Creating Catalyst-containing Nanostructures via Self-assembled Block Copolymer Templates for Rationally Synthesis of 1D nanostructures

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Carbon Nanotubes

Excellent mechanical properties: Composite

100 to 200 times stronger than steel

Excellent electron transport property: Transistors

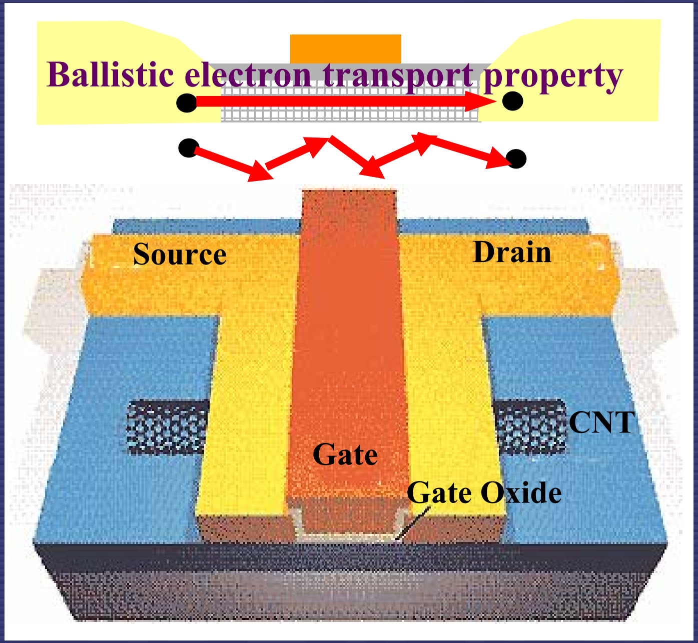
μ ~ 3000 to 20,000 cm^2/V-sec max reported in p-type CNTFETs

μ ~ 500 cm^2/V-sec Si-pFETs

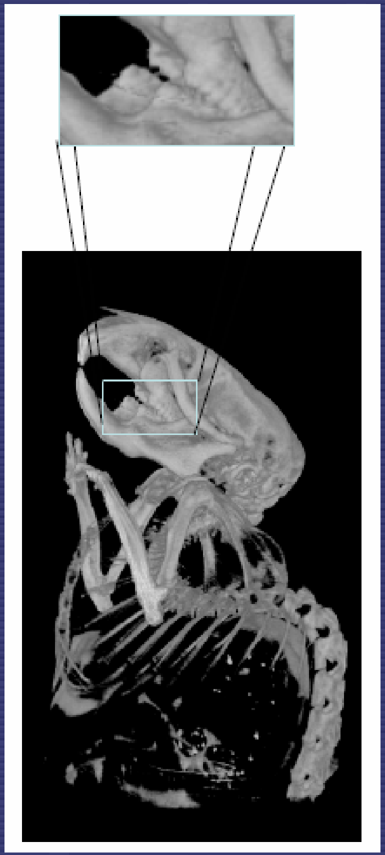
High aspect ratio, huge current capability: Field emission tips

CNT: $10^9 A/cm^2$ Metal: $< 10^6 A/cm^2$ Si: $< 10^3 A/cm^2$

Space cable (NASA)



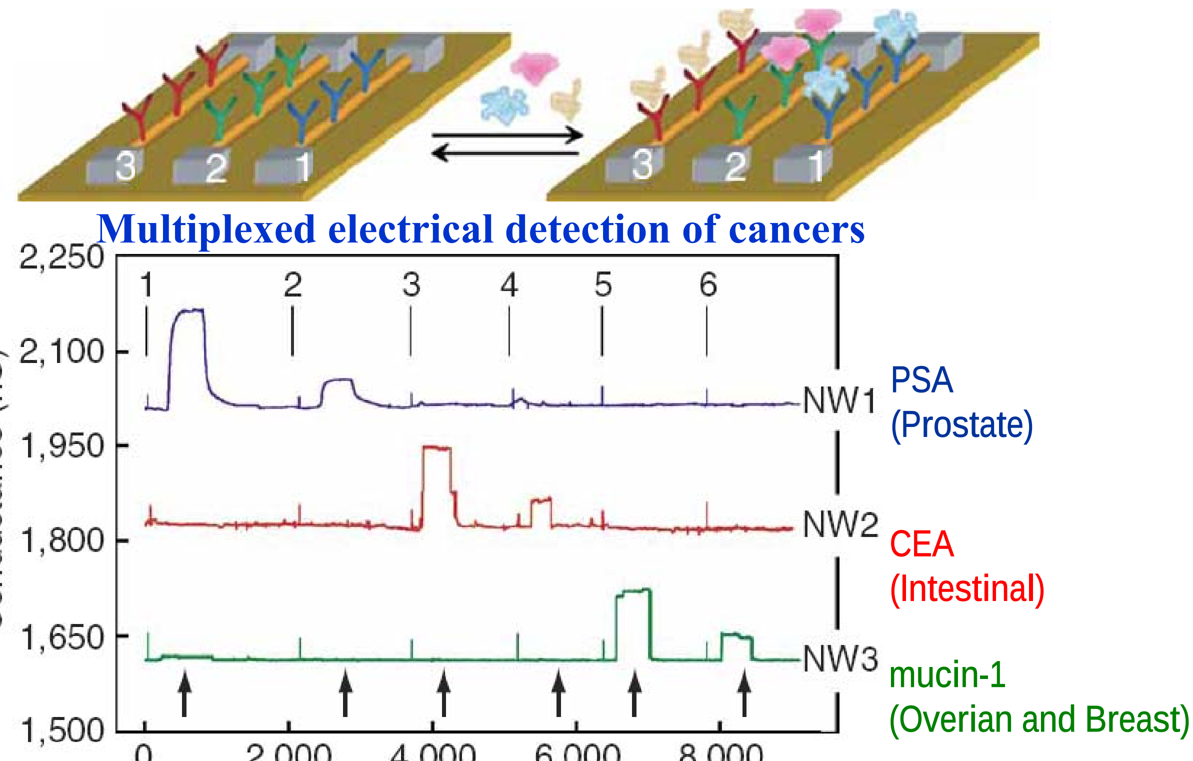
CNTFET(IBM)



CNT-based X ray (UNC)

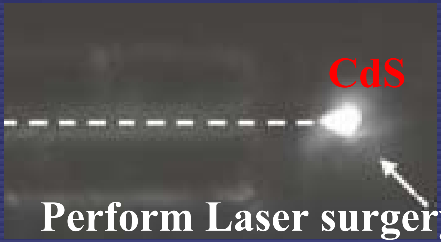
Nanowires

Electronic based sensor



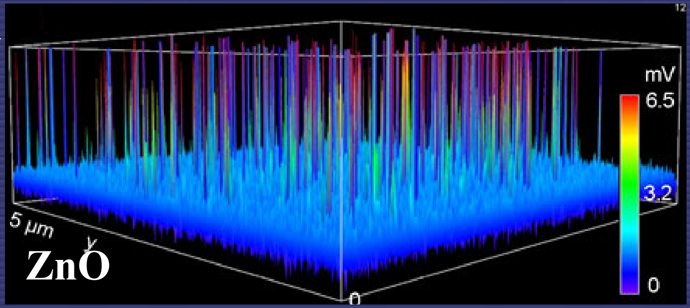
G. Zheng, F. Patolsky, Y. Cui, W.U. Wang, C.M. Lieber, Nat. Biotechnol. , 23, 1294 (2005)

NanoLaser



Nano-electricity generators

Z.L. Wang Georgia Tech

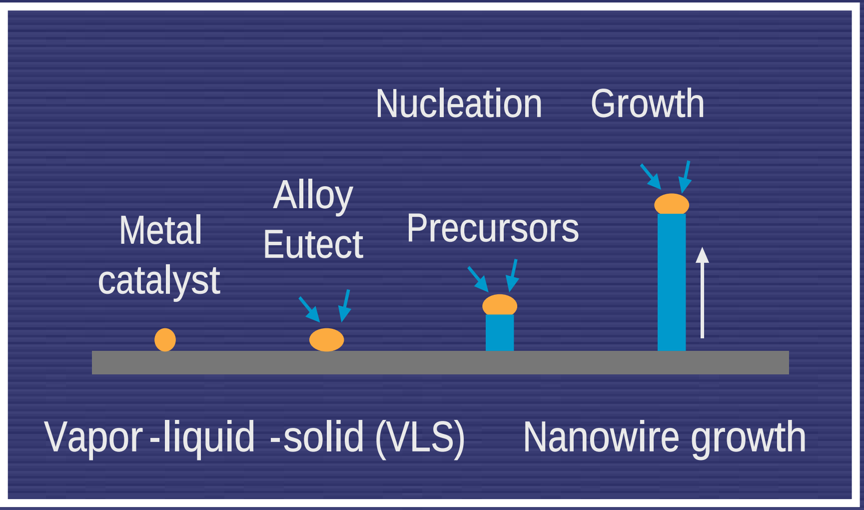


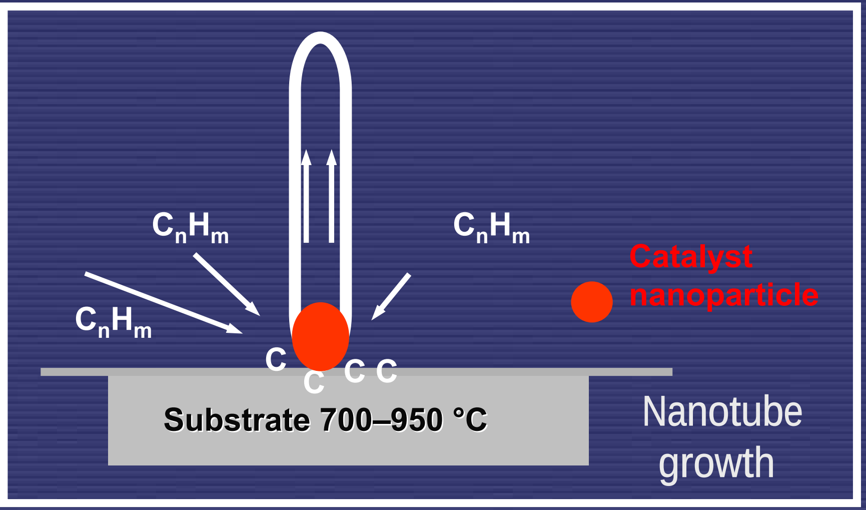
X. Duan, Y. Huang, R.Agarwal. C.Lieber. Nature 421, 241–245 (2003)

Challenges

Lack of <u>controllable synthesis</u> prevents realizing their highly touted properties

Commercialization
Nanotechnology !!! ⇐ Controllable synthesis (Locations, Orientations, Properties) Predictable, Consistent





<u>Location and diameter are determined by catalyst</u>

Challenges

Controllable growth → Catalysts with controlled size and spacing at predefined locations

Transition metal

- **Carbon nanotubes: Fe, Co, Ni**
- **Nanowires:** Au: *InP, InAlAs, GaN, Si*; Ni: *GaN, SiC, Si*

Catalyst nanoparticle size

- ≤ 3 nm for single-walled carbon nanotubes
- ≤ 20 nm for nanowires

Current top-down lithography (✗)

Self-assembled block copolymer

Outline

- Background: Block copolymers

- Iron-containing nanostructures for CNT growth

    Thin film self-assembled iron-containing block copolymers

- Catalytically active transition nanoparticles for CNT and Si nanowire growth

    Solution self-assembled metal modified block copolymers

- Conclusion

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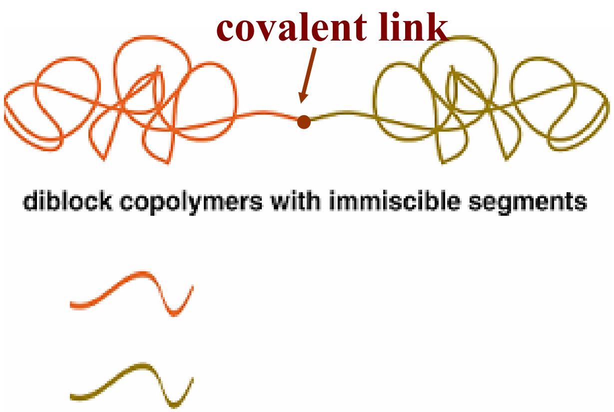
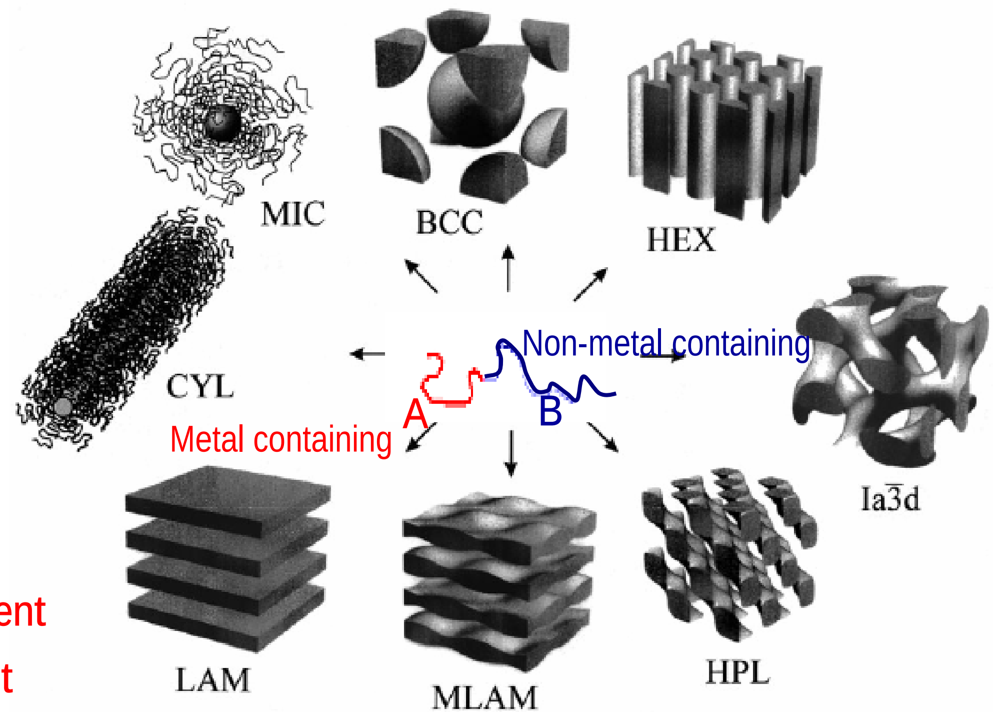
Nanomorphologies Produced by Diblock Copolymer





Morphology← Volume fraction of component

Microdomain size← Total molecular weight

< 60 nm

S. Föster et al, Adv. Mater. 10, No. 3, 1998

- Self-organize metal-containing block copolymer to produce metal-based nanostructures (A) with periodic size and spacing surrounded by (B)

Template for generating metal-containing nanostructures

Outline

- **Background: Block copolymers**

- **Iron-containing nanostructures for CNT growth**

  Thin film self-assembled iron-containing block copolymers

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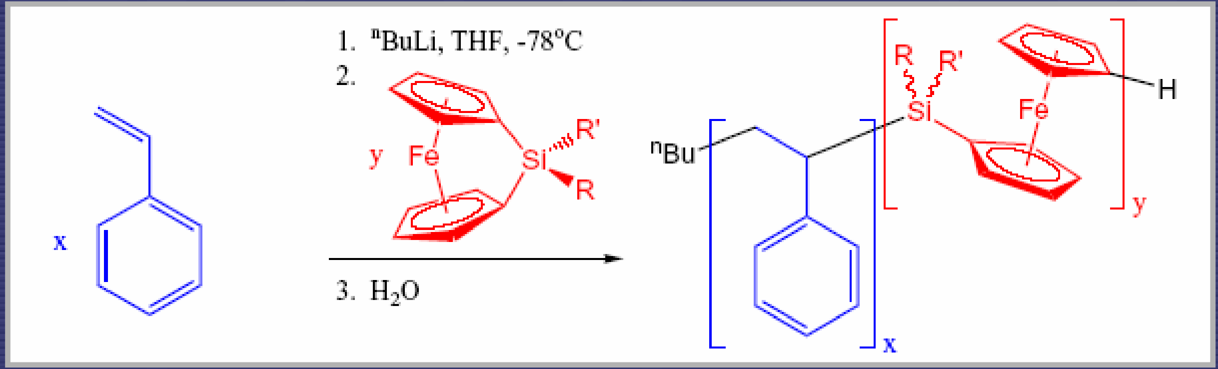
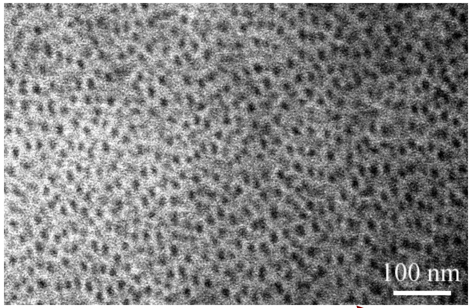
- **Conclusion**

Iron-containing Ferrocenylsilane Block Copolymers

Iron is a well-known catalyst system for CNT growth

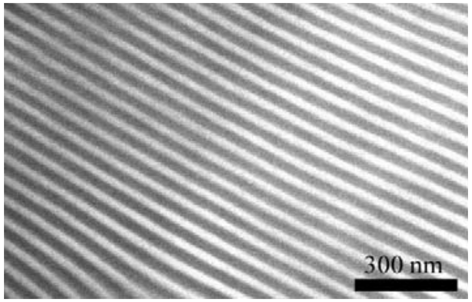


PS$_{450}$-b-PFEMS$_{25}$ (Φ_{PFEMS}=0.10)

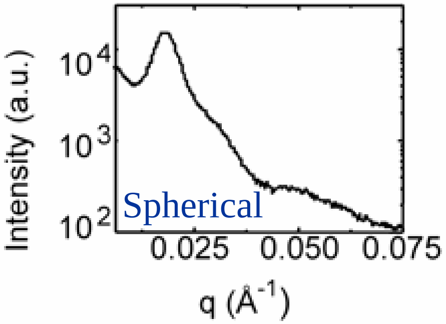


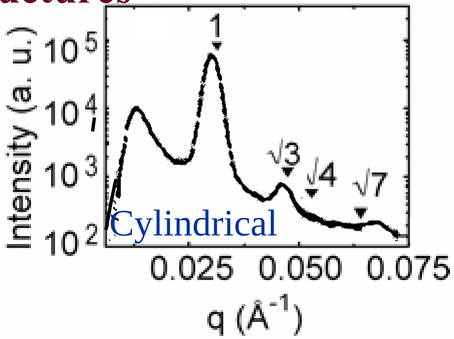
PS$_{389}$-b-PFEMS$_{108}$ (Φ_{PFEMS}=0.36)

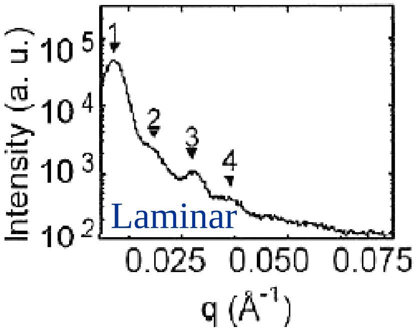
PS$_{539}$-b-PFEMS$_{296}$ (Φ_{PFEMS}=0.53)



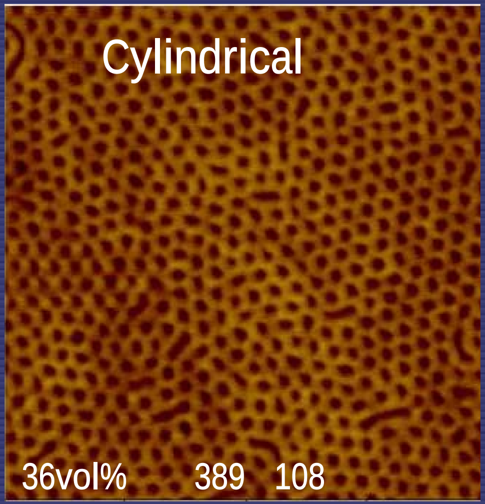
Discrete nanostructures

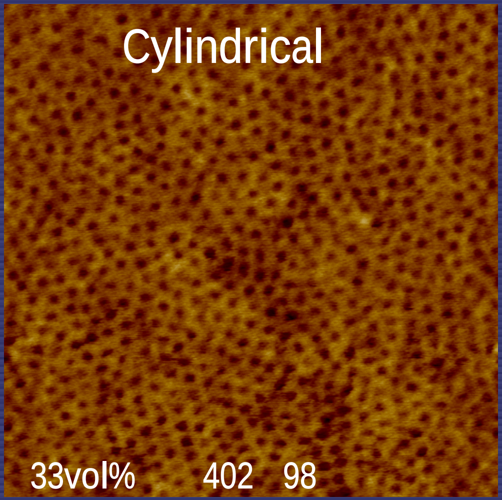


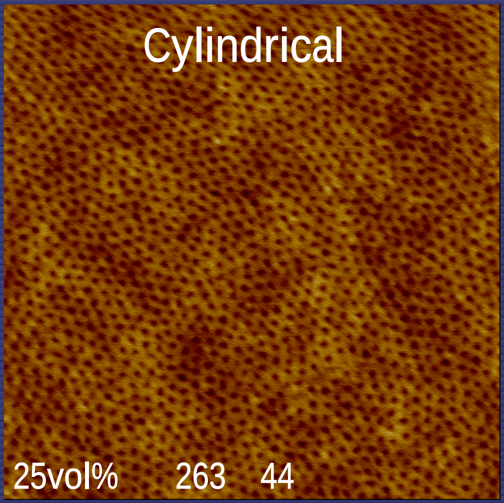




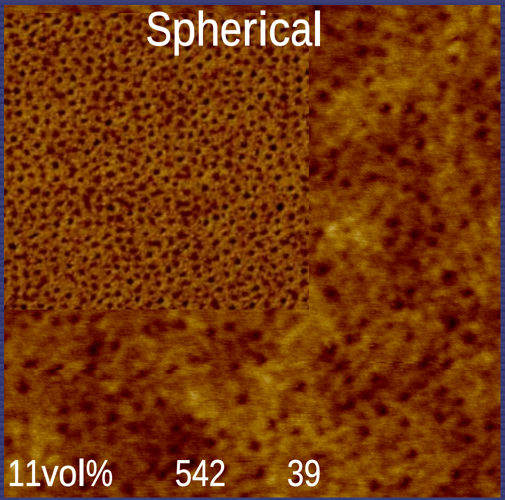
Thin film Self-assembled Morphologies







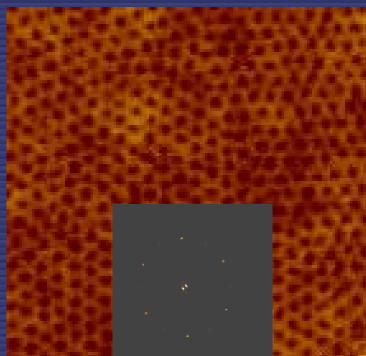
$Ø_{PFS}$	PS	PFS	Domain size	Spacing
0.33	253	44	14	28
0.25	402	98	22	36
0.36	389	108	31	45



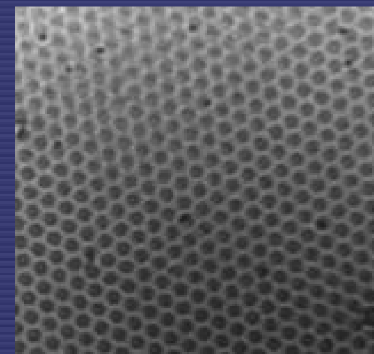
Size and spacing can be adjusted by chain lengths

Iron-Containing Nanostructures for CNT growth

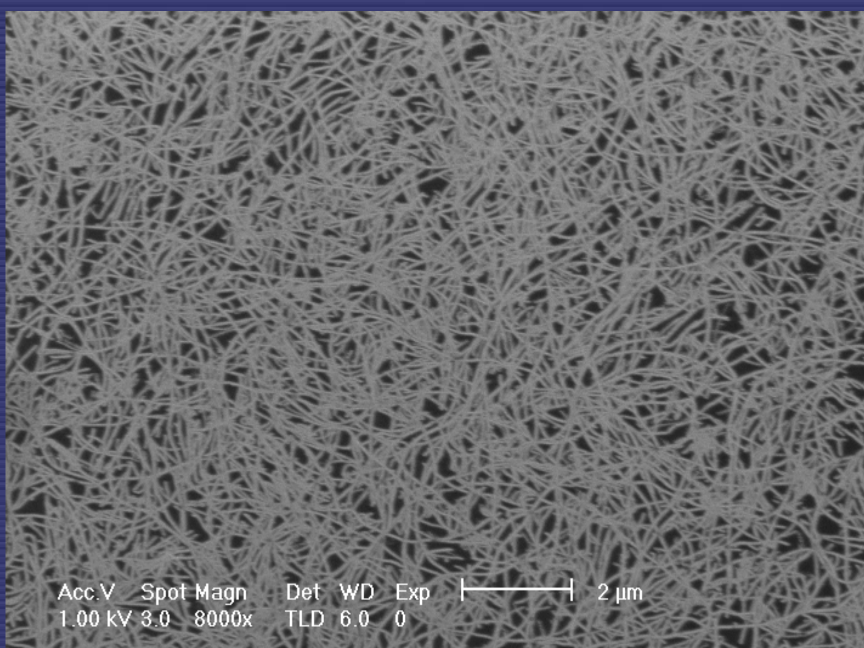
Self-assembled polymer thin film | **Fe-containing silica posts**



Oxygen plasma →



CNT growth →

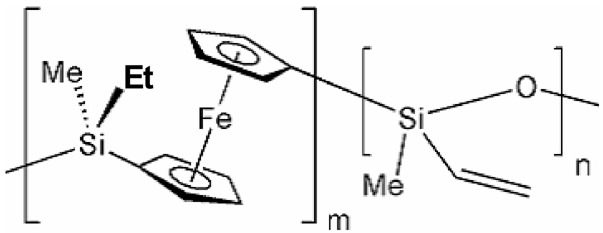


Carbon nanotube uniformly distributed over a large surface area!

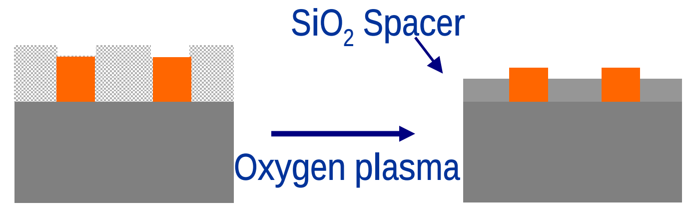
AFM and Raman analysis:

- 1 nm in diameter on average
- very few defects in CNTs

Si Rich Ferrocenylsilane-based Copolymer Systems



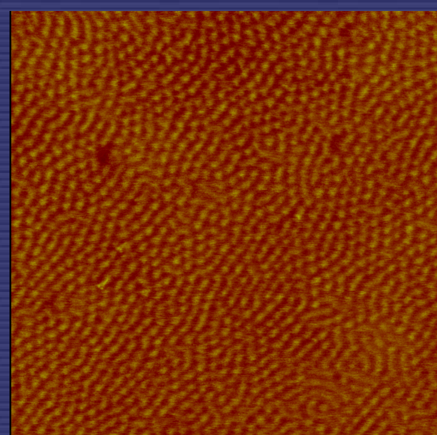
SiO_2 may further reduce aggregation

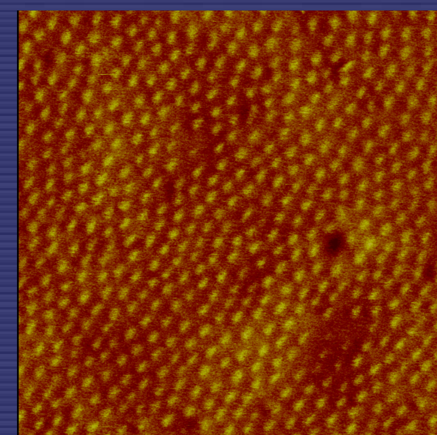


PMVS$_{377}$-b-PFEMS$_{25}$ (13vol% PFEMS) PMVS$_{837}$-b-PFEMS$_{45}$ (11vol% PFEMS)

AFM height image

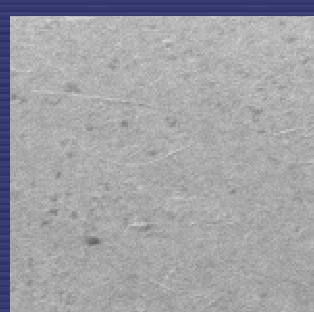
1 μm by 1 μm scan
10 nm in height

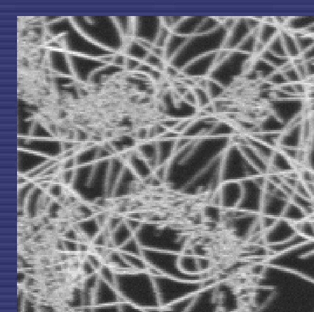




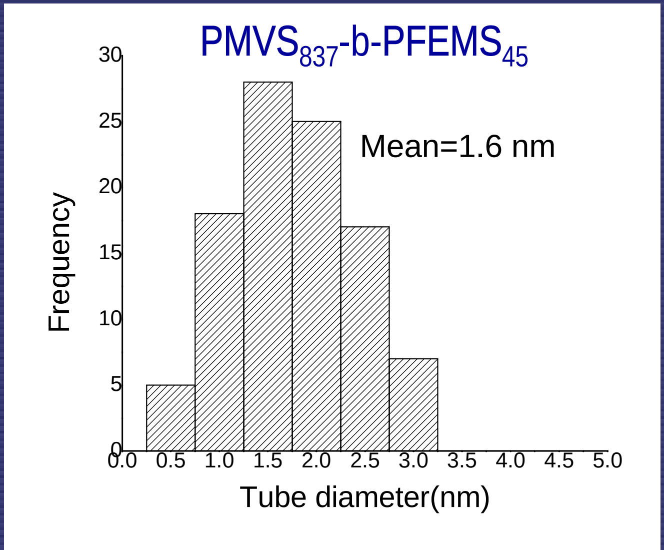
SEM image

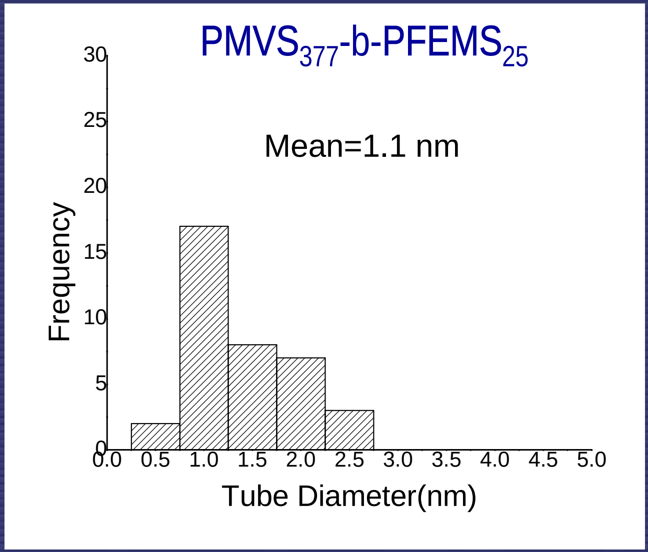
4 μm by 4 μm





Tailoring CNTs by Adjusting Block Lengths





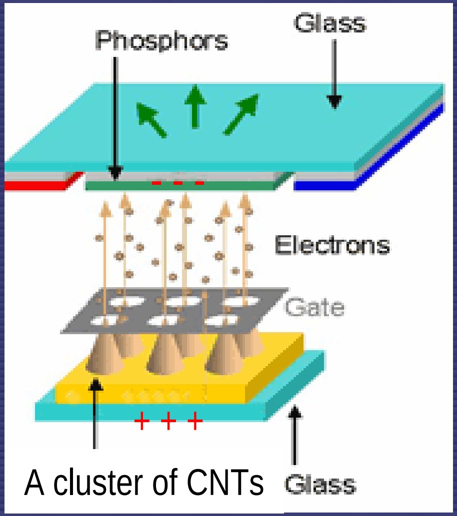
Tailoring polymer chain lengths
→ Fe-containing nanostructure size & density
→ CNT diameter & density

Rationally synthesize CNTs with predictable and tunable size and density

$PMVS_{377}$-b-$PFEMS_{25}$ G/D= 6 (1.1 nm)
$PMVS_{837}$-b-$PFEMS_{45}$ G/D= 12 (1.6 nm)

Growth condition for producing defect-free CNTs is sensitive to catalyst size.

CNTs for Display Application



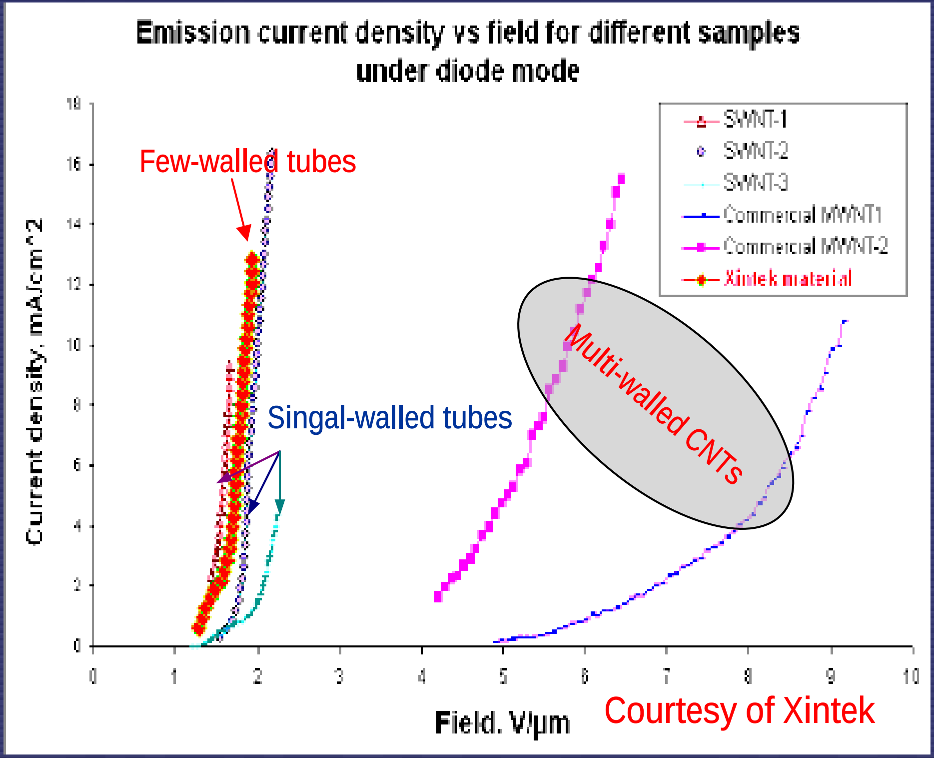
Display Market: $50 billion per annum

- Thinner
- Brighter
- Better color reproduction
- Faster response time
- Lower power consumption

Few-walled CNTs

- Excellent field emission properties
- Superior mechanical integrity

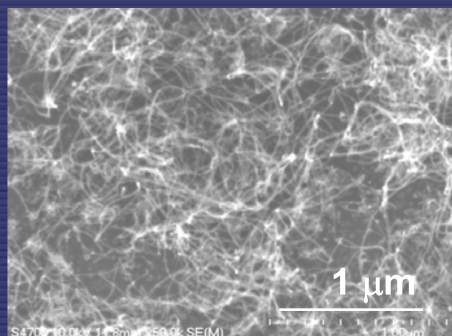
Directly grow uniform upright few-walled CNTs on ITO coated glass

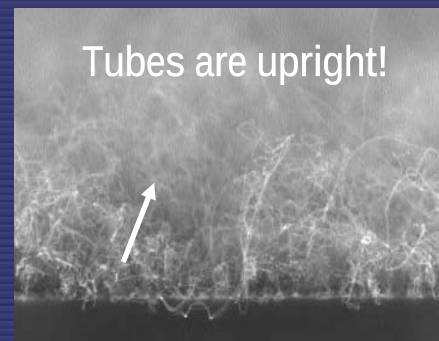


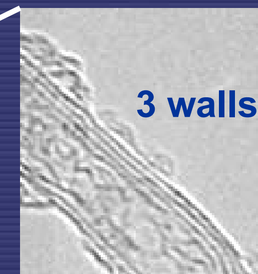
CNTs for Display Application

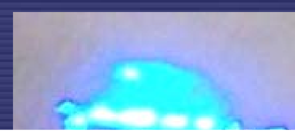
Catalyst: Fe-containing nanostructures (PS_{389}-b-$PFEMS_{108}$)

Carbon nanotube growth condition: PECVD, 600ºC









Excellent Field emission!

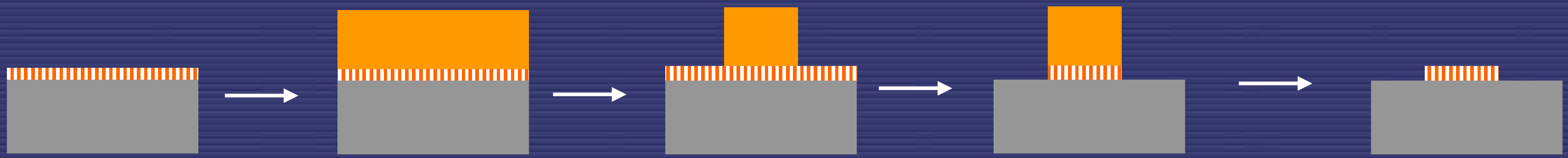
PS-b-PFEMS block copolymer template:

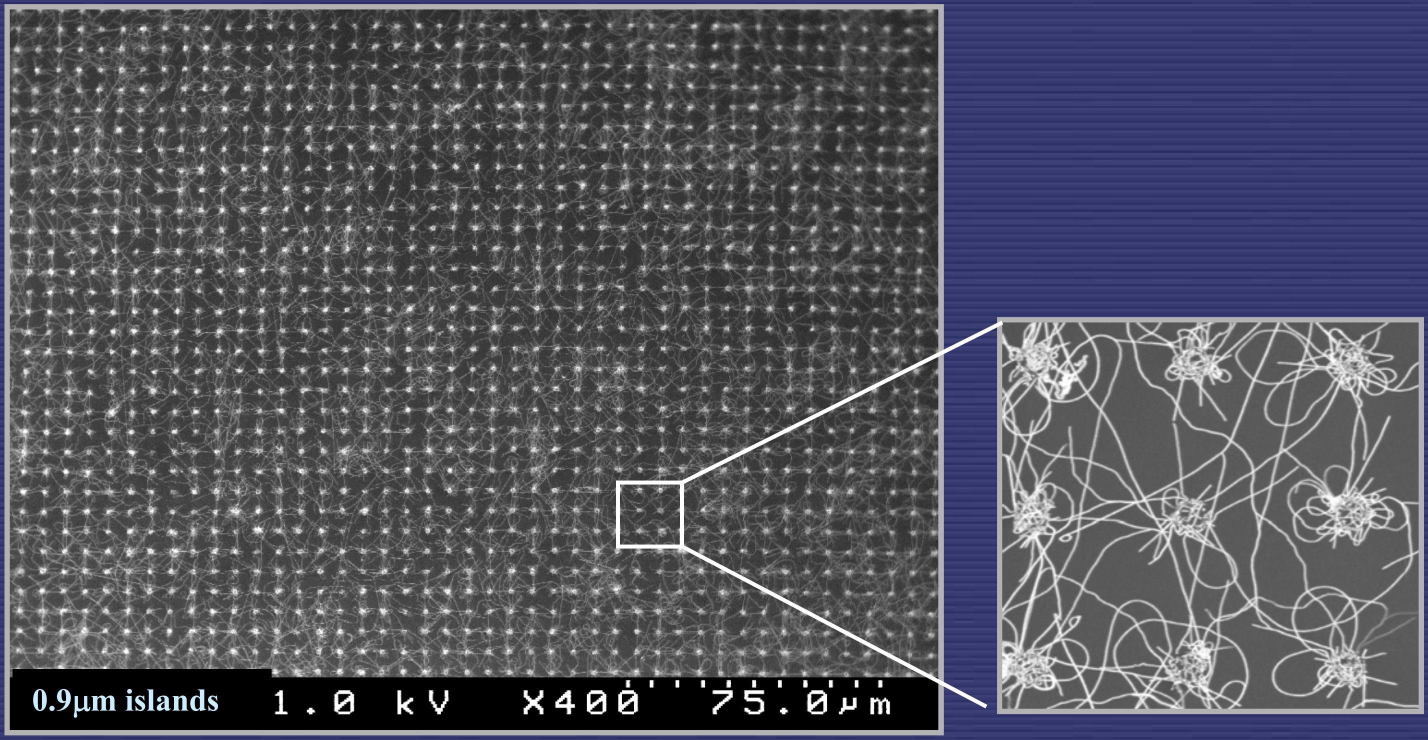
Tailoring block lengths → Upright few-walled CNTs → Excellent emission properties

Uniformly dispersed catalyst species → Evenly populated CNTs → Uniform emission

Selective Growth of CNTs

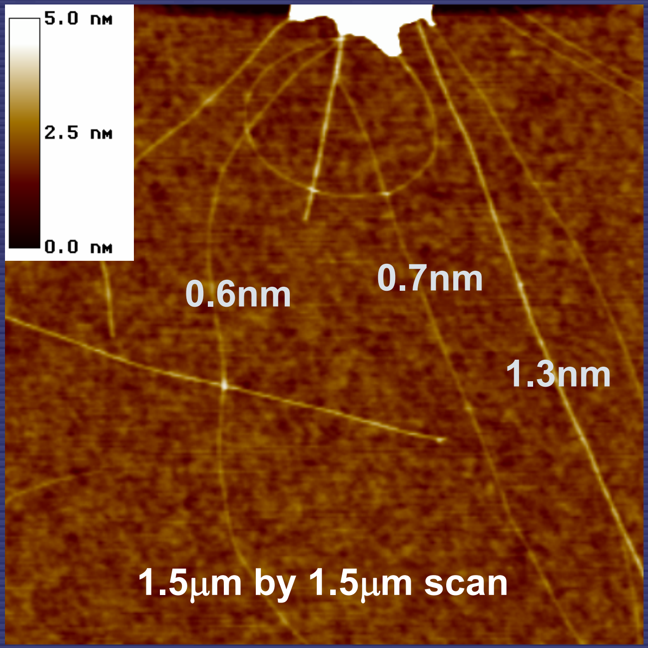
Combination of top-down litho with bottom-up self-assembly

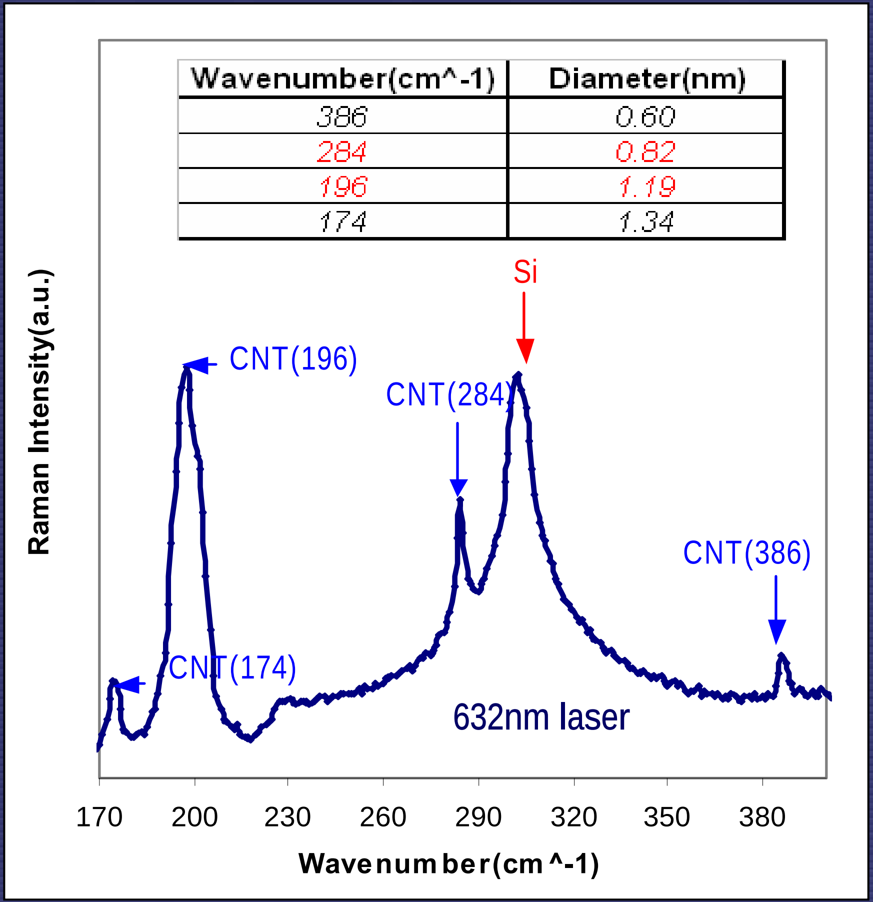




Self-assembly and lithography patterning processes on a 3 inch wafer format

Diameters of CNTs Grown from Catalyst Islands



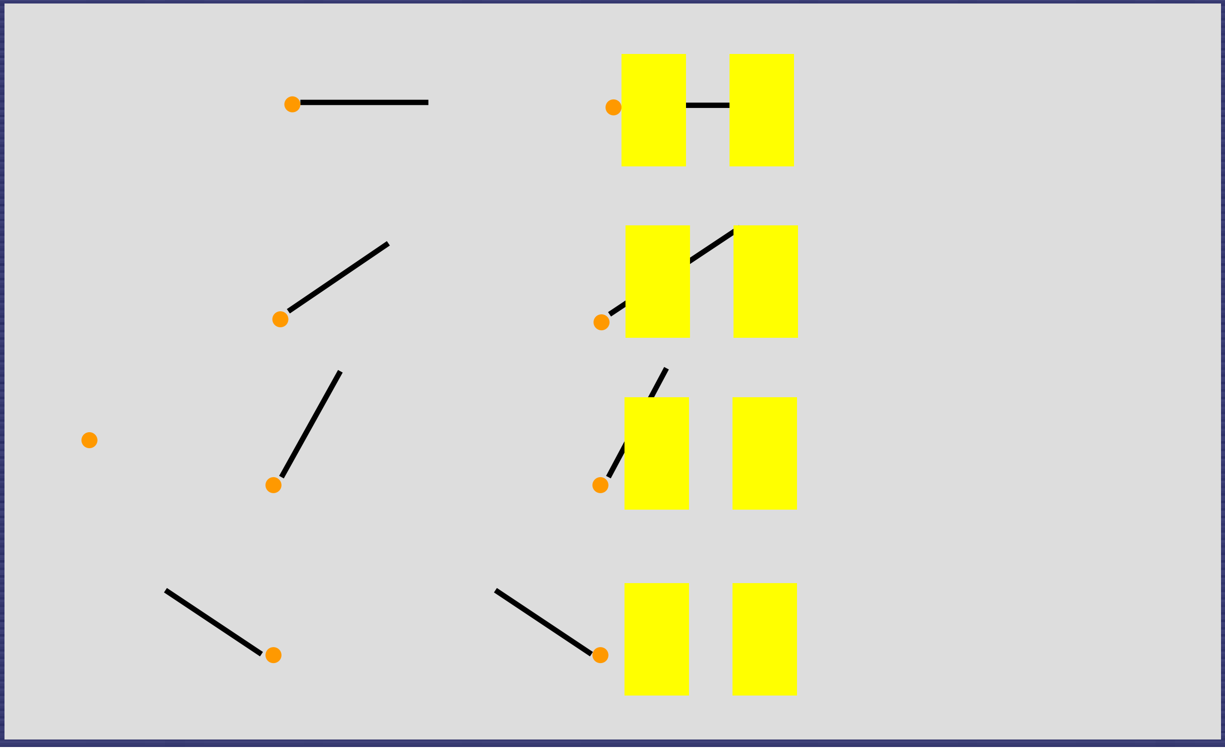


Majority of tubes have diameters around or less than 1nm

Conventional Transistor Design

Either directly growing CNTs or dispensing as-synthesized CNTs,

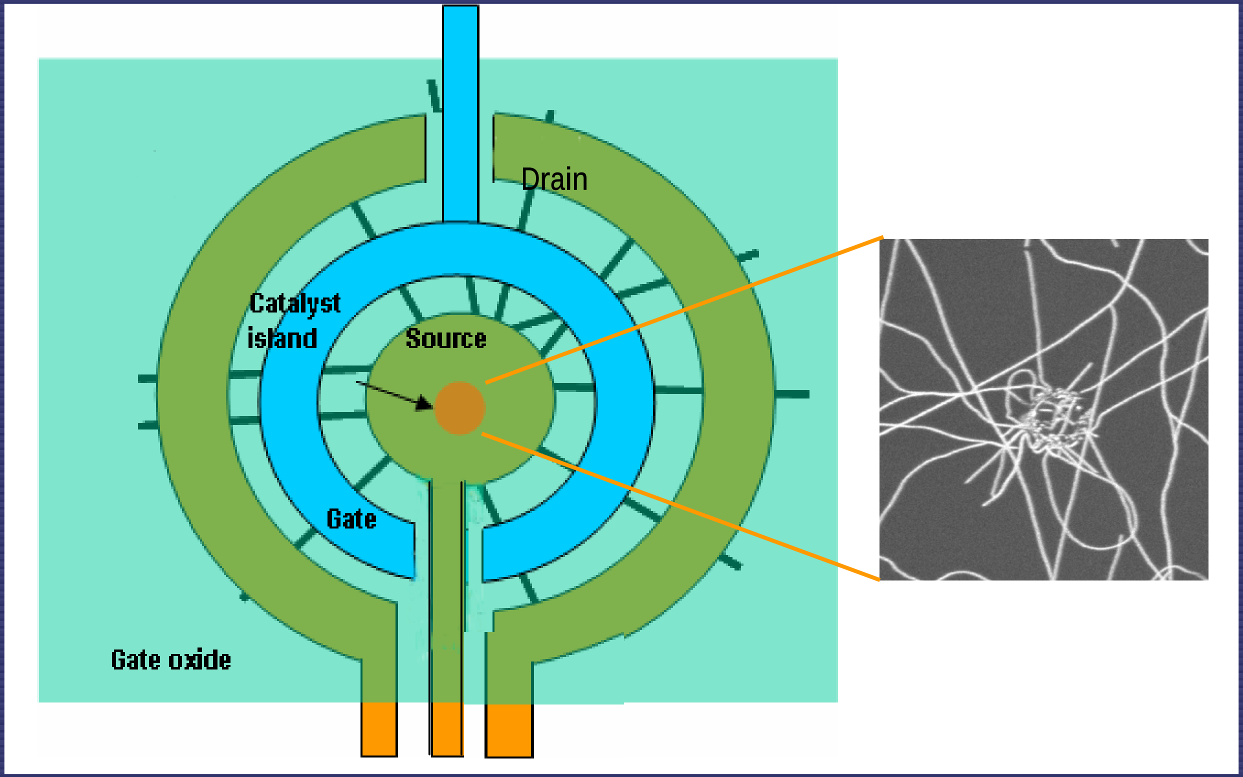
electrical contact is a random event! not manufacturable process!



Variations in **Channel length** / **Eg (diameter, chirality)** → **Unpredictable** / **Inconsistent** **Device performance**

- ✓"Mod3" tubes, tubes with n-m=3i(i=integer) are small gap semiconductor with $E_g \sim 1/d^2$
- ✓ All other tubes are moderate gap semiconductor with $E_g \sim 1/d$

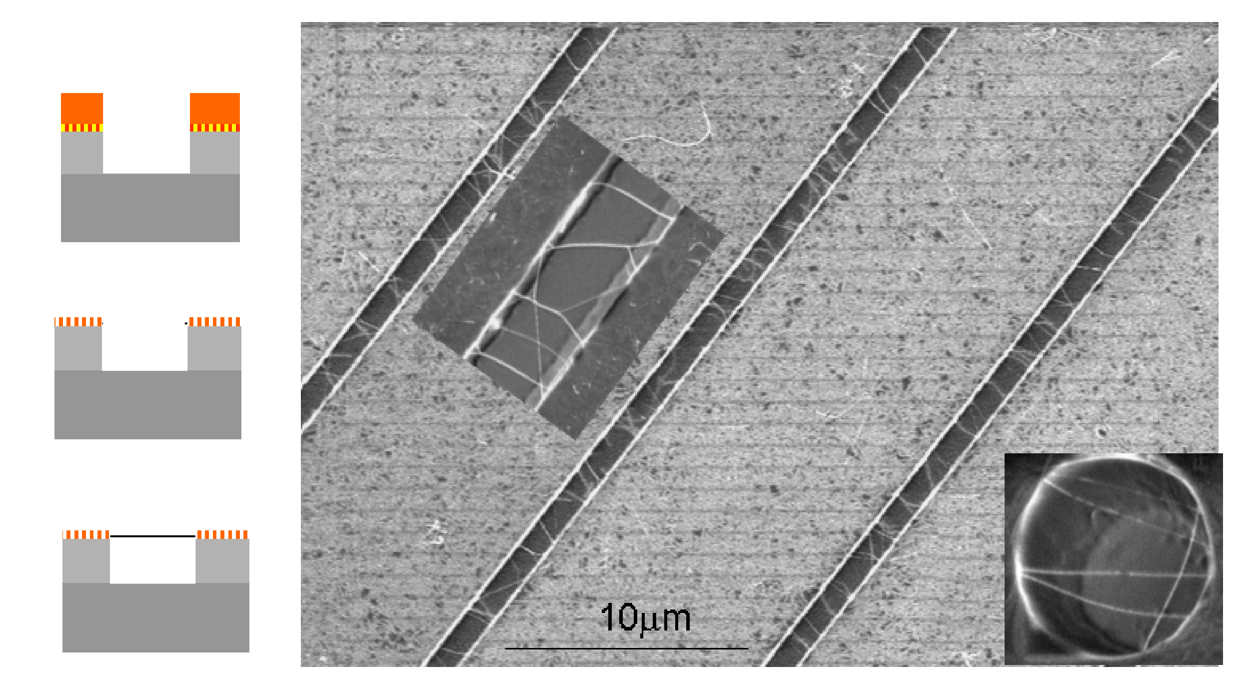
Circular Transistor Design



- Weighted average of many tubes ⟶ **Greatly improve consistency and predictability**
- Increase current carrying capacity and g_m

Alleviate requirements
- Diameter and chiral arrangement
- Orientation
- Length

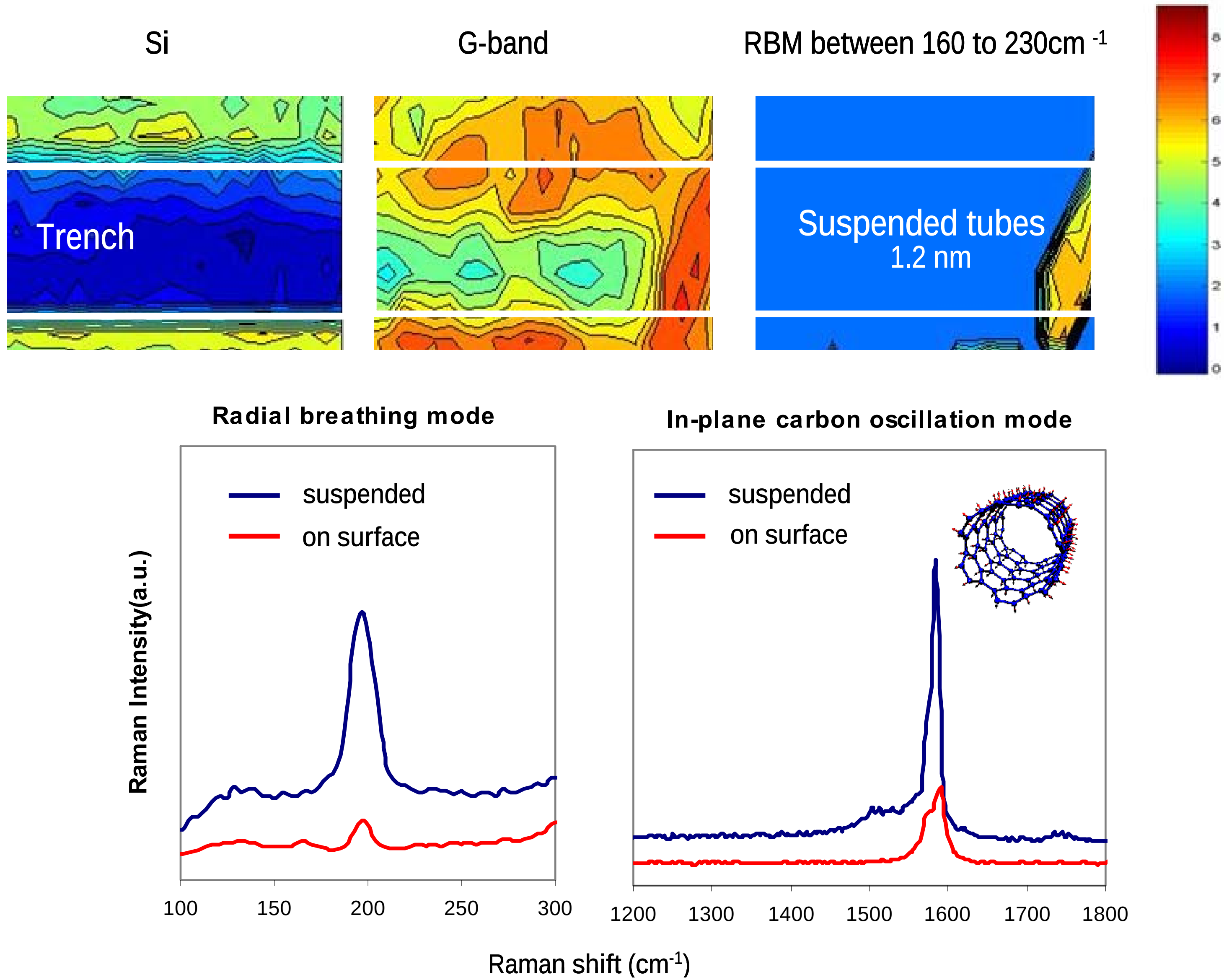
Selective Growth of Suspended CNTs



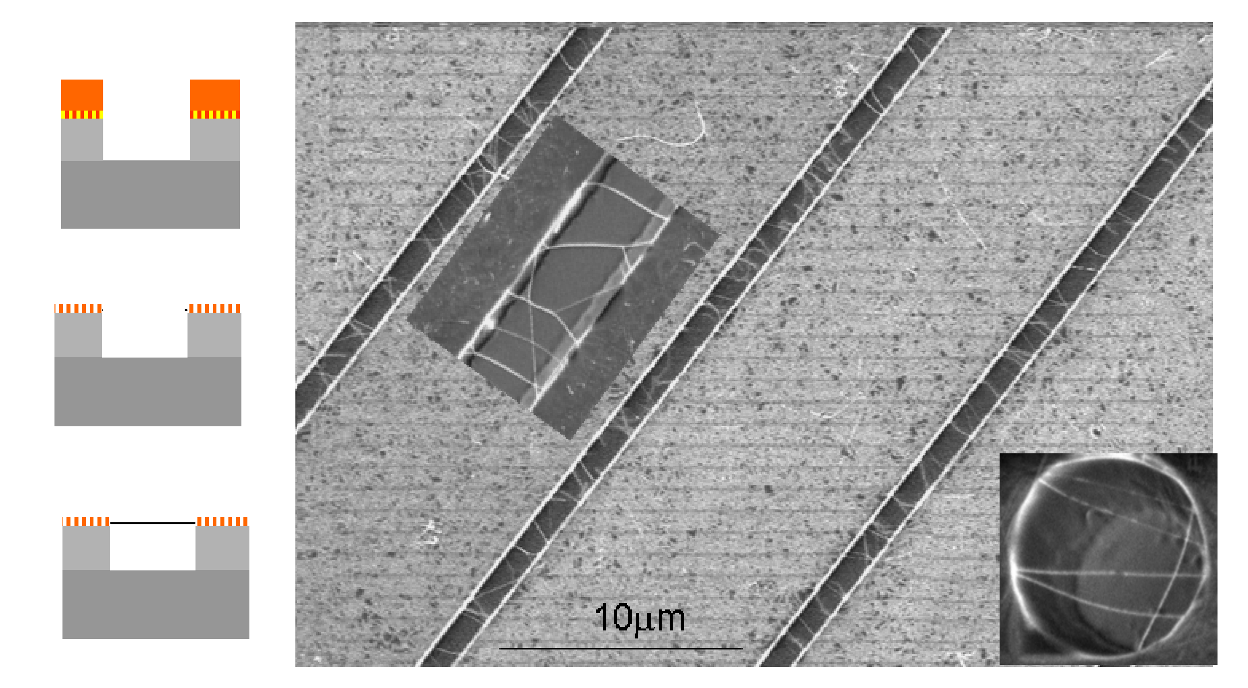
Suspended tubes are free of interaction with underlying substrates

Characterize CNTs by optical means

Raman Characterization



Selective Growth of Suspended CNTs



Suspended tubes are free of interaction with underlying substrates

- Characterize CNTs by optical means
- Ideal p-n junction diode (GE)
- Greatly enhanced IR emission (IBM)

Nanoelectromechnical applications

- Ultra-sensitive Mechanical Sensor
  - Mechanical perturbation induces change in resistance
- Nano-mechanical Switch
  - CNTs mechanically deflected to establish electrical contact
- Nano-oscillator

Block copolymer → controllable synthesis suspended CNTs → facilitate device applications

Summary: Thin film self-assembled
Ferrocenylsilane-based Block Copolymers

- Iron-containing nanostructures with precise control in size and spacing have been generated by this block template
- Uniformly distributed and high-quality CNT mats have been produced
- Selective growth of CNTs on a surface or in suspension has been demonstrated
- CNTs with diameters ~1 nm
- Few-walled, upright CNTs have been synthesized at 600ºC with excellent emission properties
- CNT's size and density can be adjusted by tailoring block lengths

For a given growth condition, the amount of dangling bonds varies with catalyst size.
To achieve defect-free CNTs with consistent properties,
it is essential to have uniform sized catalytically active nanostructures.

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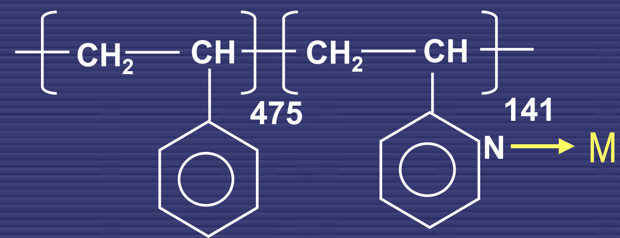
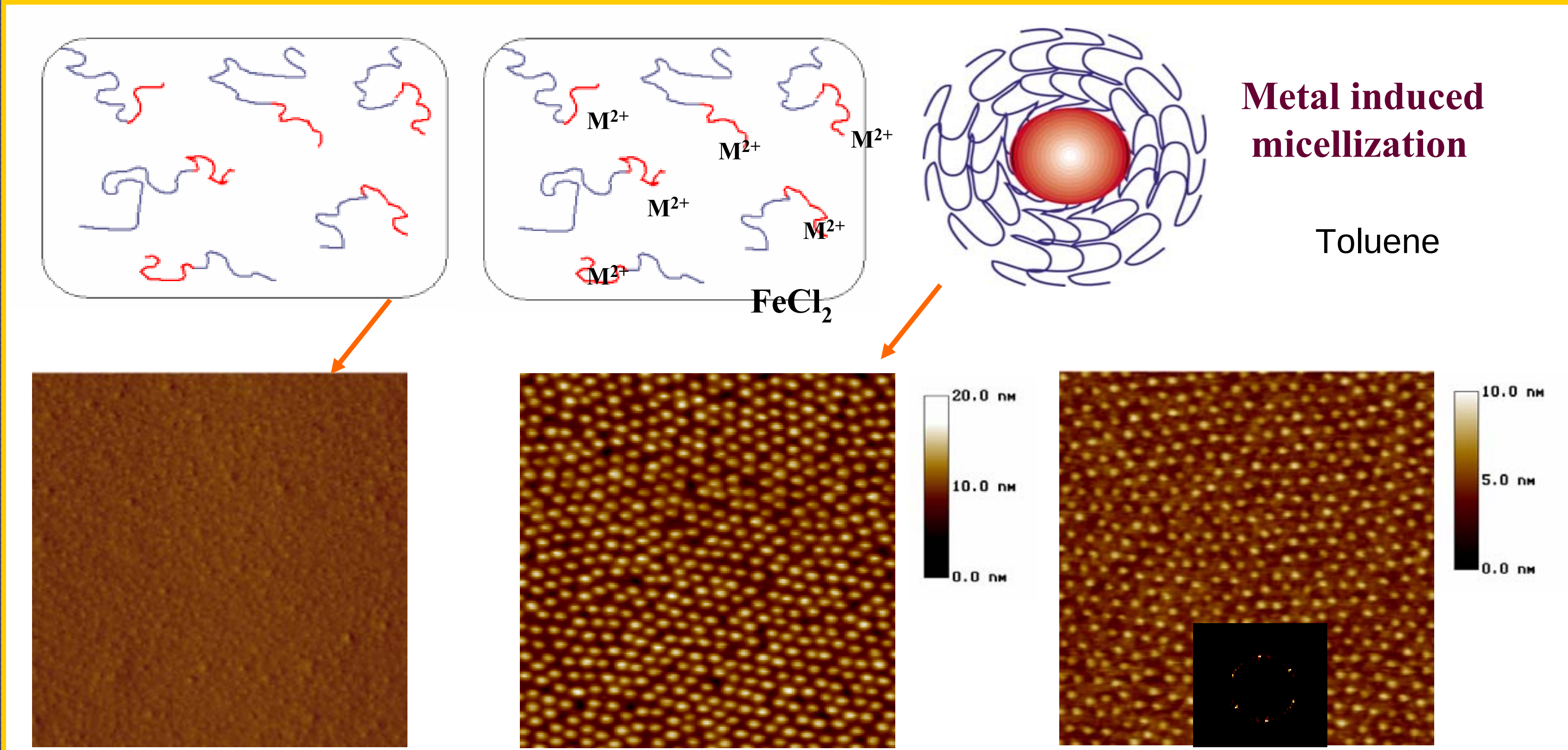
PS-b-P2VP:Metal-induced Micellization

PS -b-P2VP





No surface micelles ! PS-b-P2VP

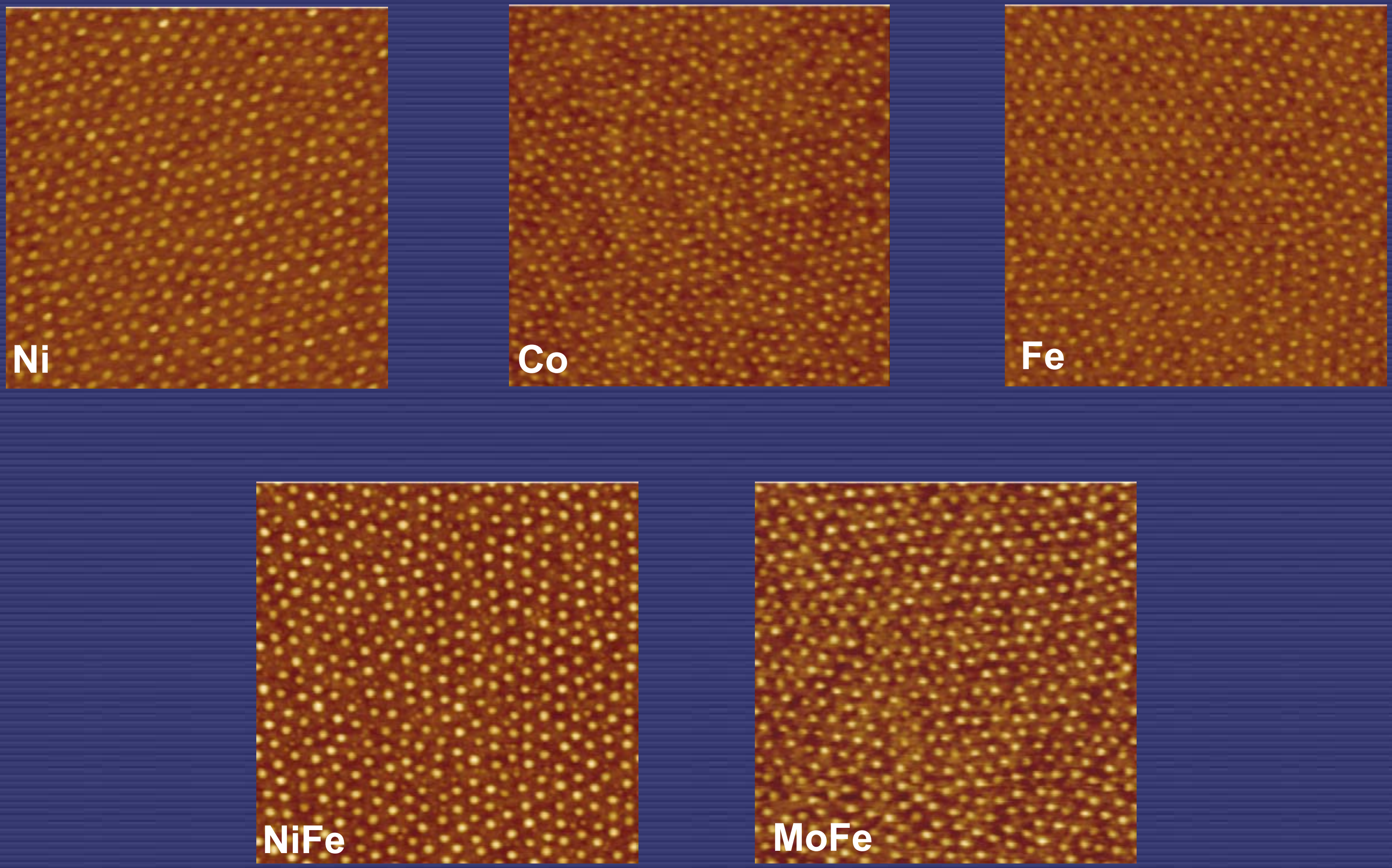
Surface micelles iron-complexed PS-b-P2VP

Iron nanoparticles

2 nm!

AFM height images
1 by 1μm scan

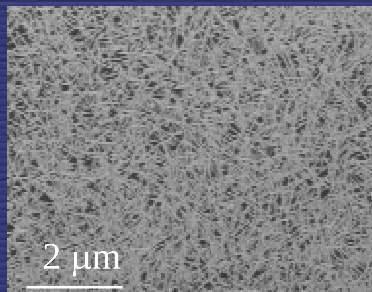
Solution Self-assembly: Various Metal Nanoparticles



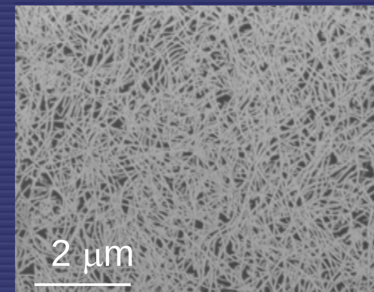
AFM height images:10 nm in Z scale, 1 by 1μm scan

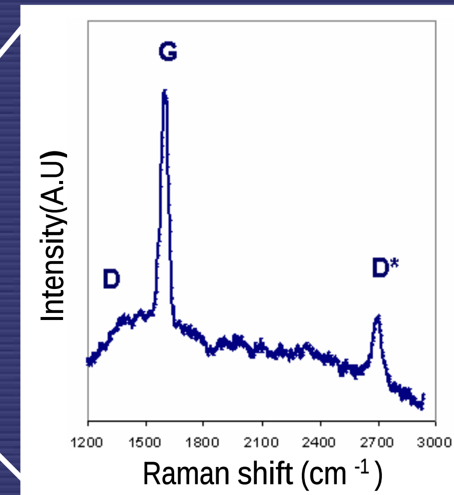
CNT Mats

Fe

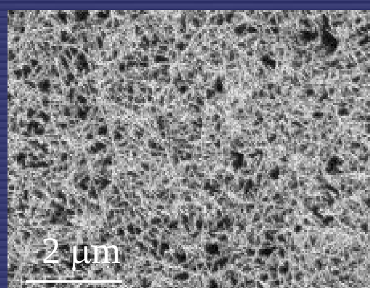


Co

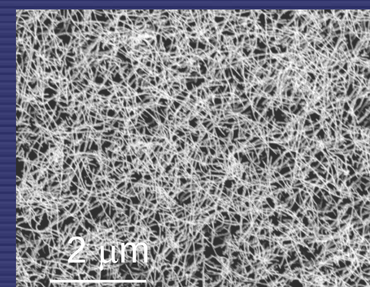




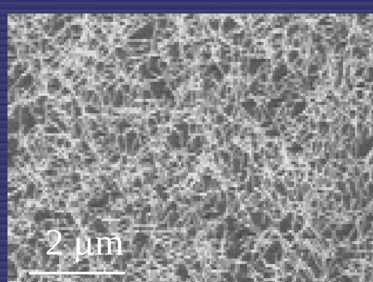
Fe/Mo=1:8



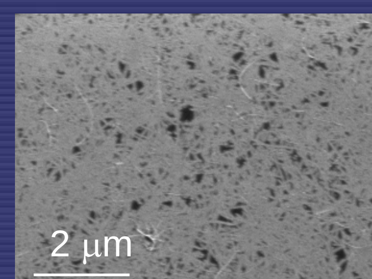
Co/Mo=1:3



Ni



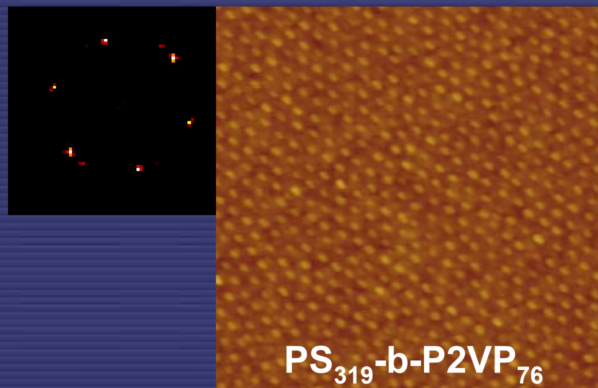
Fe/Ni



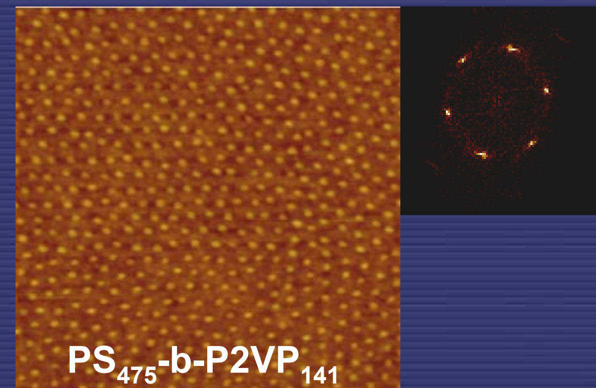
High quality CNTs and uniformity maintained over a large surface area

Growth mechanism: Effect of catalyst composition

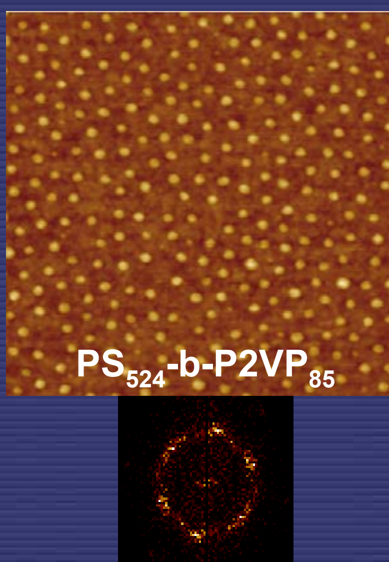
Tuning Size & Spacing



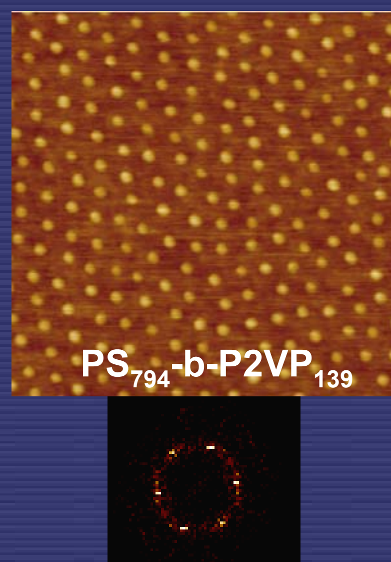
1.8 nm, 39 nm



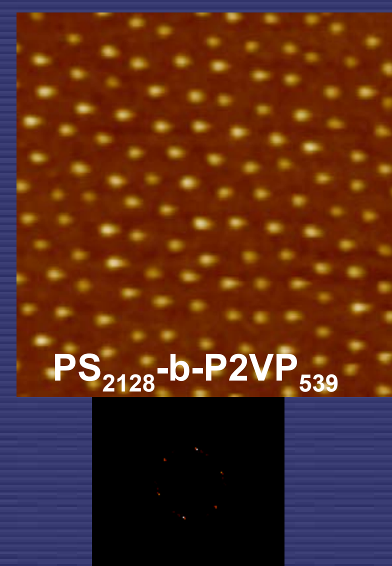
2.6nm, 45 nm



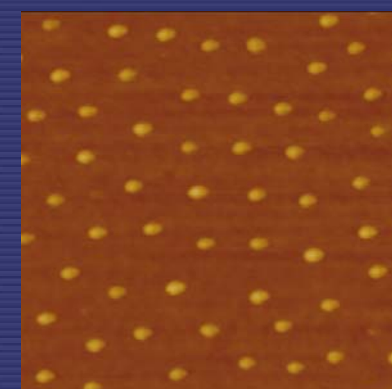
3.3 nm, 49 nm



4.2 nm, 70 nm



7.5 nm, 81 nm



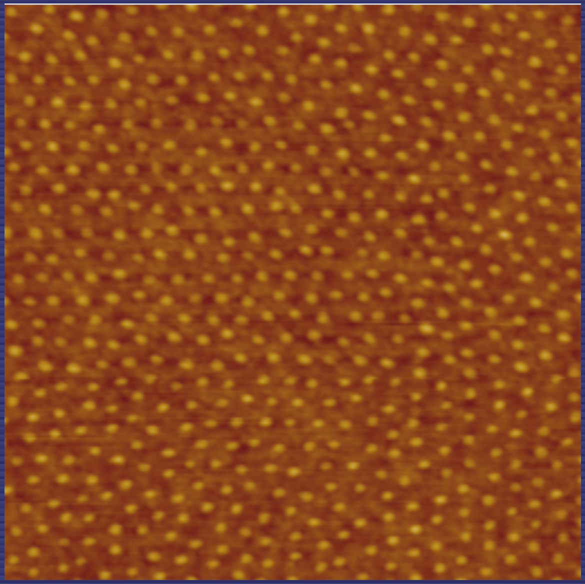
3.8 nm, 140 nm

AFM height images
1 by 1μm scan

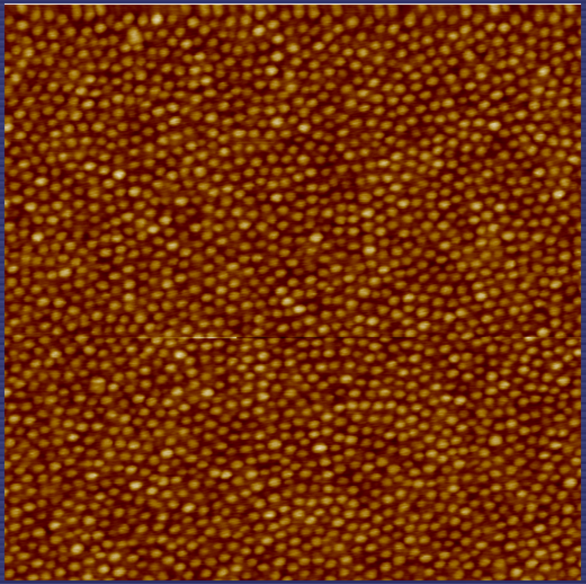
Size and spacing dictated by block lengths

Narrowing Spacing by Adjusting Solution Concentration

0.5 wt % PS_{475}-b-$P2VP_{141}$



1.0 wt % PS_{475}-b-$P2VP_{141}$



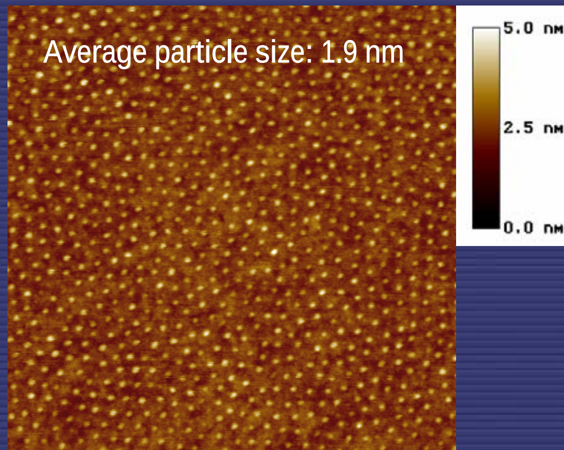
An array of closely packed cobalt nanoparticles to promote vertically oriented CNTs can be formed!

AFM height images
1 by 1μm scan

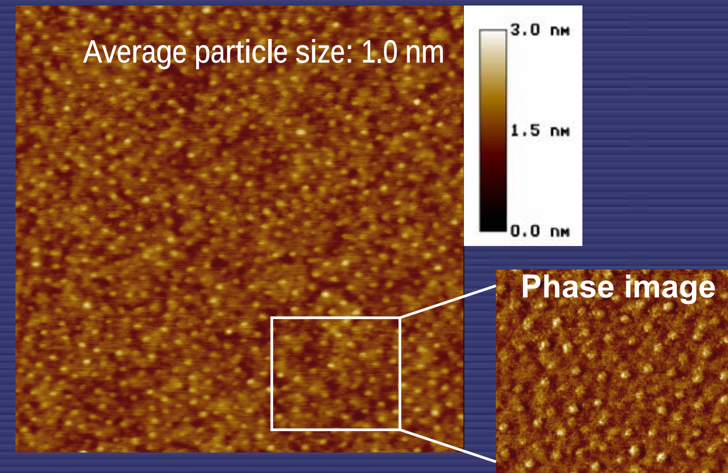
CNT Diameter Control

AFM height images
1 by 1μm scan
Iron nanoparticles

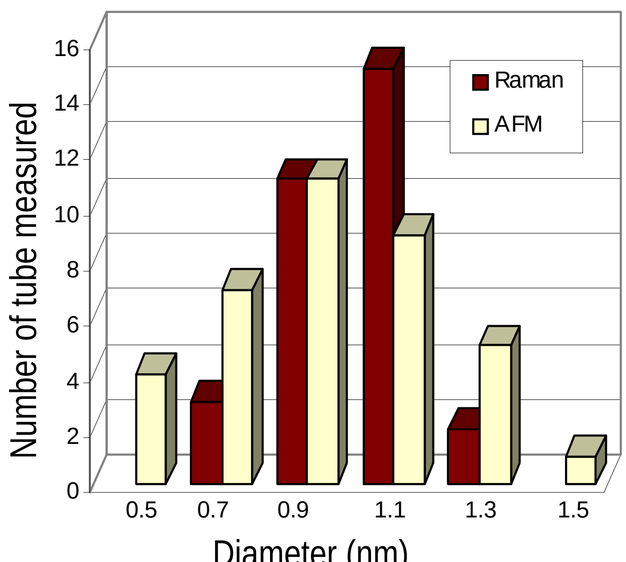
After UV-Ozonation



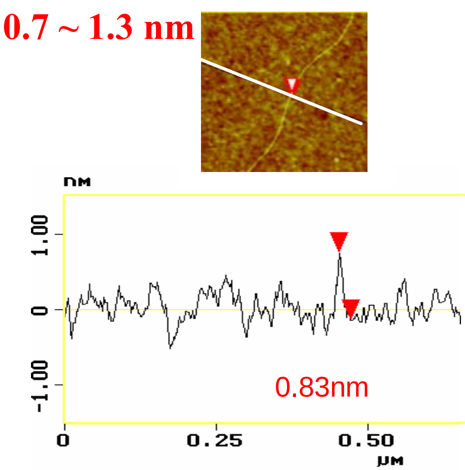
After thermal treatment (900°C/20min in H_2)



Catalyst nanoparticles do not agglomerate at high growth temperature

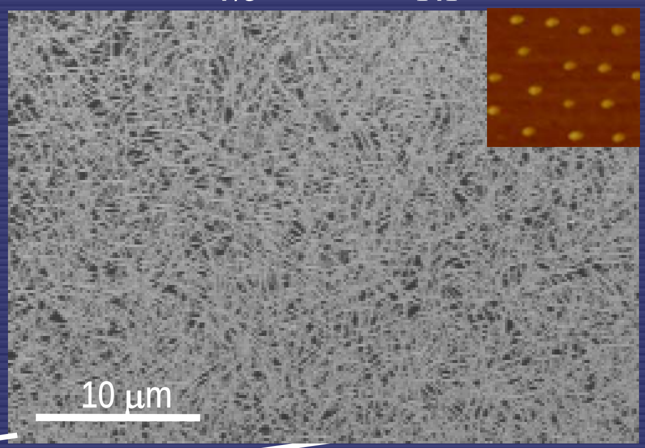


AFM: 0.5 ~ 1.5 nm
Raman: 0.7 ~ 1.3 nm

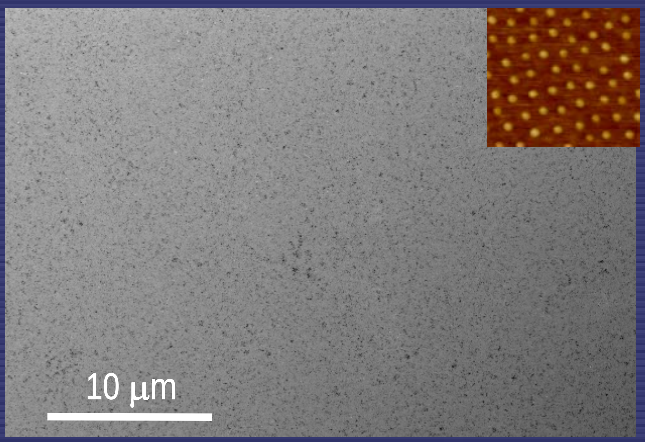


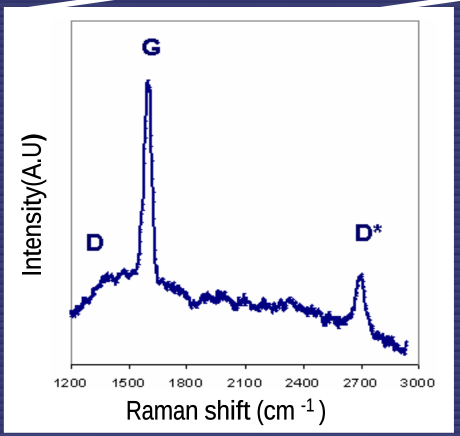
CNT 2D film

PS_{475}-b-$P2VP_{141}$



PS_{794}-b-$P2VP_{139}$





	Nanoparticle size (nm)	CNT diameter (nm)
PS_{475}-b-$P2VP_{141}$	2.2 (±0.1)	1.1(±0.4)
PS_{794}-b-$P2VP_{139}$	3.8 (±0.2)	1.7(±0.5)

Electronic signal: Average properties of the individual CNTs

Only density matters!

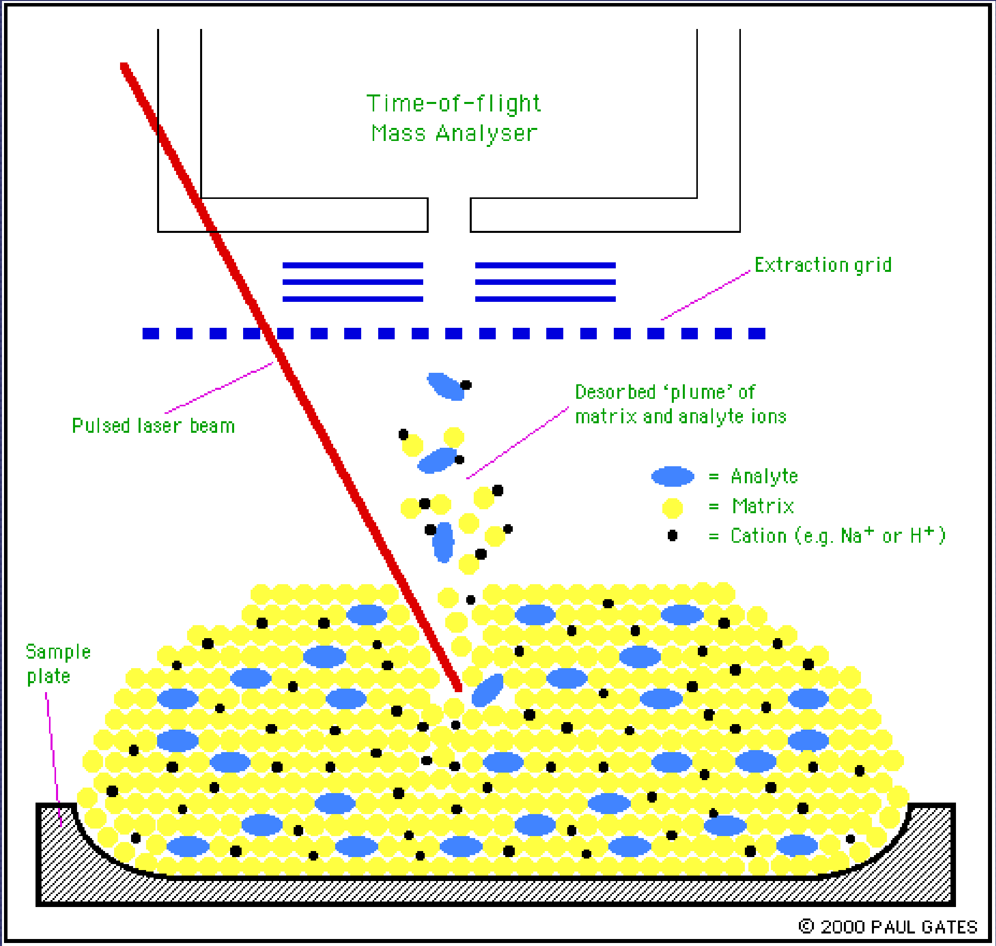
Controlled by the block copolymer approach

- **Thin-film transistor (high carrier mobility)**
- **Sensor**
- **MALDI-MS target**

MALDI-MS

MALDI(Matrix Assisted Laser Desorption and Ionization)

is a technique for ionization of large molecules for Mass Spectroscopic detection



Biopolymer is dissolved in a solvent

Matrix molecule is added (e.g. trans-cinnamic acid, 10,000 times more than biopolymer).

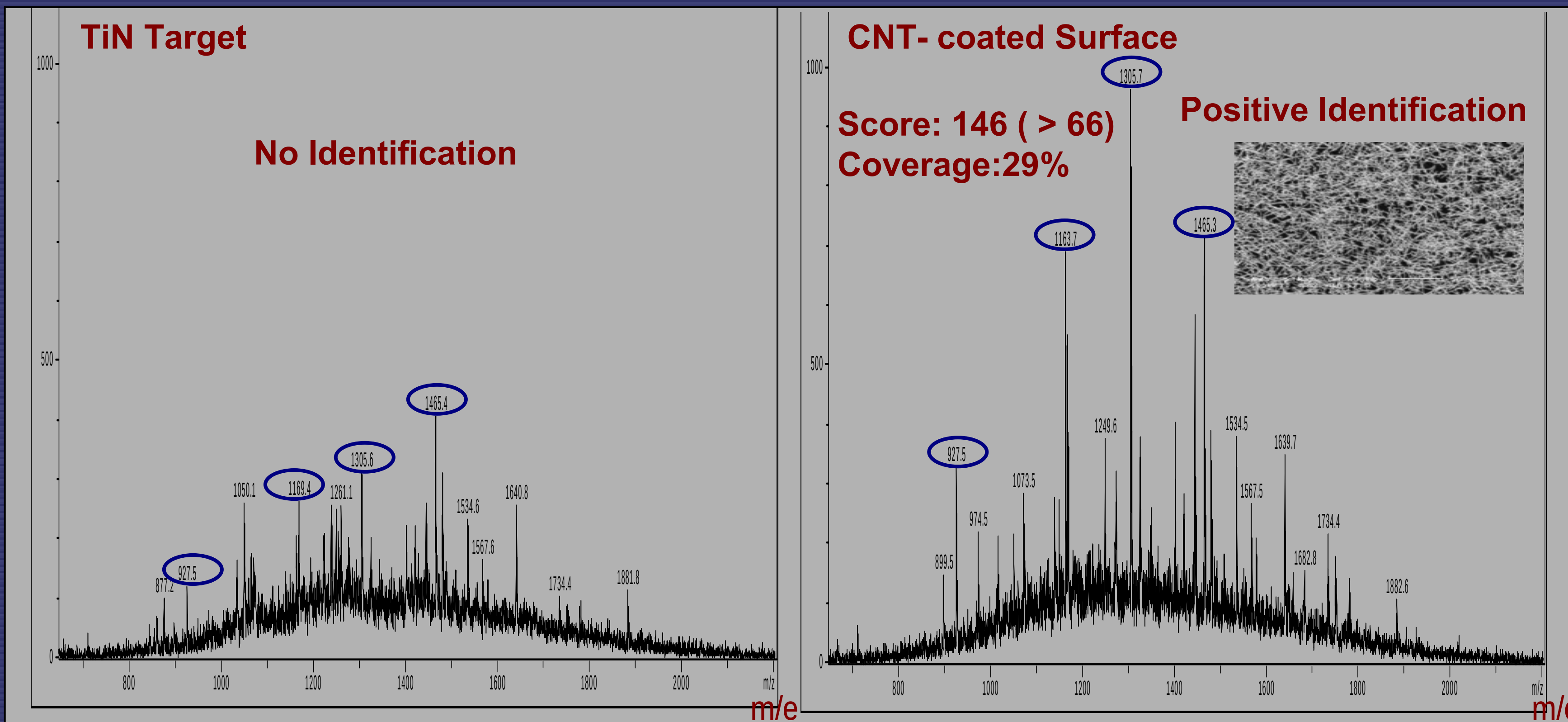
UV-Laser causes the disintegration of matrix

Evaporation and ionization of biopolymers

Positively charged fragmented ions are accelerated and detected

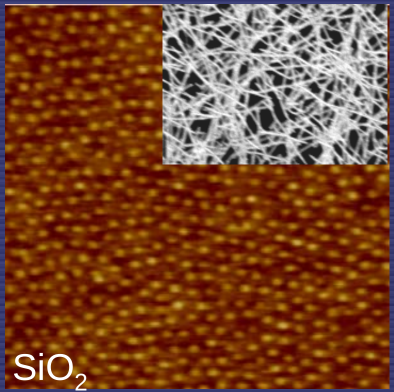
Carbon Nanotube Coated Surface as MALDI Target

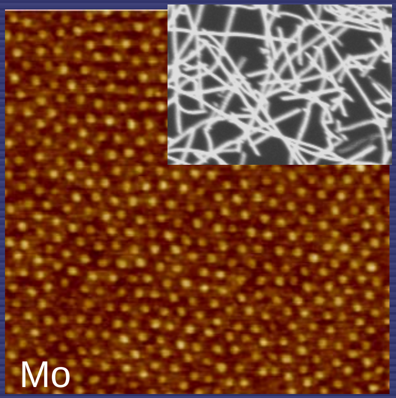
500 attomoles BSA (bovine serum albumin) in 0.25 mg/mL CHCA matrix

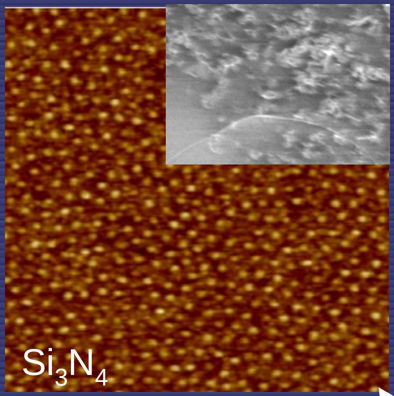


<u>**Able to identify 500 attomoles of bovine serum albumin using CNT surfaces**</u>

Catalyst Support







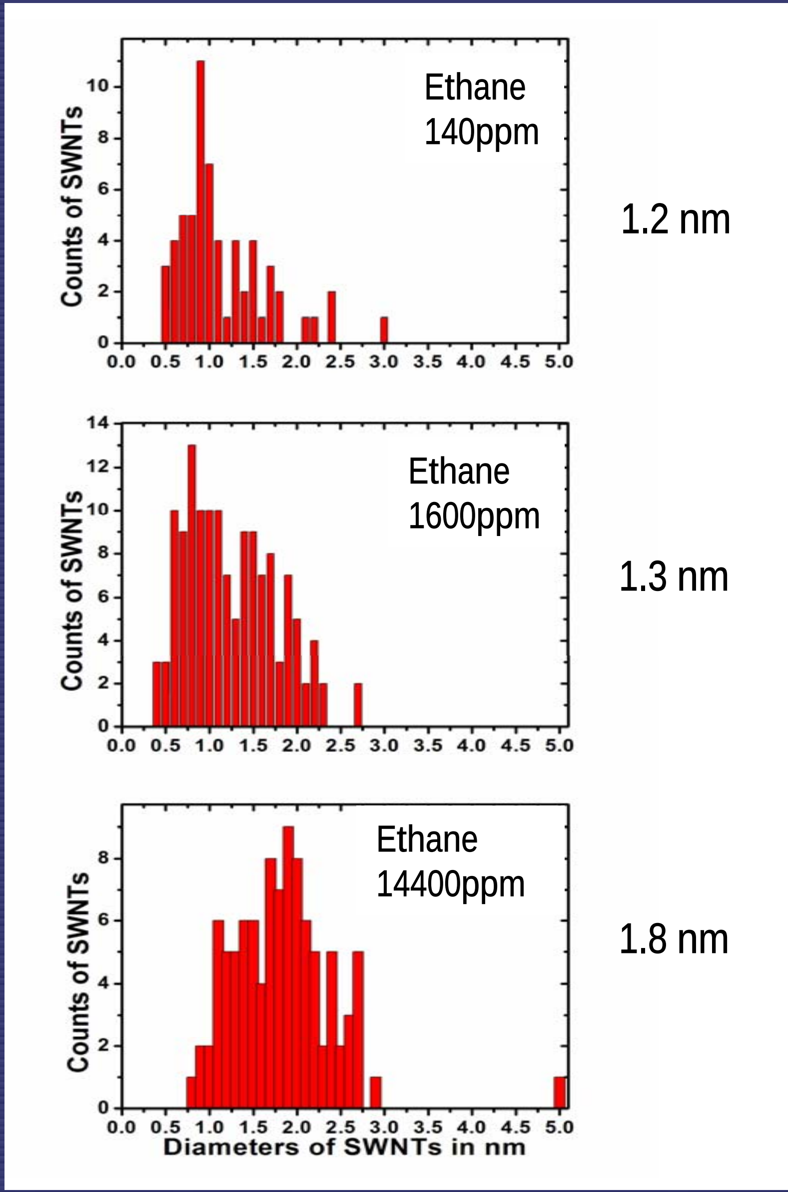
Fail to reduce to 0

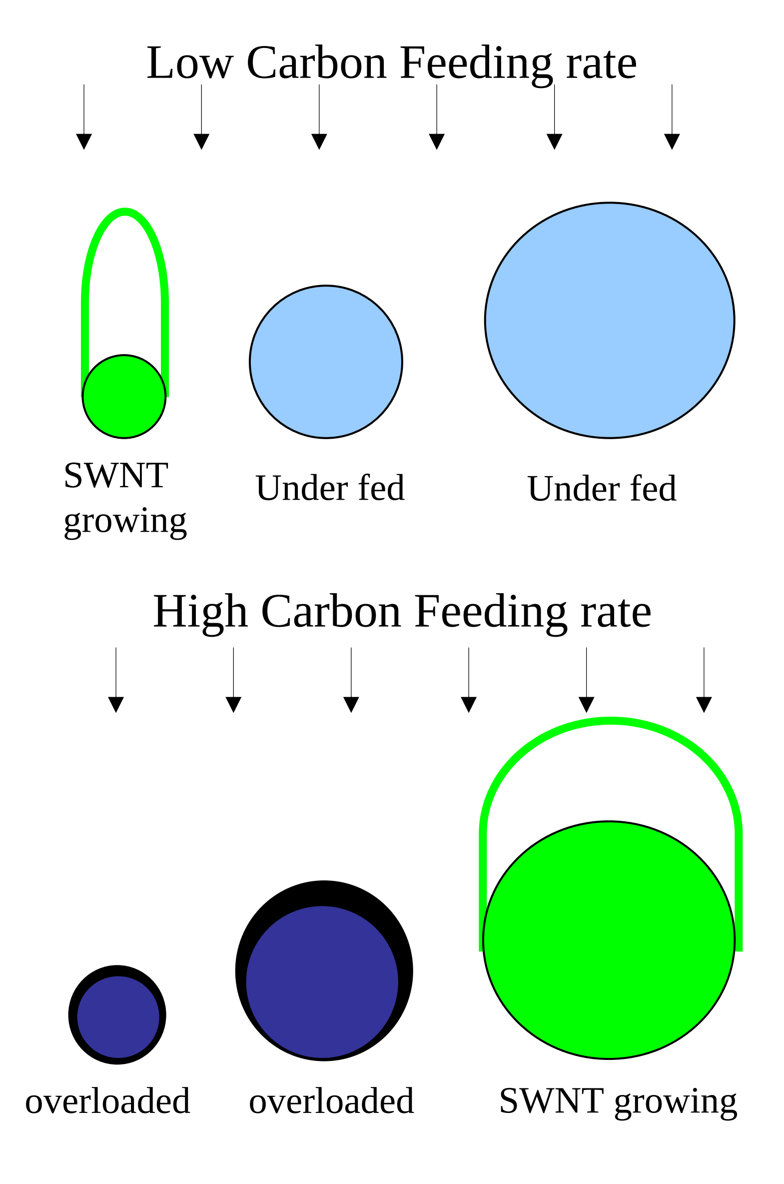
	SiO_2	Mo	Si_3N_4
CNT	dense, long, small	sparse, short , large	No CNTs
Fe Before growth	0.53% (+3)	0.56% (+3)	0.52% (+3)
Fe After growth	0.21% (0)	<0.1%(0)	<0.1%(+2, +3)

Fe nanoparticles adhere poorly on Mo and Si_3N_4 surfaces

Growth mechanism: Effect of catalyst support

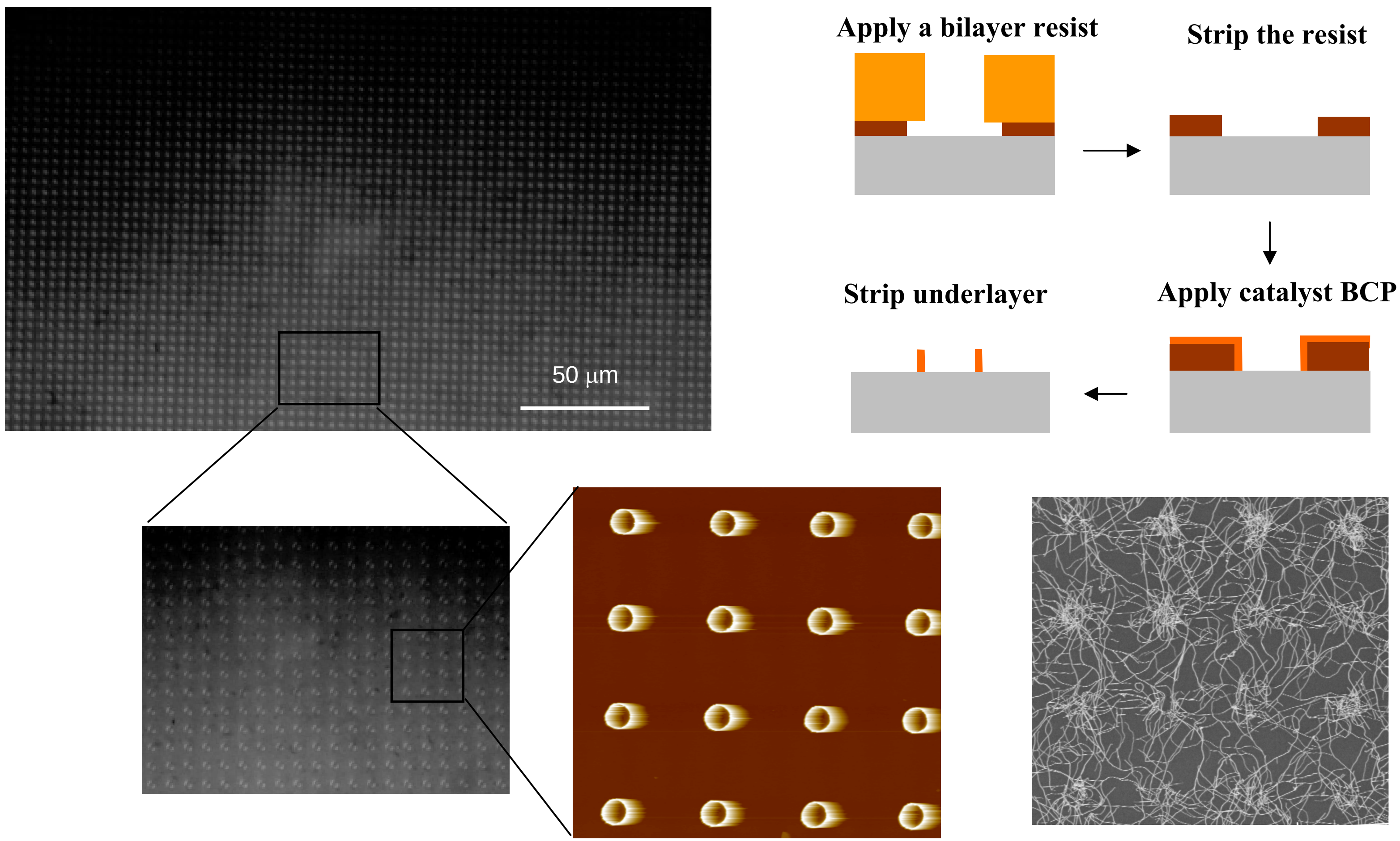
Growth Mechanism: Carbon feed rate





Collaboration with Duke

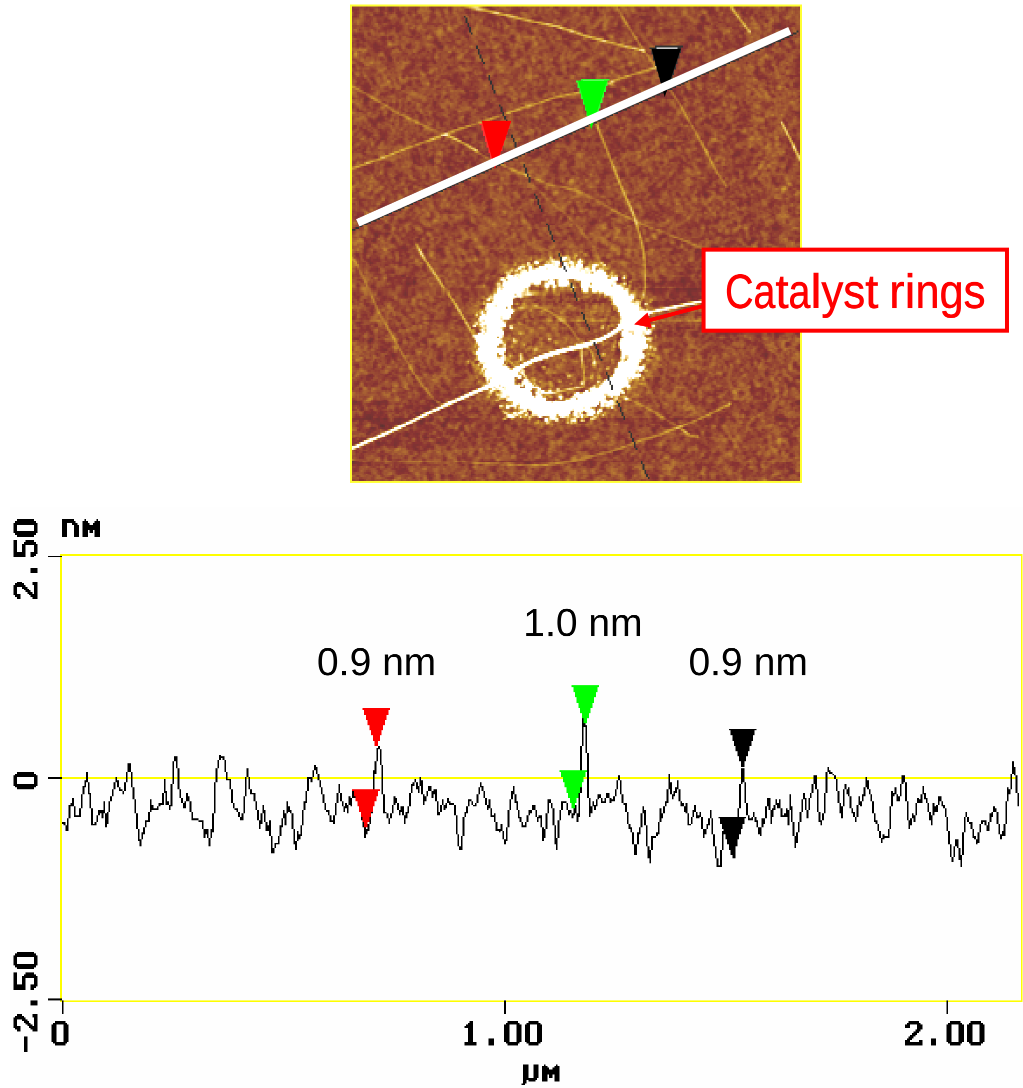
Lithographic Selective Growth



Patterned PS-b-CoPVP

Selective growth of CNTs over a large surface area!

CNT Growth Results



Electrical Test Results

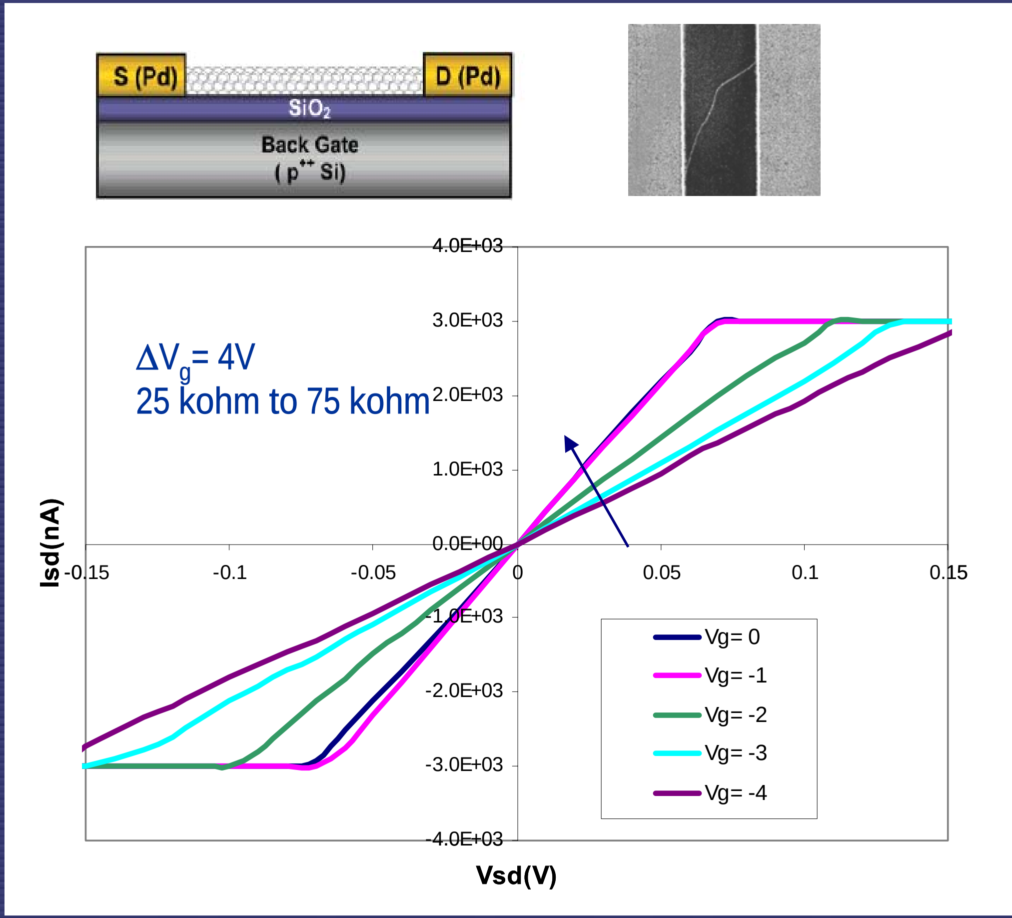
Optical lithography to define catalyst nanostructure arrays on a wafer format

↓

CNT growth

↓

Source and Drain



- Resistance is 30 kΩ at zero bias
- >7 μA pass through

→

- Decent tubes
- Good metal contact

3 inch process! However, tube density is extremely low!

Wafer level processing for fabricating CNT- based electronics

Summary: Solution Self-assembled
PS-b-PVP Micelles

- Highly ordered nanoparticles with tunable composition, size and spacing on various surfaces can be produced
- Uniformly distributed and high-quality CNT mats have been obtained
- CNTs with diameters ~ 1 nm have been synthesized using Co nanoparticles
- Selective growth of CNTs on a surface or in suspension has been demonstrated
- Wafer–level fabrication of CNT-based electronic devices has been established

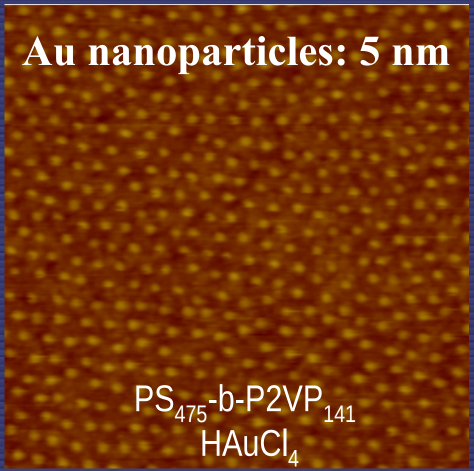
Provide an opportunity of studying the growth mechanism

Catalyst composition

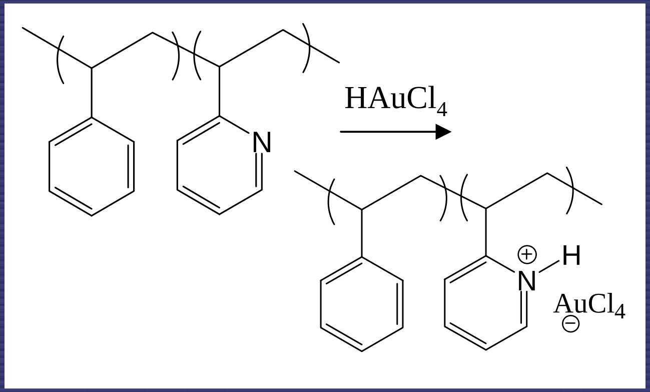
Catalyst support

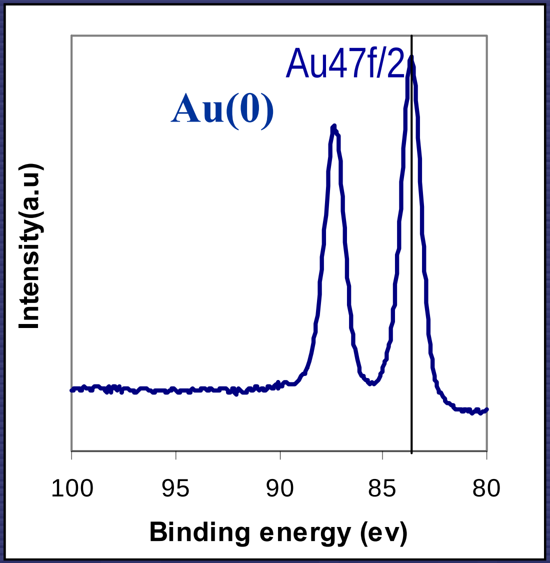
Carbon stock feed rate

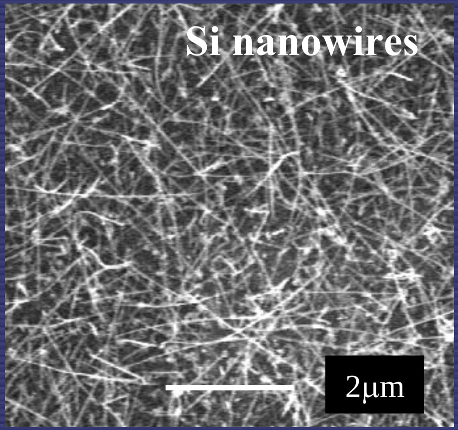
Silicon Nanowires from Au Nanoparticles

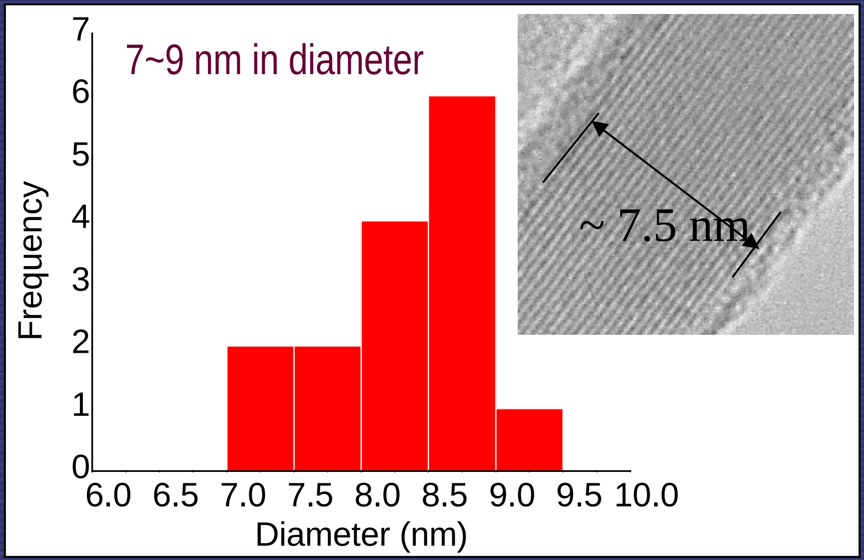


AFM height images
1 by 1μm scan, 10 nm in height









(20~80 nm from catalyst breaking up 1 nm Au thin film)

Outline

- Background: Block copolymers

- Iron-containing nanostructures for CNT growth

  Thin film self-assembled iron-containing block copolymers

- Catalytically active transition nanoparticles for CNT and Si nanowire growth

  Solution self-assembled metal modified block copolymers

- Conclusion

Important Attribute of Block Copolymer Template

Nano

Size and Spacing: Mw of each segment

Number of metal atoms incorporated onto a polymer chain

Micro and sub-micro

Lithography

Macro

Superior film forming capability

serves as a carrier to uniformly distribute nanostructures across a wafer

Ability to control at nano-, micro- and macro-scales simultaneously

→ **Controllable synthesis of 1D nanostructures on a wafer format**

Fully compatible with existing semiconductor processes

Conclusion

Thin film self-assembly
Ferrocenylsilane-based diblock copolymer

Solution self-assembly
Various metal-complexed PS-b-PVP

} Metal-containing nanostructures with controllable and tunable size, spacing and composition

CNTs and Si nanowires: uniform density, narrow diameter distribution, spatially controlled

Predictable and reproducible nanofabrication method

Applications: Transistor, Display, MALDI-MS targets, NEMS

Understanding growth mechanism:
- Catalyst size
- Catalyst support
- Carbon stock feeding rate

Current Collaborators

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David Rider

MIT

Prof. Mildred Dresselhaus

Hyungbin Son

Duke University

Prof. Jie Liu

Chen Qian

University of North Carolina at Chapel Hill

Prof. Otto Zhou

Eric Peng

Bristol University

Prof. Ian Manners

Thanks you!