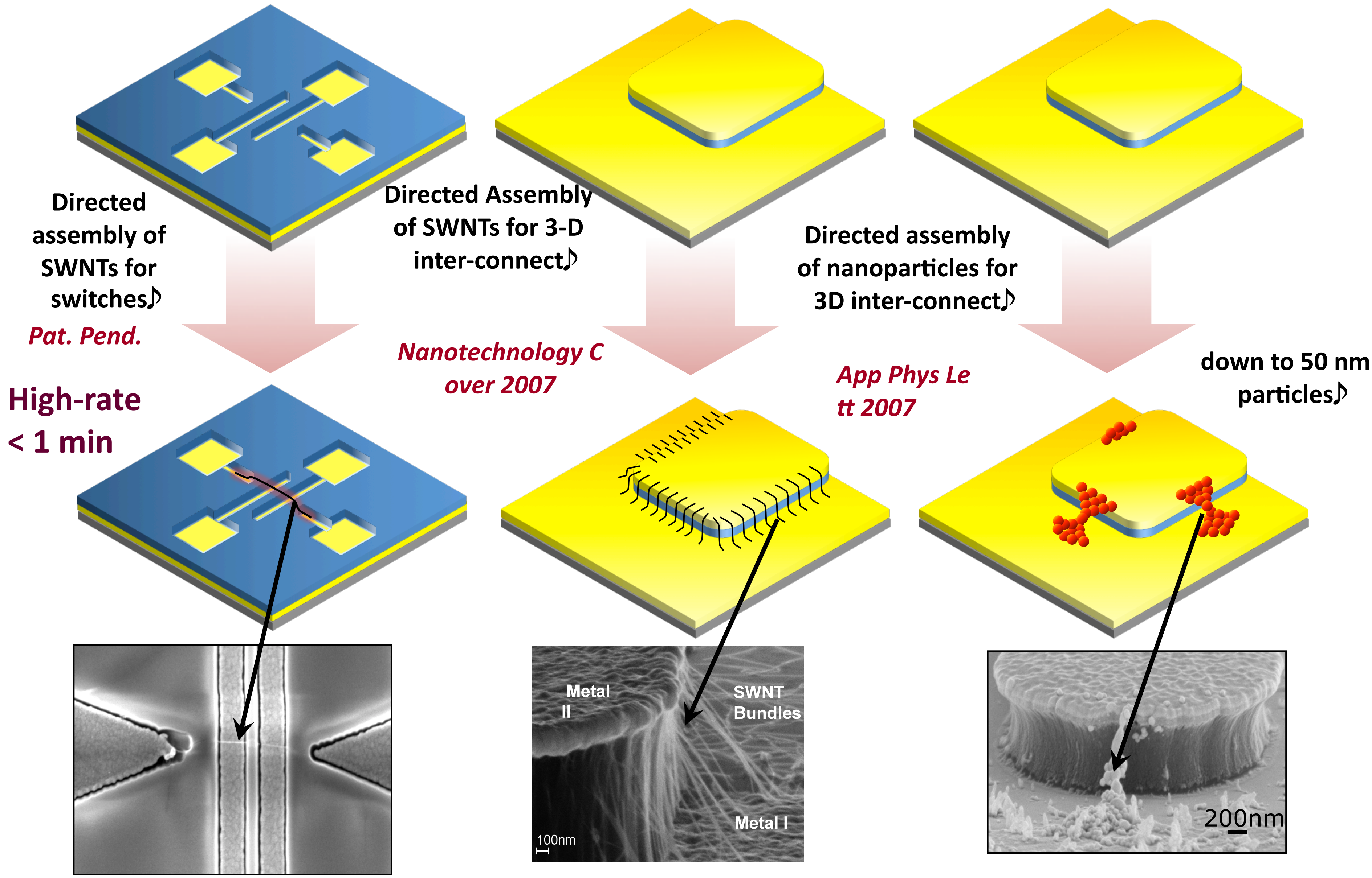


- Alignment occurs when trench width is 1/10 length of nanotubes → gives semiconducting behavior

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

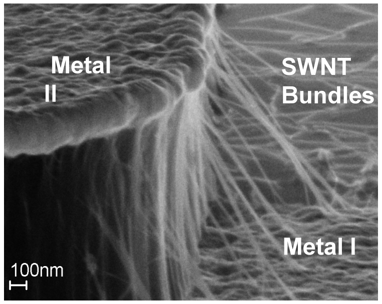
Template-free Dielectrophoretic Directed Assembly

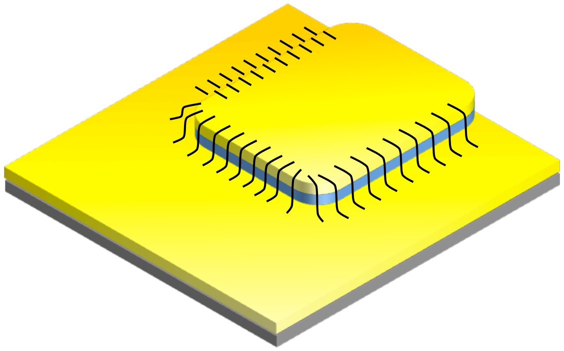
Assemble Directly on Devices Using Circuit Components♪

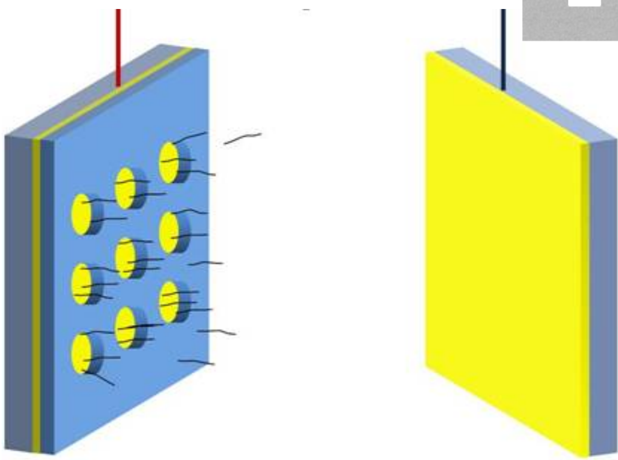


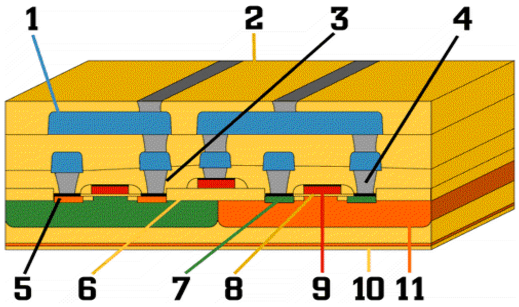
CMOS Technology Interconnects

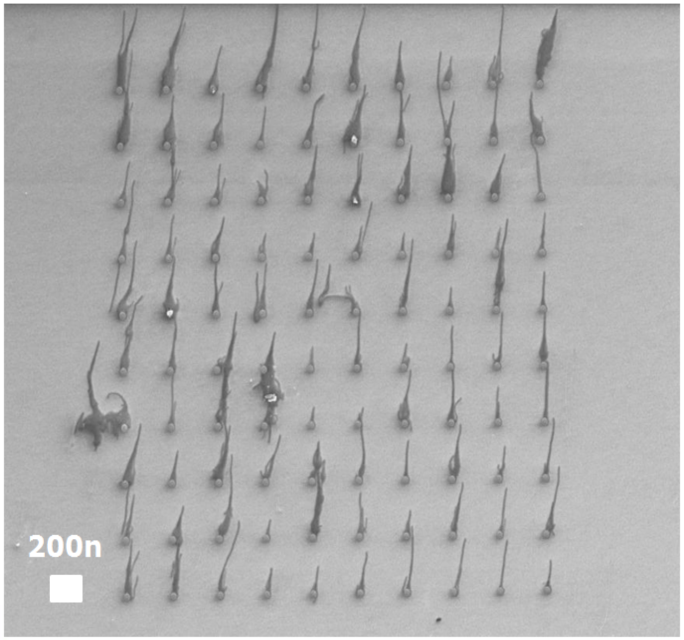
Room temperature 3D assembly of CNTs for CMOS interconnects





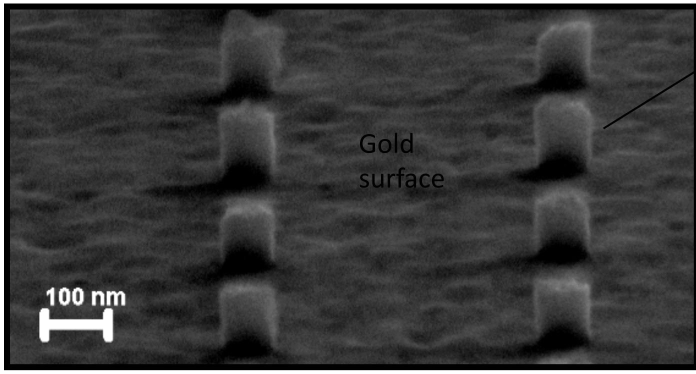




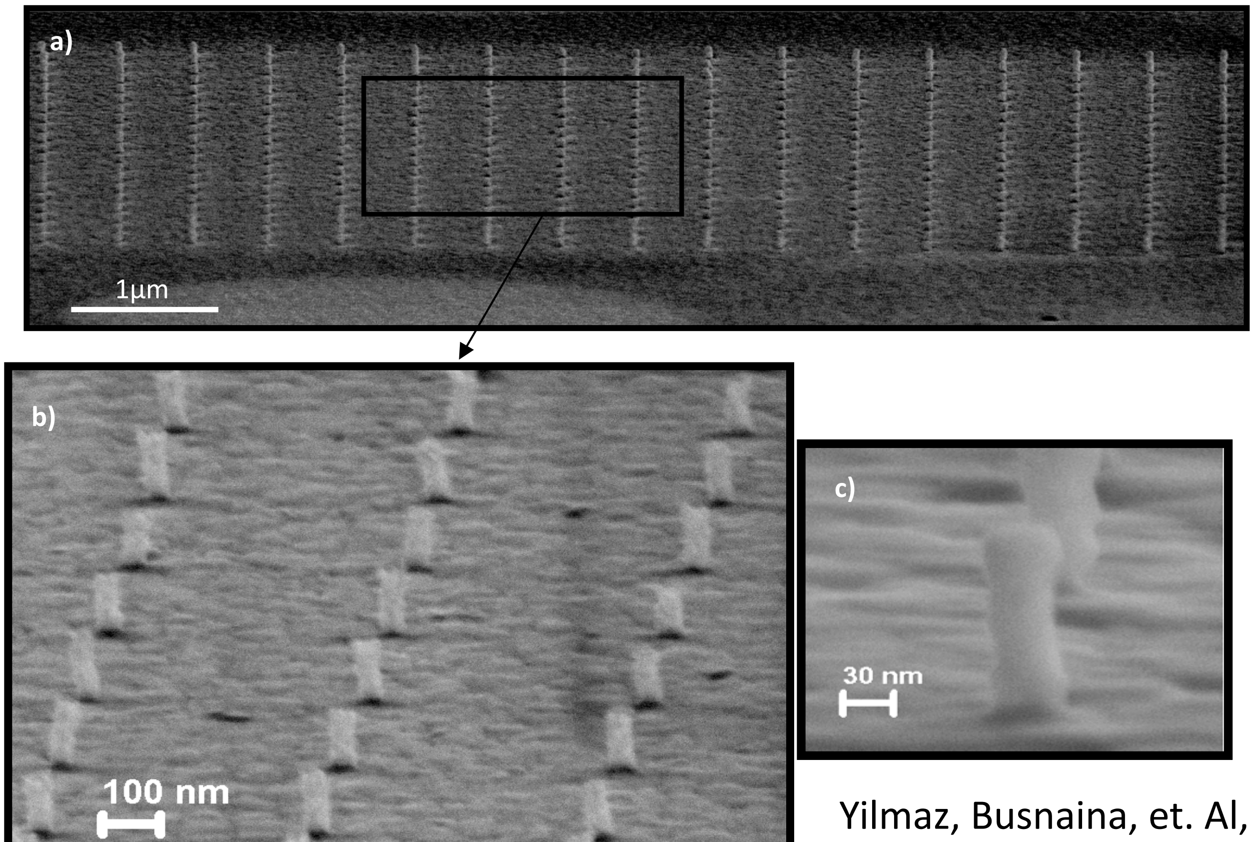


3-D Assembly of SWNT in CMOS vias over a wafer level

Interconnects and Nanorods



A high angle SEM of fabricated 100nm nanorods. 12Vpp was applied to the 5nm gold nanoparticles at the frequency of 10 kHz.



a) SEM image of 50nm nanorods over 10µ x 10µ area.

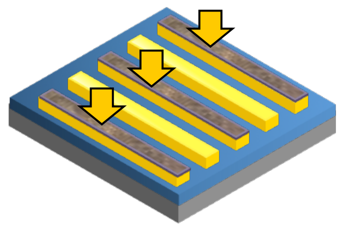
b) A magnified image of the Nanorods array.

c) High magnification image of a single rod.

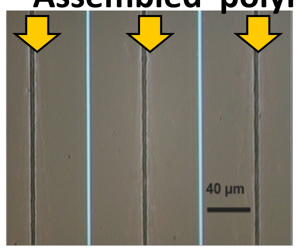
Yilmaz, Busnaina, et. Al, ***IEEE Trans on Nanotechnology* 2010**

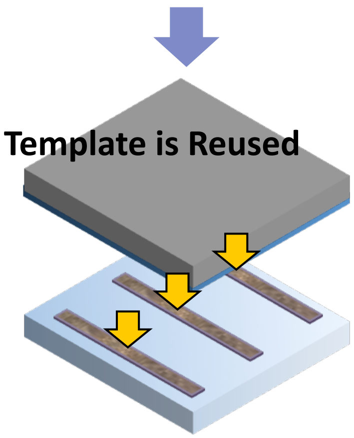
High-rate Transfer (< 1 min)

Transfer of conductive polymer wires

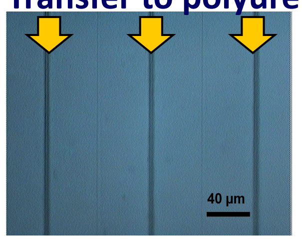


Assembled polymer♪





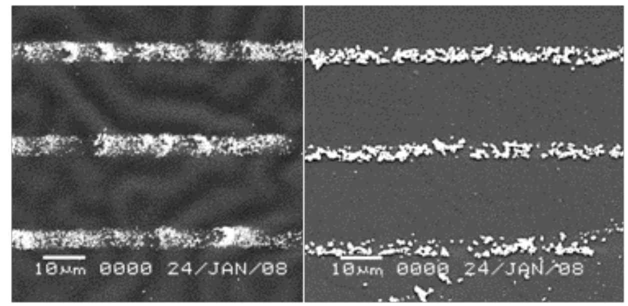
Transfer to polyurethane



Template after transfer

***J. of Macromolecular Rapid Comm*, 2006**

Transfer of assembled nanoparticles

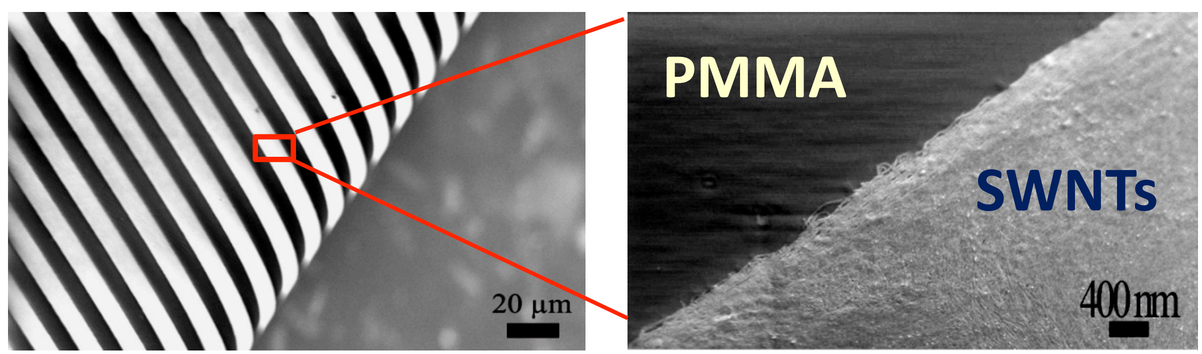


***Langmuir*, 2009**

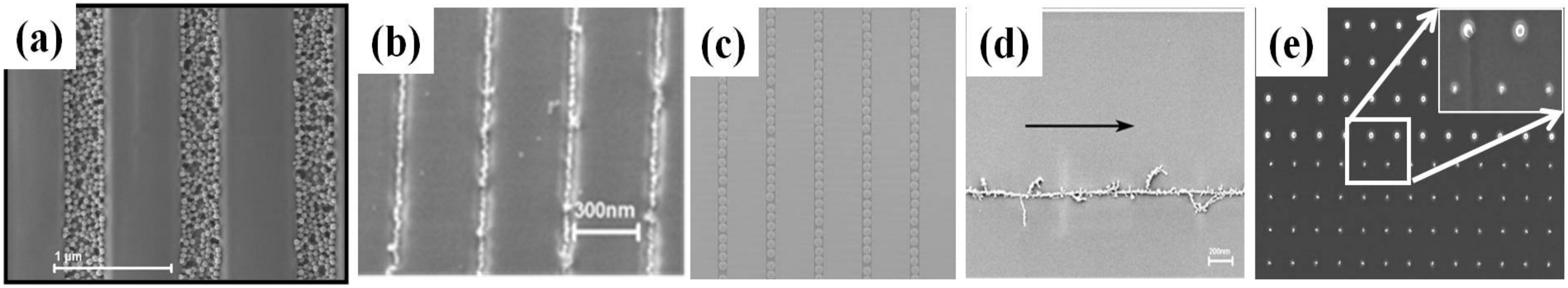
Peeling Off SWNT/Polymer Film

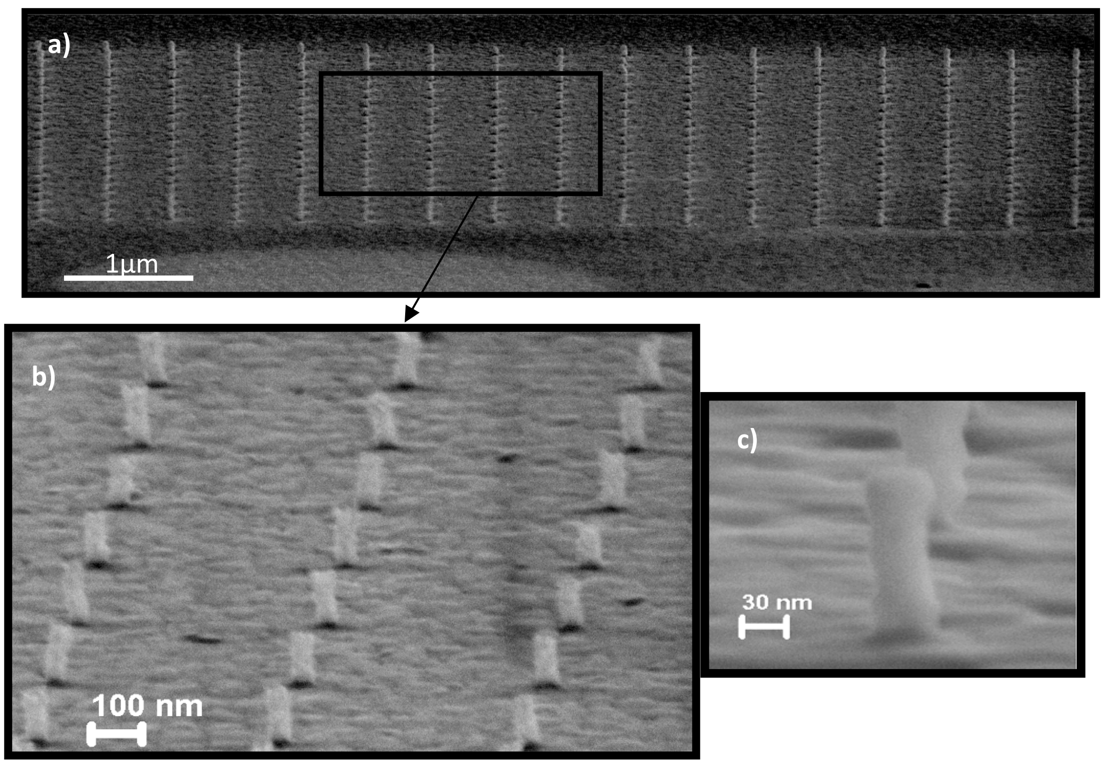
Polymer Spin Coating

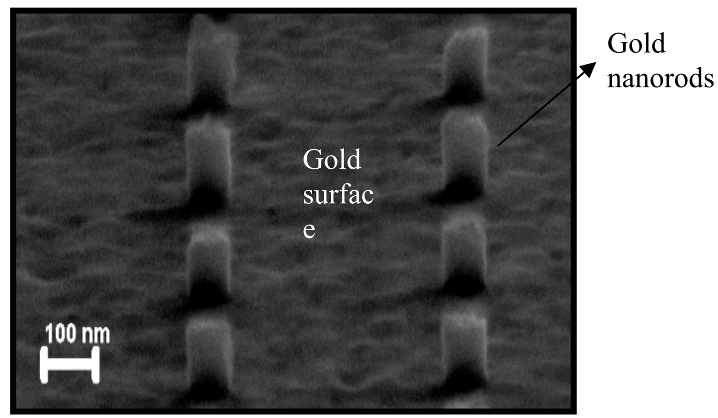
Transfer of assembled SWNT Wires



Directed Assembly of Nanoparticles

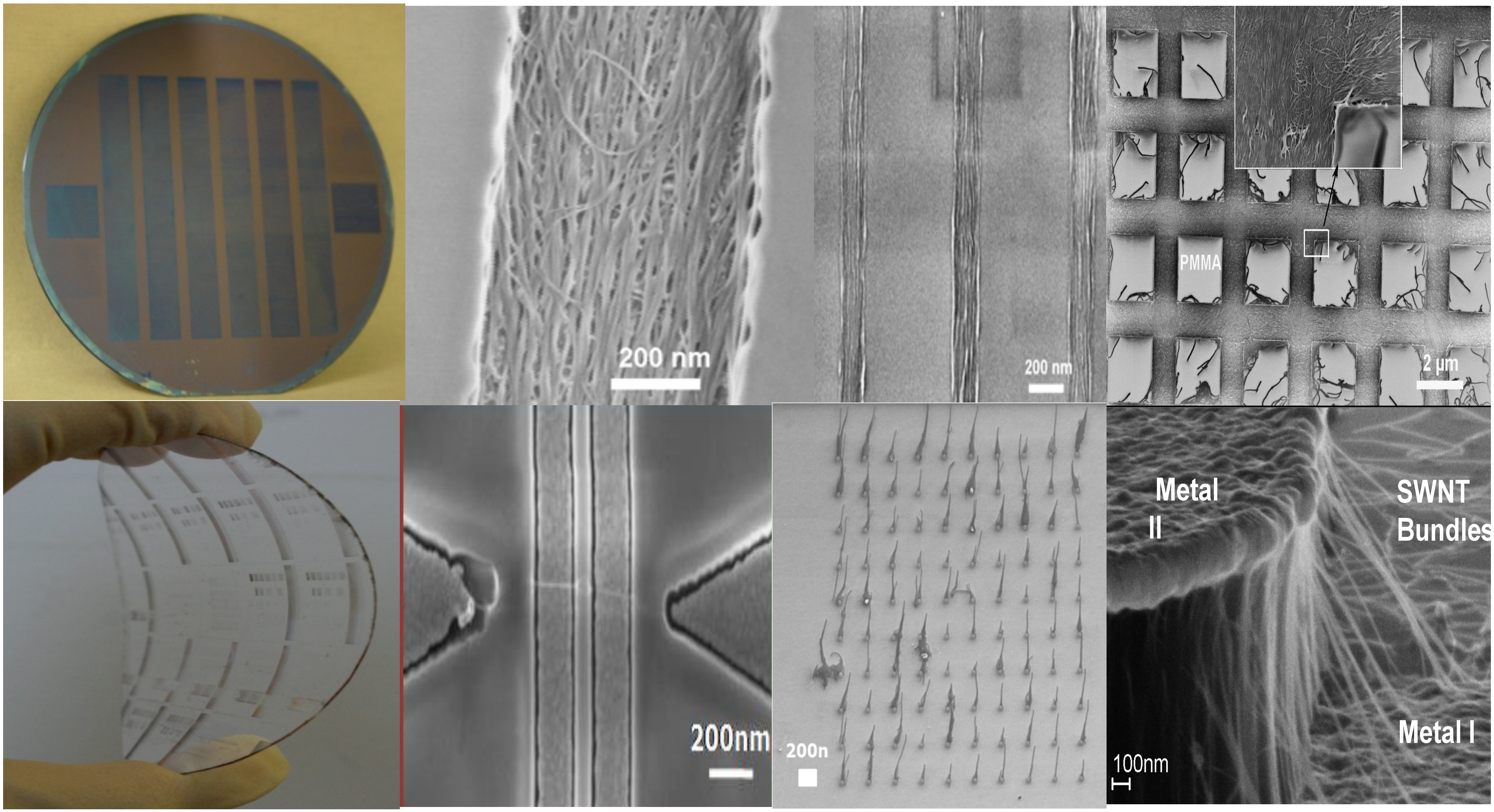




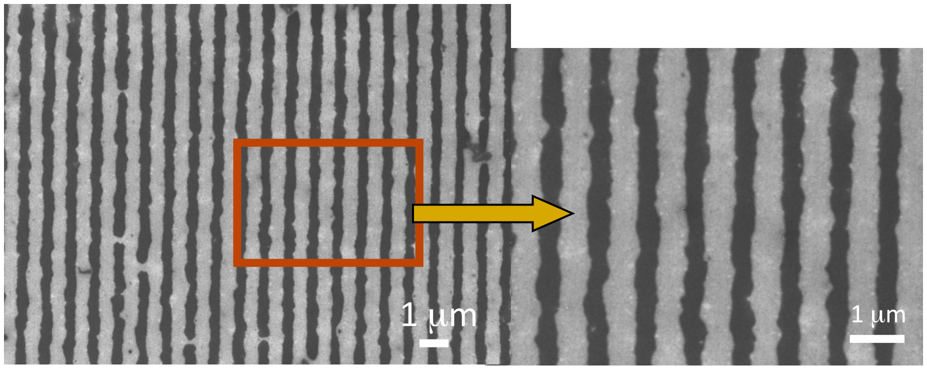


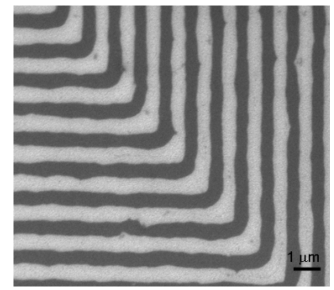
Directed Assembly of Carbon Nanotubes

Carbon nanotubes assembled in various configuration via various assembly methods

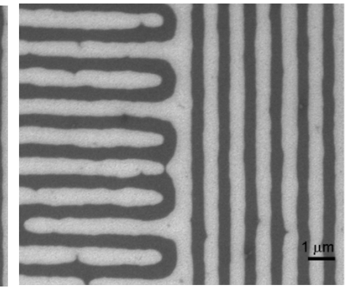


Directed Heterogeneous Assembly of Polymers

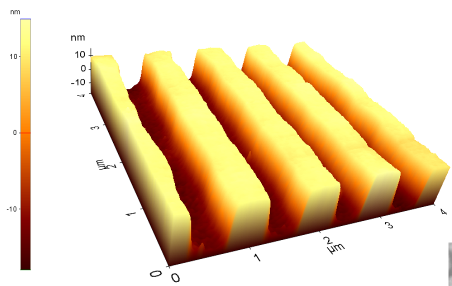


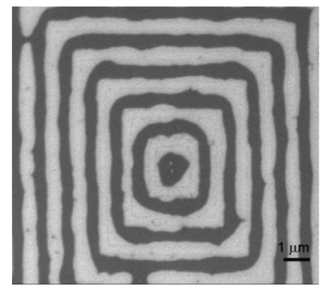


90˚ bends

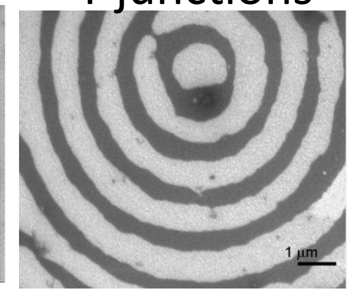


T-junctions

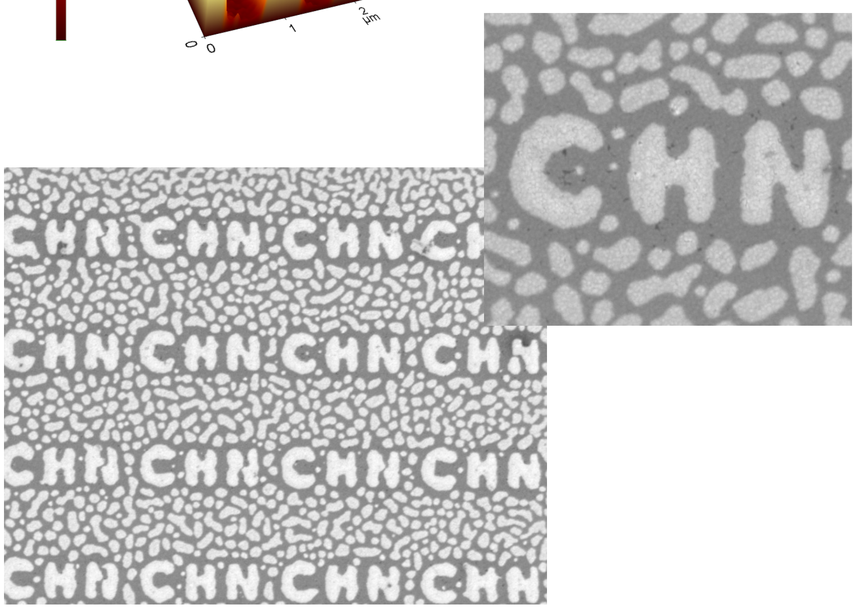


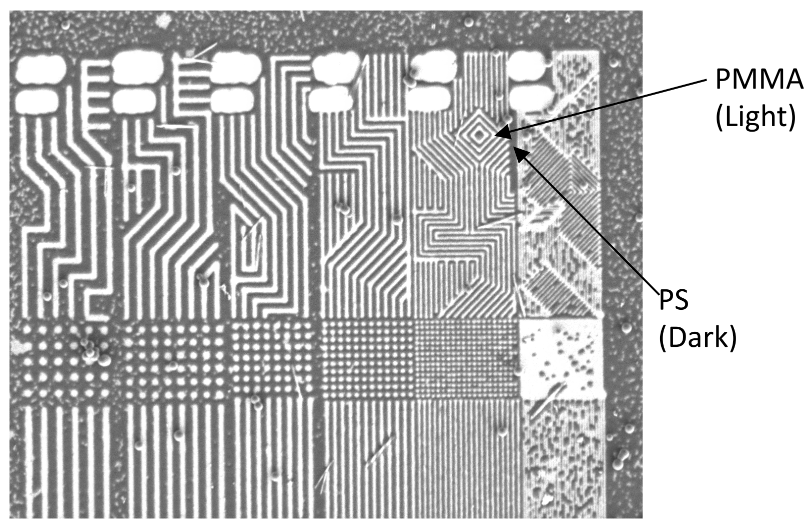


Square arrays



Circle arrays





CHN Toolbox
Connects 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
	Acenes	***Convective interfacial***			SWNT Chem Sensors
	Graphene	***Self assembly***			EMI Shielding

Process Flow for SWNT Chemical Sensors

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
	Acenes	Convective interfacial			SWNT Chem Sensors
	Graphene	Self assembly			EMI Shielding

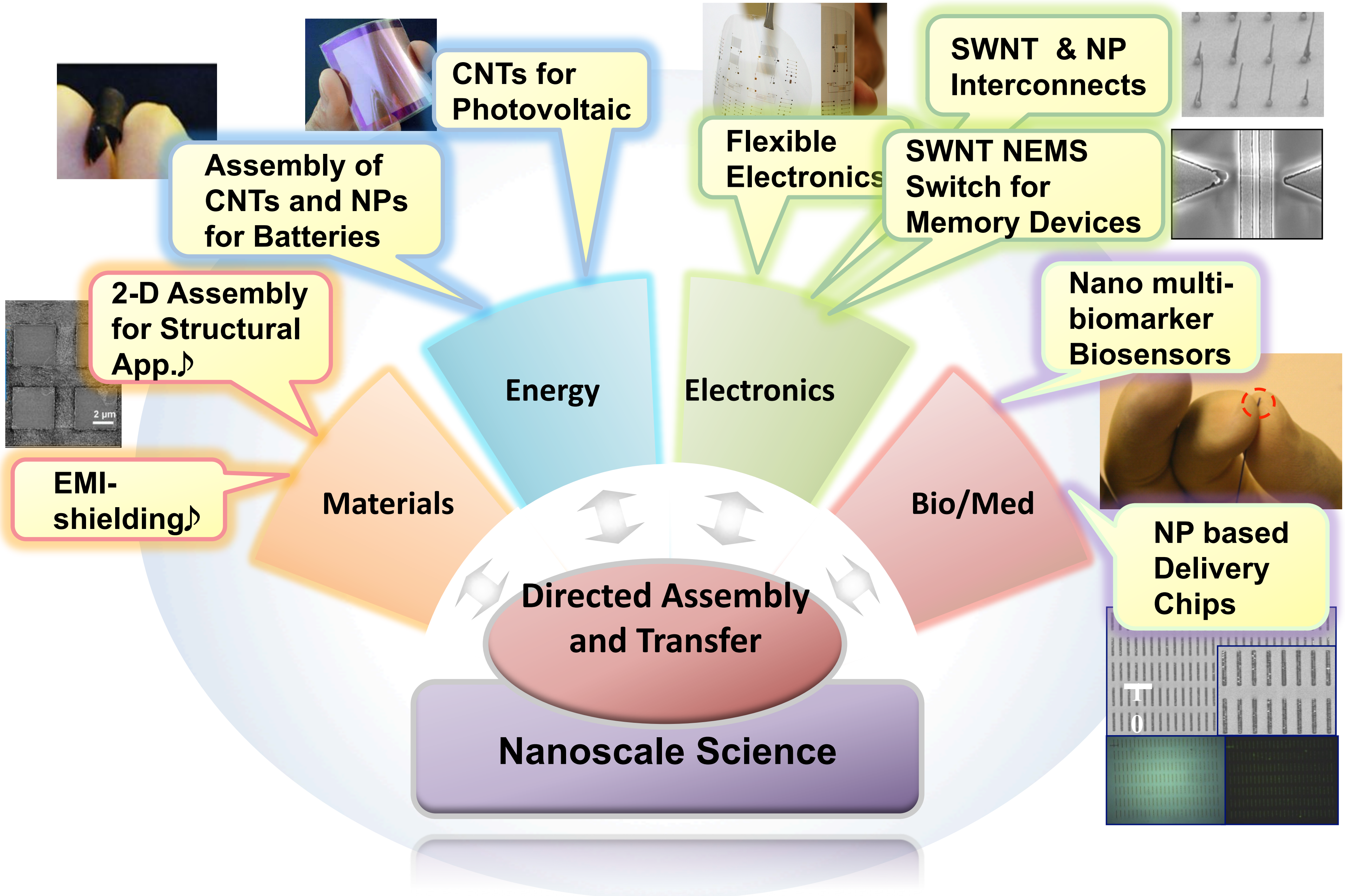
Process Flow for Nanoparticle-based Biosensors

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
	Acenes	Convective interfacial			SWNT Chem Sensors
	Graphene	Self assembly			EMI Shielding

CHN Directed Assembly Toolbox

Process	Speed	Scalability	Nanoelement property	Mechanism	Nanoelements
Electrophoretic Asssembly	Fast	Yes	Charge	Electrophoresis	Nanoparticles, CNTs, Conductive polymers
Chemical Functionalization	Fast/ slow	Yes	Functionalization	Chemistry	Polymer-based Biosensors
Electrophoretic and chemical functionalization	Fast	Yes	Charge and surface functionalization	Electrophoresis and surface energy	Nanoparticle-based Biosensors
Dielectrophoretic	Fast	Yes/No	Dielectric constant	Dielectrophoresis	SWNT Batteries
Convective	Slow	No	Surface Functionalization	Convection	Photovoltaics
Convective interfacial	Fast	Yes	Surface Functionalization and surface tension	Convection and interfacial force	EMI Shielding

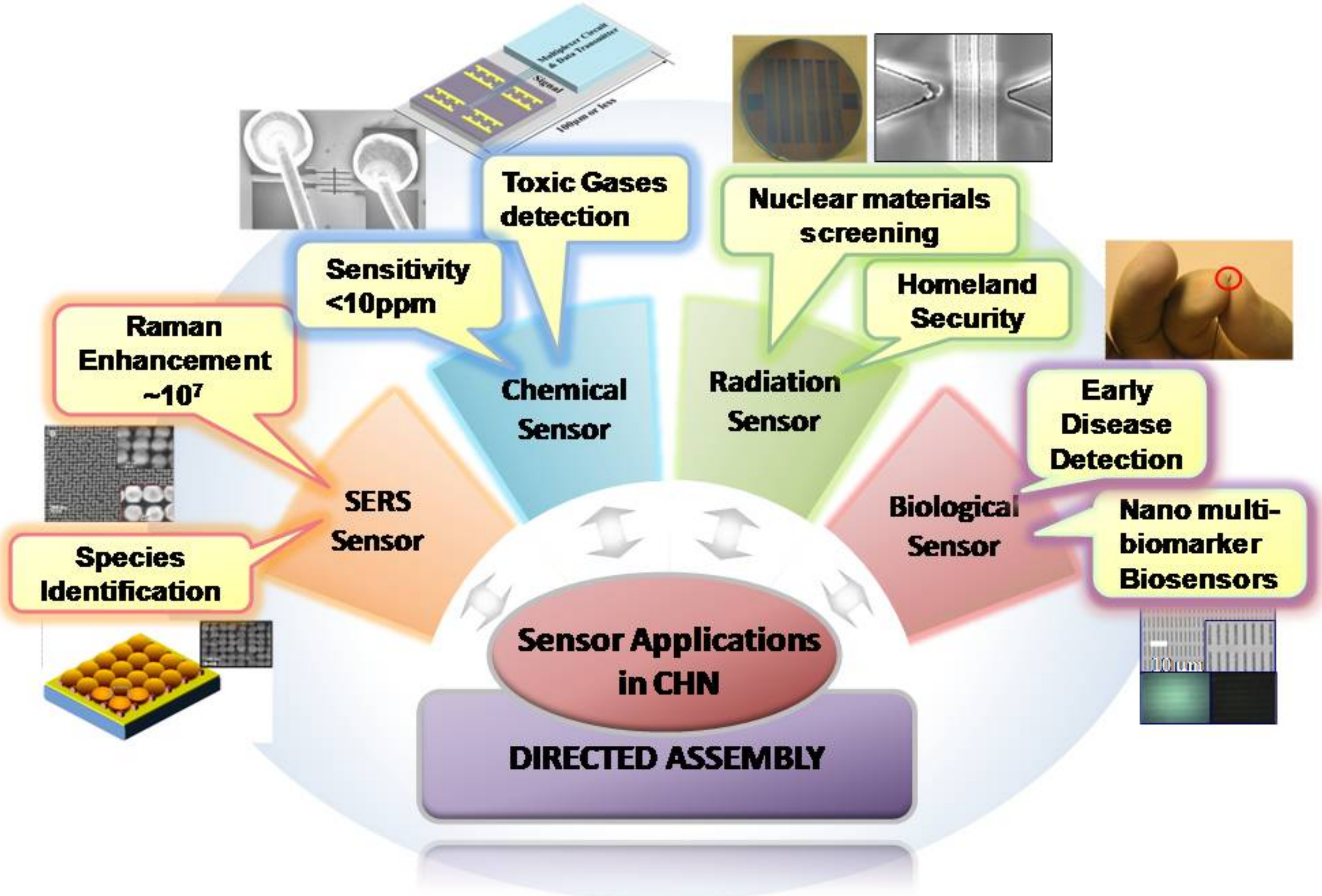
Nanomanufacturing Applications Roadmap



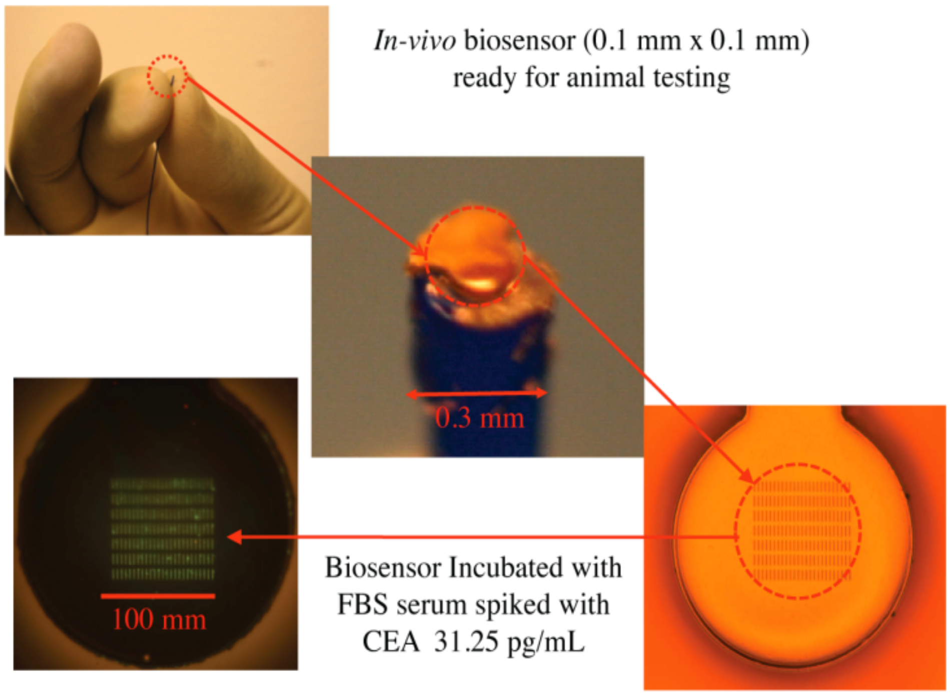
Individual Components

Sensors
Electronics
Energy Storage

Sensors Roadmap



Biological Sensors

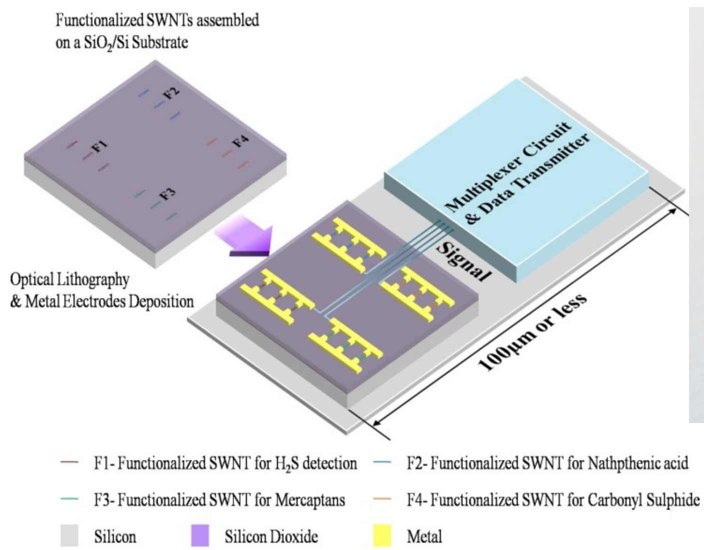


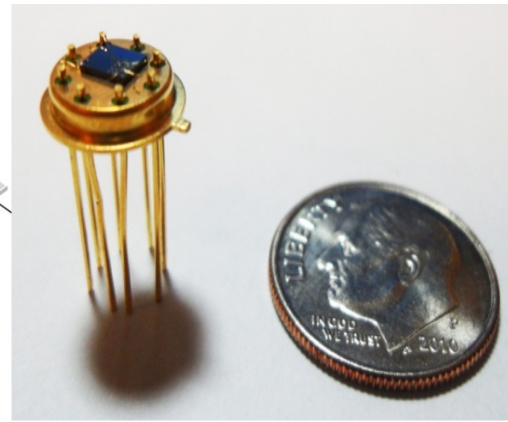
➢ Sensor active area is 100 micron squared or less
➢ Employs directed assembly
➢ ELISA based sensor
➢ Very high sensitivity ~pg/mL
➢ Fast multiple diseases detection
➢ Platform for other characterization
➢ Highly portable
➢ Suitable for *in vivo* and *in vitro* measurements
➢ When combined with peripheral components, data storage and position identification is possible

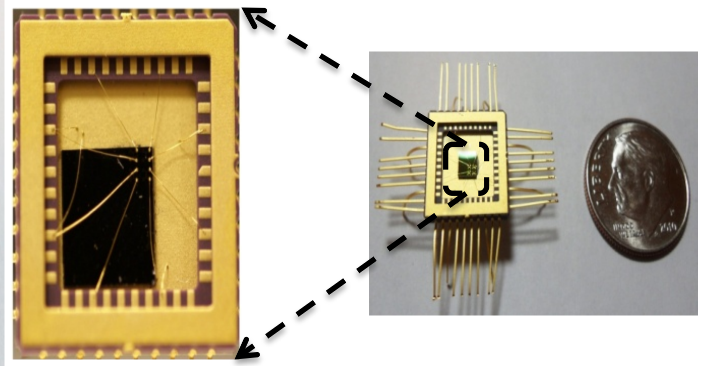
Applications

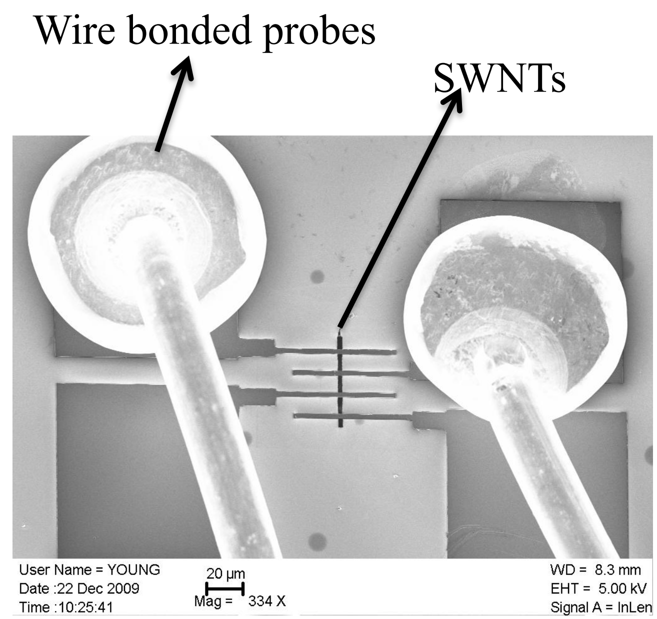
➢ Multiple Biomarker biosensor
➢ Early detection of diseases
➢ Instantaneous measurements and targeted drug delivery
➢ Environmental pathogen detection

Chemical Sensors I



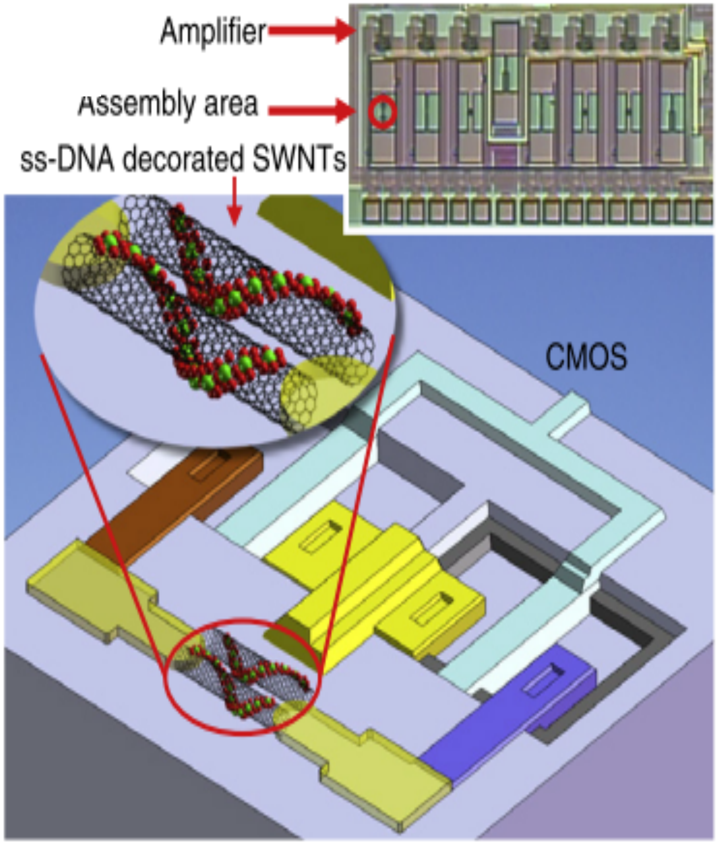


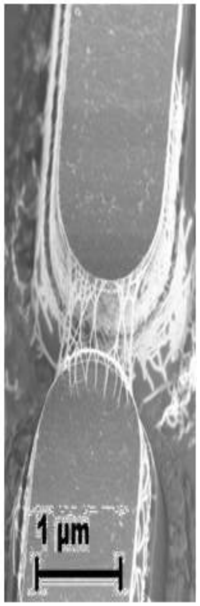




- Sensor active area is less than 10 micron squared;
- Resistance based; Very high sensitivity ~ppm
- Fast, specific Multiple species Detection
- Working in harsh environment (~250C and 25 Kpsi) already tested for 600psi and 200C
- When combined with peripheral components, data storage and communication is possible
- Potential Robust platform for low cost, high volume sensitive sensor array with size and durability to withstand reservoir injection.

Chemical Sensors II





- Sensor active area is 2 micron squared or less
- Employs directed assembly
- Resistance based
- CMOS integrated
- Alcohol sensors
- Fast detection
- Highly portable
- High sensitivity
- When combined with peripheral components, data storage and position identification is possible

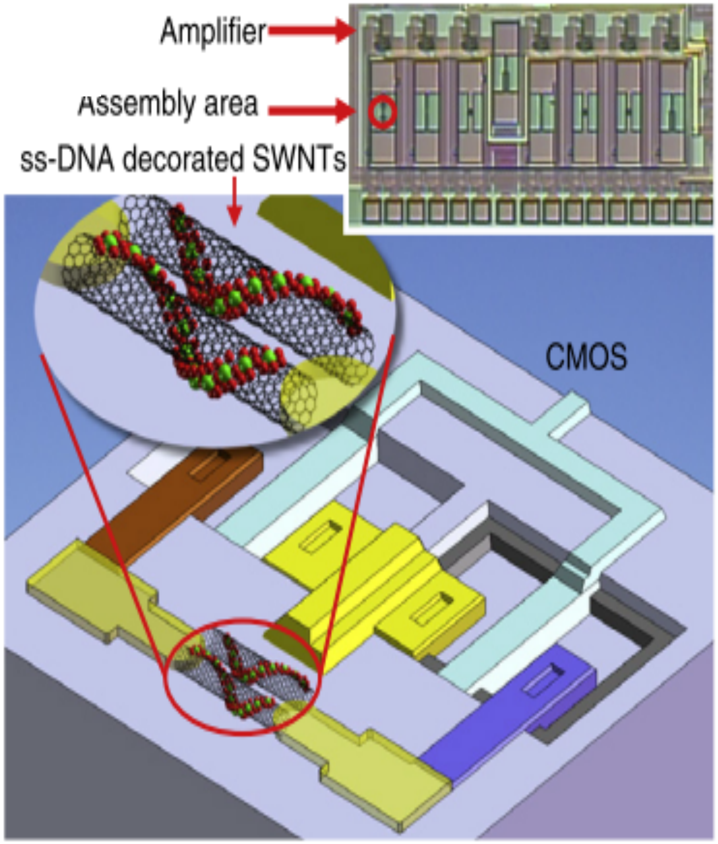
Application

Organic solvent Chemical sensors; Bio sensors

Modifications can lead to organic vapor sensors

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

Chemical Sensors II

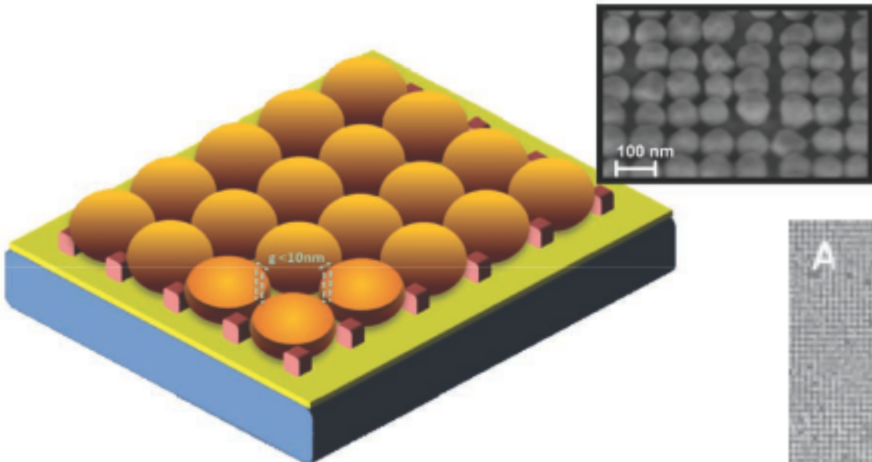


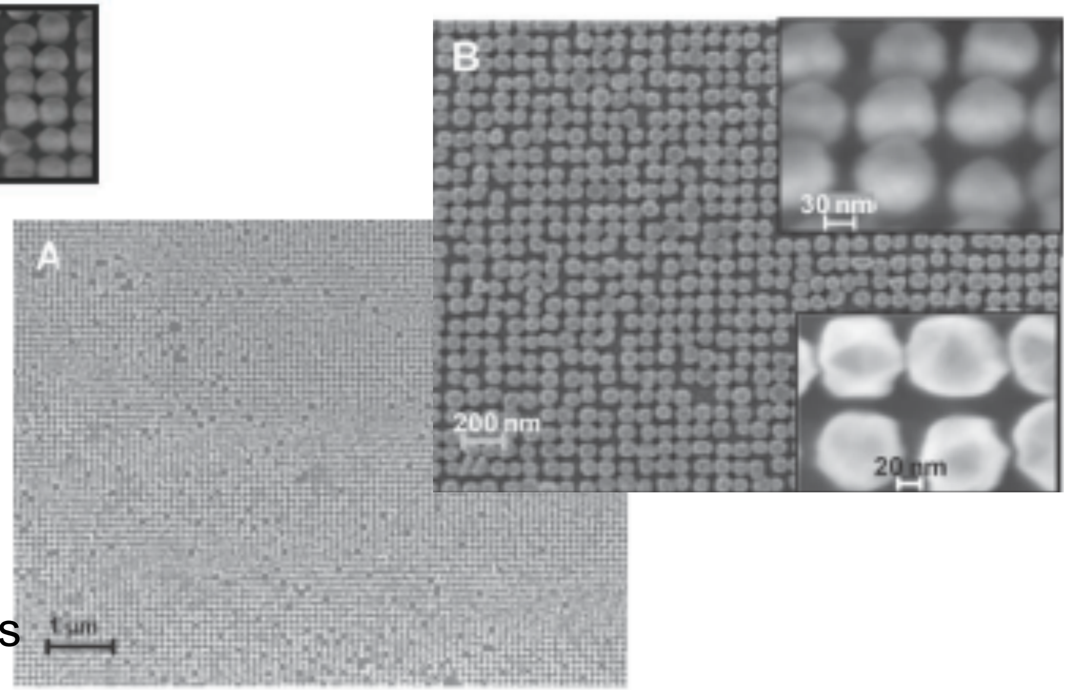
- Single-stranded DNA (ss-DNA)-decorated SWNTs onto CMOS circuitry as a chemical sensors.
- SWNTs were assembled onto CMOS circuitry via a low voltage dielectrophoretic (DEP) process.
- The the gas sensor was enhanced (up to ~300% and ~250% for methanol vapor and isopropanol alcohol vapor, respectively) compared with bare SWNTs.
- The SWNTs coupled with ss-DNA and their integration on CMOS circuitry demonstrates a step towards realizing ultra-sensitive electronic nose applications.

Application
Organic solvent Chemical sensors; Bio sensors
Modifications can lead to organic vapor sensors

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

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

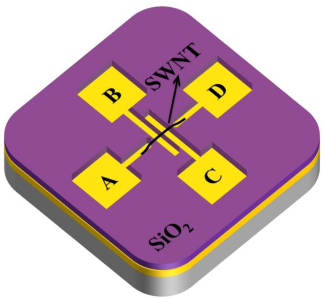
- Chemical sensors; Bio sensors
- Energy solar conversion
- Spacers
- Local field amplifiers

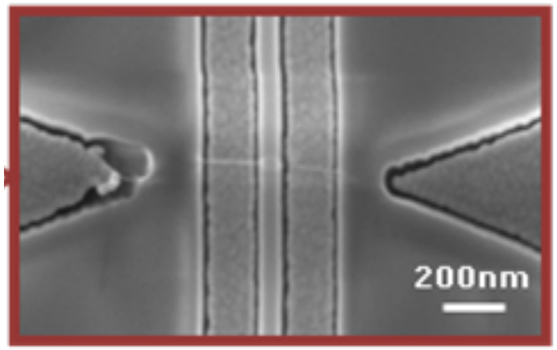
Liberman, Yilmaz, Busnaina, et. al., ***Advanced Materials 2010***

Figure of Merit –Sensors

	Nanoparticle Biosensor	Chemical Sensor	SERS Sensor	SWNT Biosensor
Size	100µm X 100µm	10µm X 1µm	15mm X 15 mm	10µm X 1µm
Opertaional power	NA	100microwatts	NA	100milliwatts
Operational voltage	NA	100millivolts	NA	500millivolts
Detection limit	30pg/L	ppm	7 orders of enhancement	mg/L
Multiple species detection	YES	YES	YES	YES
Scaling down	Yes	YES	NO	YES
CMOS intergation	YES	YES	YES	YES
Manufacturability	Cheap	Cheap	Cheap	Cheap
Gamma radiation vulnerability	YES	NO	NO	YES
Cyclability	Single Use	Multiple Use	Single Use	Multiple Use

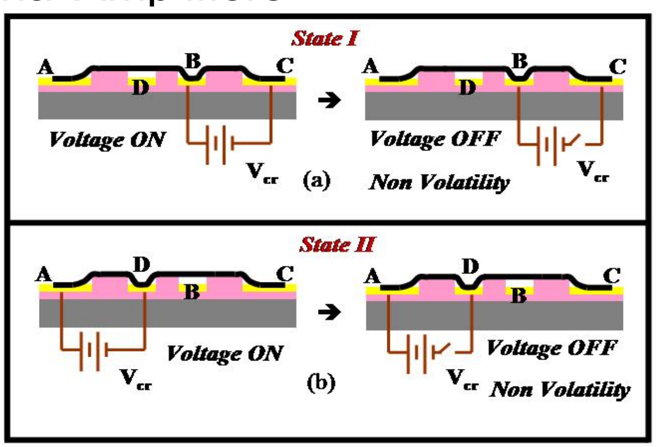
Carbon Nanotube NEMS Switch





Applications

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



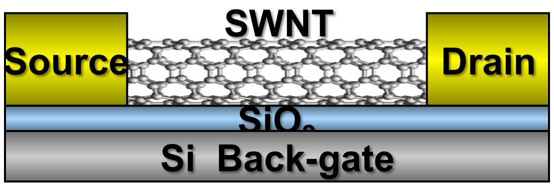
Schematic of states I and II.

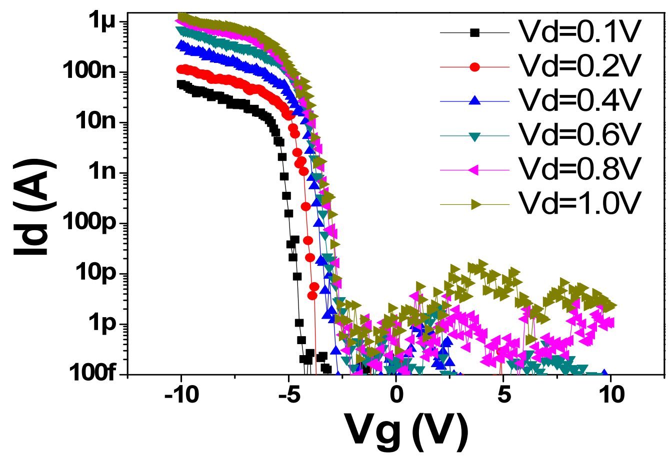
- Nano electromechanical Switch
- Non-voaltile
- Bistable Latch
- Position –Alternative state variable
- Novel State Variable Based Logic
- Fabrication employs field assisted directed assembly technique & a single mask process
- CMOS compatible

Characteristics:

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

Carbon Nanotube FET

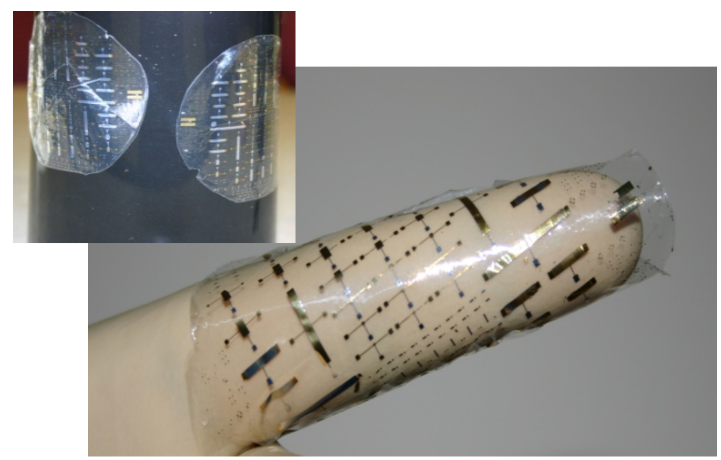




Employs Field Assisted Directed Assembly Technique

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

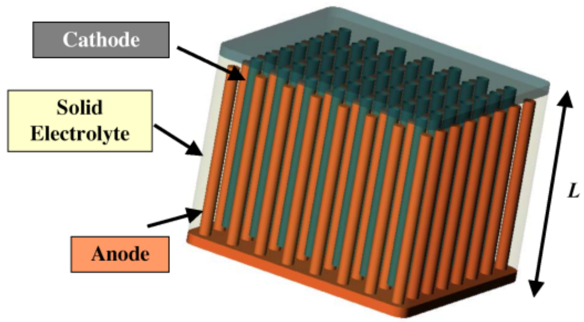
High Speed binary transistors ;
Logic gates; Analog devices;
Power amplifiers; Sensors, etc.

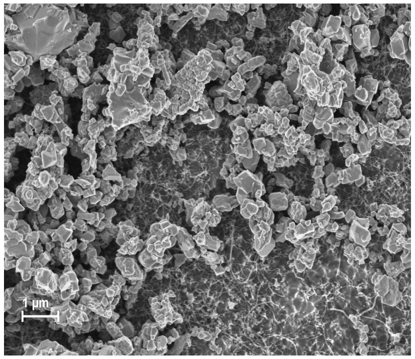
Selvarasah, Li, Busnaina, and Dokmeci, ***Appl. Phys. Lett. 97, 1 2010.***

Figure of Merit – Switch

	SWNT Switch	SWNT FET
Size	180 nm	100nm
Opertaional power	5nW	100mWatts
Operational voltage	5volts	2V
Volatility	NO	YES
Speed/cycle	40nSec	100nSec
Cell Factor	2F X 3F	2F X 2F
Scaling down	YES	YES
CMOS intergation	YES	YES
Manufacturability	Cheap	Cheap
Gamma radiation vulnerability	NO	YES
Endurance	Infinite	Infinite

Carbon Nanotube Battery





- Employs directed assembly – Cheaper cost
- Charge/discharge rate of C or greater
- Energy density of 450 Wh/kg; Higher power density
- Cycle life of 50,000 cycles; Storage life of 5 years
- Thermal cycle survivability of -55°C to +125°C
- Significant reduction or elimination of thermal runaway
- Materials are stable in the presence of g-radiation.

Applications

High Power energy storage elements for space, biomedical, electronics, transportation & stand alone sensors.

Figure of Merit – Battery

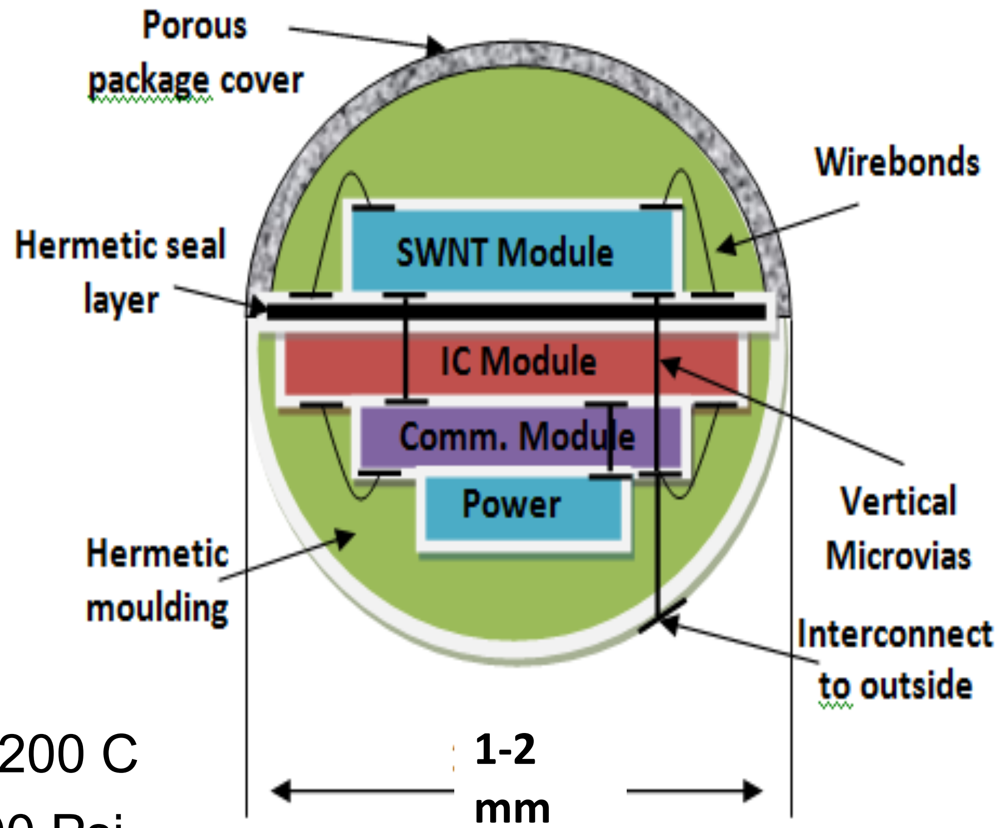
	MWNT Battery
Size	15mm X 15mm
Opertaional power	NA
Operational voltage	4.2 V
Self discharge	Microamps/ Nanoamps
Scaling down (Thin film)	YES
CMOS intergation	YES
Manufacturability	Cheap
Gamma radiation vulnerability	NO
Energy density	400Whr/kg
Cyclability	50000

Integrated Systems

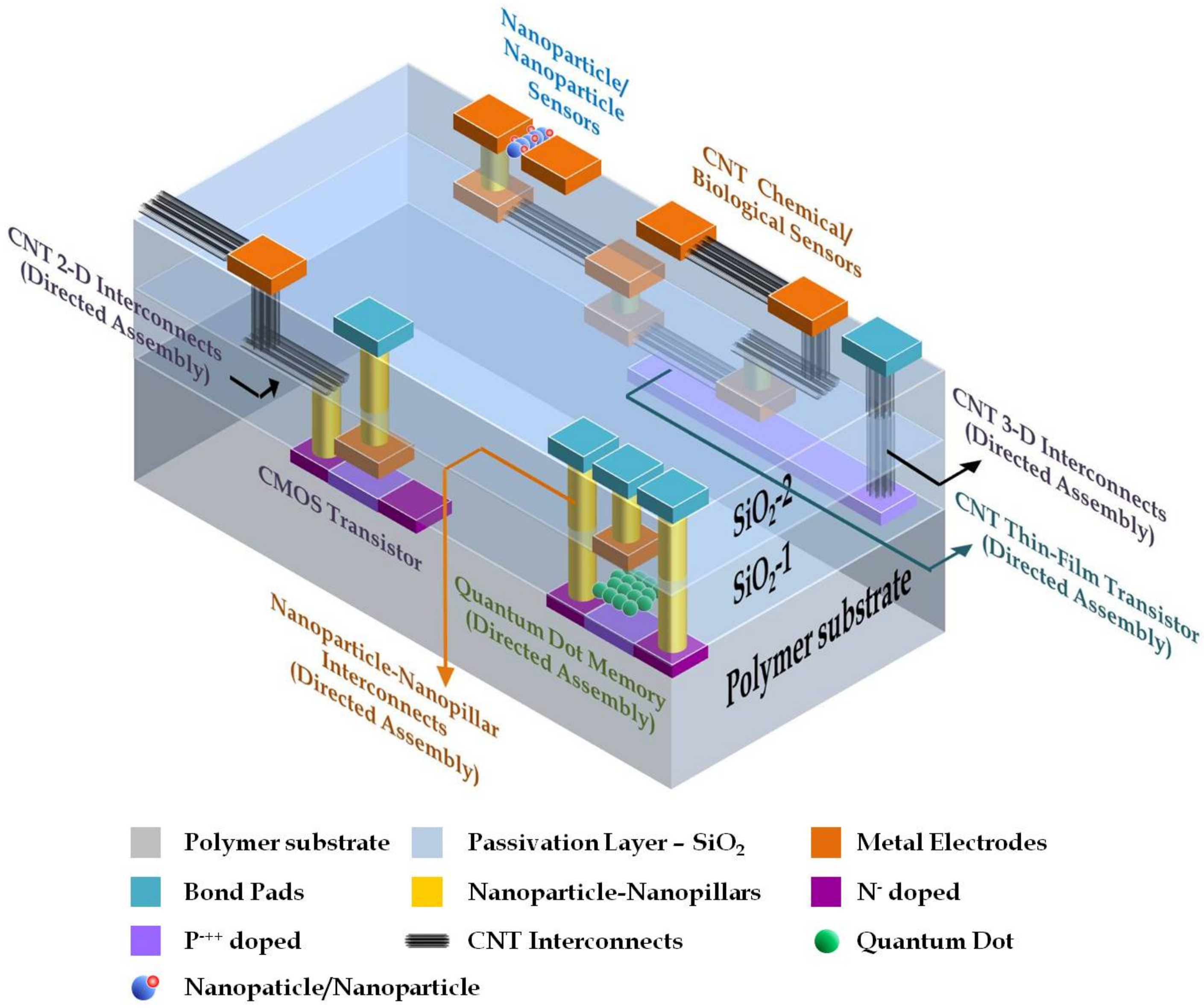
Vision

Monolithic Stand Alone Sensor Platform

- ➢ Stand alone sensor platform
- ➢ Can be chemical or biosensors
- ➢ Millimeter scale computing
- ➢ Utilize of the shelf components
- ➢ Has it own processor module communication module & power module
- ➢ Can withstand temperature up to 200 C
- ➢ Can withstand pressure up to 5000 Psi
- ➢ Communication module is used to communicate as well as recharge the battery



Monolithic Flexible IC - Directed Assembly – Reel to Reel



Strong Industrial Partnerships

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Applications Road Map

- **CHN emerging applications roadmap led to increased industrial sponsorship**
  - **SWNT sensors**
  - **Micro-nano battery**
  - **Photovoltaics**
  - **Nonvolatile memory**
  - **EMI shielding**
  - **Metamaterials**
  - **Biosensor**
  - **SWNT composites**

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What can directed Assembly do for Nanoscale Manufacturing?

1. Bottom directed assembly of nanoelements (nanoparticles, nanotubes, polymer molecules, nanowires, etc.) to build 2 or 3-D nanostructures during manufacturing.
   1. Nanostructures such as interconnects between layers or components such switches or sensor elements.
   2. Precise placement of quantum dots, SWNTs or molecules
   3. Enable new generation of devices (NEMS, quantum dot, etc.)
   4. Reduce manufacturing cost for nanoscale structures.

2. For directed assembly to be useful in manufacturing it has to be:

   Fast, repeatable, scalable, achieve high-yield and produce reliable structures

Questions?