

北京大學



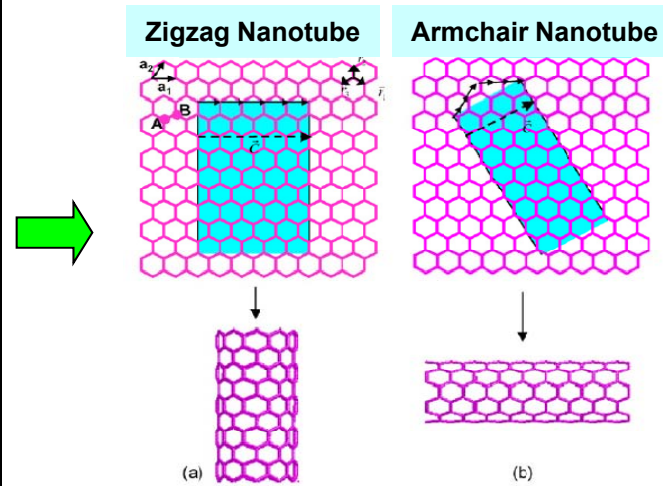
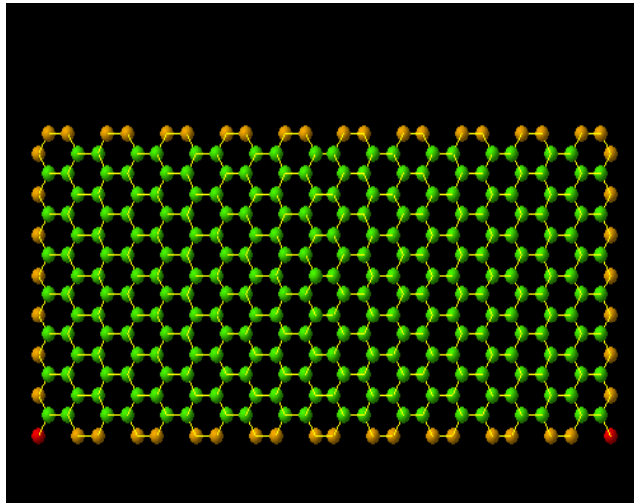
Growth of Single-Walled Carbon Nanotubes on Surface with Controlled Structures

Prof. Jin ZHANG

Center for nanochemistry
College of Chemistry and Molecular Engineering
Peking University, Beijing 100871, P. R. CHINA
Email: jinzhang@pku.edu.cn

The University of Tokyo, 1st Nov, 2010, Tokyo

Introduction of Single-walled Carbon Nanotubes

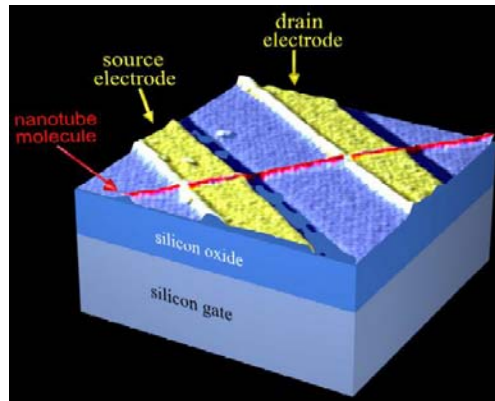


$$C_n = na_1 + ma_2 \equiv (n,m)$$

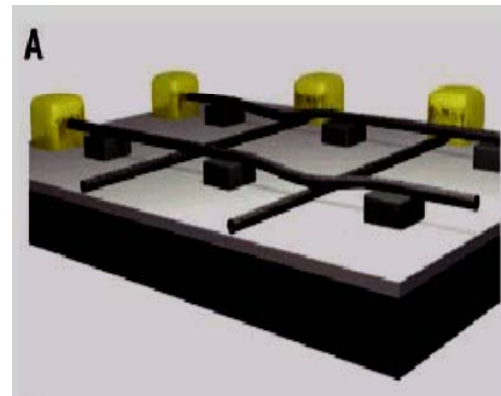
$$d_t = \sqrt{3}a_{C-C}(n^2 + m^2 + nm)^{1/2} / \pi$$

$$\theta = \tan^{-1}\left(\frac{\sqrt{3}m}{2n+m}\right)$$

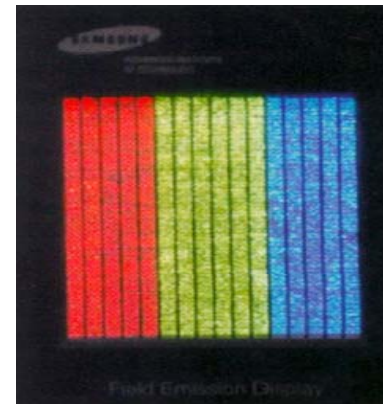
$$n - m = \begin{cases} 3p & \text{metal} \\ 3p \pm 1 & \text{semiconductor} \end{cases}$$



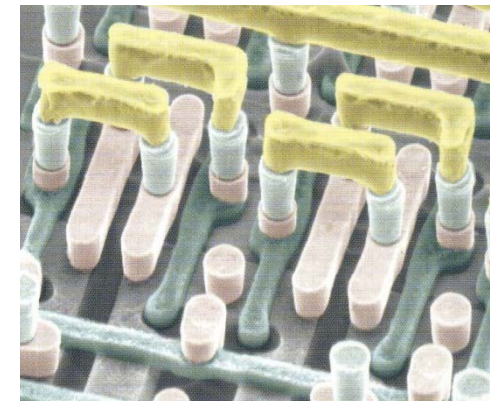
Nanotube transistor



Nanotube RAM

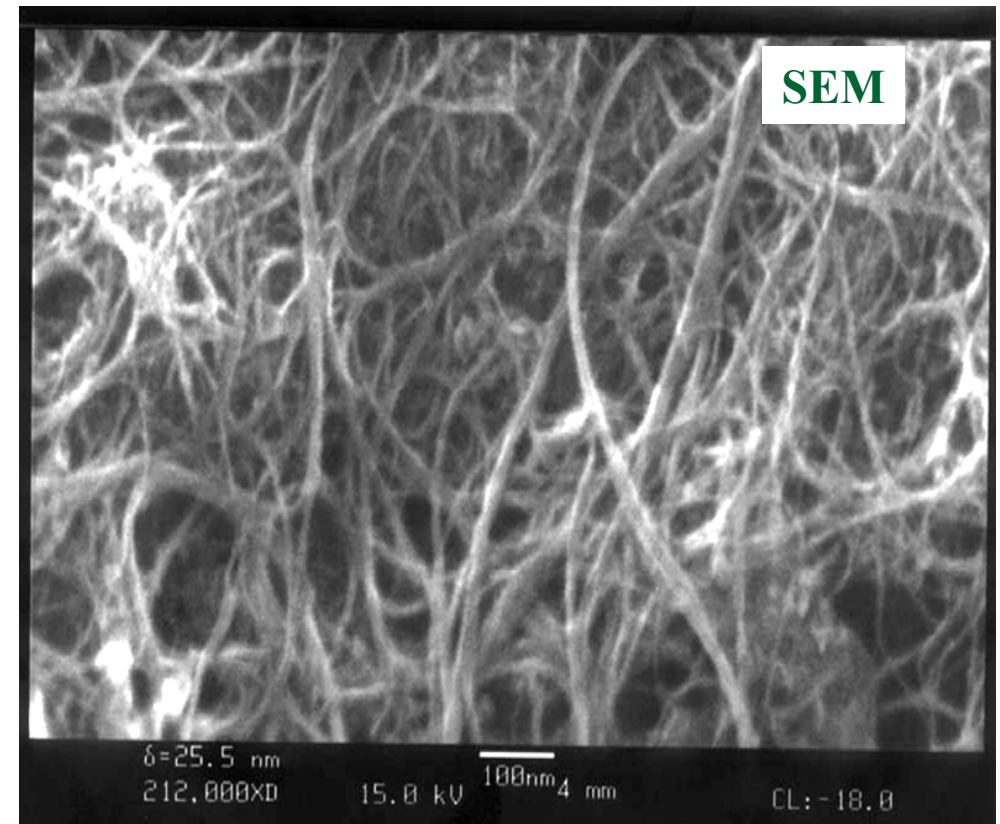
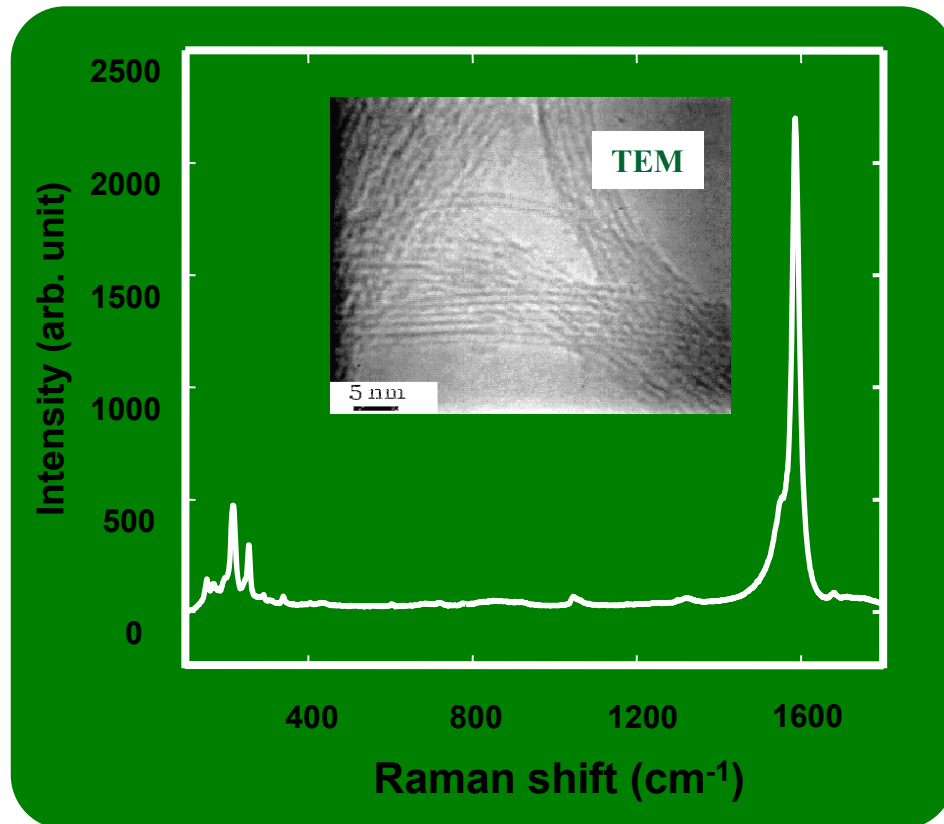


Flat panel display



Nanotube interconnect

A Scalable CVD Synthesis of High-Purity SWNTs with Porous MgO as Support Materials

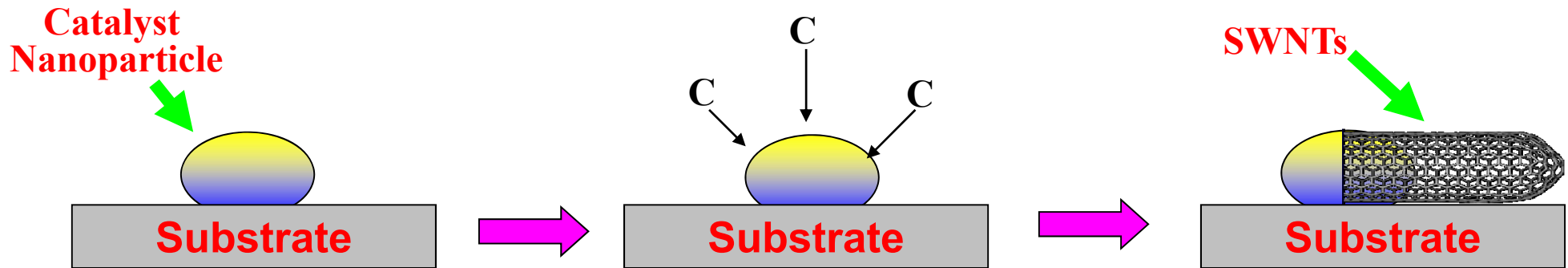


Support: MgO; Catalysts: Fe; Carbon Source: CH₄

J. Zhang et. al. , J Mater Chem, 12(4): 1179-1183, 2002; Carbon, 40(12): 2282-2284, 2002; Carbon, 40(14): 2693-2698, 2002

Surface Growth of SWNTs by CVD

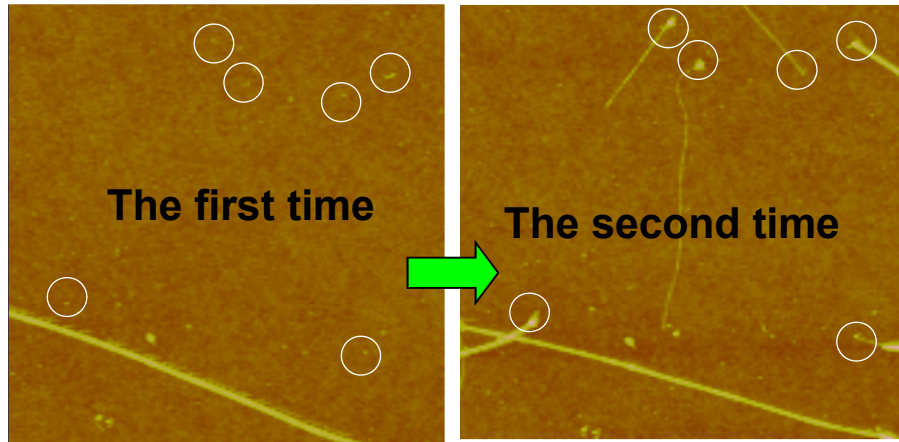
Growth Process:



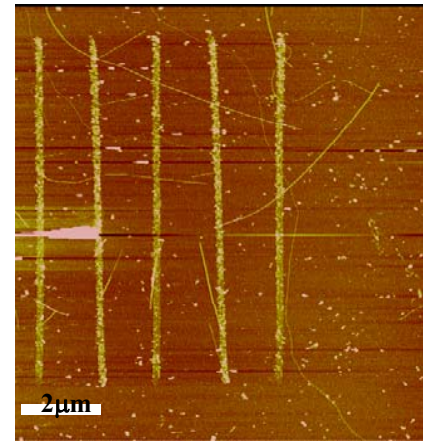
Questions:

1. Growing SWNTs on Surface Directly with Controlled Density, Position and Orientation
2. Growing SWNTs on Surface with Controlled Diameter
3. Growing SWNTs on Surface with Controlled Metallic and Semi-conducting Properties
4. Growing SWNTs on Surface with Controlled Chirality

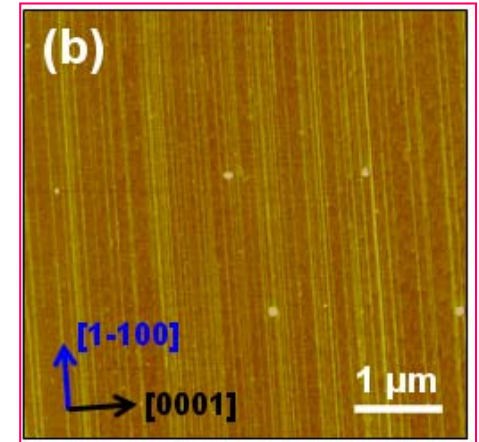
Controlled CVD Growth of SWNTs on Surface



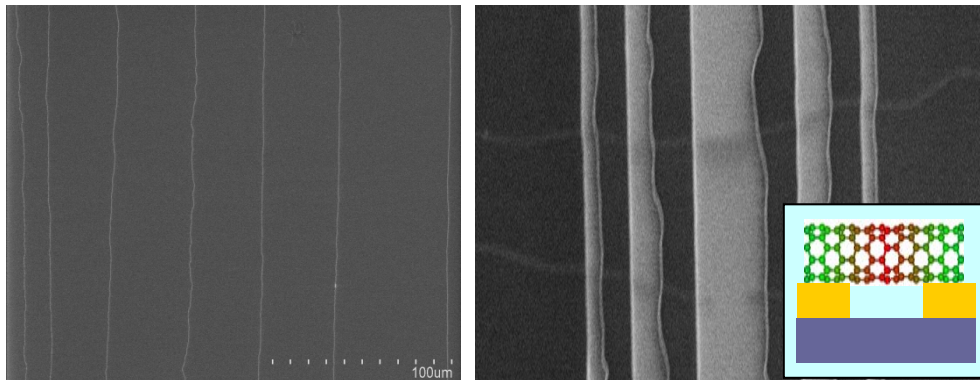
J. Phys. Chem. B. 2004, 108, 12665



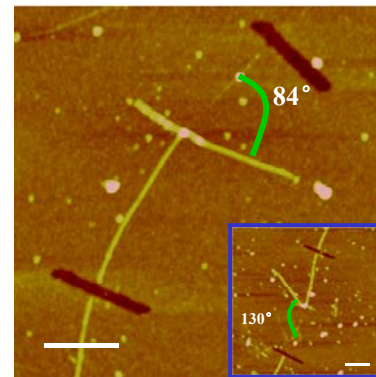
J. Phys. Chem. B, 2005, 109, 10946



J. Phys. Chem. C, 2008, 112, 8319

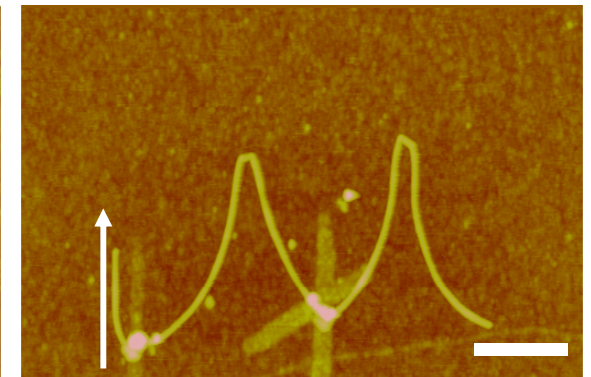


J. Am. Chem. Soc. 2005, 127, 17156



J. Am. Chem. Soc. 2005, 127, 8268.

J. Phys. Chem. B, 109 (2005) 2657-2665



Challenges for the Application of Carbon Nanotubes in Future Device

- 1) How to achieve a structure-controlled synthesis of nanotubes ?
 - Diameter
 - Lattice geometry (armchair, zigzag, chirality)
 - Semiconducting or Metallic Nanotubes

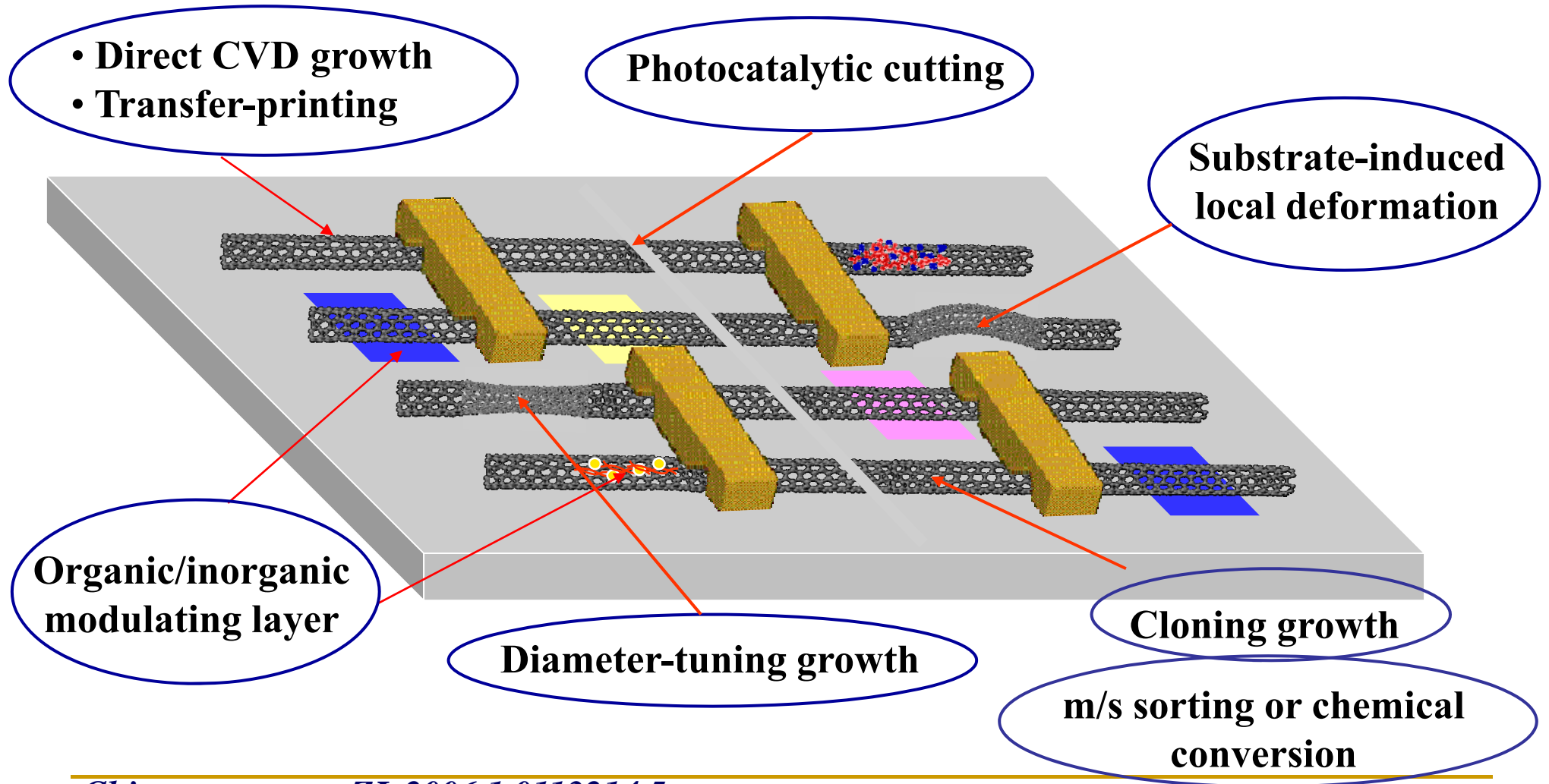
 - 2) How to fabricate a desired device structure ?
 - Controlled surface growth
 - Manipulation

 - 3) What architecture should the nanotube device have ?

 - 4) How to integrate trillions of individual nanotube devices ?
-

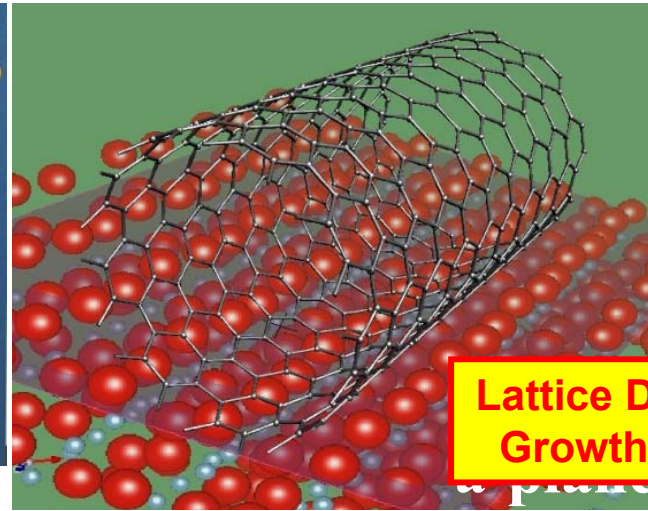
Our strategy towards SWNTs-based CMOS chips

— Axial Band Structure Engineering

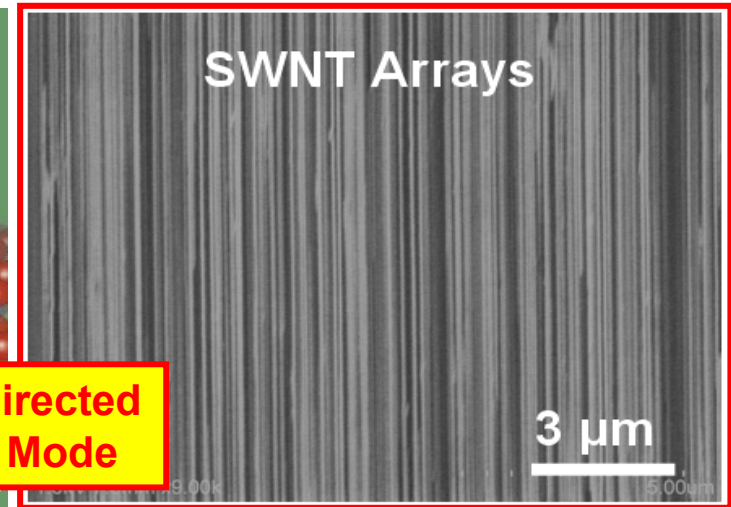


*Chinese patent : ZL 2006 1 0113214.5
ZL 2006 1 0113212.6*

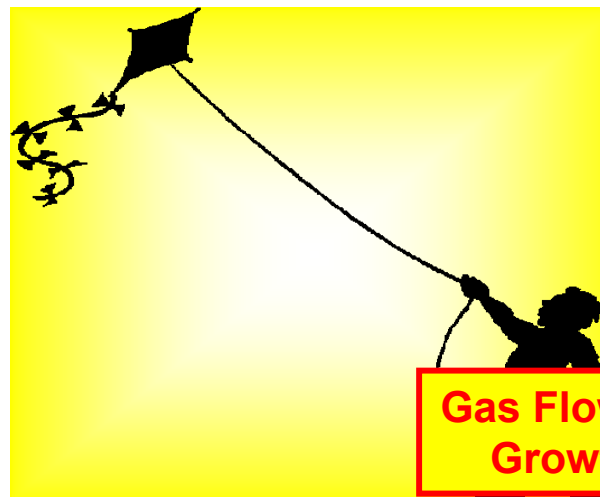
Catalytic CVD Growth of SWNTs Arrays on Surface



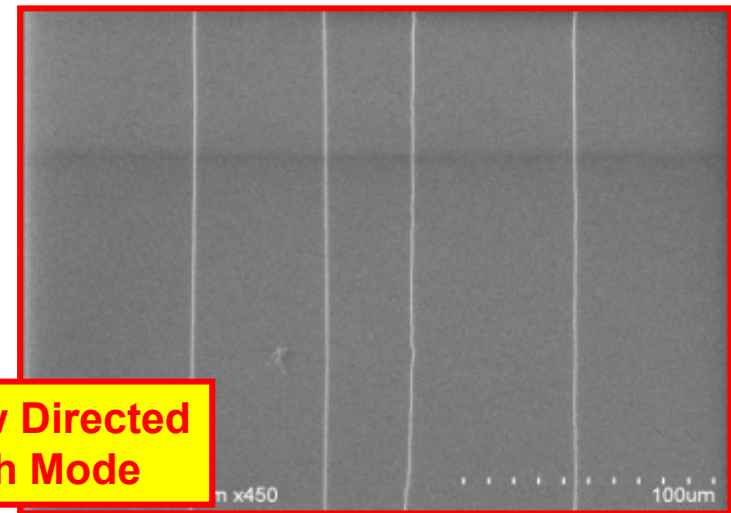
Lattice Directed Growth Mode



Carbon source : Methane, ethanol, etc
Substrate: Sapphire, quartz, SiO₂/Si, etc

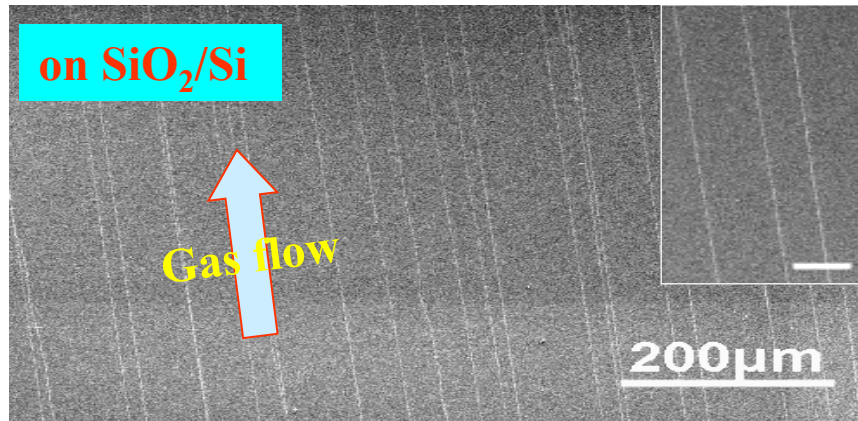


Gas Flow Directed Growth Mode

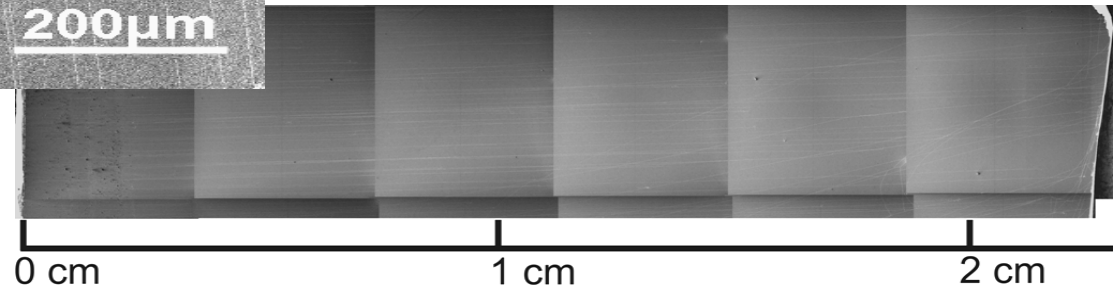


Lattice Directed Growth vs. Gas Flow Directed Growth

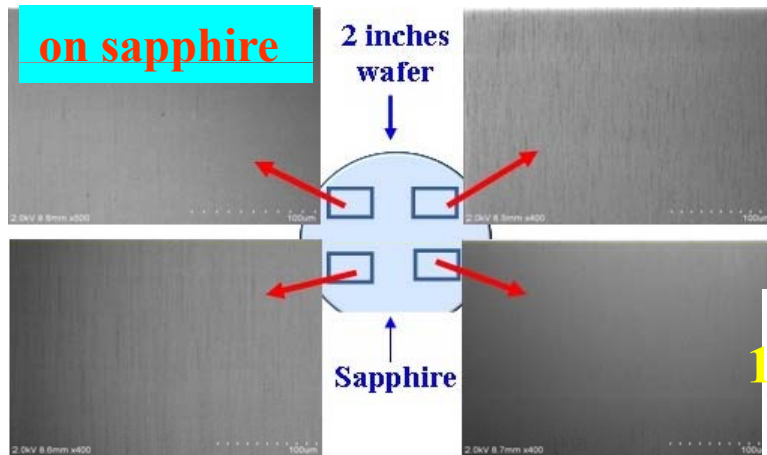
Gas flow directed
CVD growth



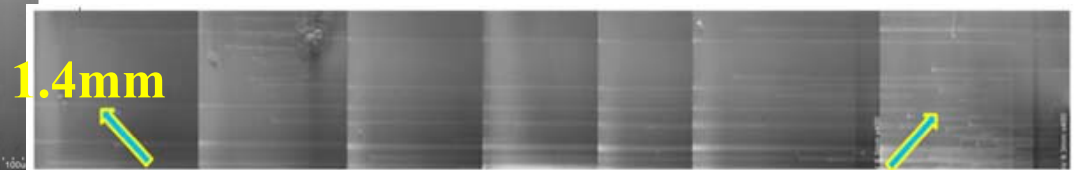
- ◆ Tube diameter: 1-2 nm
- ◆ Length: > 5 cm
- ◆ Spacing: 1-50 μm



Lattice oriented
CVD growth

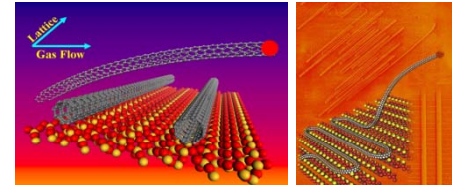


- ◆ Diameter: ca. 1 nm
- ◆ Length: ca. 1 mm
- ◆ Spacing: $\sim 0.2 \mu\text{m}$

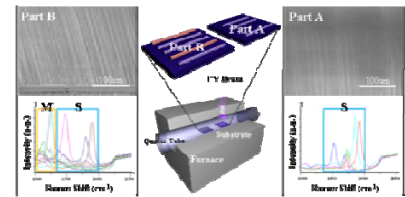


Outline

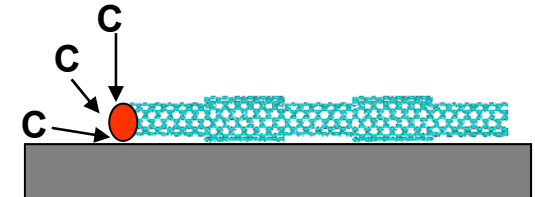
✓ Controlling Morphology of SWNTs on Surfaces



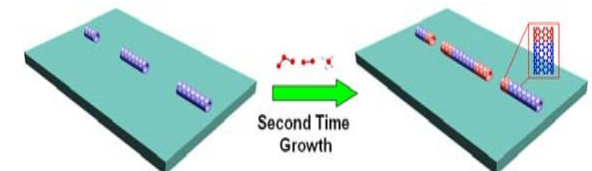
✓ Direct Growth of Semiconducting SWNT Arrays

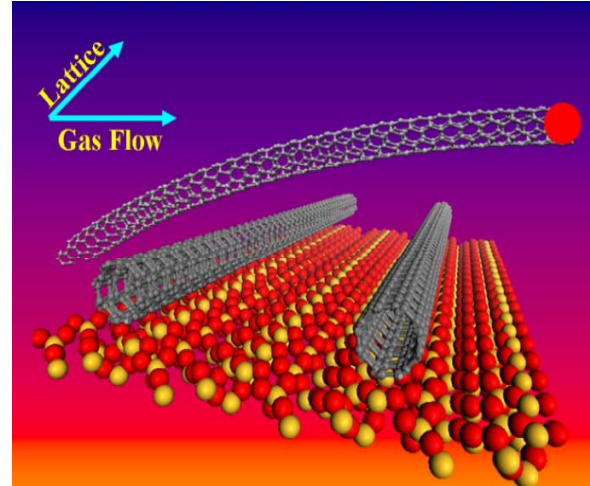
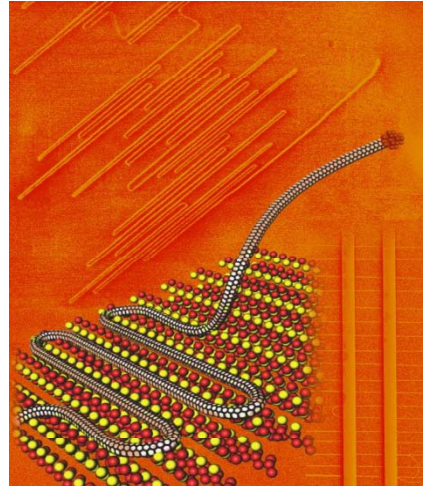


✓ Tuning Diameters of SWNTs by Temperature



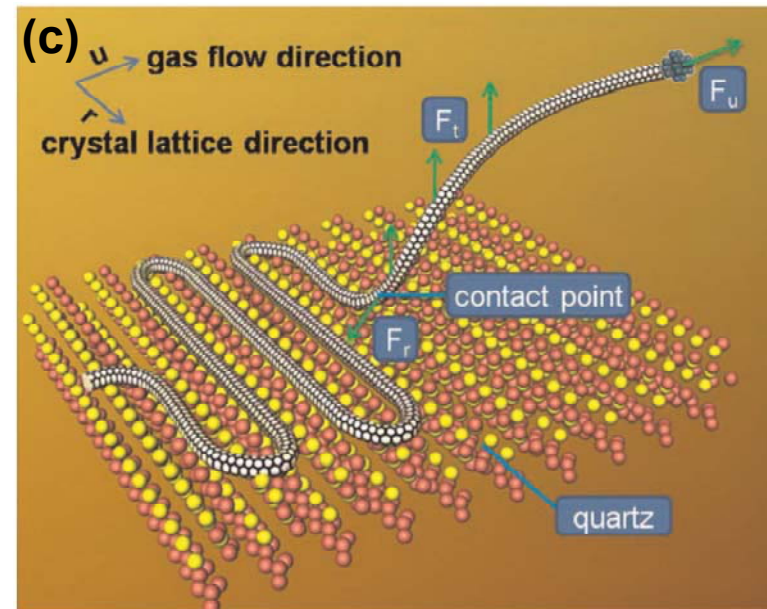
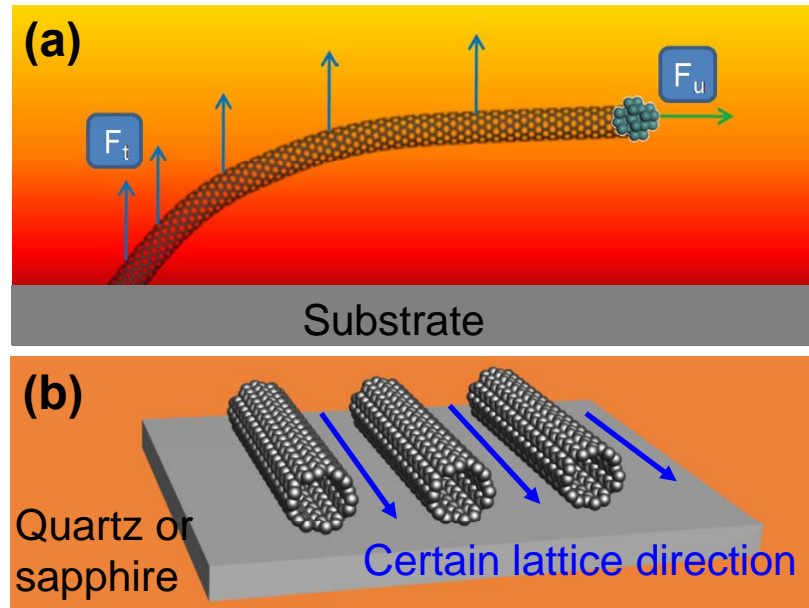
✓ Cap-engineering for SWNTs Growth with Controlled Chiralities





Controlling Morphology of SWNTs on Surfaces by Combining the Two Growth Modes

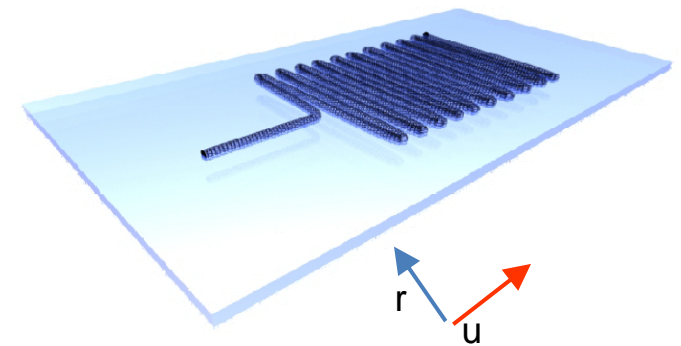
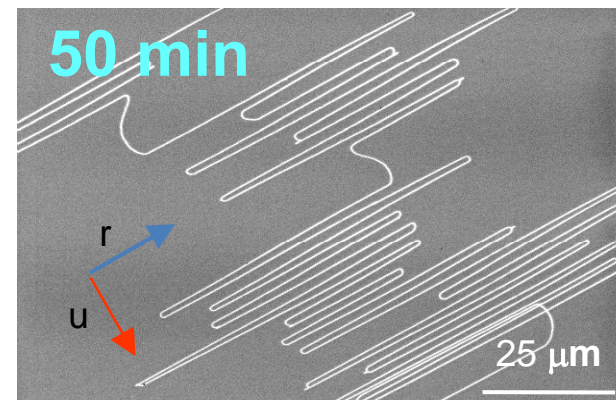
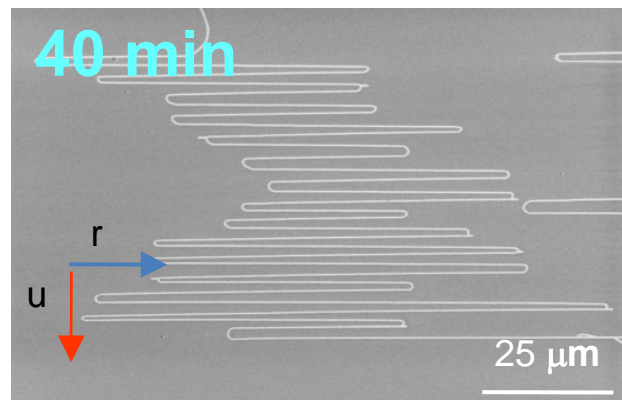
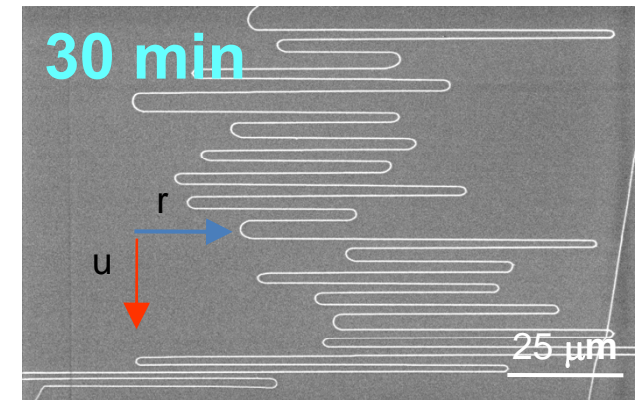
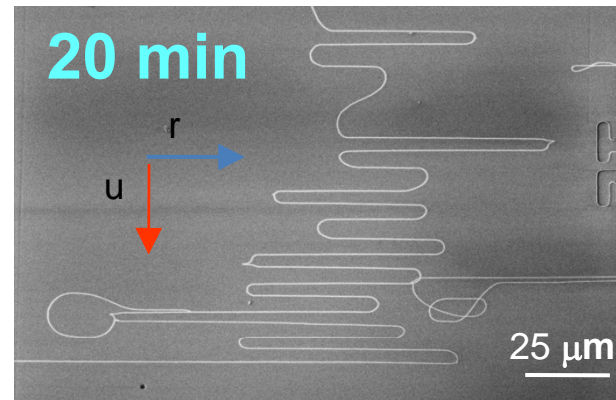
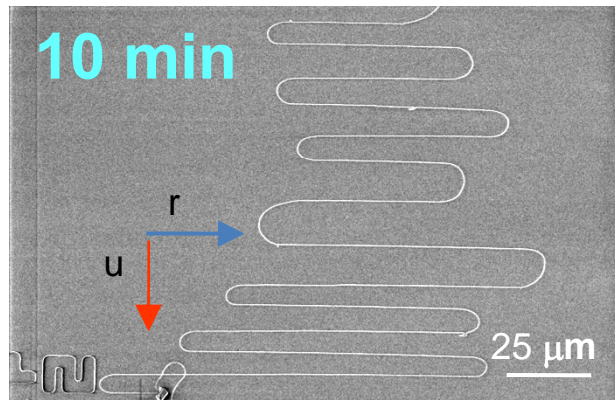
Growth of serpentine SWNTs



- ◆ The spacing between two parallel sections is mainly determined by the landing rate of the ultralong SWNT.
- ◆ The landing rate can be controlled by cooling rate.

Therefore, the folding density of serpentine SWNTs can be controlled by cooling rate.

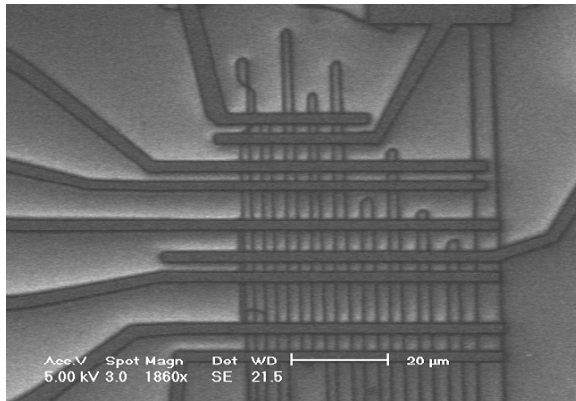
Serpentine SWNTs grown at different cooling rates



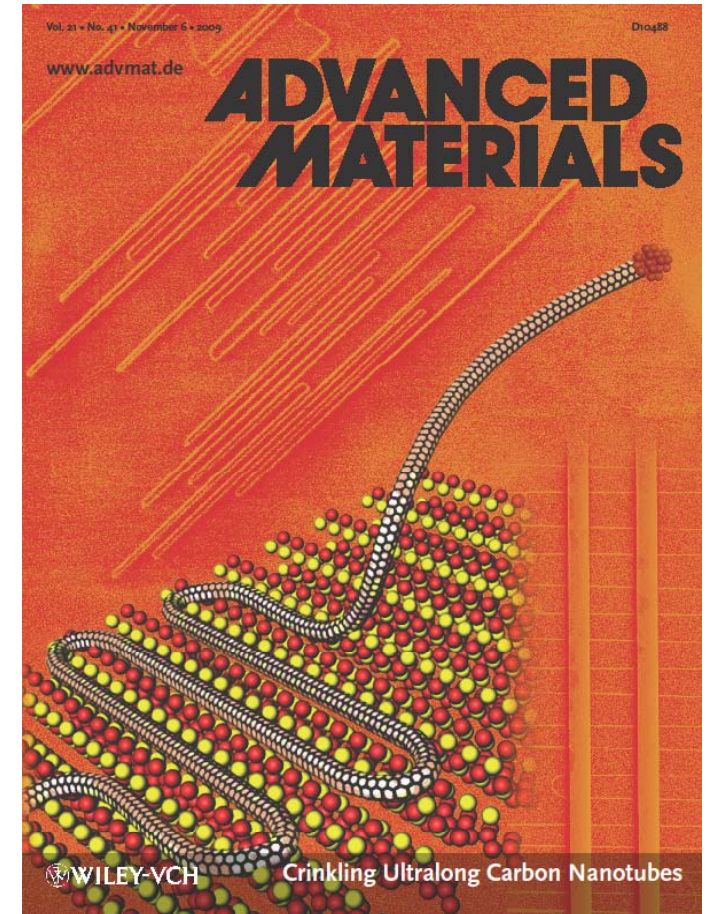
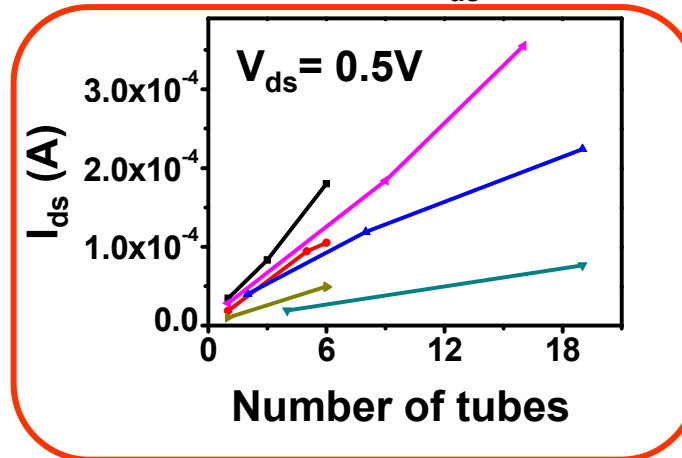
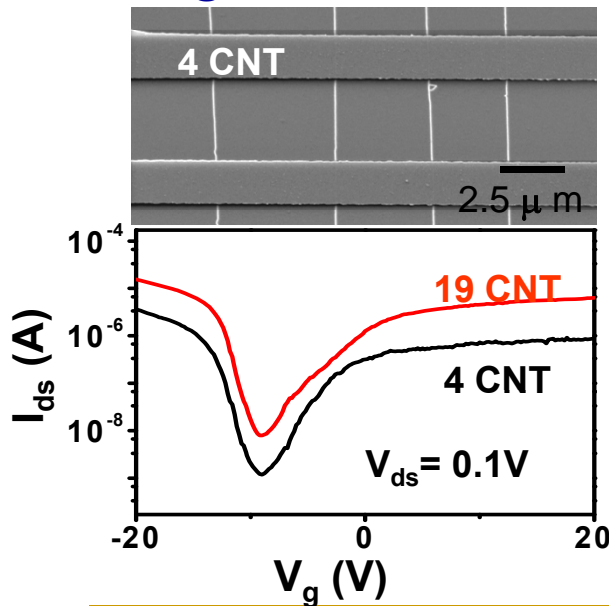
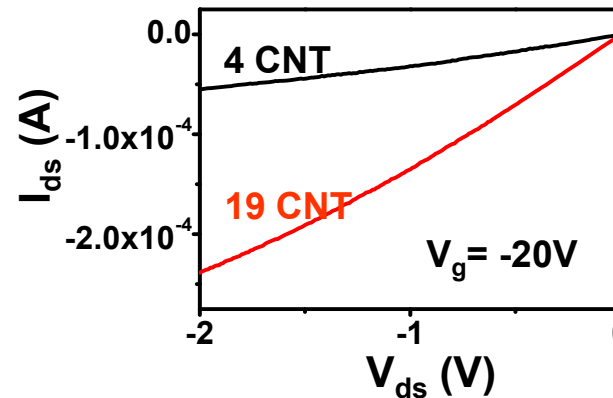
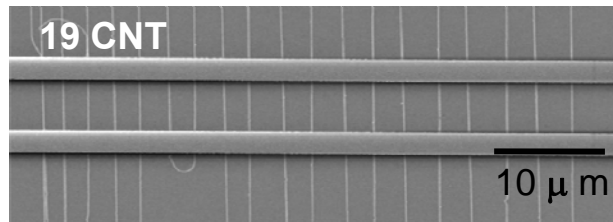
T from 975°C to 775 °C.

The slower the cooling speed, the higher the tube folding density.

High Performance SWNT-FET with Identical Chirality

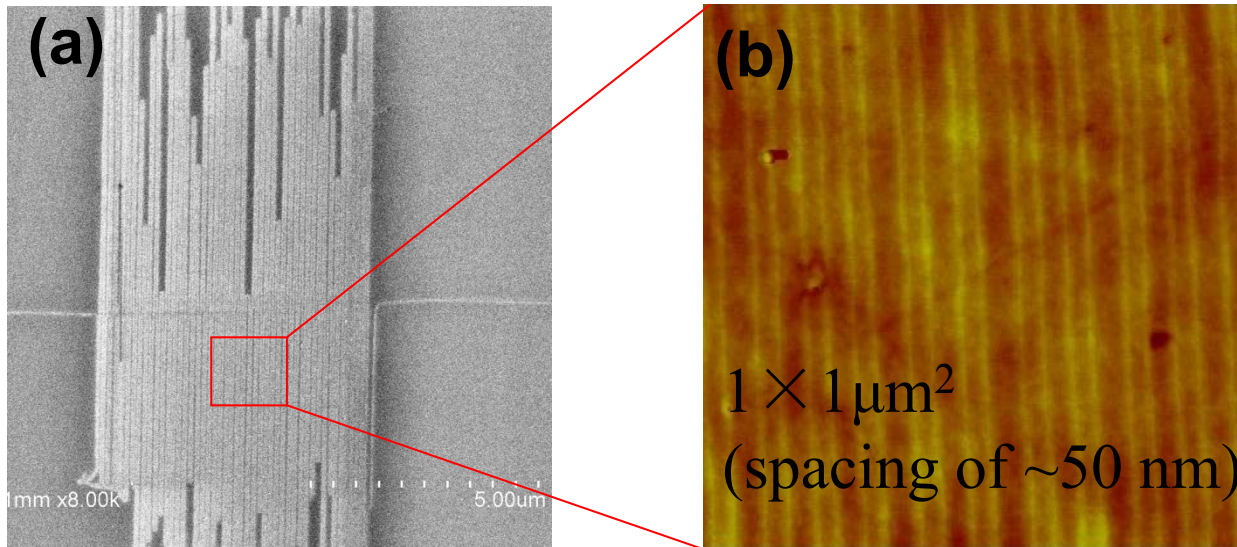


Pd electrode, 800nm SiO₂ gate dielectric

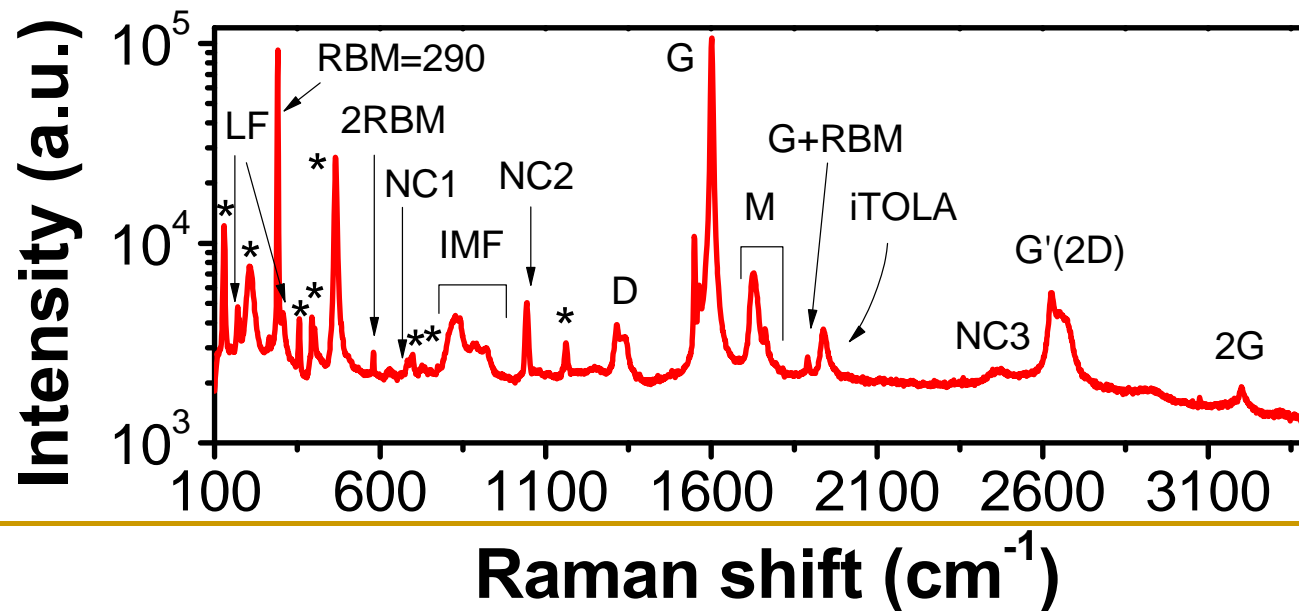


J. Zhang, et al., Adv. Mater. 2009, 21, 4158-4162. (Inter Front Cover Paper).

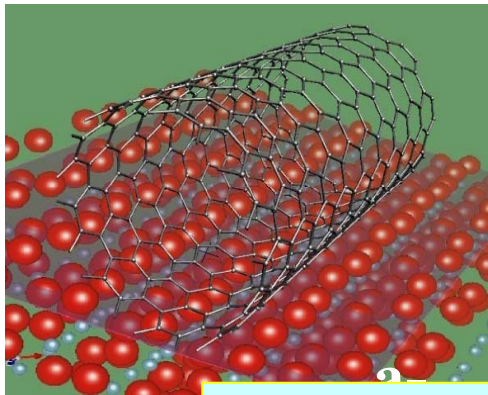
The highest density we have achieved



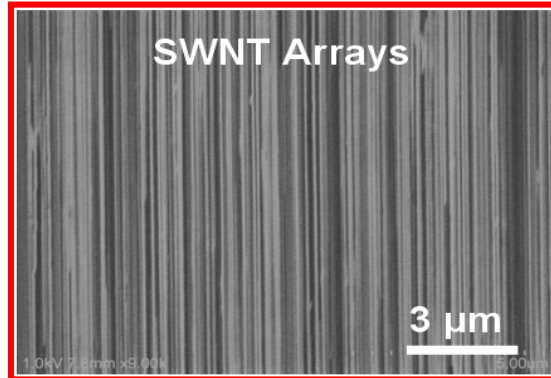
High density of SWNTs make it possible to observe various weak second-order Raman from SWNTs.



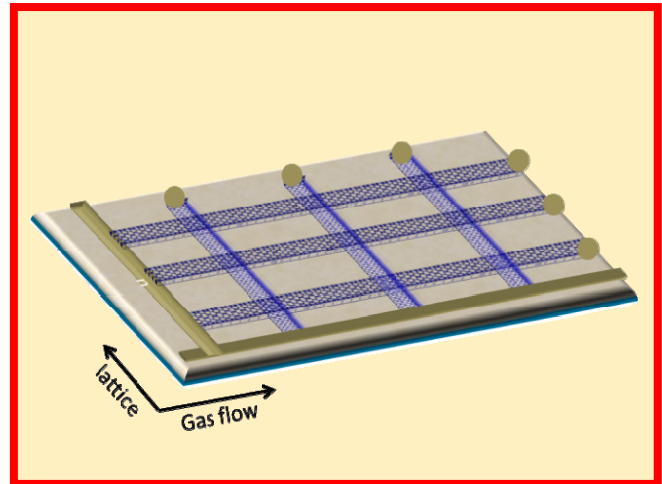
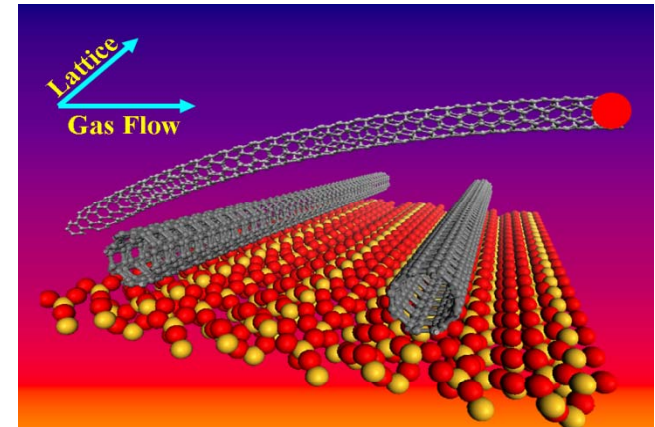
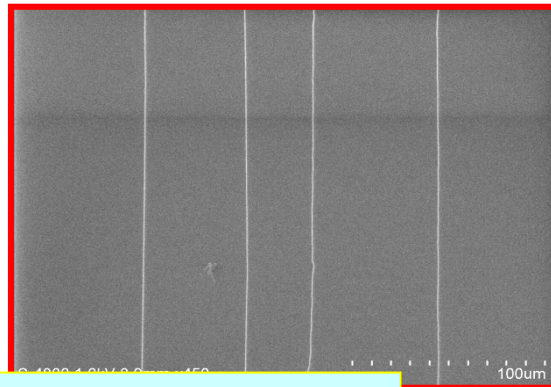
Grow SWNT cross-bars in one batch



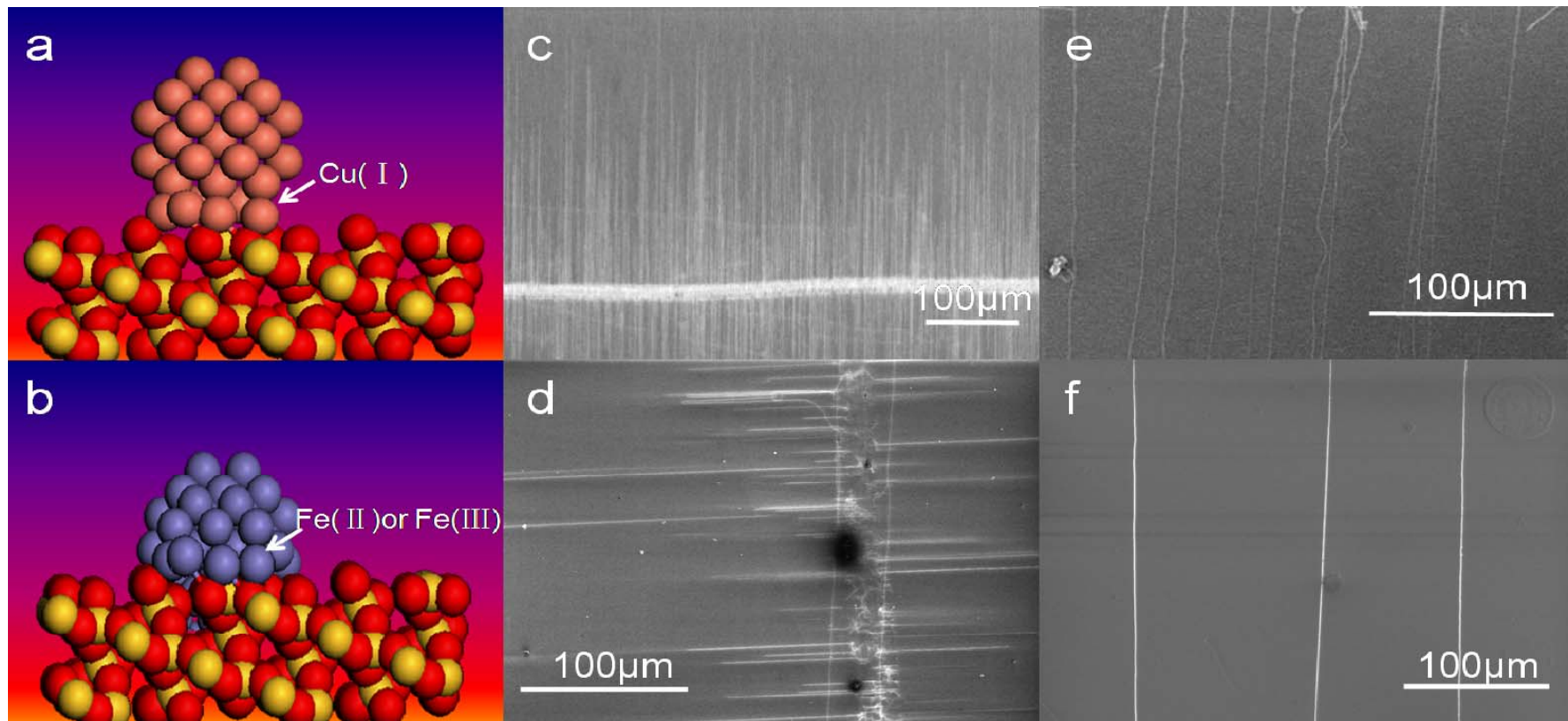
Lattice Directed Growth Mechanism



Gas Flow Directed Growth Mechanism



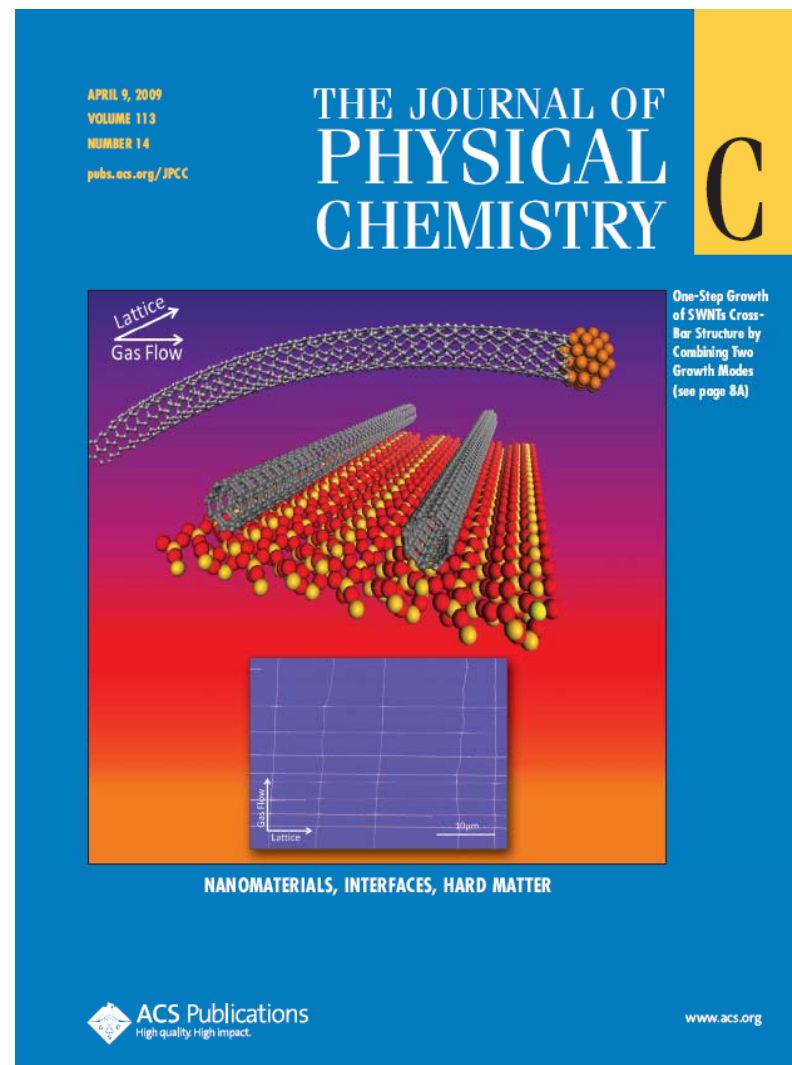
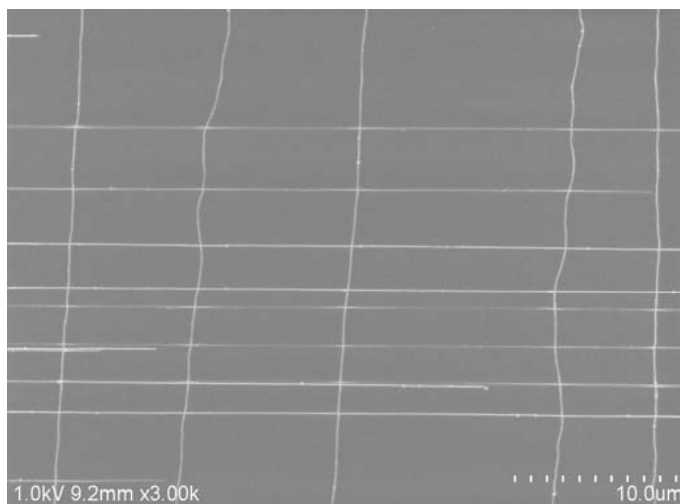
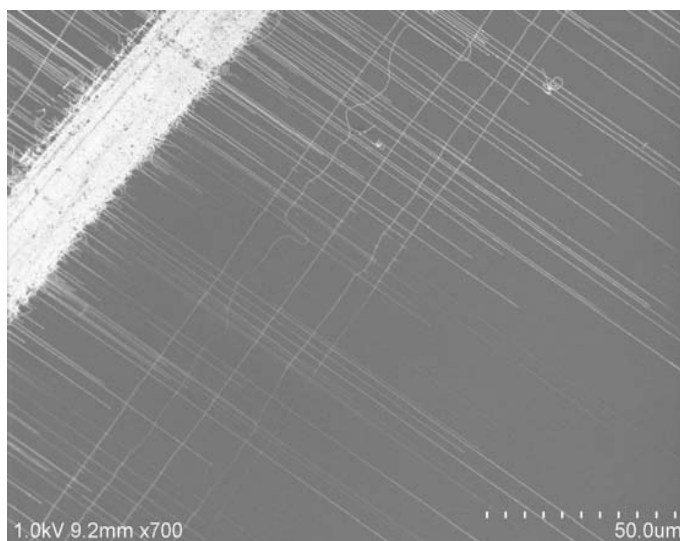
Interaction between Cu, Fe Catalysts and Quartz Surface



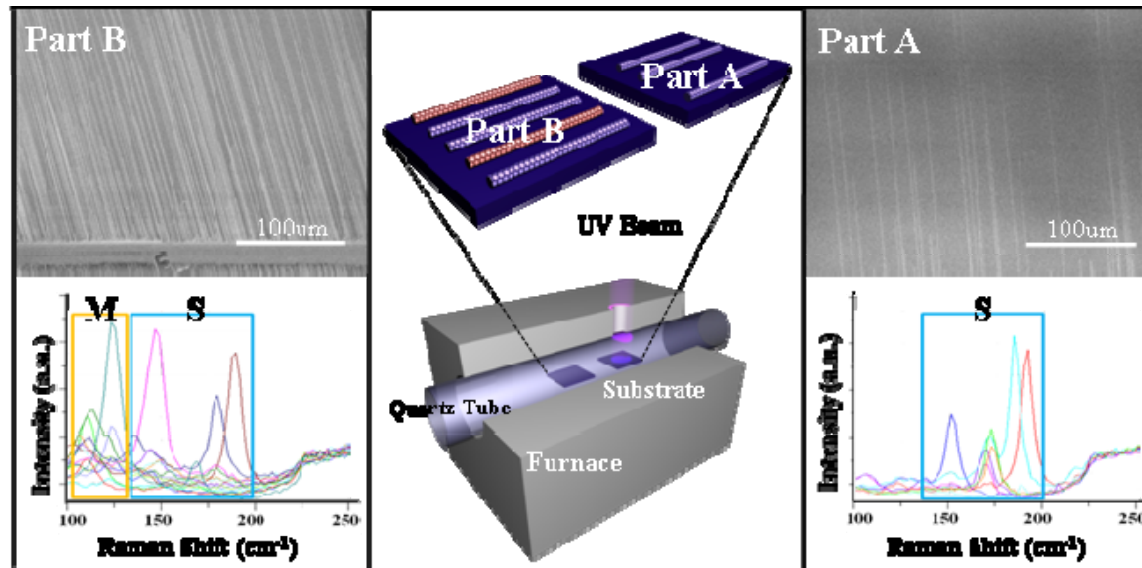
a) and b) illustrate the interaction between Cu, Fe nanoparticles and surface of quartz, the red balls represent oxygen atoms. c) and d) High-magnification SEM image of the lattice assisted SWNTs catalyzed by Cu and Fe. e) and f) Results of gas flow directed growth of carbon nanotubes where Cu and Fe are used as catalysts respectively.

SWNT Cross-bars and Its Potential Application

Low temperature favors for lattice oriented growth mode and high T for gas flow directed growth mode. With a moderate 930-950°C, crossbar can be grown.



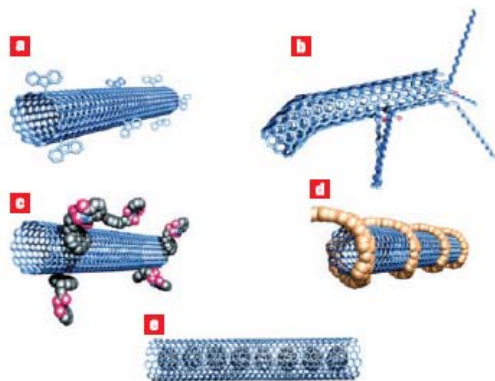
J. Zhang et al., J. Phys. Chem. C. 2009, 113, 5341-5344 (cover)



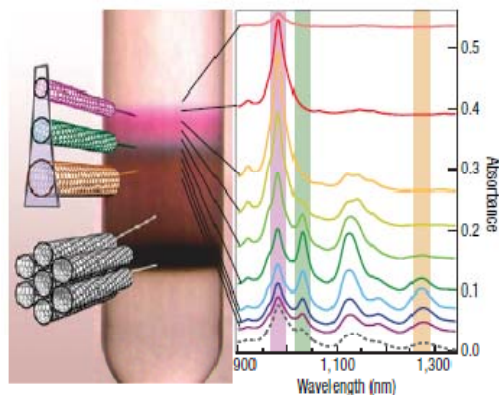
Direct Growth of Semiconducting SWNT Arrays by UV Irradiation Assistance CVD

Separation of s-SWNTs and m-SWNTs after Growth

Functionalization



density gradient ultracentrifugation

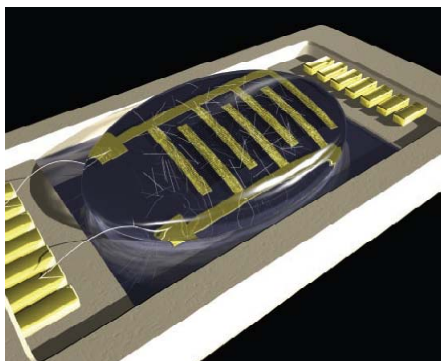


Ion-exchange chromatography



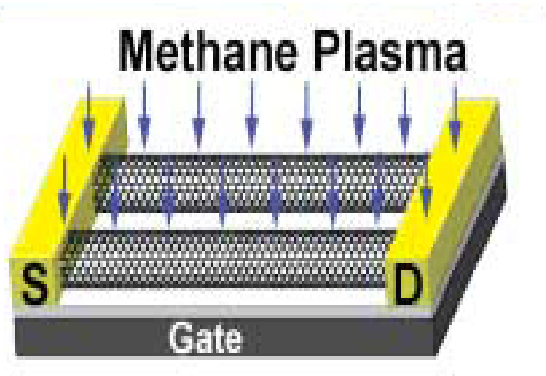
A. Hirsch, *Angew. Chem. Int. Ed.*, 2002 M. S. Arnold, *Nature Nanotech.*, 2006 M. Zheng, *Nature Mater.*, 2003

alternating current dielectrophoresis



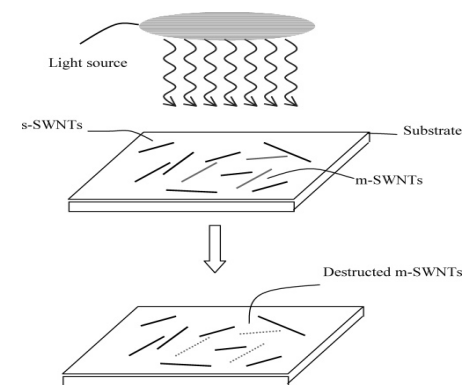
R. Krupke, *Science*, 2003

gas-phase plasma hydrocarbonation



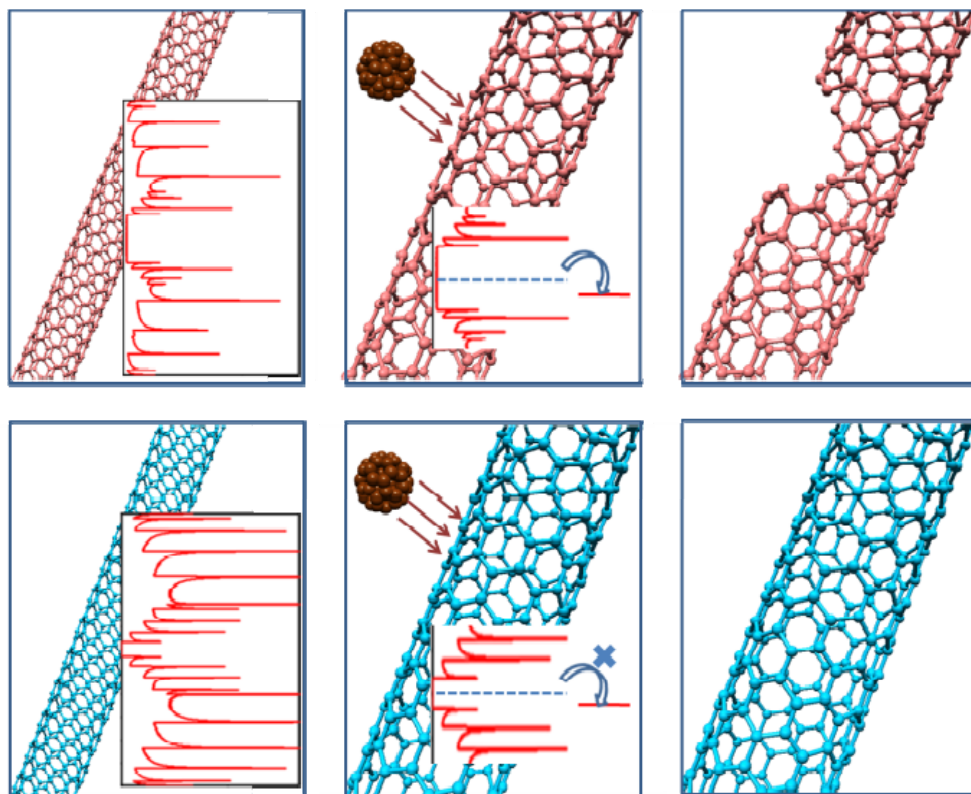
H. J. Dai, *Science*, 2006

Laser Irradiation

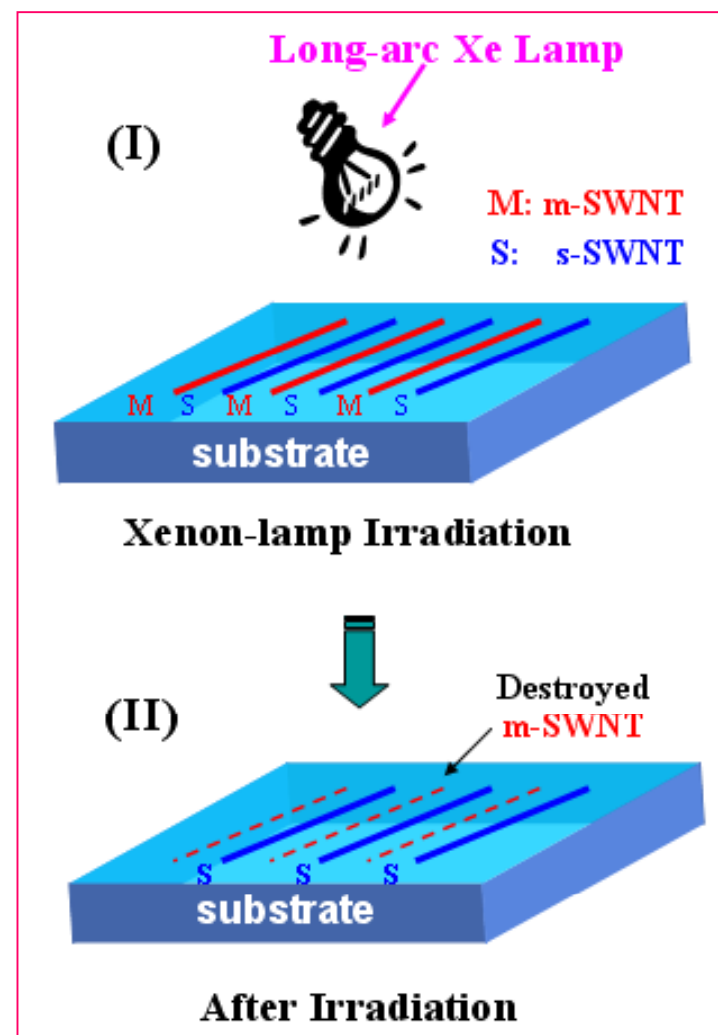


H. J. Huang, *J. Phys. Chem. B*, 2006

Why s-SWNTs and m-SWNTs can be Separated

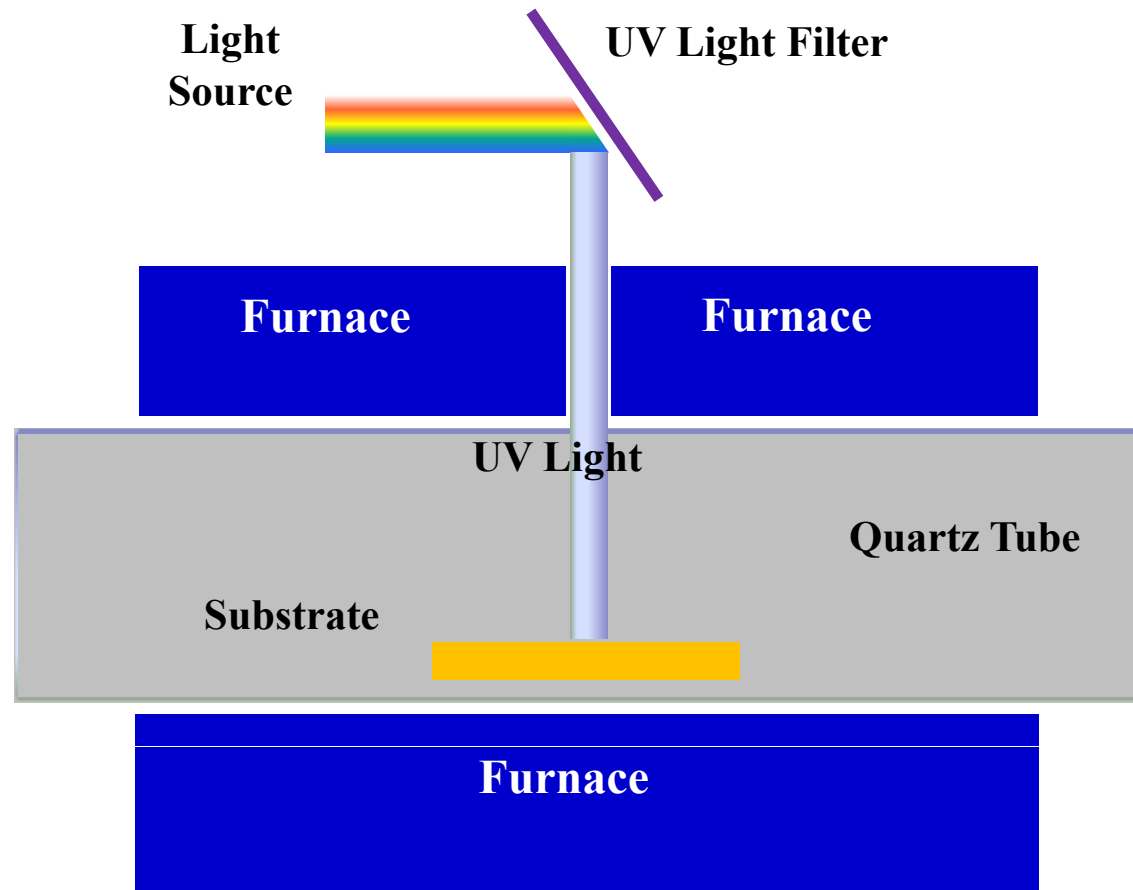


When a reactant comes near the SWNT, the electron can transfer from the metallic SWNT, but cannot transfer from the semiconducting SWNT. After that, the metallic SWNT can be damaged and the semiconducting SWNT still survived .

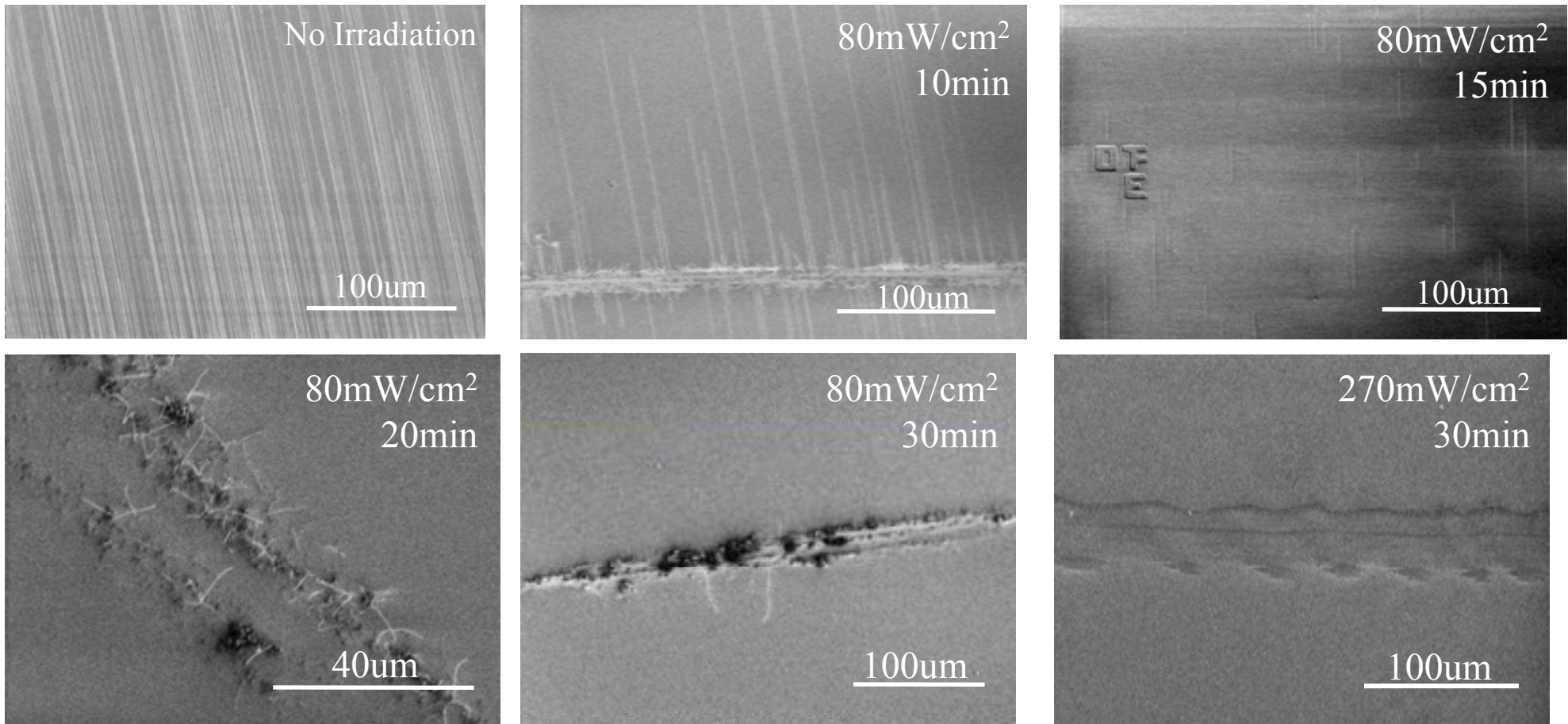


J. Zhang, et. al., J. Phys. Chem. C 112, 3849, (2008)

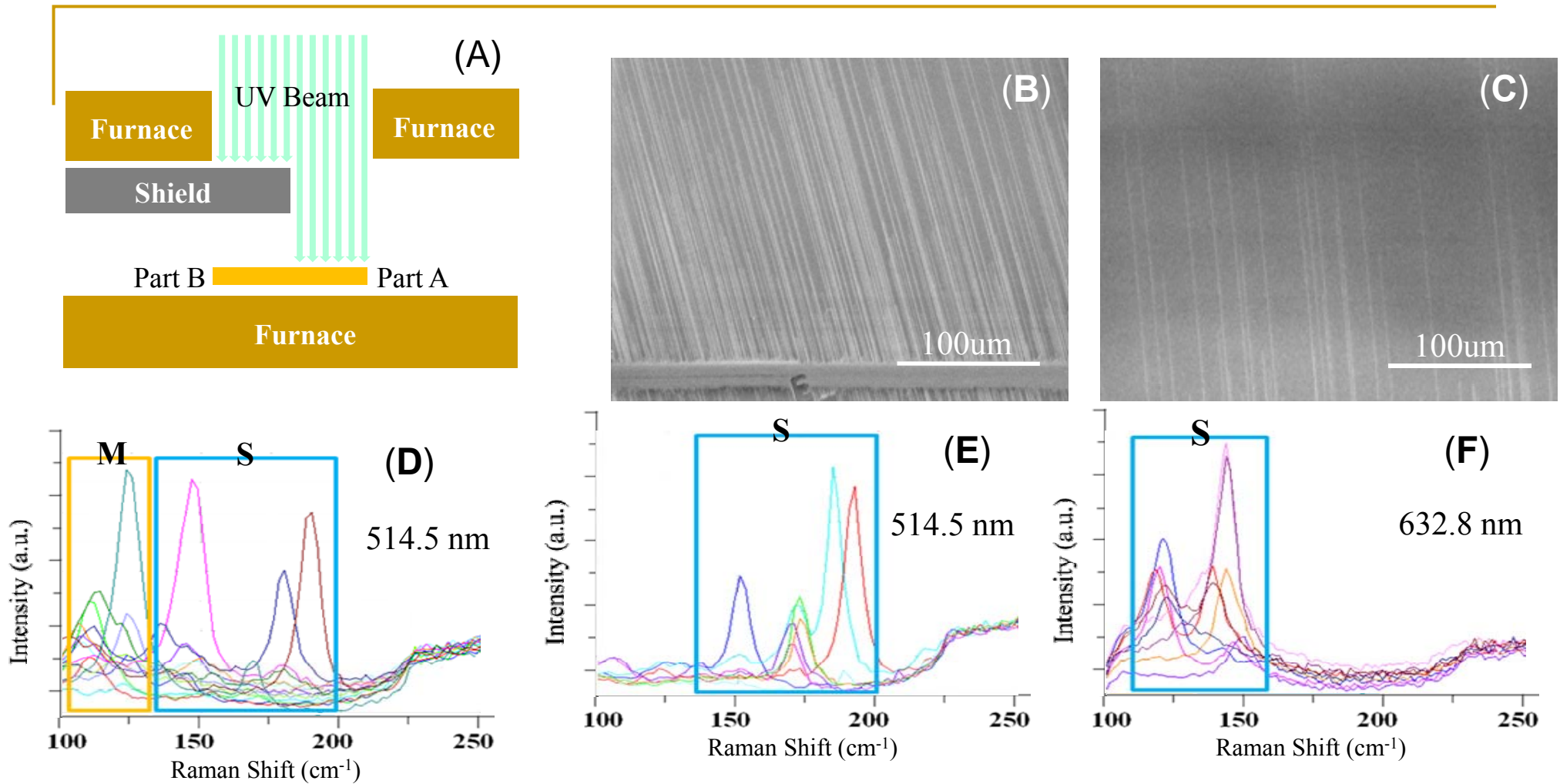
Setup of Our Home-Made CVD System



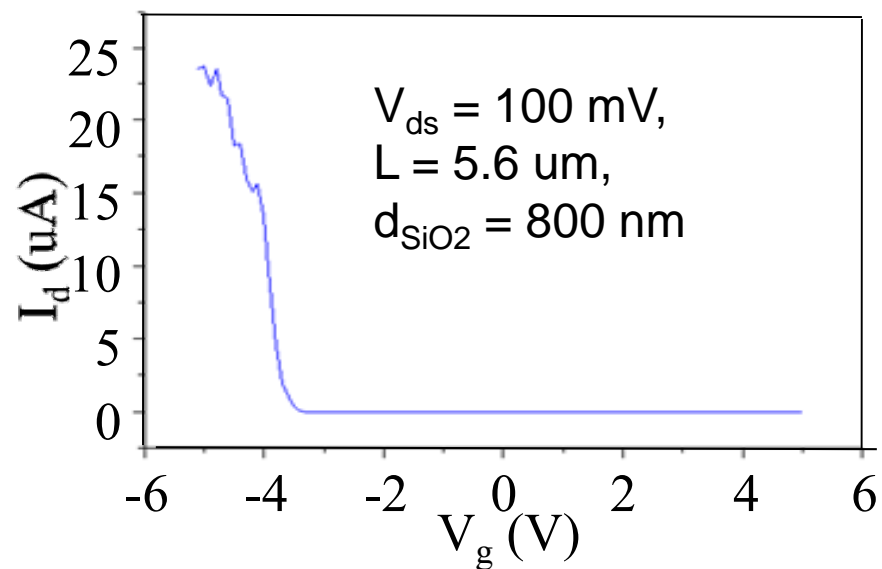
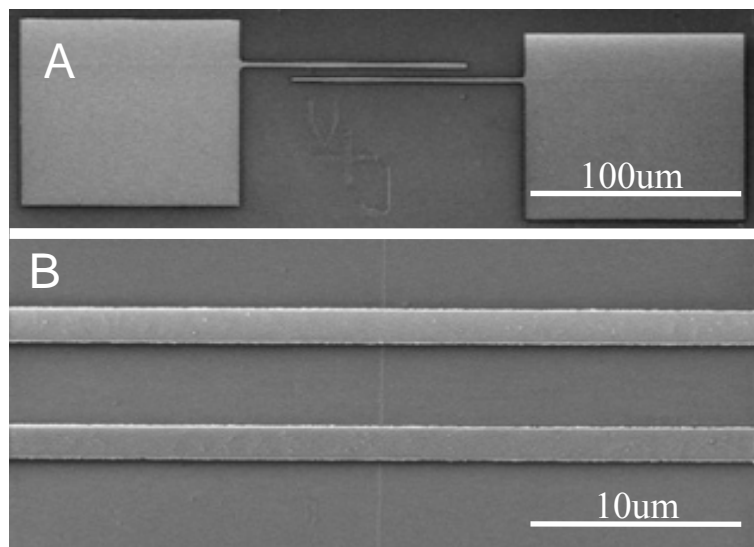
SEM images of SWNTs arrays under different irradiation time



When UV beam acted on the substrate, the density of the SWNT array decreased obviously. From above, the shorter the irradiation time, the longer and denser the SWNTs were. If we continued increasing the irradiation time or the irradiation intensity, SWNTs would become shorter and shorter, and disappeared eventually

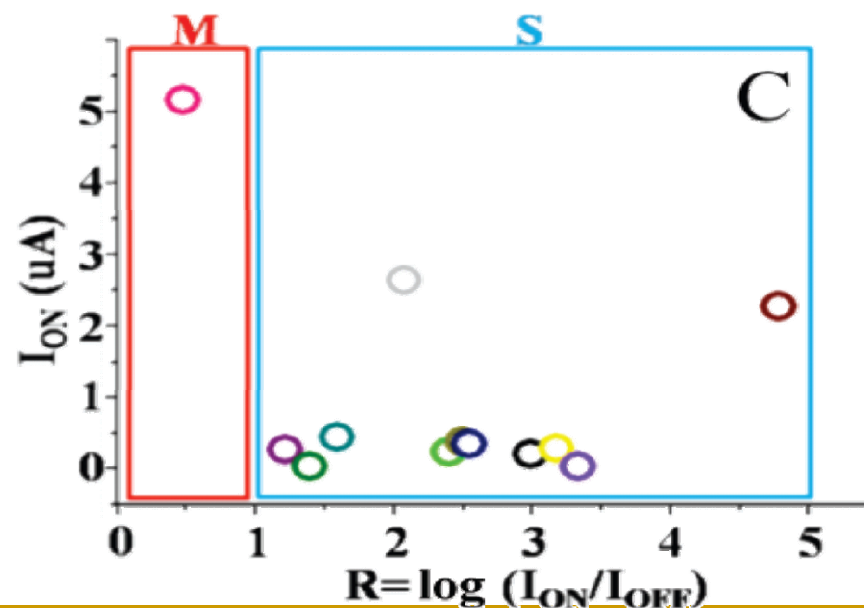


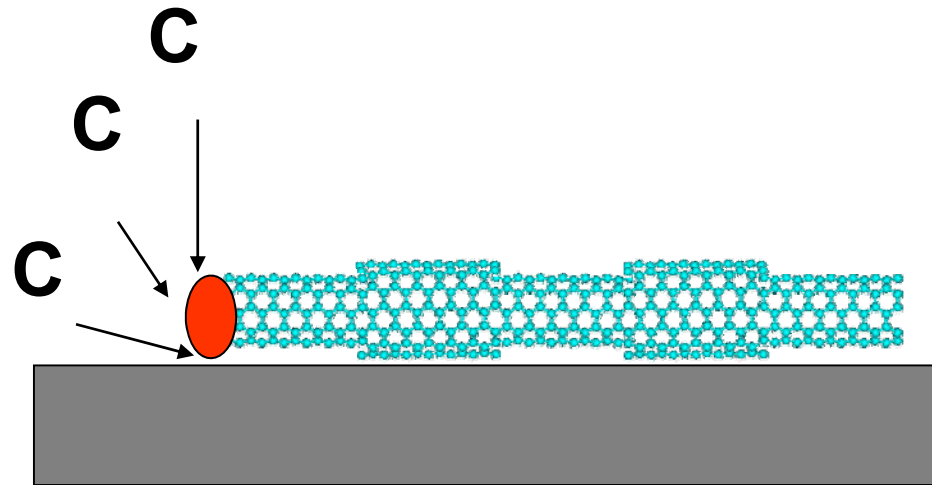
(A) Sketch map of the comparison experiment for SWNT growth with and without UV irradiation. (B)/(C) SEM image of the growth result without/with UV irradiation. (D) Raman spectrum for part B with 514.5 nm excitation. (E)/(F) Raman spectrum for part A with 514.5/632.8 nm excitation. The metallic SWNTs signals were collected in the yellow rectangle while the semiconducting SWNTs signals were collected in the blue rectangle separately for all the three spectra.



Raman spectra demonstrated an amazing result that almost 100% SWNTs were semiconducting.

Electrical measurement data showed that 21 out of 22 SWNTs (~95%) were semiconducting.

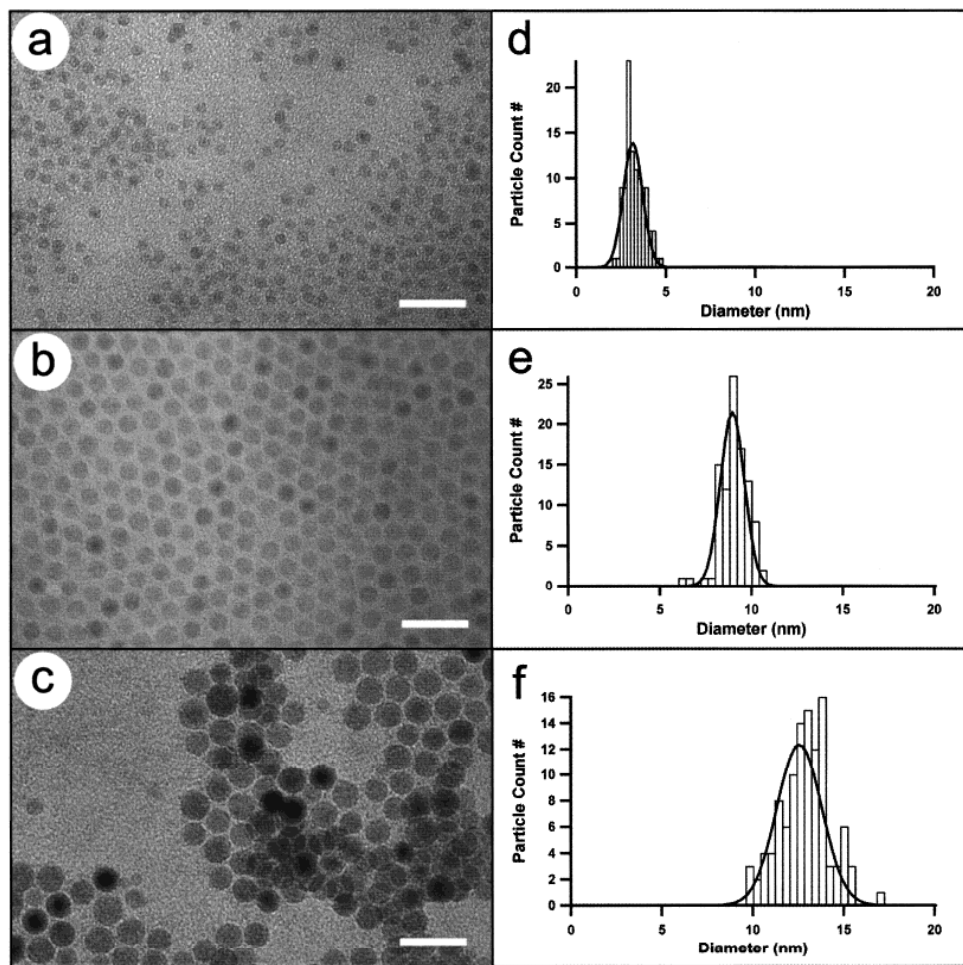




Tuning Diameters of SWNTs by Temperature-oscillation CVD growth

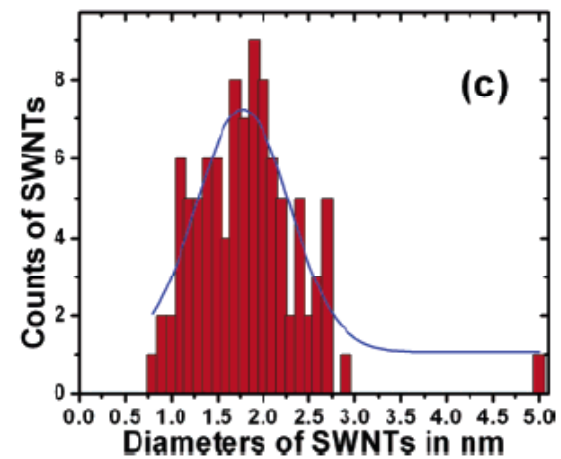
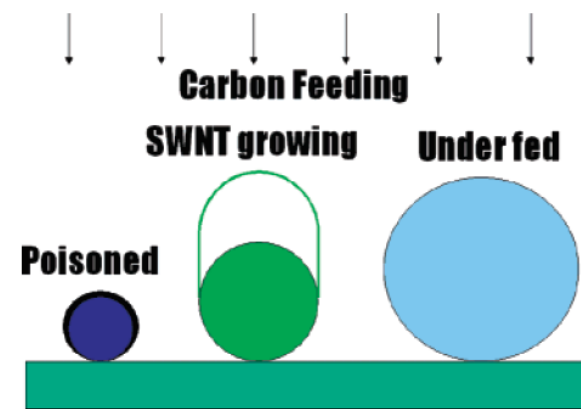
Controlling Diameters of SWNTs

By Catalyst Particle



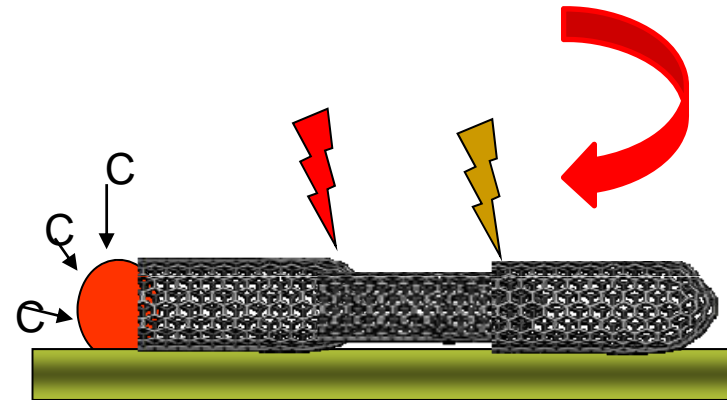
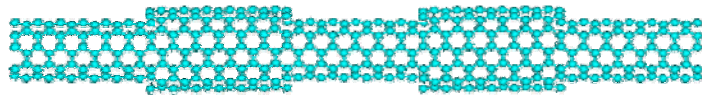
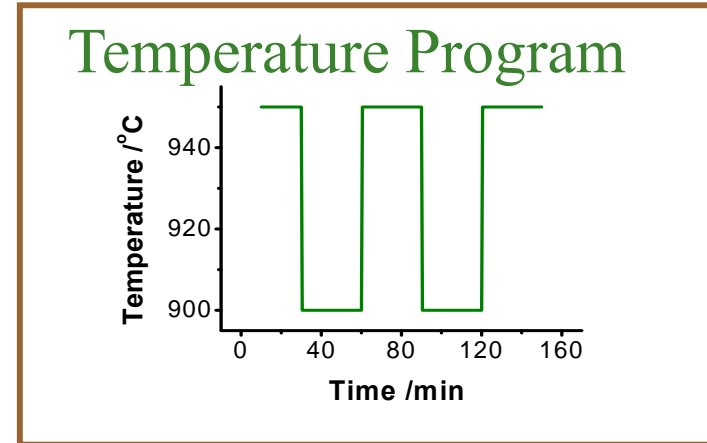
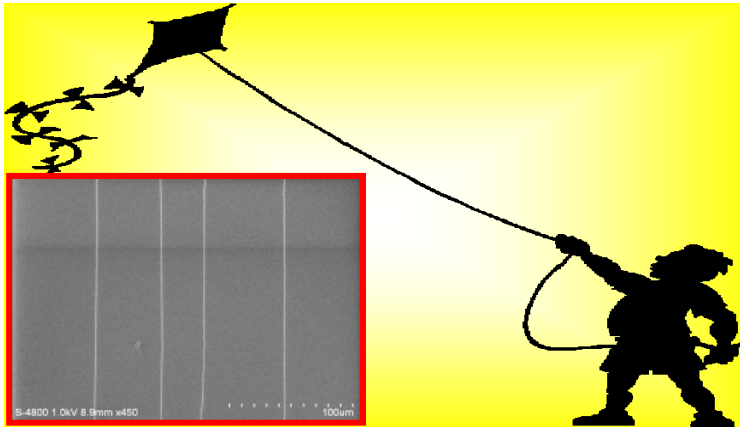
J. Phys. Chem. B. 2002, 106, 2429-2433

By Carbon Feeding

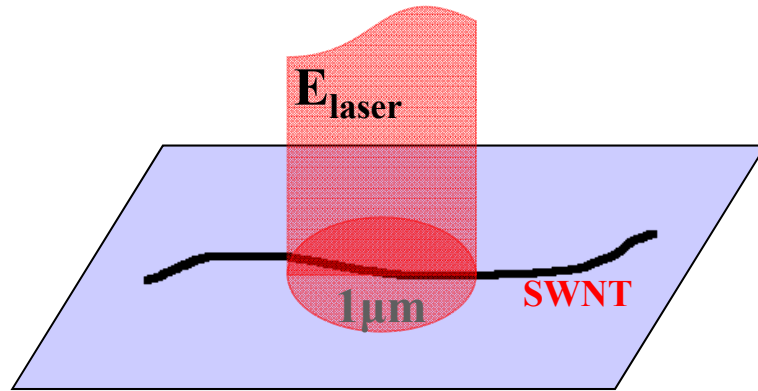


J. Phys. Chem. B. 2006, 110, 20254-20257

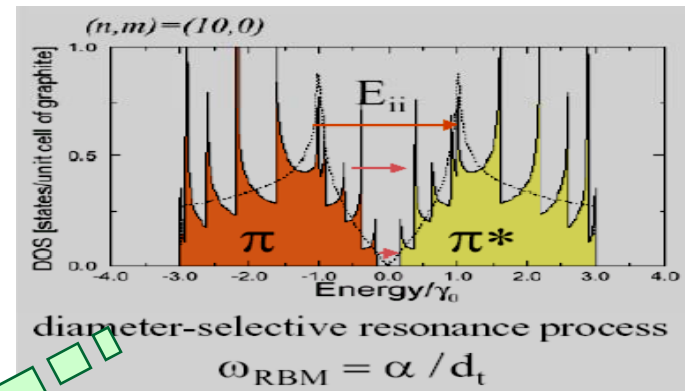
Our Approach: Tune the Diameter of SWNTs by Temperature



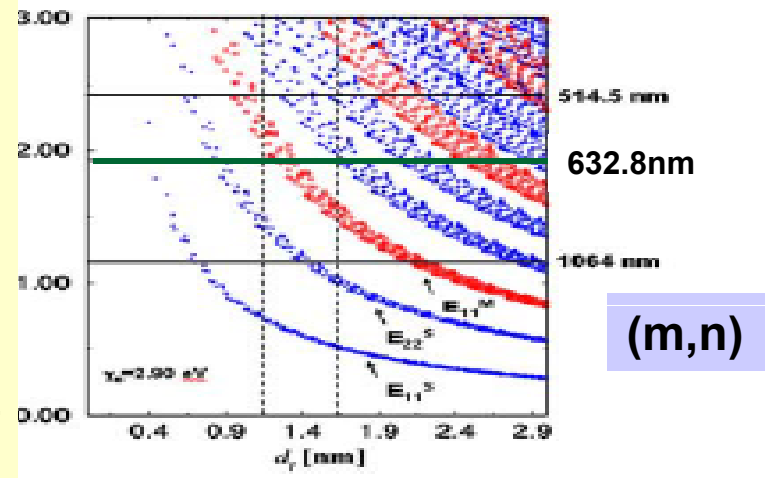
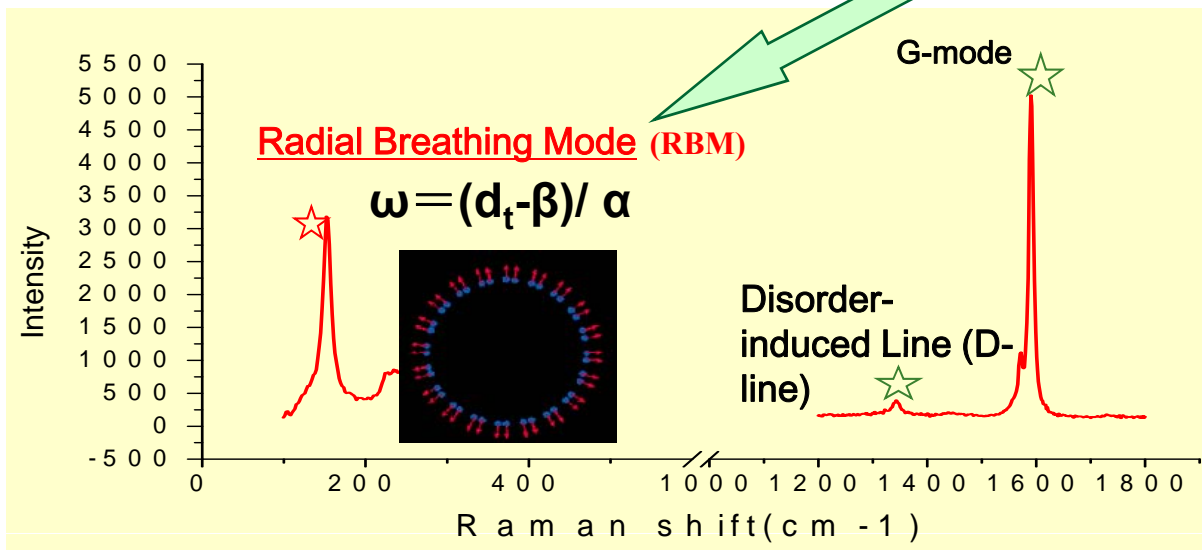
Micro-Resonance Raman Spectrum of Individual SWNTs



Micro-Raman spectroscopy

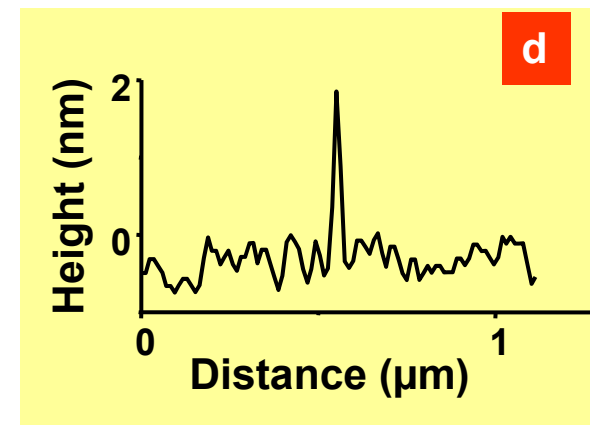
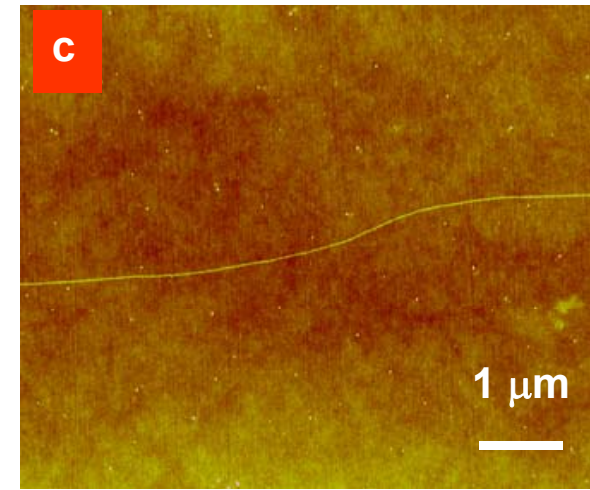
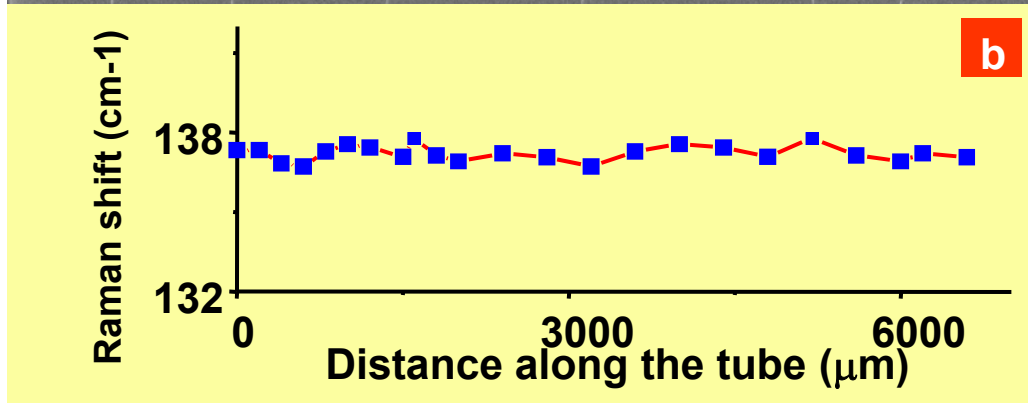
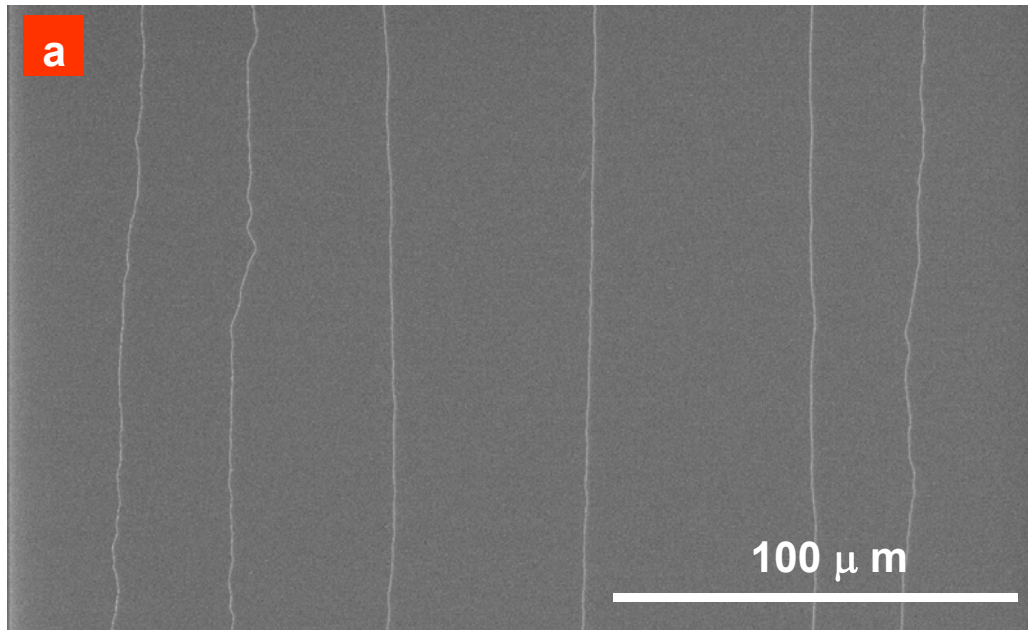


Resonance condition: $E_{laser} = E_{ii}$

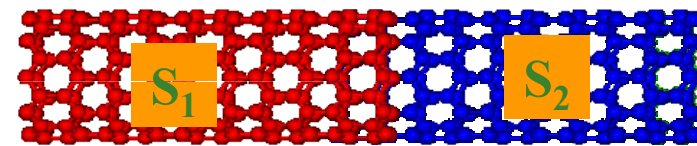
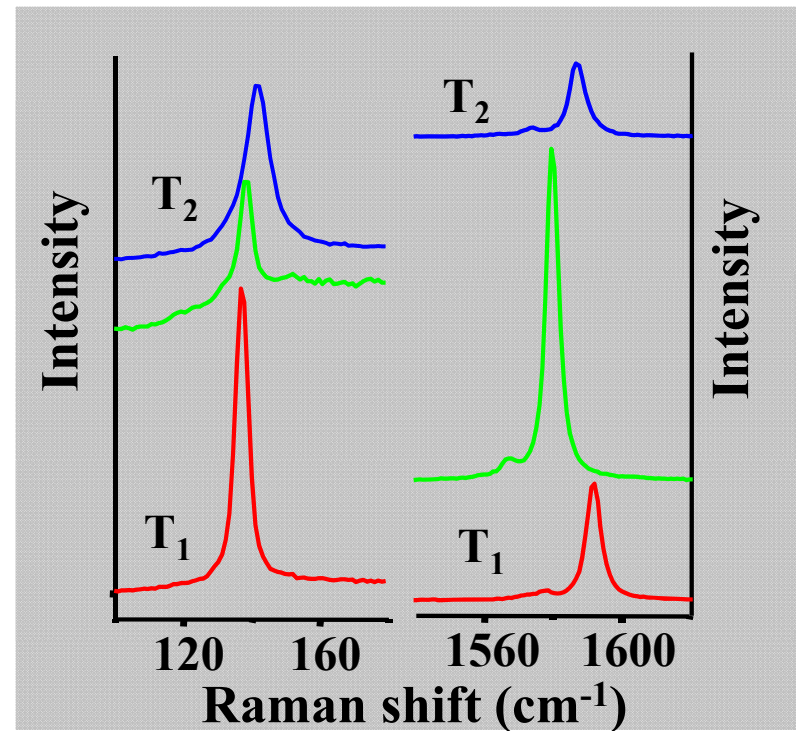
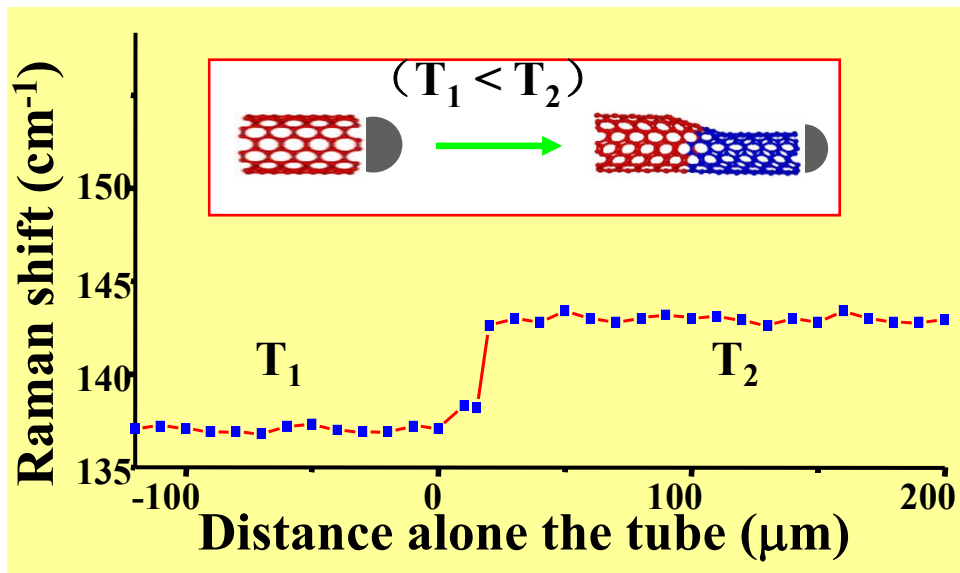
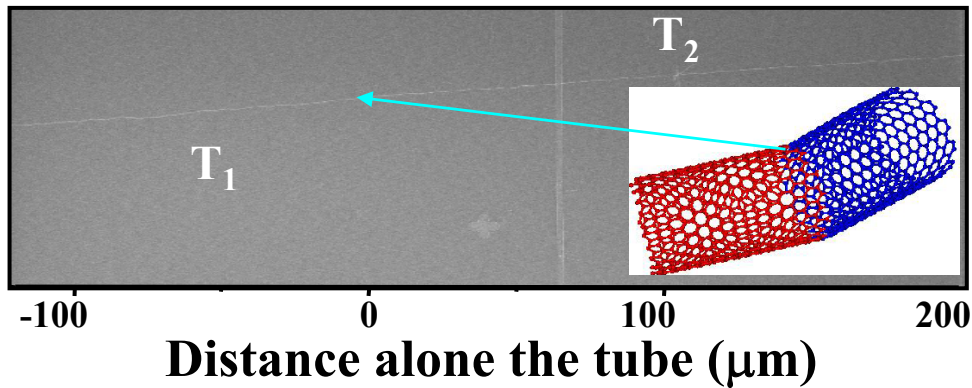


A power tool for both the atomic and electronic structure of SWNT !

Constant-temperature CVD

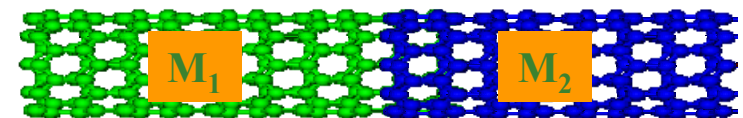
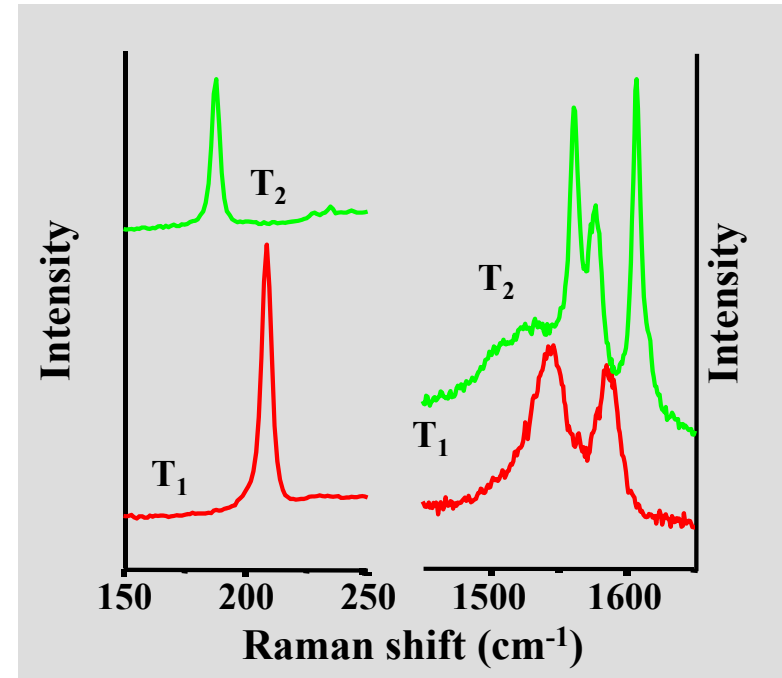
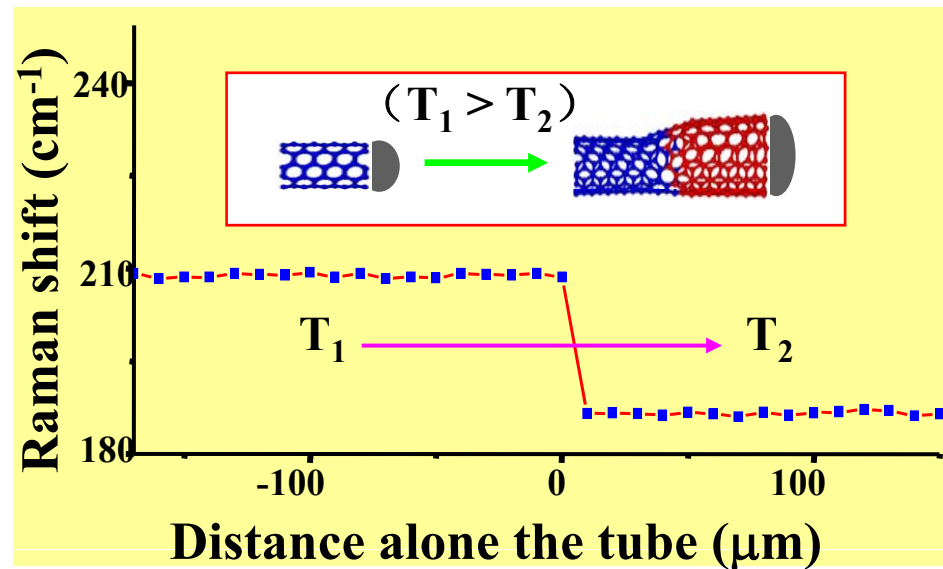
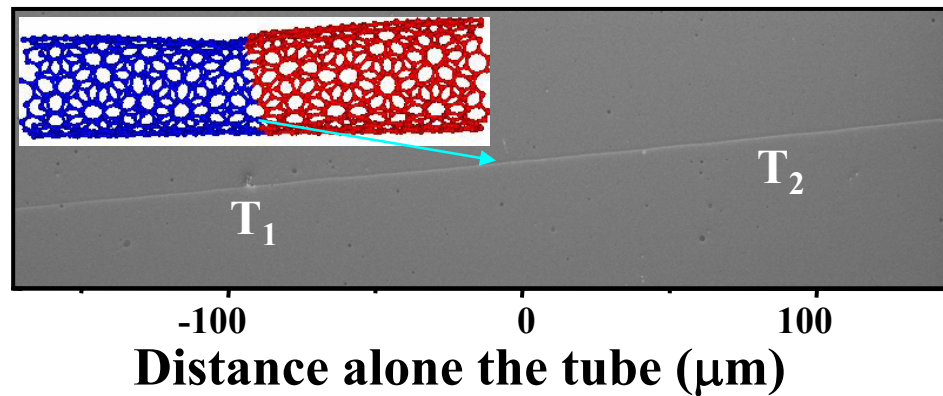


SWNTs Grown by one Time Temperature Oscillated CVD (From 900°C to 950°C)



**Semiconducting—
Semiconducting Nanojunction**

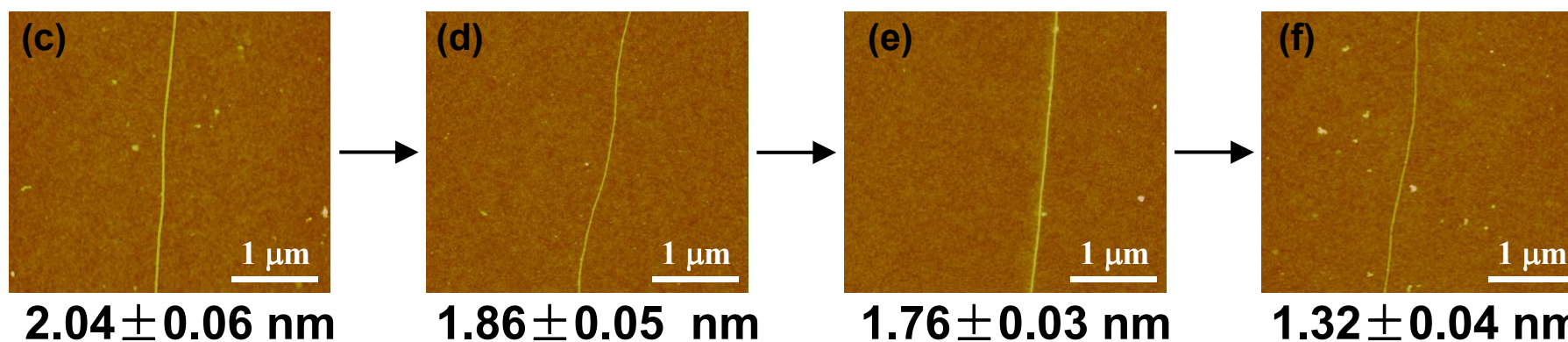
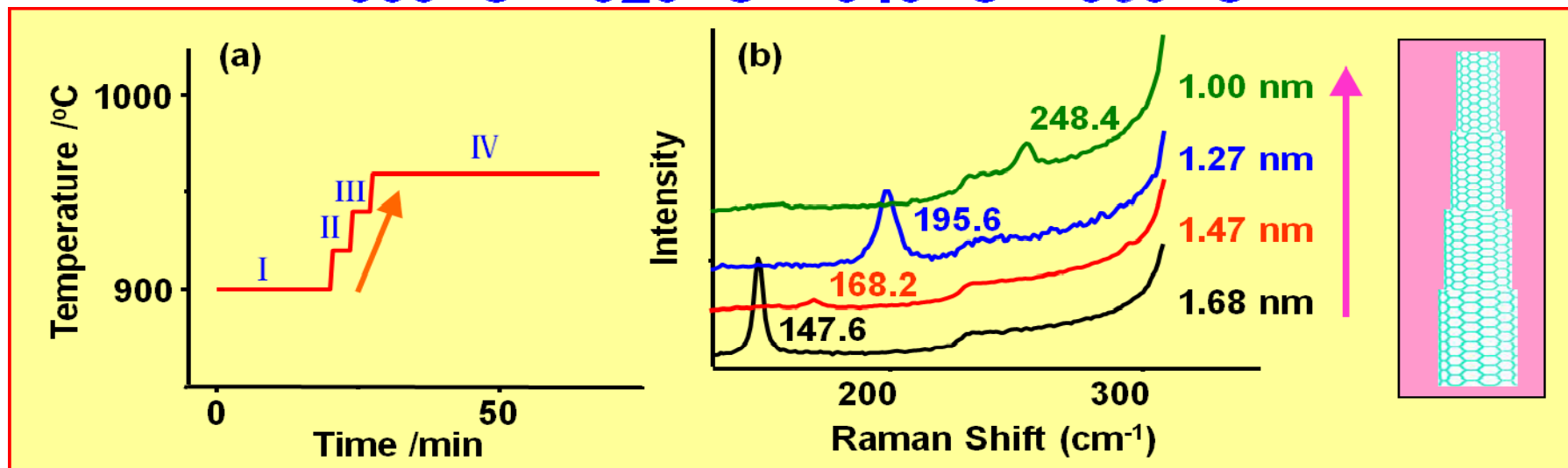
SWNTs Grown by one Time Temperature Oscillated CVD (From 950°C to 900°C)



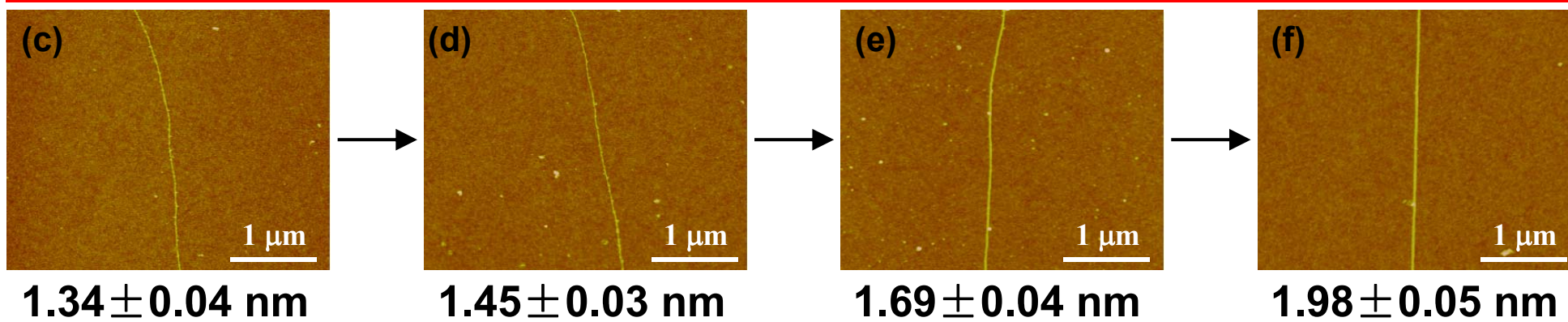
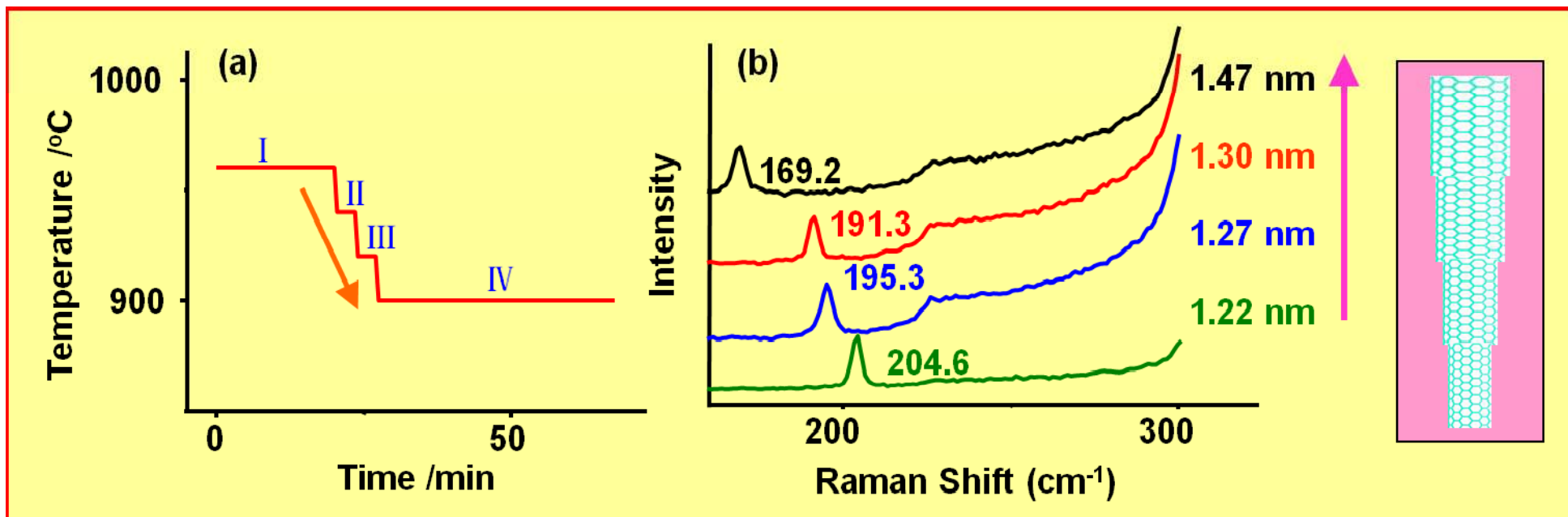
Metallic—Metallic Nanojunction

Controlled Thinning of SWNTs via Temperature Step-Up

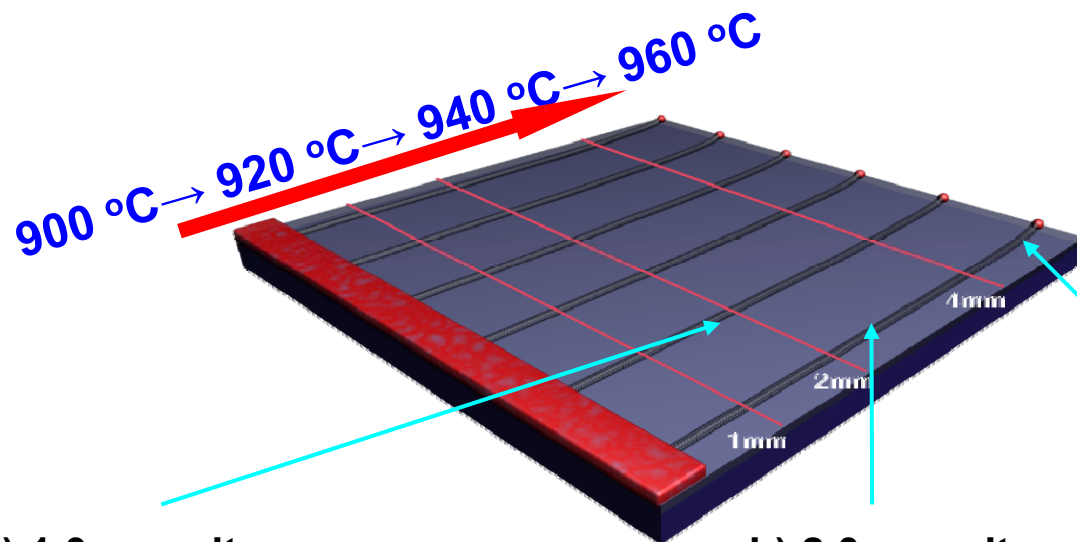
900 °C → 920 °C → 940 °C → 960 °C



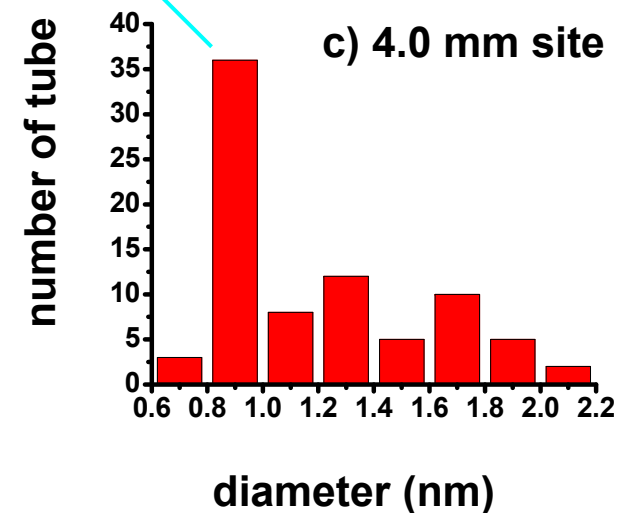
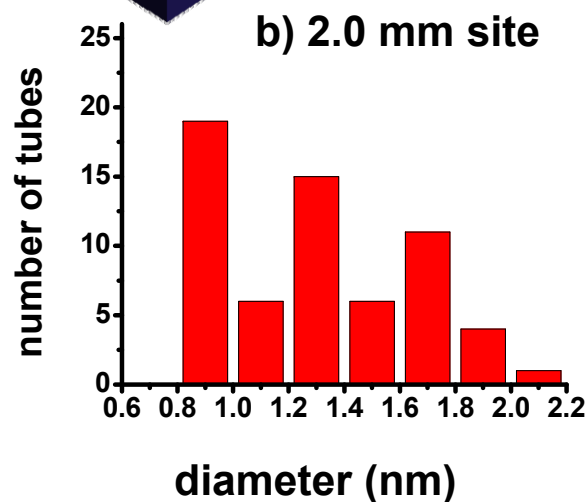
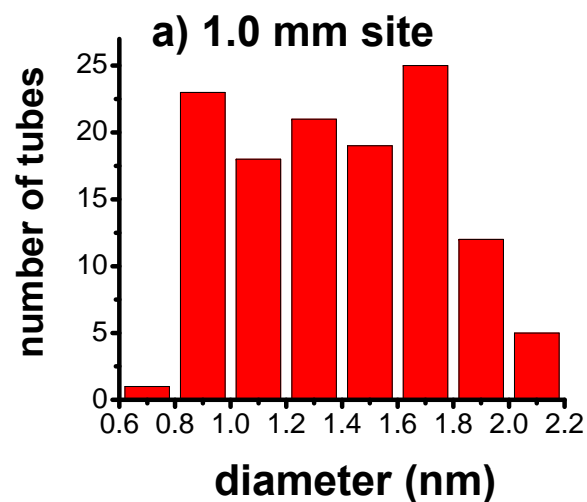
Controlled Thickening of SWNTs via Temperature Step-Down



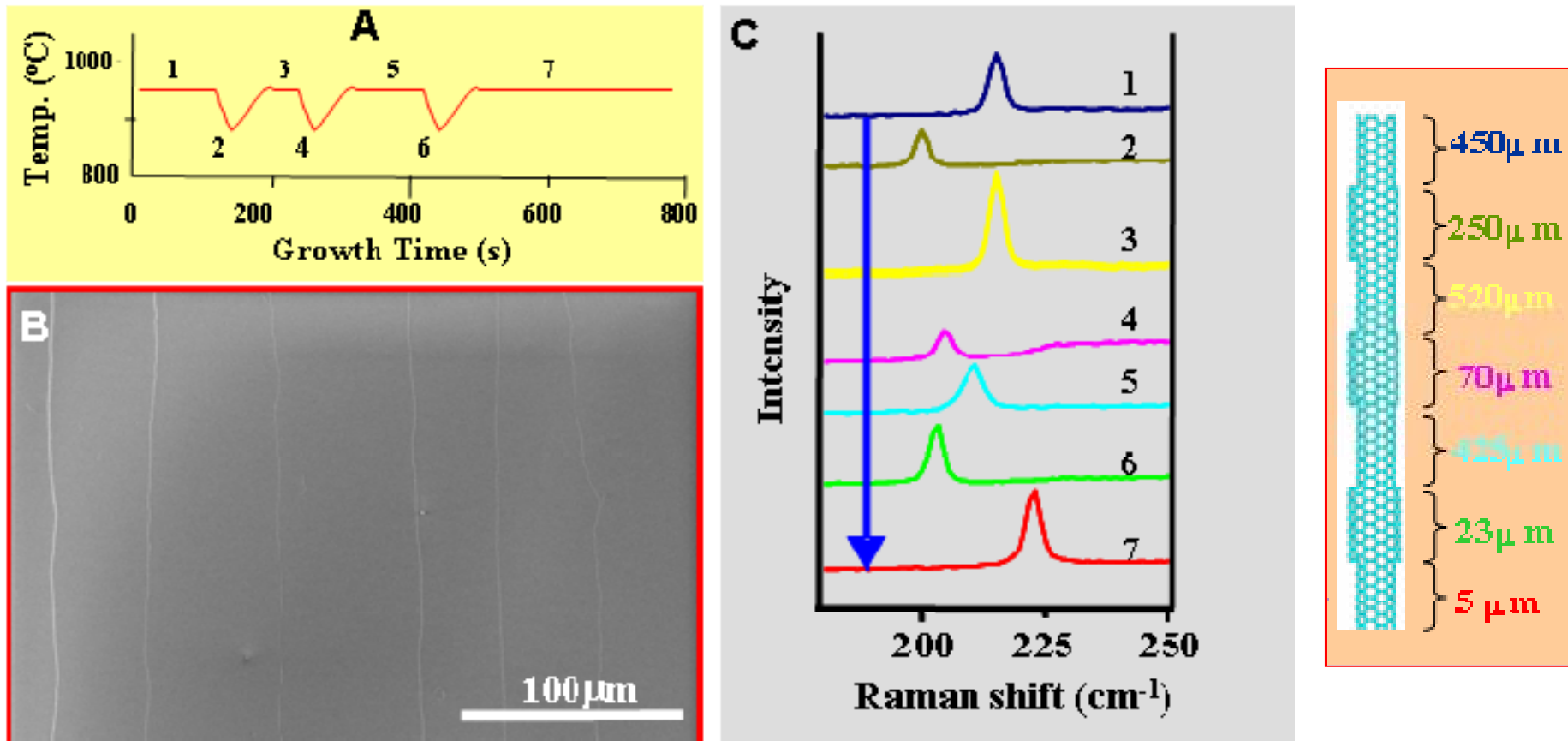
Tube Diameter from Wide to Narrow Distribution



Narrowing the distribution of tube diameters by sequential temperature step-up or step-down



Multiple Intratube Nanojunctions by Repeating Temp. Oscillation



Six intramolecular junctions were induced by three temperature oscillations between 950°C and 880°C during CVD. (A) shows the scheme of temperature oscillation with time; (B) is an SEM image of several parallel ultralong SWNTs grown during the temperature oscillation; (C) shows Raman RBM peak positions along a SWNT, each peak corresponds to a time period in (A).

J. Zhang et al., Nature Materials, 2007, 6, 283



nanotoday

www.nanotoday.com

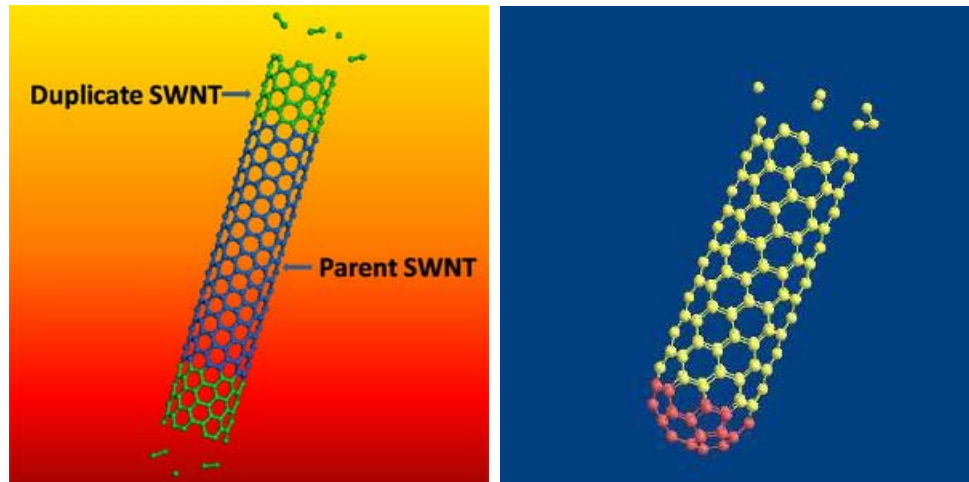
JUNE 2007 | VOL 2 | NO 3

But carbon nanotubes could, in the future, provide more than just thermal management, they could form the basis of electronic devices themselves. To realize such a goal, it will be necessary to find a means of creating intramolecular junctions in a controlled manner. Researchers from Peking University, China and Los Alamos National Laboratory claim to be able to form single-walled carbon nanotube (SWNT)

intramolecular junctions simply by varying growth temperature [Yao et al., Nat. Mater. (2007) 6, 293].

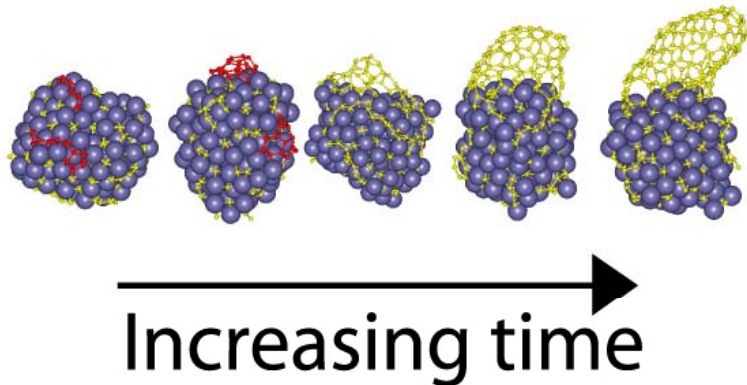
It is currently accepted that the size of the catalytic particle used to grow a nanotube determines its diameter. However, the Chinese researchers observe that the diameter of a SWNT varies with growth temperature during catalytic CVD, even with the same catalytic particle. The results show that if the growth temperature is increased from 900°C to 950°C, the diameter of the SWNT decreases by ~4%. Conversely, when the growth temperature is decreased, the SWNT diameter increases. With the change in nanotube diameter comes a change in chirality and, hence, bandgap. However, if the growth temperature is held constant, the researchers observe nanotubes of uniform diameter.

"These strategies provide a potential approach to grow SWNT intramolecular junctions at desired locations, sizes, and orientation," says Jin Zhang of Peking University. If such a simple method could reliably produce SWNT intramolecular junctions, it could be a significant step toward next-generation, carbon-nanotube-based electronic circuits and devices.

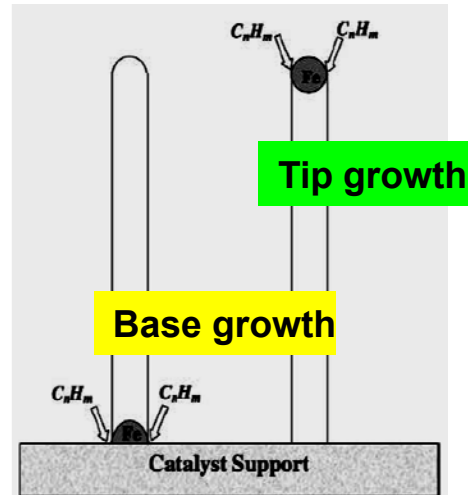


Cap-engineering for Growing SWNT with Controlled Chiralities

Growth Mechanism of SWNT



www.adm.hb.se/~KIB/nanotubes.htm



1. Cap formation on catalyst

2. Carbon atoms bound to the cap and form a SWNT

The cap structure determines the structure of the formed SWNT.

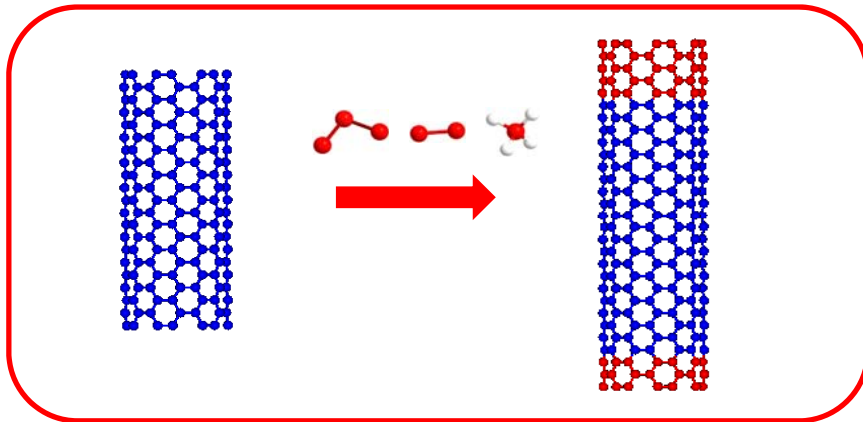
However, it is hard to control the cap structure by controlling the structure of catalyst nanoparticles.

It follows the Vapor – Liquid – Solid (VLS) Mechanism

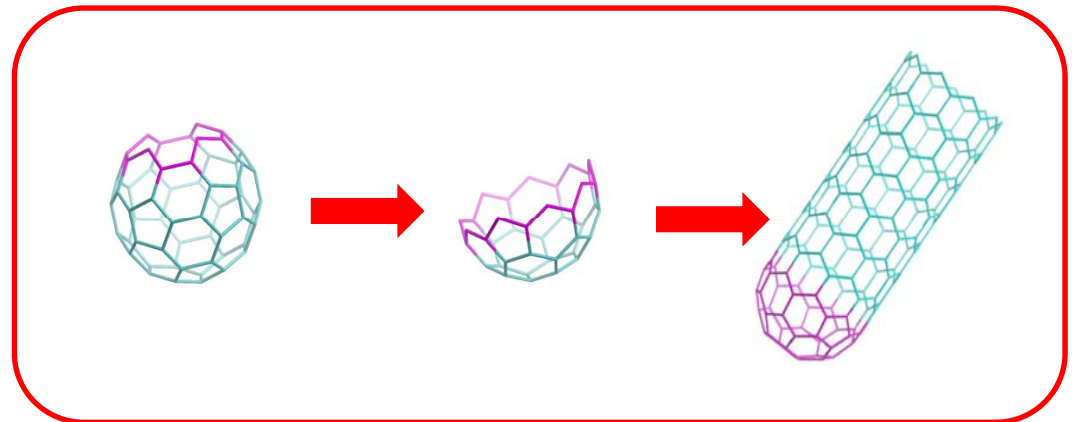
Our Strategies ----- Cap-engineering

Based on the concept of SWNTs Cloning, using an open end SWNT or opened C_{60} as seed/cap to grow SWNT. The structure of the open end SWNT or opened C_{60} determines the structure of the formed SWNT.

Open-end SWNT as seed/cap



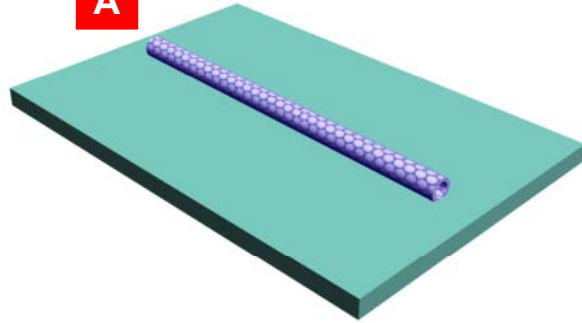
Opened C_{60} as seed/cap



Vapor-Solid Growth Mechanism / Open-End Growth Mechanism

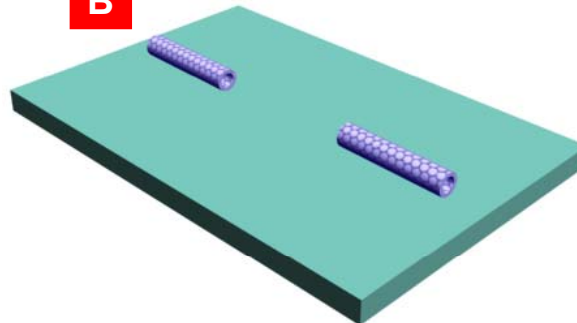
Our experimental scheme

A



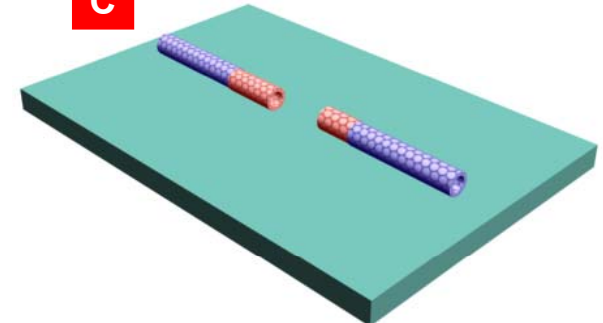
Original "seed" catalyst

B

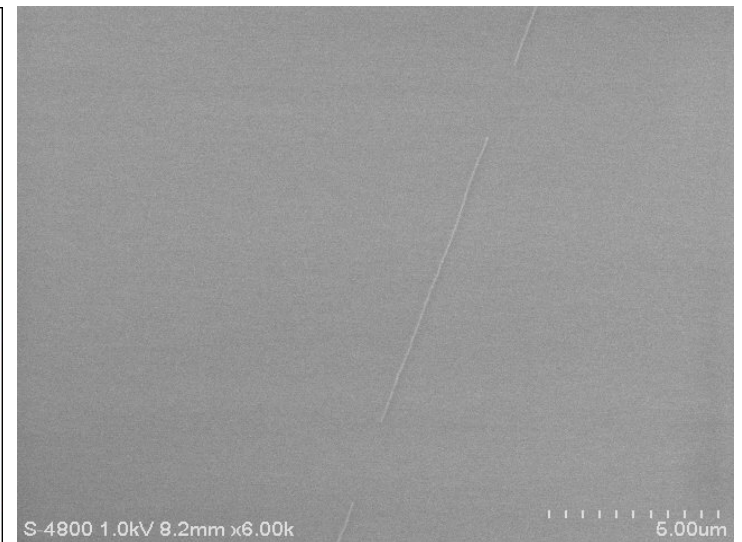
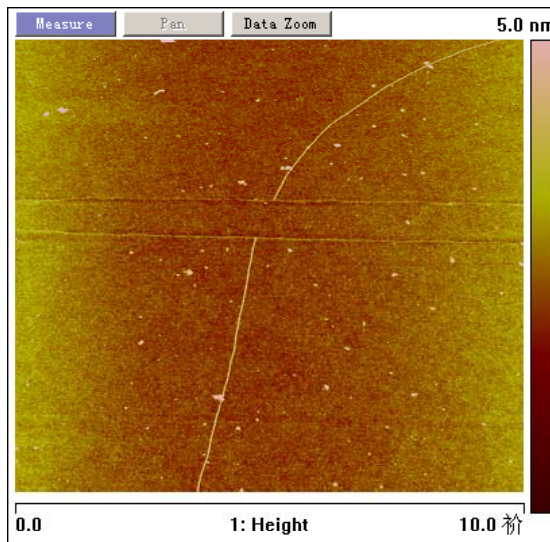
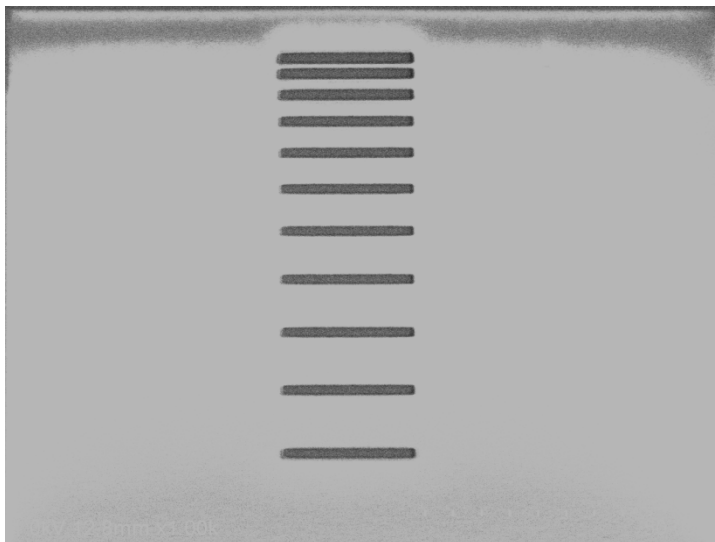


EBL+O₂ plasma

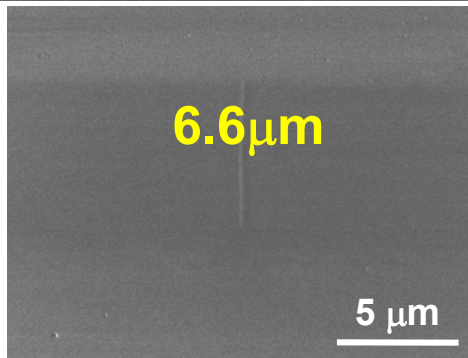
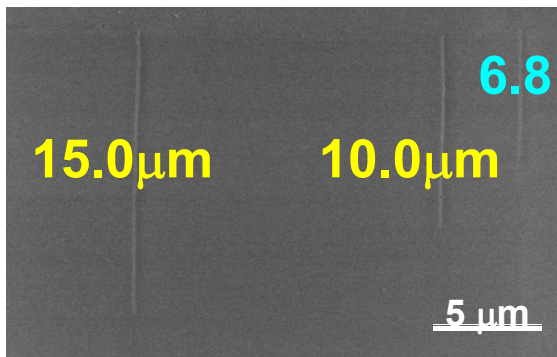
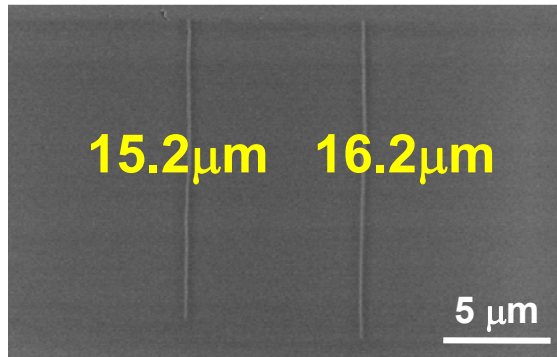
C



Second growth



Cloning SWNTs on Quartz Surface



Before growth

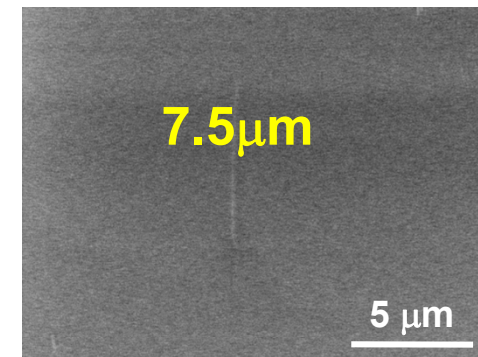
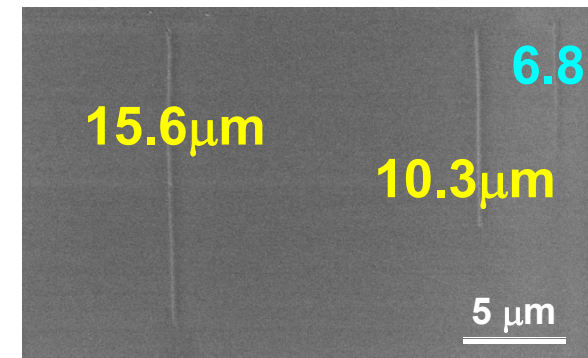
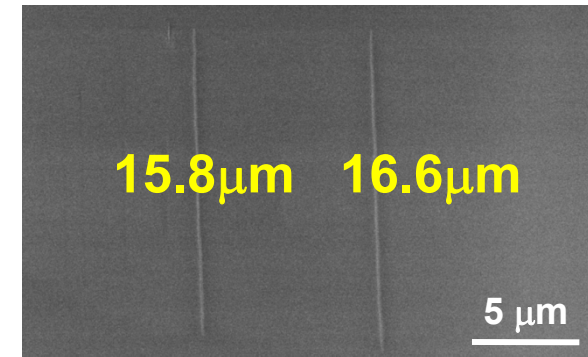
Tube length
increase:

0 μm – 1 μm

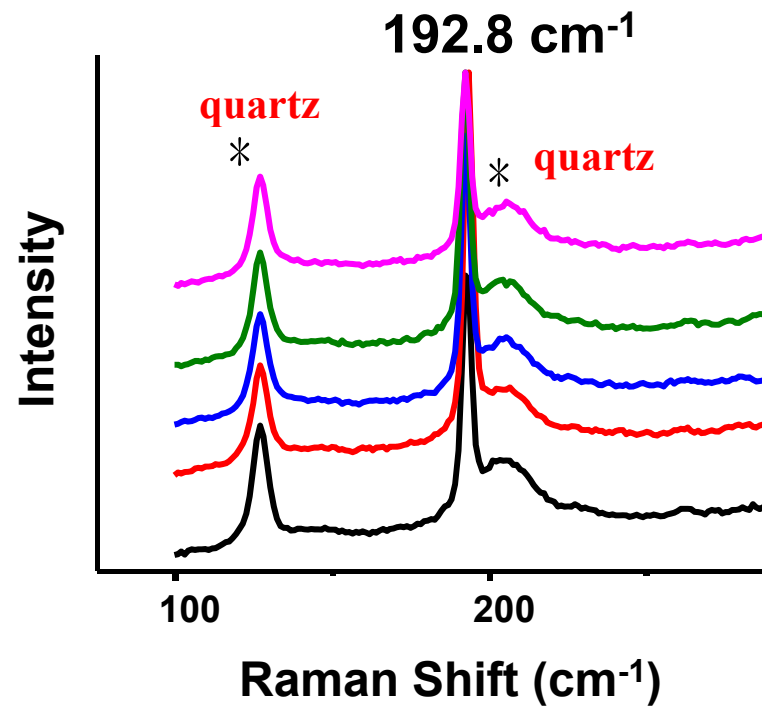
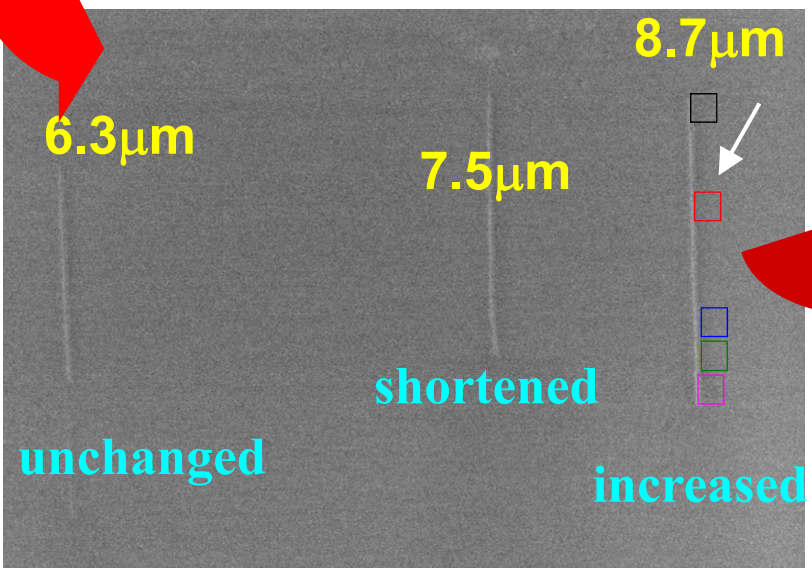
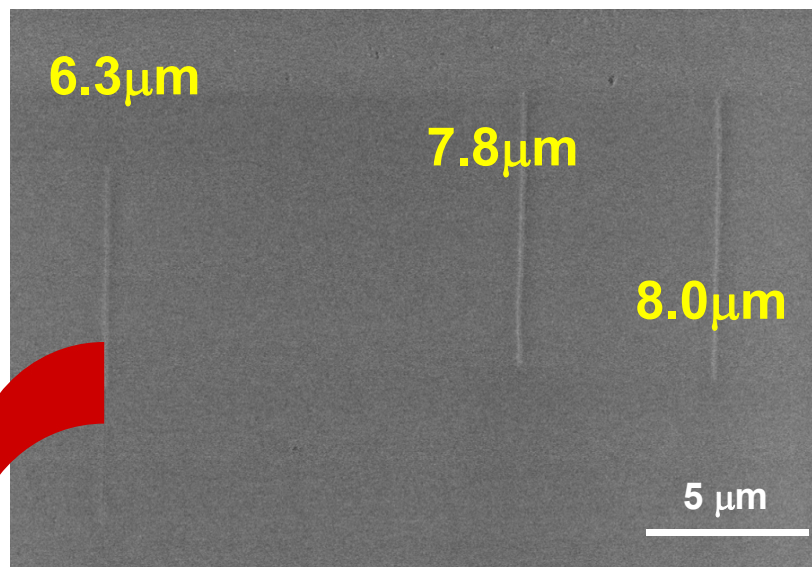


Rate of success
for cloning:

$24/59 = 40.7\%$

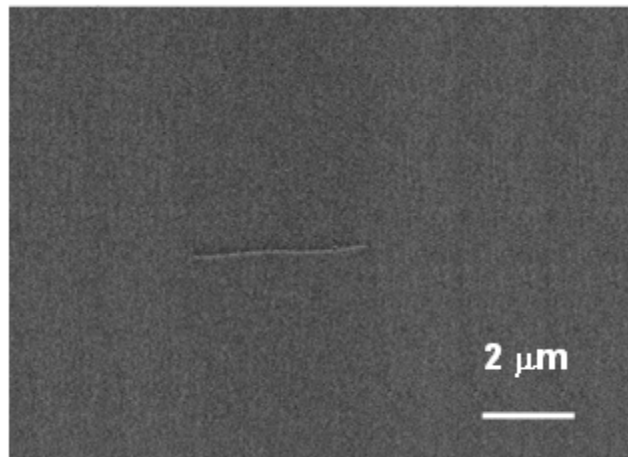
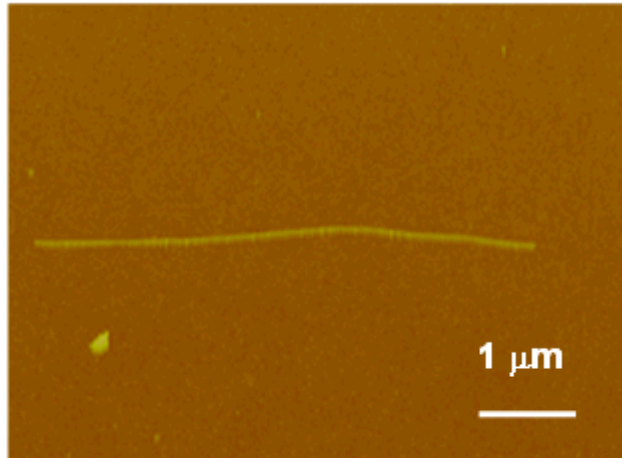


After growth



**Tube diameter & chirality
keep unchanged after
cloning growth**

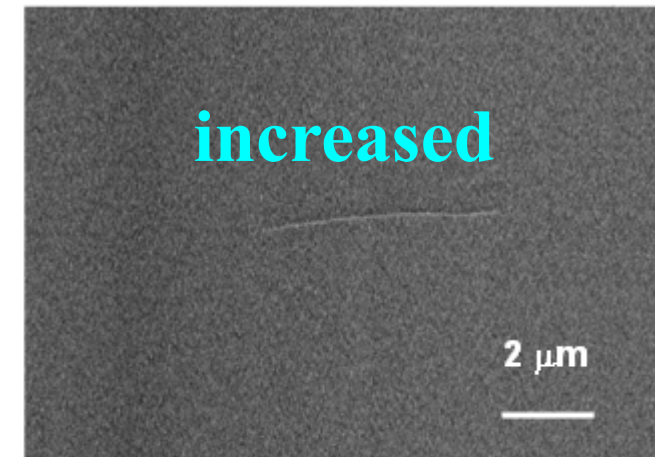
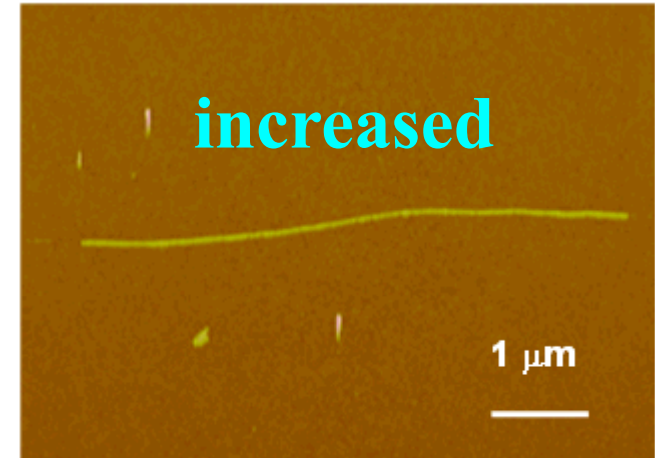
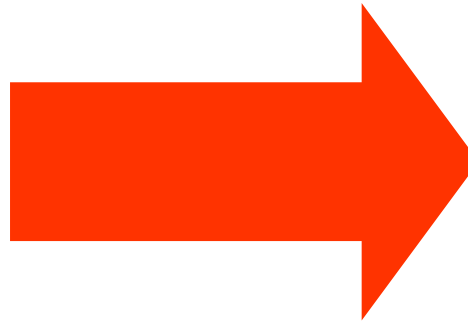
Cloning SWNTs on SiO₂/Si Surface



Before growth

Tube length
increase:

0 μm – 4.6 μm



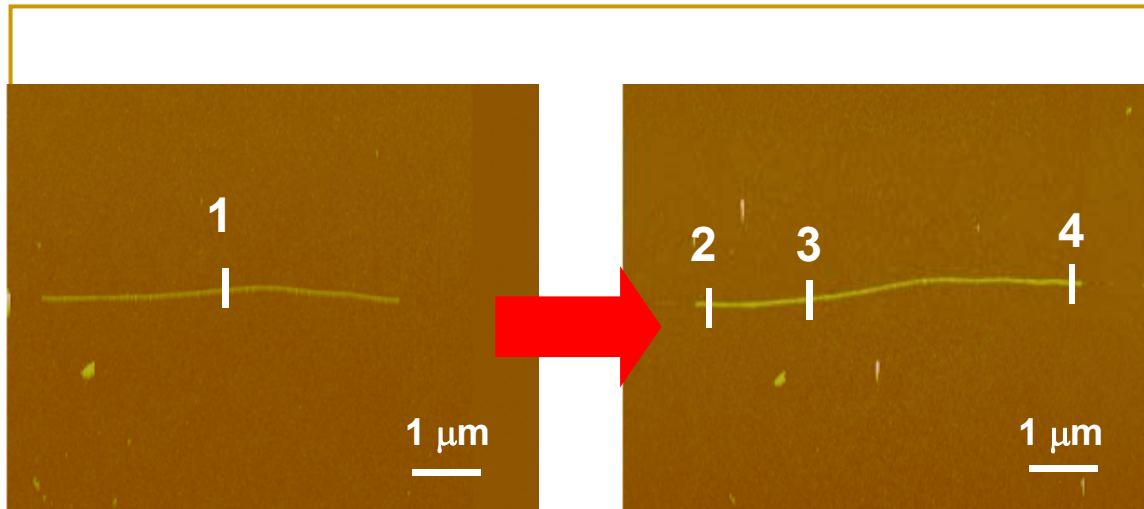
After growth

Rate of success
for cloning:

$56/600 = 9.3\%$

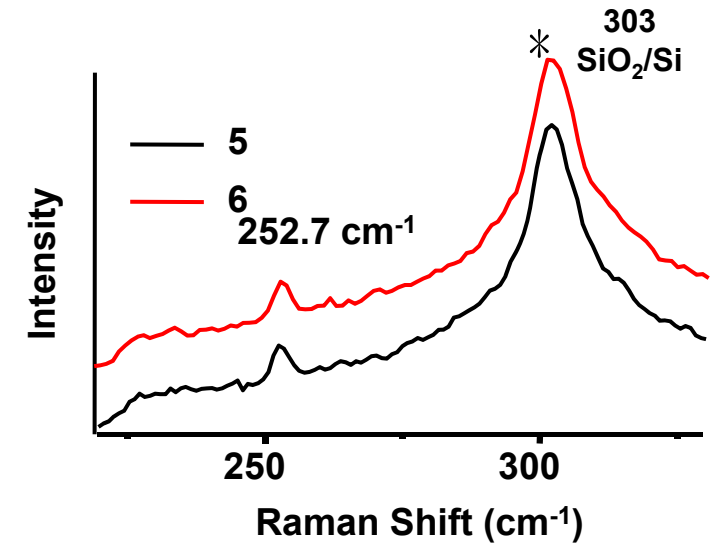
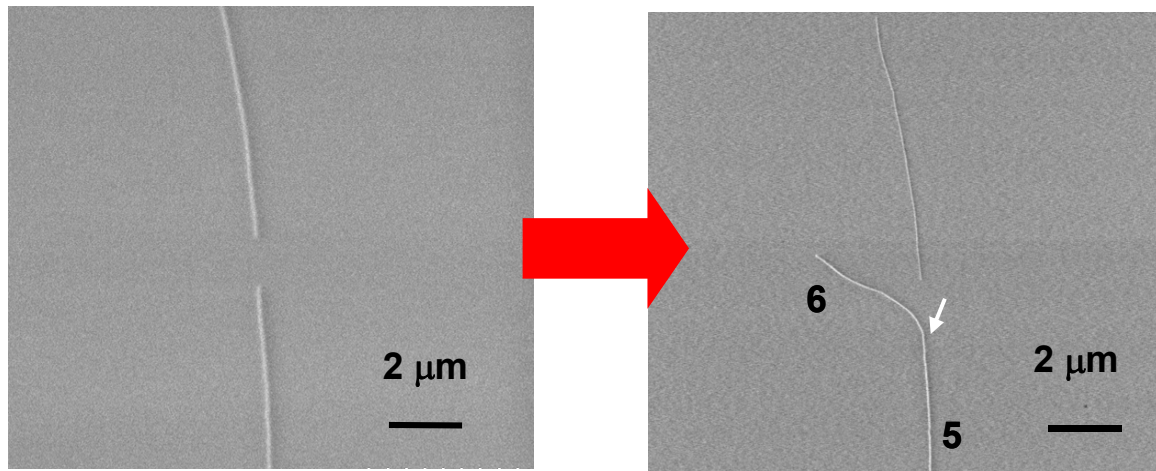
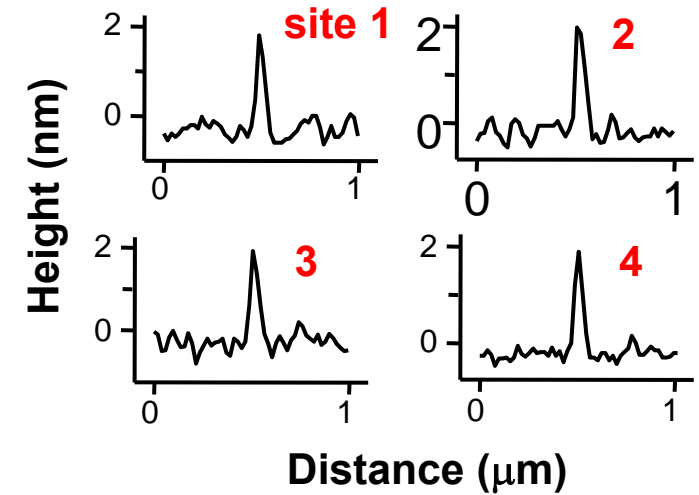
• $CH_4/C_2H_4/H_2=100/5/300$

• Growth $T=975^\circ C$ for 15min



Before growth

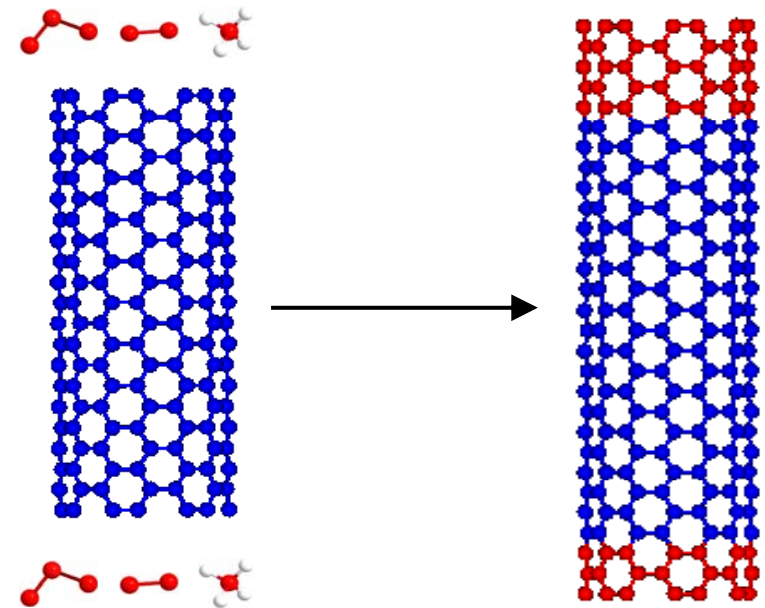
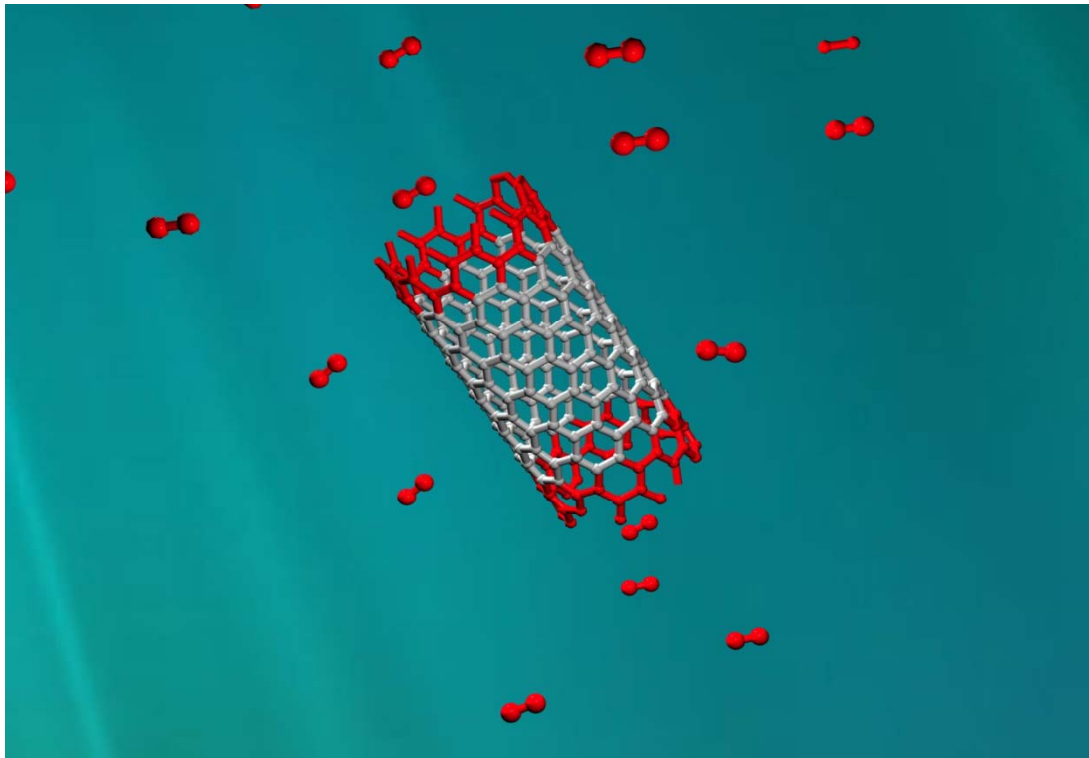
After growth



AFM and Raman evidence for the diameter & chirality maintenance

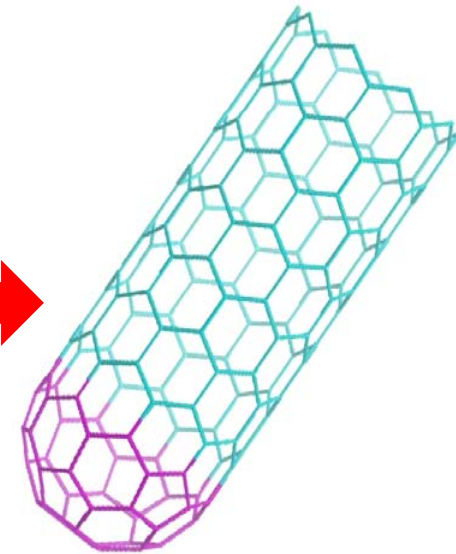
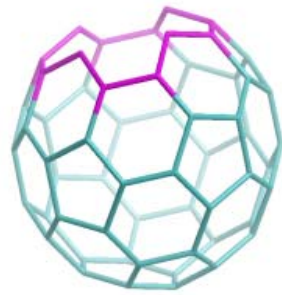
J. Zhang et al., Nano Lett., 2009, 9, 1673

Open-End Growth Mechanism

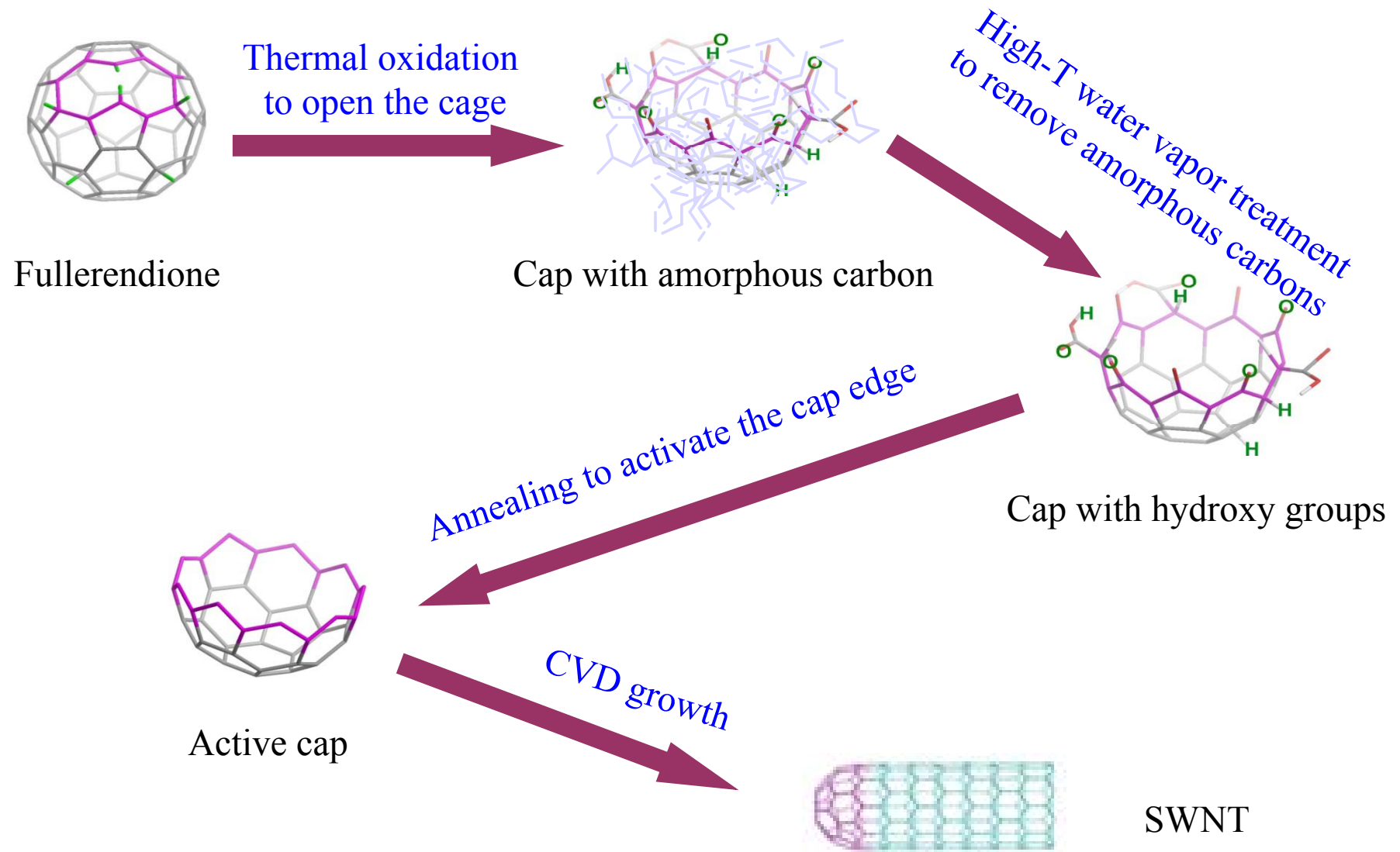


“VS” growth model ?

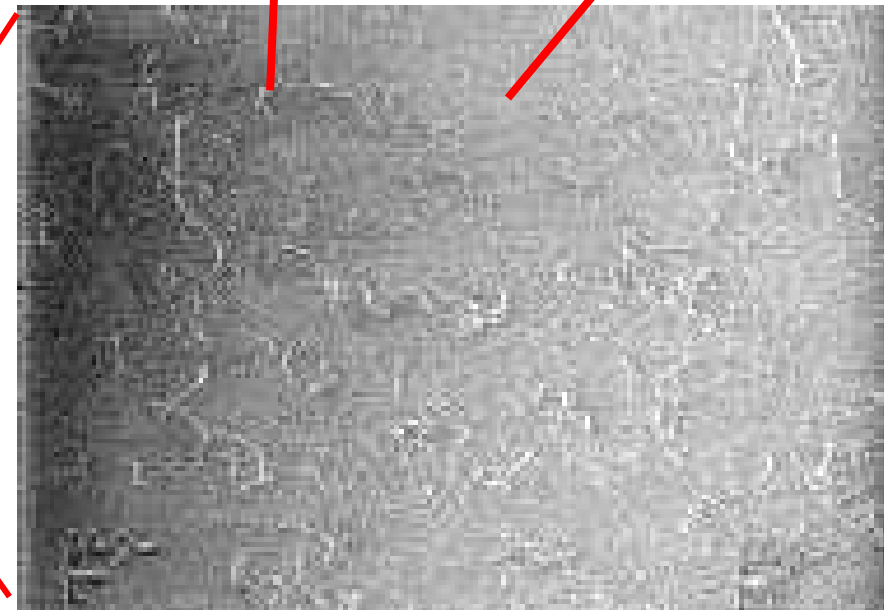
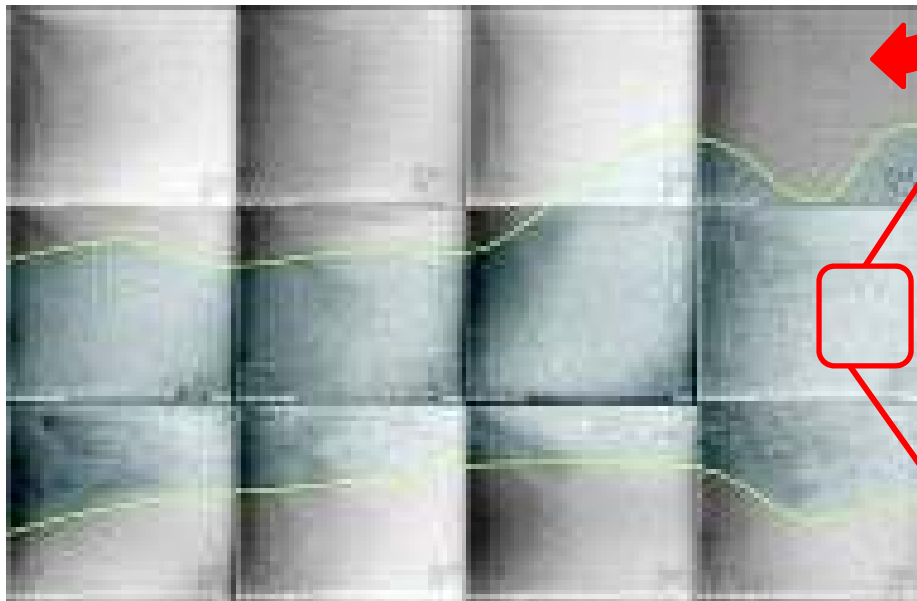
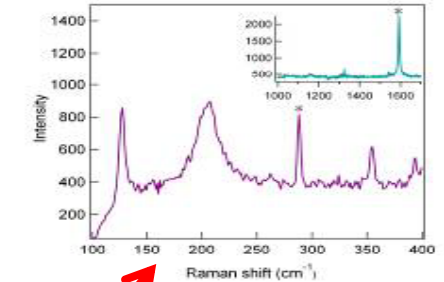
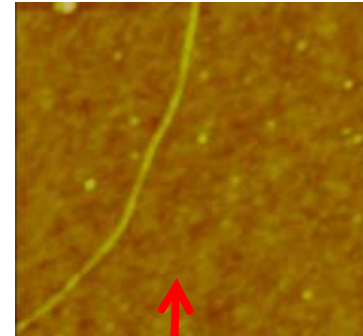
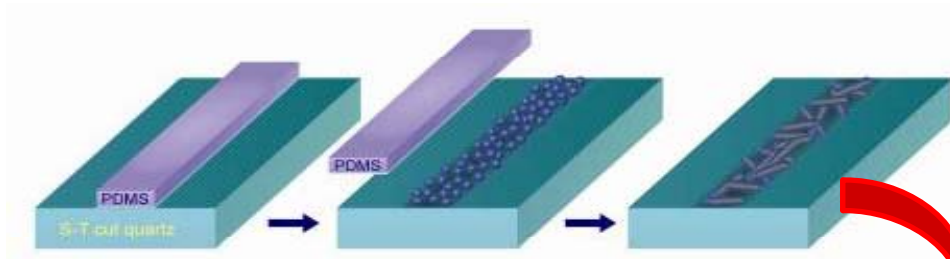
Using C_{60} cap to grow SWNTs



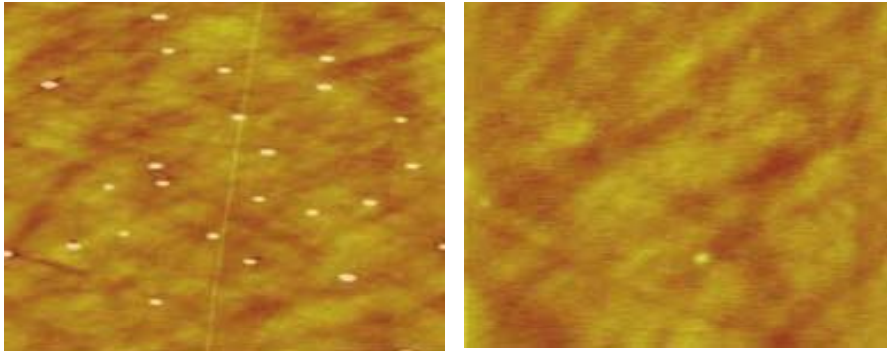
Experiments



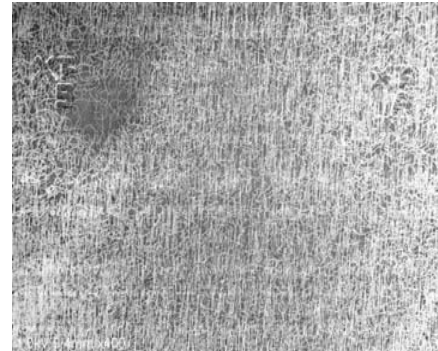
Growing SWNTs Using Opened C_{60} as Seeds: Growth Result



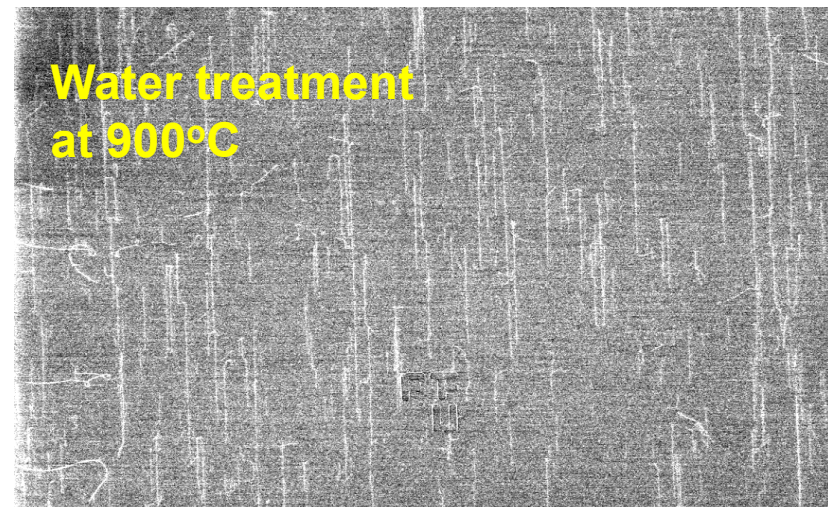
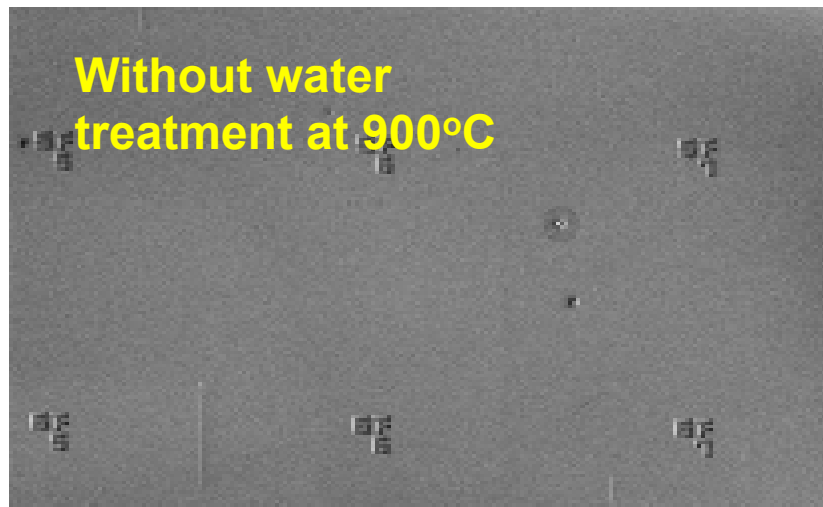
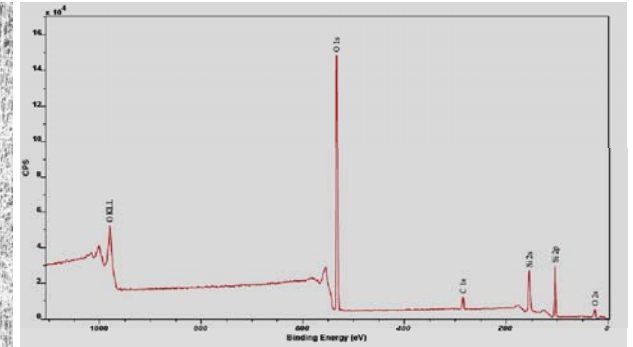
Evidence of SWNTs Grown from Opened C₆₀



Morphological a SWNT grown from opened C₆₀ and after heat treatment

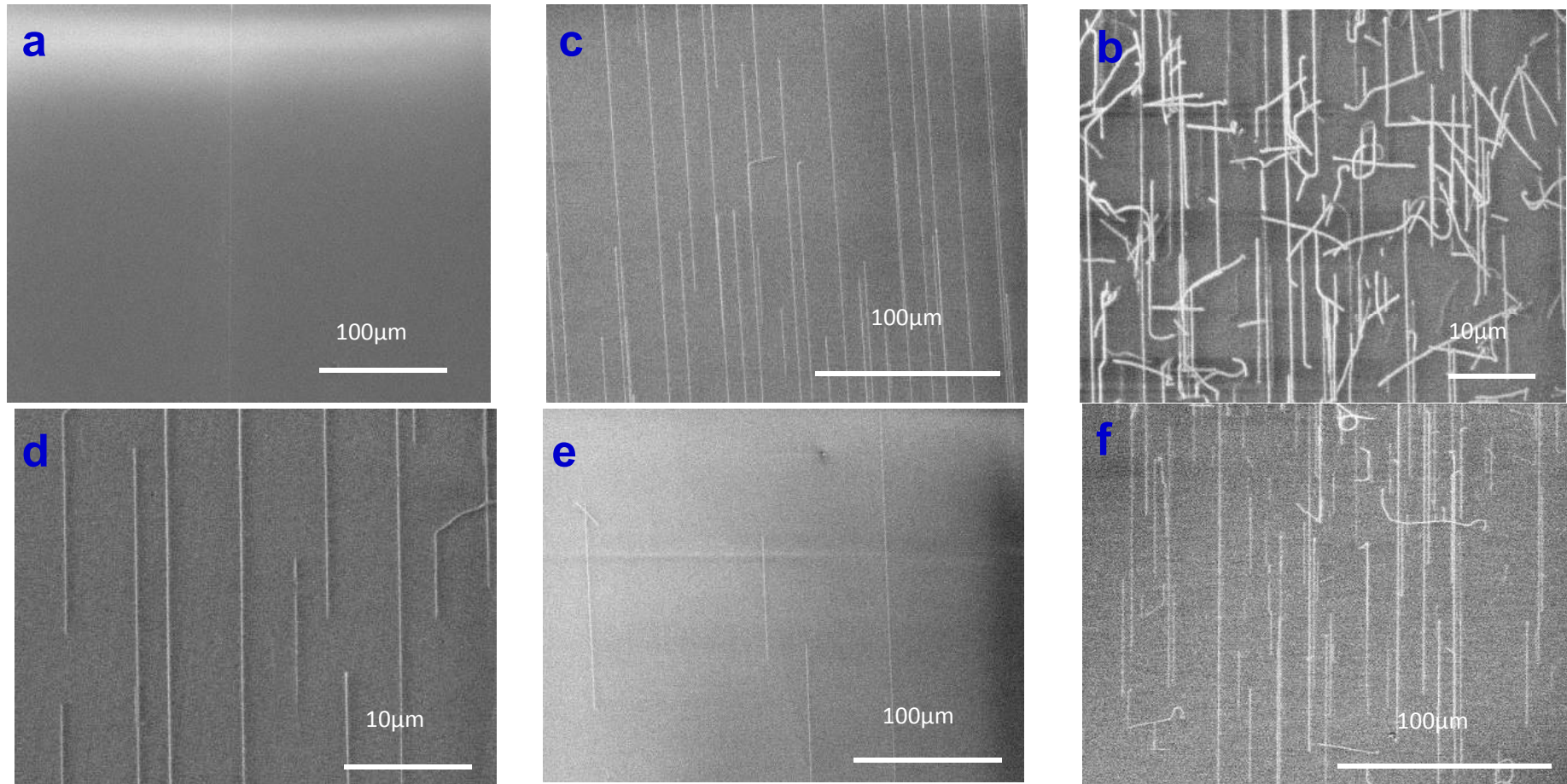


SEM image of a SWNT grown from opened C₆₀ and XPS of the SWNTs sample



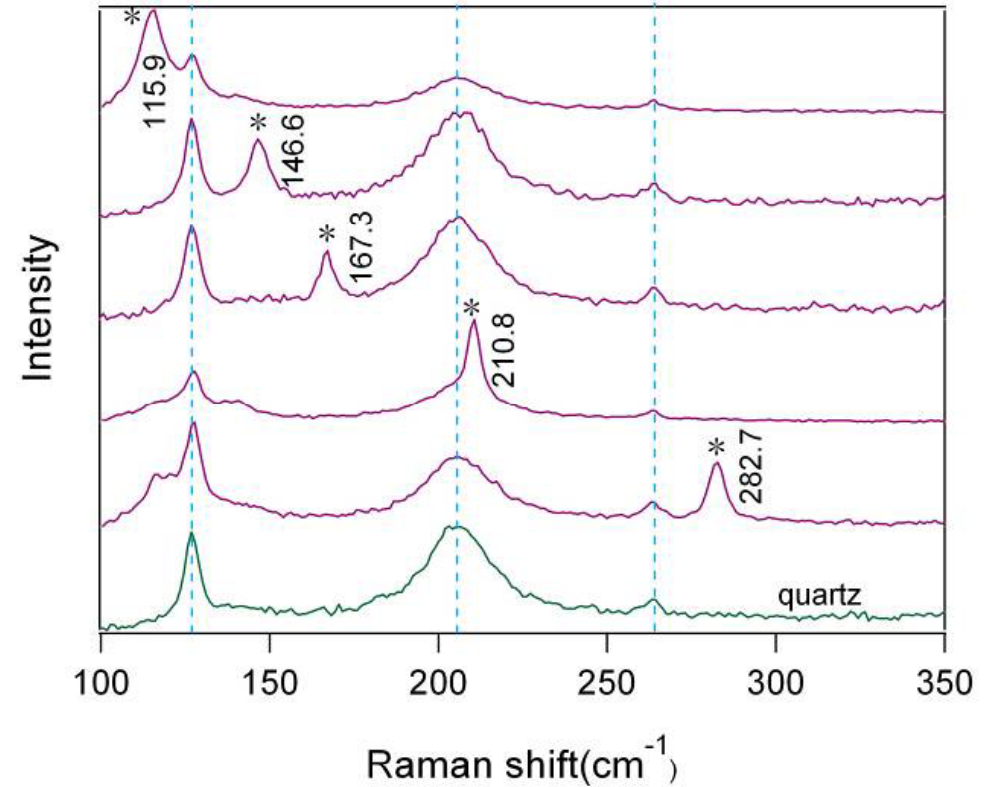
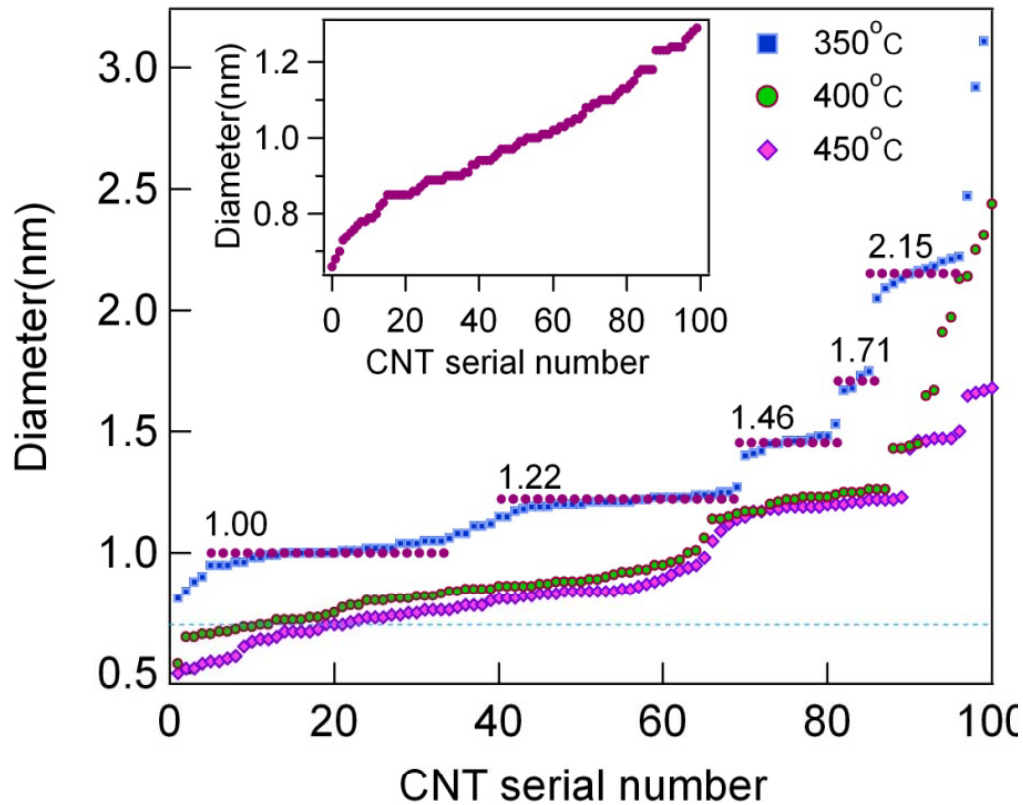
Water treatment is very important for SWNTs growth!

Different thermal oxidation temperature



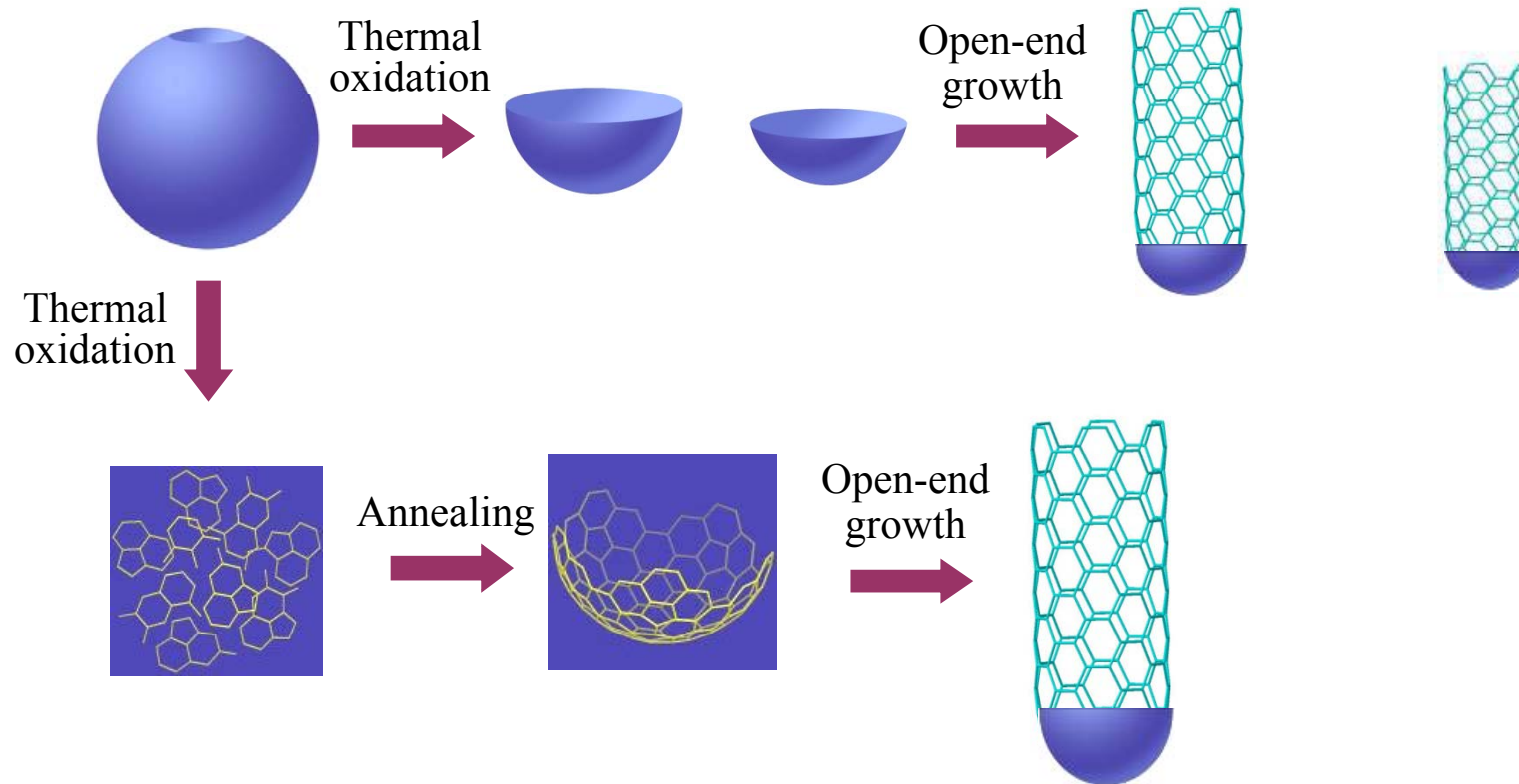
(a)-(e) SWNTs grown from fullerendione using thermal oxidation temperatures of 300, 350, 400, 450 and 500 °C respectively. (f) SWNTs grown from pristine C₆₀ using an oxidation temperature of 500 °C

Diameter Distribution of SWNTs grown by using Opened C₆₀ caps



Diameter distribution of SWNTs grown from fullerene under different oxidation conditions (measured from AFM).

Possible Growth Mechanism



The caps from C₆₀ has a discrete diameter distribution.

The formed SWNTs are expected to have a discrete diameter distribution.

Carbon nanotubes: Perfect clones

Published online 29 June 2009

Although methods for producing single-walled carbon nanotubes have advanced considerably in recent years, growing nanotubes with specific structures remains difficult. Nanotubes can be semiconducting or metallic in character depending on the orientation of carbon hexagons within the structure, and controlling this behavior is crucial for future nanoscale electronic applications.

Now, Jin Zhang and colleagues¹ from Peking University in China have devised a novel method for the growth of single-walled carbon nanotubes that allows precise control of the nanotube properties. Using seeds cut from existing nanotubes, the researchers grew new extensions that retained the original structure — perfect 'clones' of the parent segments (Fig. 1).

Working with ultralong single-walled carbon nanotubes grown by chemical vapor deposition, Zhang's group first covered the nanotubes with a lithographic mask. Then, using electron-beam lithography and oxygen plasma ion etching, the researchers prepared short, open-ended segments of the nanotubes as seeds. These small sections were then remove any impurities.

To grow new nanotube extensions, a stream of gas containing carbon by the seed segments. Using atomic force and scanning electron team observed new growth of several micrometers in length external Raman spectroscopy confirmed that the newly grown nanotube segments retained the original seed structure.

According to Zhang, growing the nanotube clones required accurate a mixture of acetylene and methane gases. "We used acetylene to decompose of methane gas into carbon radicals. If we didn't use growth temperature was below 945 °C, no amplified growth occurred."

Instead of requiring an external additive, the growth mechanism is the open ends of the nanotubes themselves as catalysts. The seed the nanotube structure, and any new growth via carbon radicals released from the open ends.

The researchers reported that, on a quartz substrate, over 40% of produced new cloned segments. "We think if the open-ended segments the growth efficiency would be greatly improved," says Zhang.

Zhang and colleagues are now undertaking large-scale growth trials of carbon nanotube clones.

Reference

1. Yao, Y.,¹ Feng, C.,¹ Zhang, J.,^{1*} & Liu, Z.¹ "Cloning" of single-walled carbon nanotubes. *Nano Lett.* 9, 1673-1677 (2009). | [article](#) |

Author affiliation

1. Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Nano-devices, State Key Laboratory for Structural Chemistry of Unstable and Transient Chemistry and Molecular Engineering, Peking University, Beijing 100871, China *E-mail: jinzhang@pku.edu.cn

www.afm.university.org

WWW.AFM.UNIVERSITY.ORG

Agilent

Article Tools

Printer-friendly

E-mail this article

Daily News Email Digest

Subscribe to Spotlight

Join us on Facebook

Follow us on Twitter

Nanowork News Feeds

SHARE

TOP TEN

Most Recent Spotlights

Nanotechnology fabrication technologies can be advanced by ingenious structure of biomimicry
 Posted: Aug 24th, 2009

Ten things you should know about nanotechnology
 Posted: Aug 20th, 2009

DNA nanotechnology in computers knocks down another roadblock
 Posted: Aug 18th, 2009

Re-writable photonic paper
 Posted: Aug 17th, 2009

DNA-encasing increases carbon nanotubes' tumor killing power
 Posted: Aug 13th, 2009

Towards electronic-based single-molecule DNA sequencing
 Posted: Aug 12th, 2009

Bio-interface nanosensor visually reports damage to a material
 Posted: Aug 11th, 2009

Improving solid oxide fuel cells with nanostructured electrolyte layers
 Posted: Aug 6th, 2009

Textured network devices to solve fundamental problems with CNT nanoelectronics
 Posted: Aug 4th, 2009

Plastic surgeons' dream? Scar-free surgery with nanotechnology sealant
 Posted: Jul 31st, 2009

An evolutionary tree for nanotechnology particle engineering
 Posted: Jul 29th, 2009

Cellular toxicity of titanium dioxide nanotubes and nanowires
 Posted: Jul 27th, 2009

Biosensors printed on bioactive paper
 Posted: Jul 24th, 2009

Integrating nanotube-based NEMS into large scale MEMS
 Posted: Jul 23rd, 2009

Nanotechnology listening device for neuronal talks
 Posted: Jul 22nd, 2009

Easy fabrication of carbon nanorolls could speed their use in nanotechnology applications
 Posted: Jul 22nd, 2009

Nanofluidics meets nanoplasmonic sensing
 Posted: Jul 17th, 2009

European debate on human enhancement technologies
 Posted: Jul 16th, 2009

Graphene transistors can work without much noise
 Posted: Jul 16th, 2009

Desertec - a nanotechnology-enabled bold vision for an energy revolution
 Posted: Jul 13th, 2009

Nerve interface electrodes
 Posted: Jul 9th, 2009

FluidFM: Combining AFM and nanofluidics for single cell applications
 Posted: Jul 8th, 2009

Novel electrostatic coupling method to make quantum dot

Fig. 1: Using nanotubes (SWNT) growth process

Cloning

Cloning

Cloning

Cloning

Cloning

Nano-C, Inc. Fullerenes, Carbon Nanotubes, PCBM and Other Derivatives

Elicarb™ SV Single-wall carbon nanotubes Commercial

News » Nanowork Spotlight »

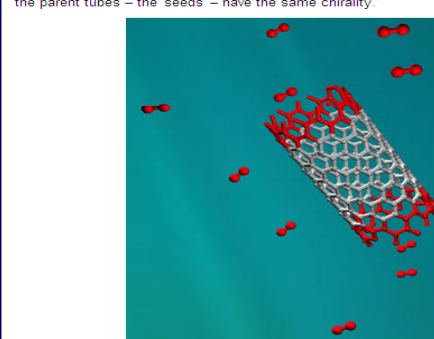
Posted: April 3, 2009

'Cloning' might solve the chirality control issue

(Nanowork Spotlight) Notwithstanding the tremendous amount of carbon nanotubes, the synthesis of single-walled carbon nanotube still has not been achieved. Current production methods for carbon nanotubes with different diameter, length, chirality and electronic properties, all blended with some amount of amorphous carbon. The separation properties remains a technical challenge. Especially SWCNT sort composition and chemical properties of SWCNTs of different type conventional separation techniques inefficient.

Using the concept of cloning, scientists in China have discovered special (n, m) indices SWCNTs.

"We found that an open-end single-walled carbon nanotube, which grown via an open-end growth mechanism," Jin Zhang tells Nanowork the parent tubes — the 'seeds' — have the same chirality."



Schematic illustration of a single walled carbon nanotube clone. Laboratory for Molecular Sciences

These findings by Zhang, a professor of chemistry and molecular Laboratory for Molecular Sciences, and his colleagues Zhongfan Li are not only helpful to understand the formation mechanism of single-walled carbon nanotubes, but also the controllable growth of SWCNT with identical chirality into nanotubes.

Moreover, this growth mechanism might be an effective way for carbon nanotubes. Furthermore, large scale cloning of single chirality SWCNTs is possible.

The scientists reported their findings in the March 13, 2009 online Single-Walled Carbon Nanotubes via Open-End Growth Mechanism.

For their technique, Zhang's team first grew ultralong (several tens micrometers) nanotubes. The nanotube length is only limited by the substrate size. Then, the ultralong SWCNTs were cut into short lithography (EBL), oxygen plasma ion etching, and lift-off, which is the stencil in the second growth.

In a third step, the SWCNT 'clones' were grown from the open-end seeds in a chemical vapor deposition (CVD) furnace to first grow functionalized SWCNTs, which could help expose the active group and C₆₀ carbon source.

"The cloned nanotubes usually grew as much as a few micrometers amplified growth was 4.6 μm" says Zhang. "We thought that if the substrate such as the open-end SWCNTs are suspending, the growth mechanism will be greatly improved."

"We have measured more than 600 short seed segments and found about 90% are SWCNTs," says Zhang. "This yield can be greatly improved up to 100%."

The key point of SWCNT cloning is to verify the duplicate SWCNT parent SWCNTs. Through atomic force microscopy and micro Raman characterization the team determined that the parent nanotube are same structure.

According to Zhang, the open-end SWCNT catalyst (seed) is more effective for the growth of SWCNTs.

"Firstly, it can not conglomerate at high growth temperature. The metal catalysts will directly add to the open-end and thus the structure of the parent SWCNTs. Thirdly, our results show that the parent SWCNTs might act as a template for the formation of SWCNTs."

By Michael Berger. Copyright 2009 Nanowerk LLC

Carbon nanotubes: Capped for growth

High-temperature oxidation reactions open fullerenes to seed carbon nanotube growth.

Single-walled carbon nanotubes (SWNTs) are poised to play central roles in future nanoelectronic devices, but it remains necessary to develop methods to reliably control their structures. Even small changes in the width of the tubes or the orientation of carbon atoms can alter the conductivity of SWNTs, determining whether they behave as a semiconductor or metal. Now, in a collaboration between Peking University in China and the Samsung Advanced Institute of Technology in Korea, Jin Zhang, Jae-Young Choi, Zhongfan Liu and co-workers¹ have developed a 'cap engineering' method that generates SWNTs with well-defined diameters.

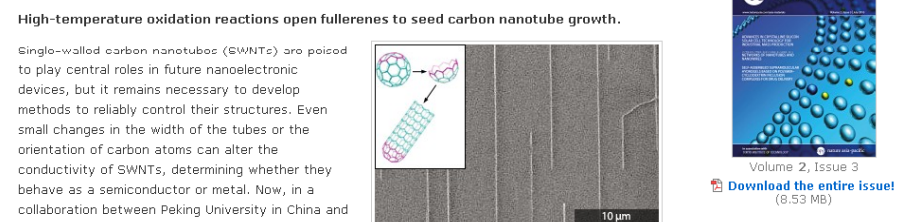


Fig. 1: Schematic representation of the growth of a single-walled carbon nanotube from an opened fullerene cap (inset), and a scanning electron microscopy image of the prepared nanotubes.

Typical SWNT syntheses rely on the formation of hemispherical carbon-based nanostructures, or 'caps', on metal nanoparticle catalysts at high temperature. These caps initiate the growth of nanotubes, and also define their final structure. The extreme conditions required for synthesis, however, make it difficult to generate caps of uniform size. "We think that if the SWNTs can be grown from existing carbon caps through a vapor – solid or open-ended growth mechanism, the structure of SWNTs could be controlled," says Zhang.

The team developed a method using fullerenes (C₆₀) and derivatives called fullerendiones, which can open to form caps with predetermined diameter. After depositing these ball-shaped carbon structures on a quartz substrate, the team cracked opened the carbon – carbon bonds by high-temperature oxidation. Treating the caps with water eliminated any amorphous carbon from the structure, and subsequent heating removed oxygen-containing groups. The activated caps were finally exposed to ethanol at 900 °C, which induced the growth of uniform SWNTs (Fig. 1). Ethanol releases carbon radicals that are added directly to the cap ends, resulting in the growth of nanotubes by an open-ended growth mechanism.

The researchers found that the oxidation temperature was crucial in determining the diameter of the fullerene-derived caps, and therefore for controlling the SWNT structure. Higher temperatures caused the breakage of more carbon – carbon bonds, giving smaller caps and resulting in thinner SWNTs. The team also observed that at lower temperatures, the oxidation produced oxygen-bridged 'opened fullerenes' that further coalesced into larger caps, leading to larger-diameter nanotubes.

"We are now working on controlling the chirality of SWNTs during growth using this cap engineering approach," says Liu.

From Ref. 1. Reproduced with permission. © 2010 ACS

Reference

1. Yu, X.,¹ Zhang, J.,^{1*} Choi, W.M.,² Choi, J.-Y.,² Kim, J.M.,² Gan, L.¹ & Liu, Z.^{1*} Cap formation engineering: from opened C₆₀ to single-walled carbon nanotubes. *Nano Lett.* 10, 3343 (2010). | [article](#) |

Author affiliation

1. Center for Nanochemistry, Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Key Laboratory for the Physics and Chemistry of Nanodevices, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

2. Samsung Advanced Institute of Technology, Nongseo-Dong, Gyeonggi-Dong, Yongin, Gyeonggi-Do 446-712, Korea

*E-mail: zliu@pku.edu.cn

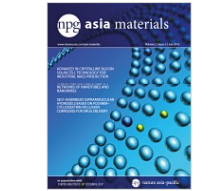
top home

Register today for:

- ✓ FREE PDF downloads
- ✓ FREE email alerts

Register

Volume 2, Issue 3



Download the entire issue! (8.53 MB)

site resources

- email alert signup
- RSS feed
- Follow us on Twitter (NPG Nature Asia-Pacific)

search & explore

search

GO

explore

- photonic crystal
- crystal
- ferrite films

more keywords

TOKYO TECH Pursuing Excellence

TOKYO TECH Global-COE

NANOMATERIALS in ASIA

news & events

AsiaNANO 2010, Tokyo, Japan: 1 – 3 Nov 2010

AsiaNANO 2010, the fifth Asian Conference on Nanoscience & Nanotechnology, will be held in Tokyo, Japan, 6th Asian Photochemistry Conference, Wellington, New Zealand: 14 – 18 Nov 2010

The 2010 Asian Photochemistry Conference will provide an opportunity for researchers in photochemistry...

Summary

Single-Walled Carbon Nanotubes

Application the SWNTs in Future Devices

Growing SWNTs on Surface
with Controlled Structures

Although it is still difficult to make a precise control of the diameter, chirality and local band structure of single-walled carbon nanotubes, there exists a big space for further efforts.

Acknowledgement

Collaborates:

Prof. Zhongfan Liu

PKU

Prof. Jing Kong

MIT

Prof. Mildred Dresselhaus

MIT

Fund Support:

NSFC (20725307, 50521201);

MOST(2006CB932701)



Welcome to Peking University!

Welcome to Beijing!

