



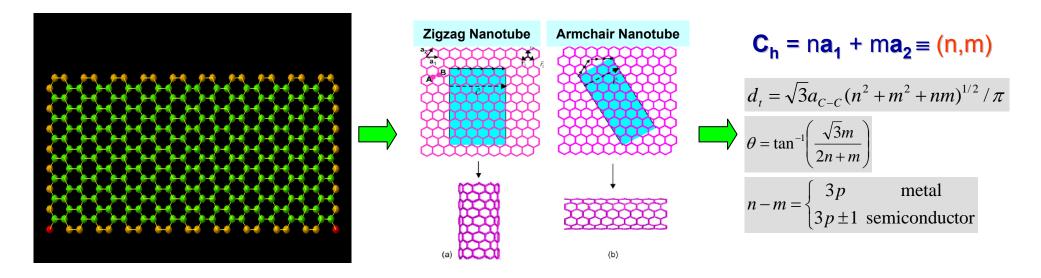
Structure Controlled Growth of Singlewalled Carbon Nanotubes on Surface

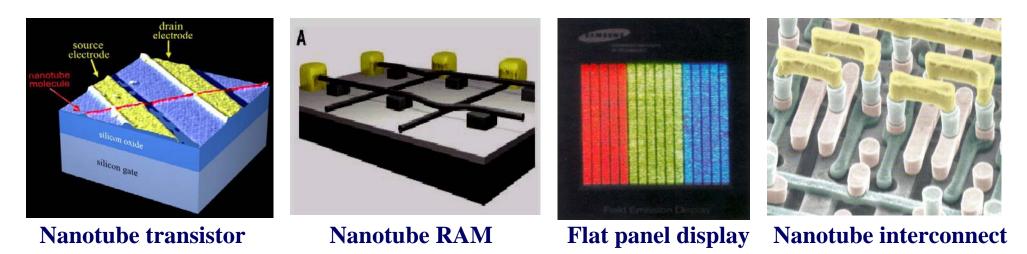
Jin ZHANG (张 锦)

Beijing National Laboratory for Molecular Sciences(BNLMS) College of Chemistry and Molecular Engineering Peking University, Beijing 100871, P. R. CHINA Email: jinzhang@pku.edu.cn

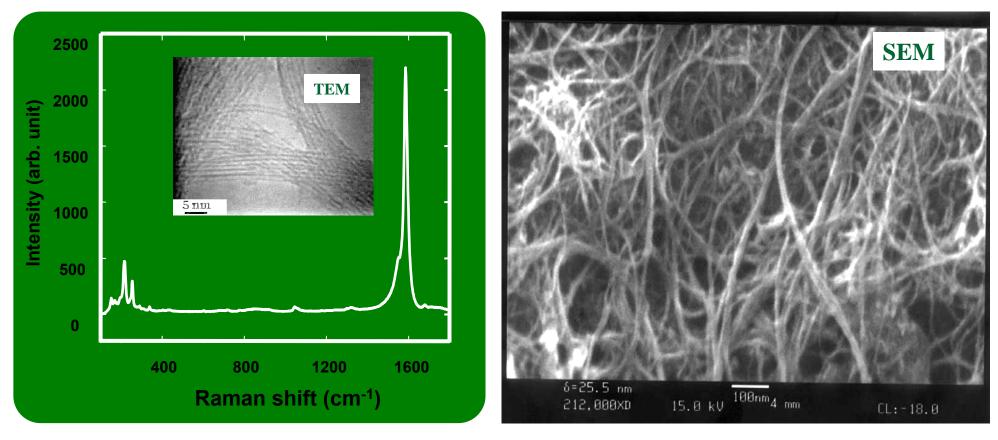
北京大学物理学院,2009年10月22日

Introduction of Single-walled Carbon Nanotubes





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

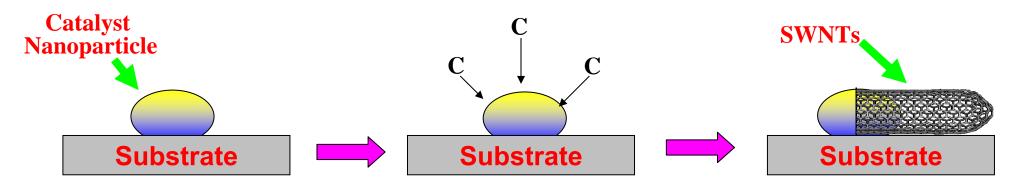


Support: MgO; Catalysts: Fe; Carbon Source: CH₄

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

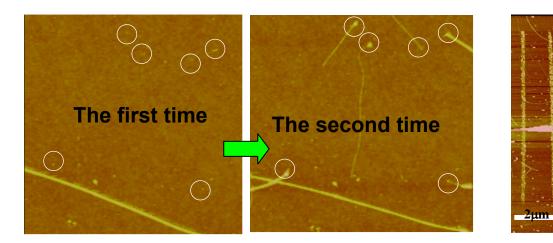
Growth Process:

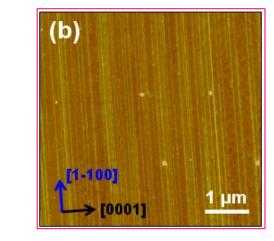


Questions:

- 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 Semiconducting Properties
- 4. Growing SWNTs on Surface with Controlled Chirality

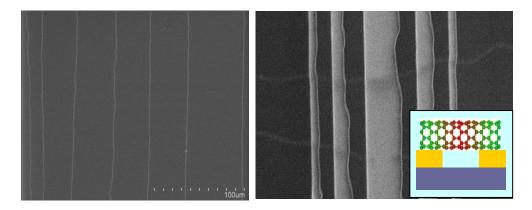
Controlled CVD Growth of SWNTs on Surface



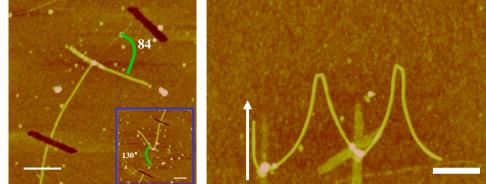


J. Phys. Chem. B. 2004, 108, 12665

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)
 - Semiconduting 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 ?

Outline

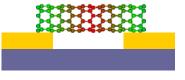
Control of local deformation of SWNTs
Growth on designed surface

Control of local tube diameters of SWNTs —— Temperature-oscillation growth

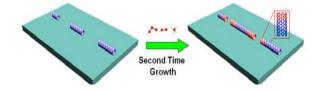
Control of chirality of SWNTs
Cloning growth

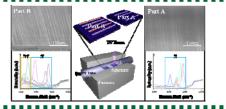
Control of metallic-/semiconducting- of SWNTs
UV irradiation assistance CVD growth

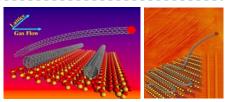
Control of local conformation and architectures
— Cooperative growth of floating and lattice oriented modes

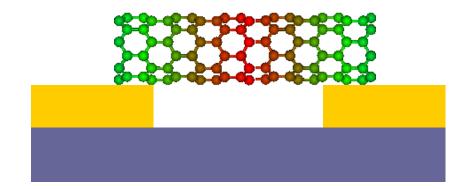






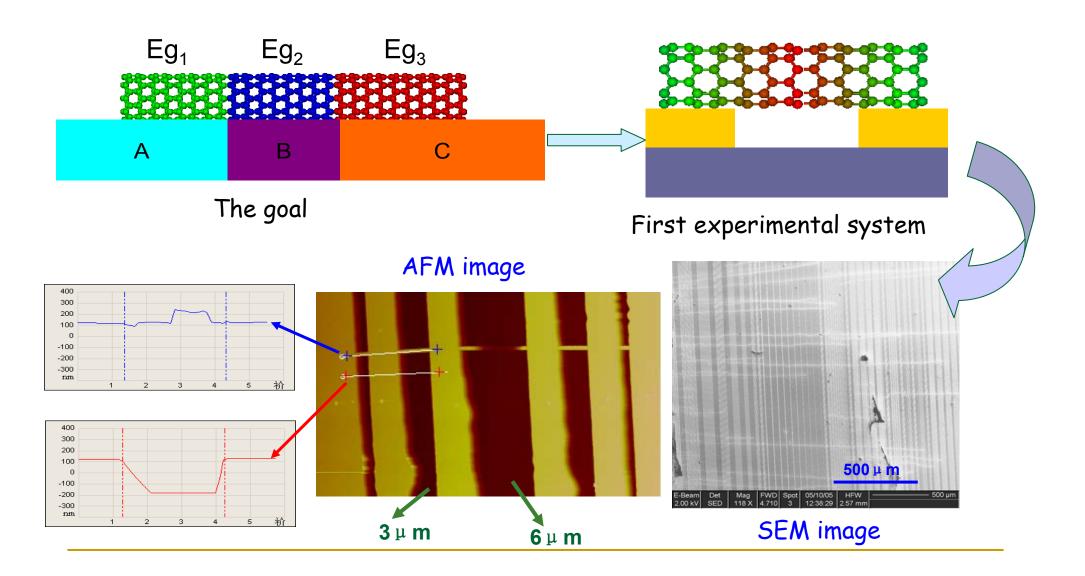




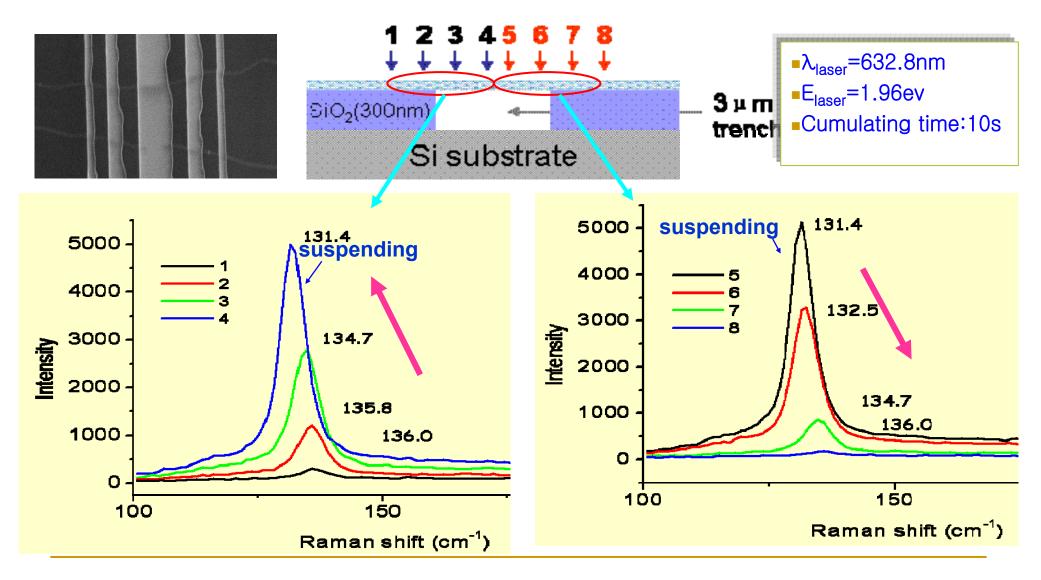


Control of local deformation of SWNTs —— Growth on designed surface

Substrate-Induced Band Structure Variation

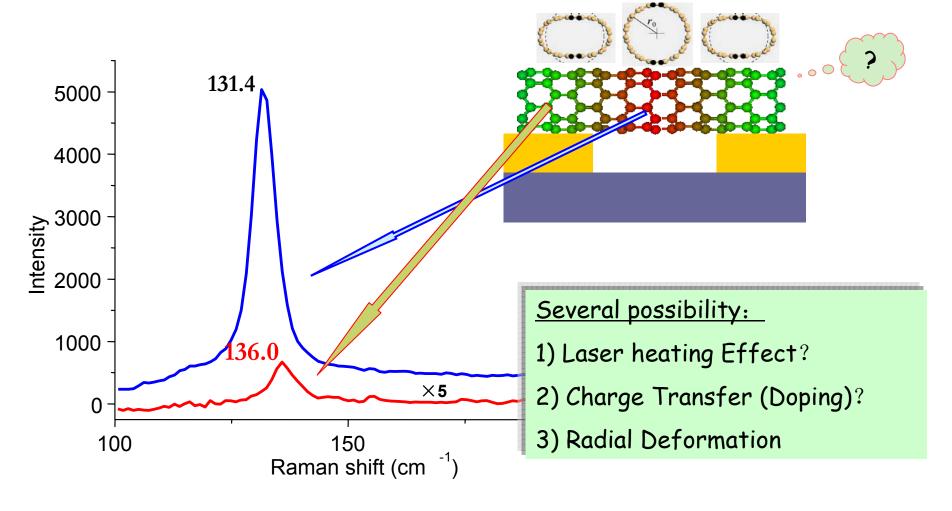


Raman Mapping of Partially Suspended SWNT



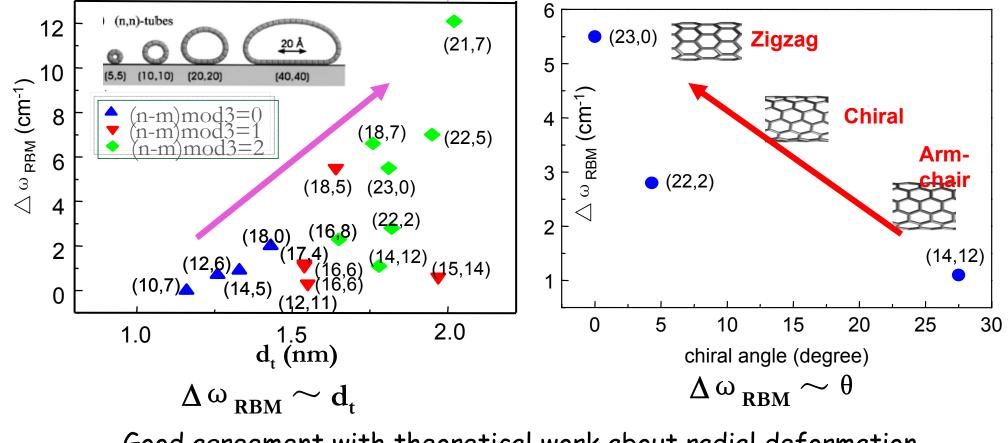
J Zhang et al, J. Am. Chem. Soc, 2005,127,17156

What is the Origin of Raman Spectrum Variation ?



J. Phys. Chem. C., 111(2007)1983-1987; 111(2007)1988-1992.

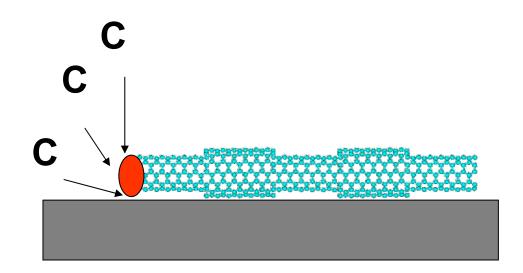
Dependence of $\triangle \ \omega$ RBM on Diameter and Chiral Angle



Good agreement with theoretical work about radial deformation.

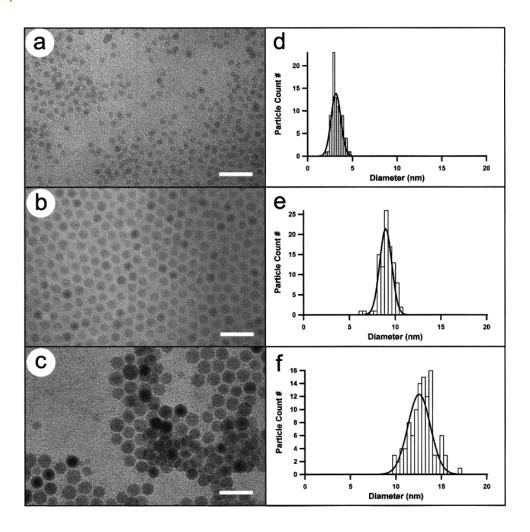
Band Structure Variation between Suspended and Non-suspended SWNT

No.	Location	ω _{RBM} (c m ⁻¹)	I _{AS} /I _S	E _{ii}	E _{ii} (eV)	∆E _{ii} (meV) (SiO₂-Sus)	(n,m)	(2n+m) MOD3
1	Suspended	282.7	0.12	E22S	1.9522	-3.1	(7,5)	1
	SiO ₂	282.7	0.085		1.9491			•
2	Suspended	243.6	1.26		1.9736	-4.8	Difficult	
	SiO ₂	244.8	0.95		1.9688			
3	Suspended	200.4	0.13	E11M	1.9514	~0	(13,4)/(14,2)/(15,0)	
	SiO ₂	200.4	0.14		1.9511			0
4	Suspended	187.3	0.13	E11M	1.9517	+0.9	(11,8)	0
	SiO ₂	188.3	0.15		1.9526			
5	Suspended	169.7	0.40	E33S	1.9584	-2.1	(14,7)	2
	SiO ₂	169.4	0.28		1.9563			
6	Suspended	159.7	0.94	E33S	1.9640	-0.6	(12,11)/(16,6)/(17,4)	2
	SiO ₂	159.8	0.79		1.9634			
7	Suspended	156.4	0.91	E33S	1.9671	-9.4	(12,11)/(15,8)/(20,1)	2
	SiO ₂	156.7	0.39		1.9577			
8	Suspended	148.3	1.16	E33S	1.9640	-3.7	(16,8)	1
	SiO ₂	148.2	0.60		1.9603			/
9	Suspended	129.5	2.11	E44S	1.9698	-14.1	(24,1)/(18,10)/(19,8)/23,3)	1
	SiO ₂	129.9	0.44		1.9557			
10	Suspended	116.8	0.55	E44S	1.9588	+4.3	(25,3)/(23,7)/(20,10)	2
	SiO ₂	116.8	1.20		1.9631			
11	Suspended	115.9	1.50	E44S	1.9648	+2.6	(23,7)/(20,10) (25,3)	2
	SiO ₂	115.7	1.25		1.9672			4
12	Suspended	110.7	1.01	E44S	1.9670	~+26	(28,0)	2
	SiO ₂	110.8	3.07		1.9810			4



Control of local tube diameters of SWNTs — Temperature-oscillation growth

Controlling the Diameter of SWNT by Catalyst Particle



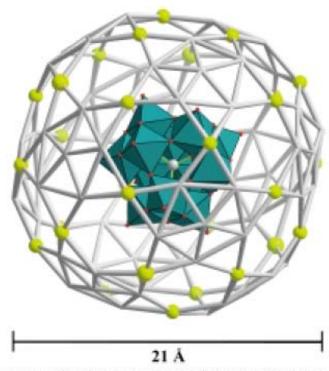
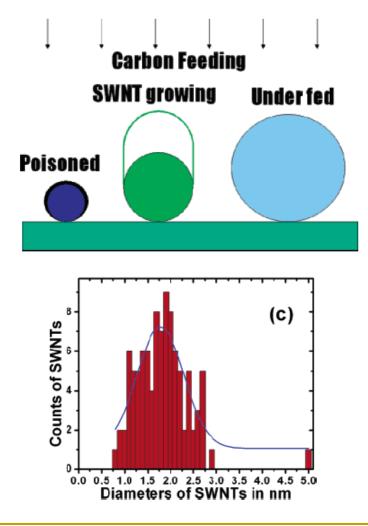


Figure 1. Demonstration of the structure of the building block of 1 with the capsule (host) and encapsulated Keggin-type cluster nucleus (guest idealized): the metal $\{Mo_{72}Fe_{30}\}$ capsule in wire frame representation—with 30 Fe^{III} centers (highlighted as yellow spheres) linking the 12 $\{(Mo^{VI})Mo^{VI}_{5}\}$ pentagons—and the Keggin nucleus in polyhedral representation.

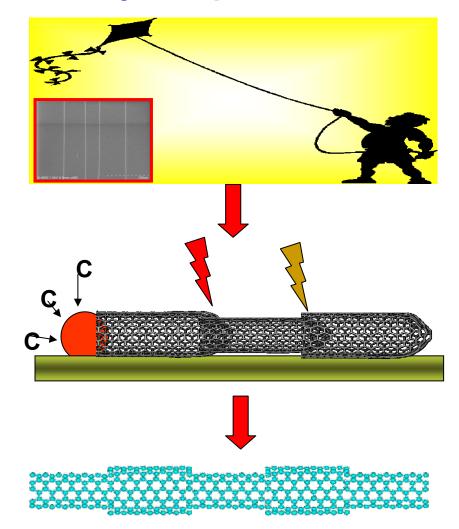
J. Phys. Chem. B. 2002,106, 2429-2433

J. Am. Chem. Soc. 2002, 124, 13688

Controlling the Diameter by Carbon Feeding

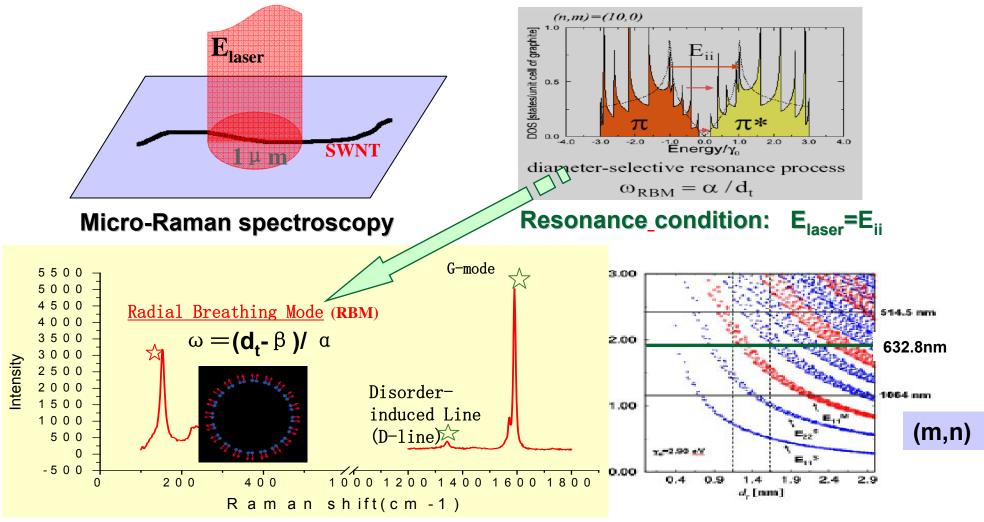


Our Approach: Tune the Diameter of SWNTs by Temperature



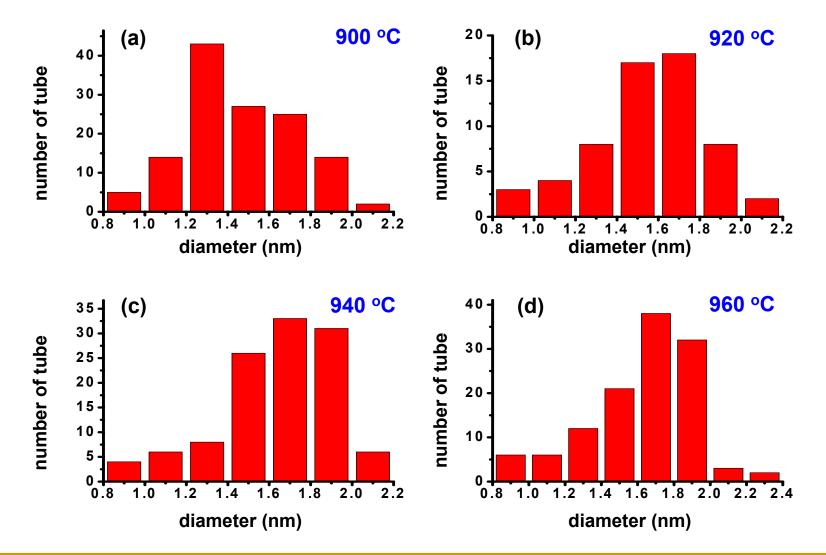
Liu, J. et. al. J. Phys. Chem. B. 2006,110,20254-20257

Micro-Resonance Raman Spectrum of Individual SWNTs



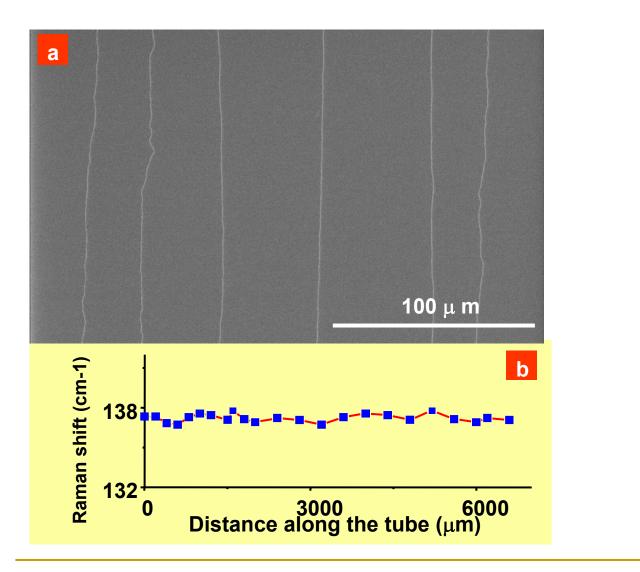
A power tool for both the atomic and electronic structure of SWNT !

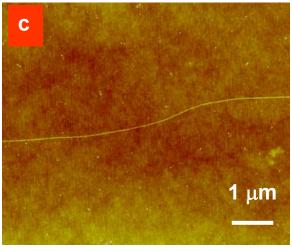
Growing SWNTs at Different Temperature

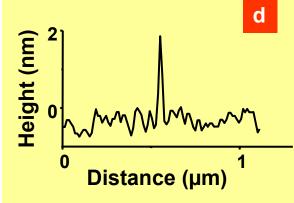


The catalyst nanoparticles might sinter or collide with each other at the high temperature

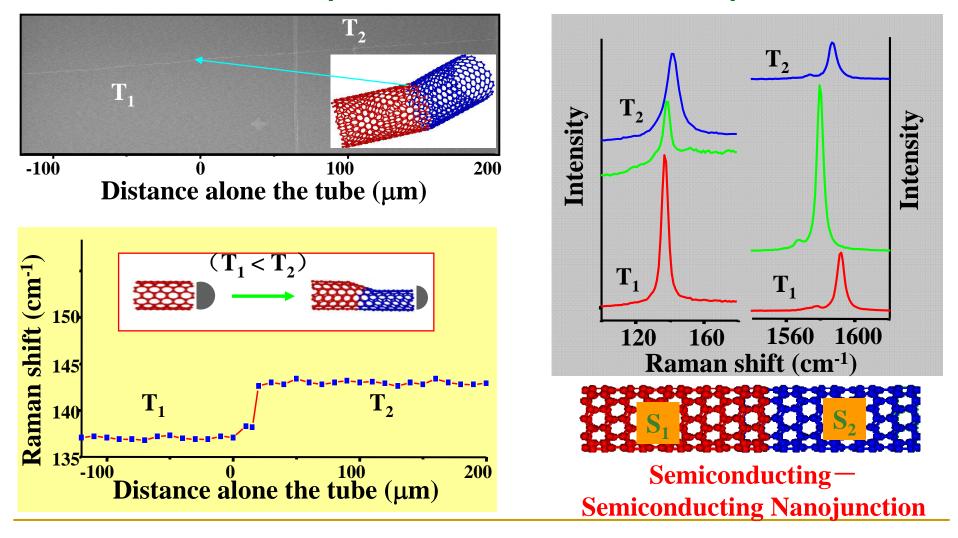
Constant-temperature CVD



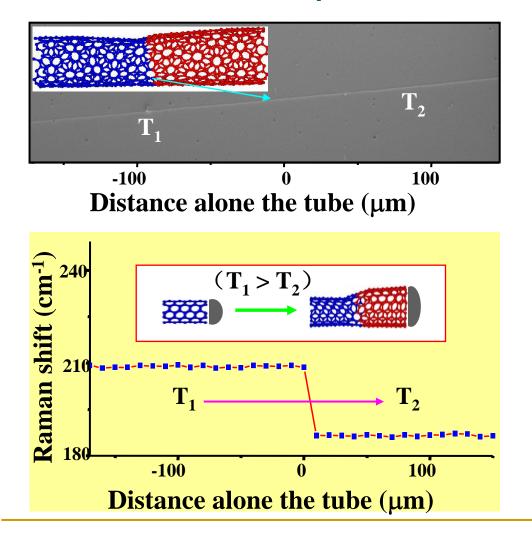


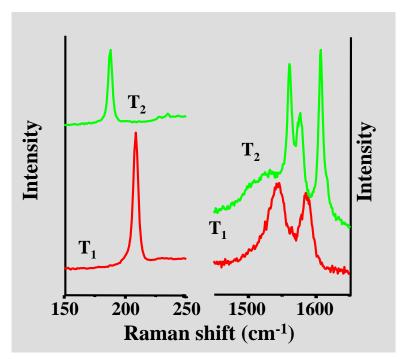


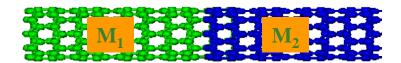
SWNTs Grown by one Time Temperature Oscillated CVD (From 900°C to 950°C)



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



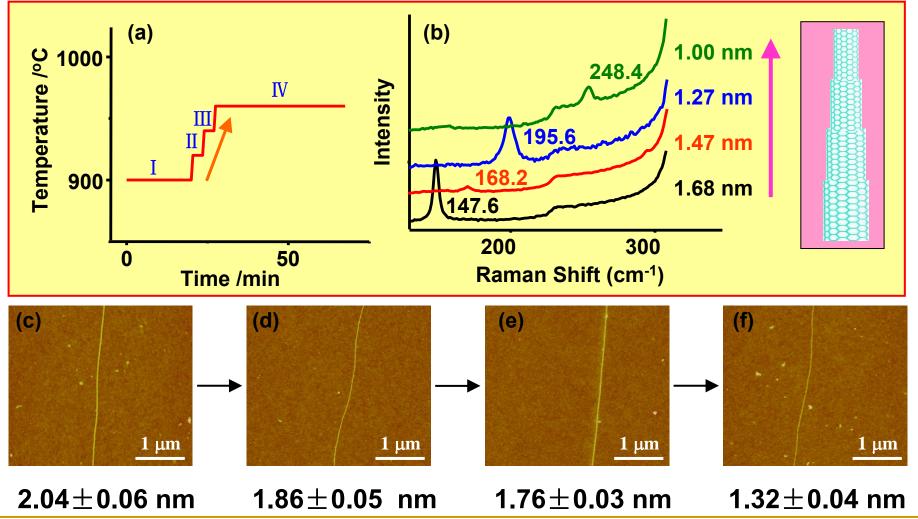




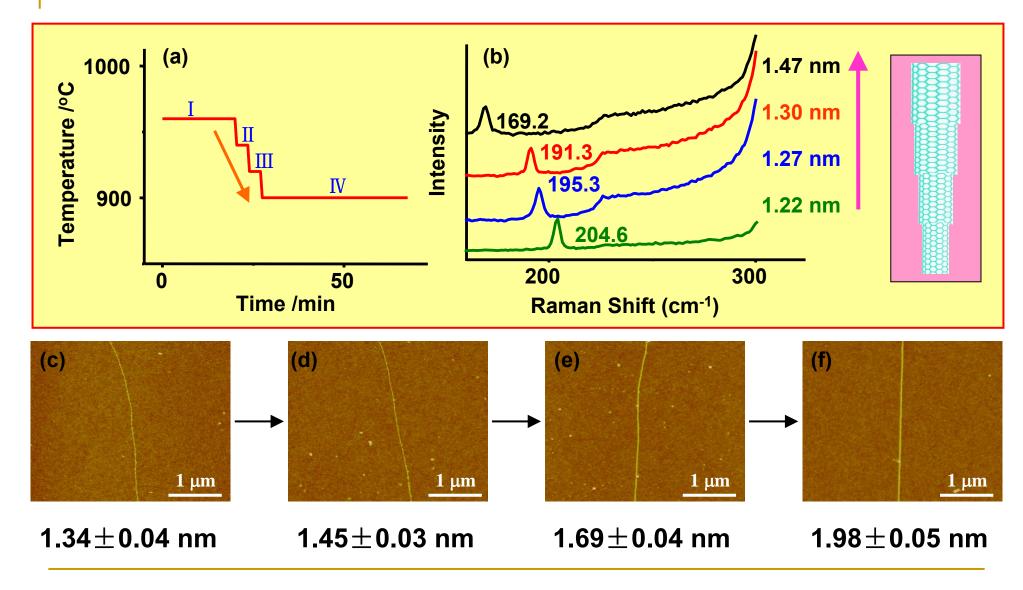
Metallic – Metallic Nanojunction

Controlled Thinning of SWNTs via Temperature Step-Up

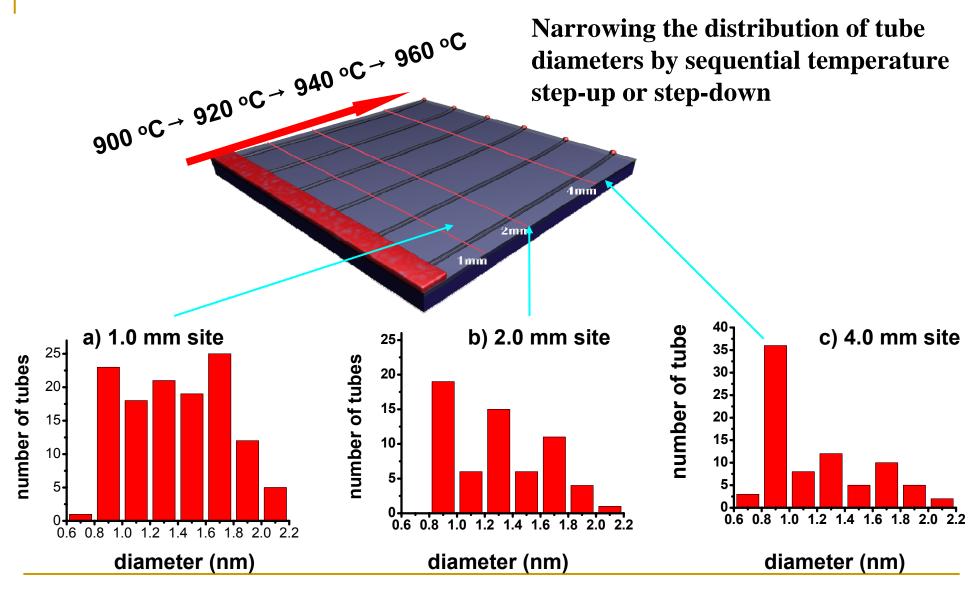
 $900 \circ C \rightarrow 920 \circ C \rightarrow 940 \circ C \rightarrow 960 \circ C$



Controlled Thickening of SWNTs via Temperature Step-Down

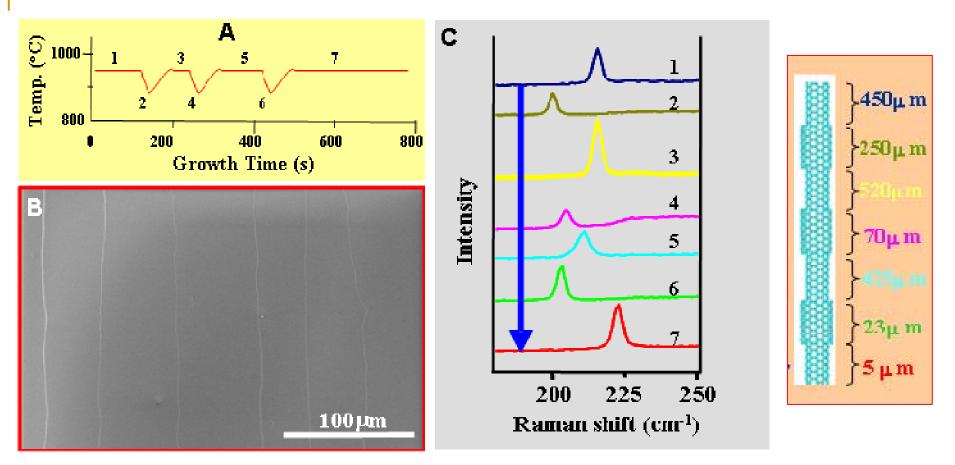


Tube diameter from wide to narrow distribution



J. Zhang et. al., J. Phys. Chem. C, 2009, 113(30),13051-13059

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).

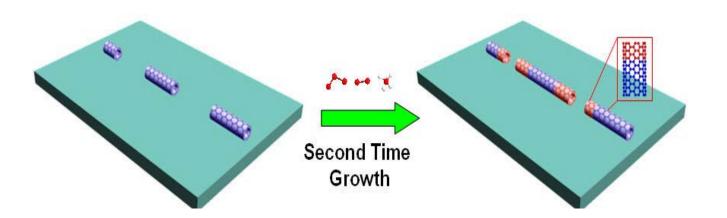
J. Zhang et. al., Nature Materials, 2007, 6, 283



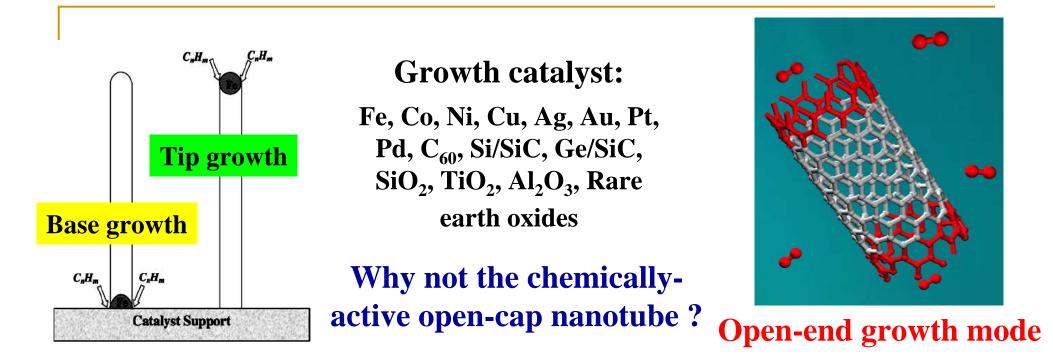
But carbon nanotubes could, in the future, provide more than just thermal management, they could form the basis of electronic devices themselves. To realize such a goal, it will be necessary to find a means of creating intramolecular junctions in a controlled manner. Researchers from Peking University, 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].

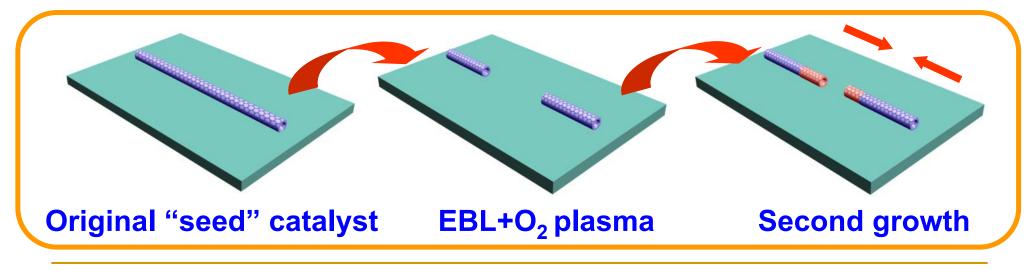
It is currently accepted that the size of the catalytic particle used to grow a nanotube determines its diameter. However, the Chinese researchers observe that the diameter of a SWNT varies with growth temperature during catalytic CVD, even with the same catalytic particle. The results show that if the 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, carbonnanotube-based electronic circuits and devices.



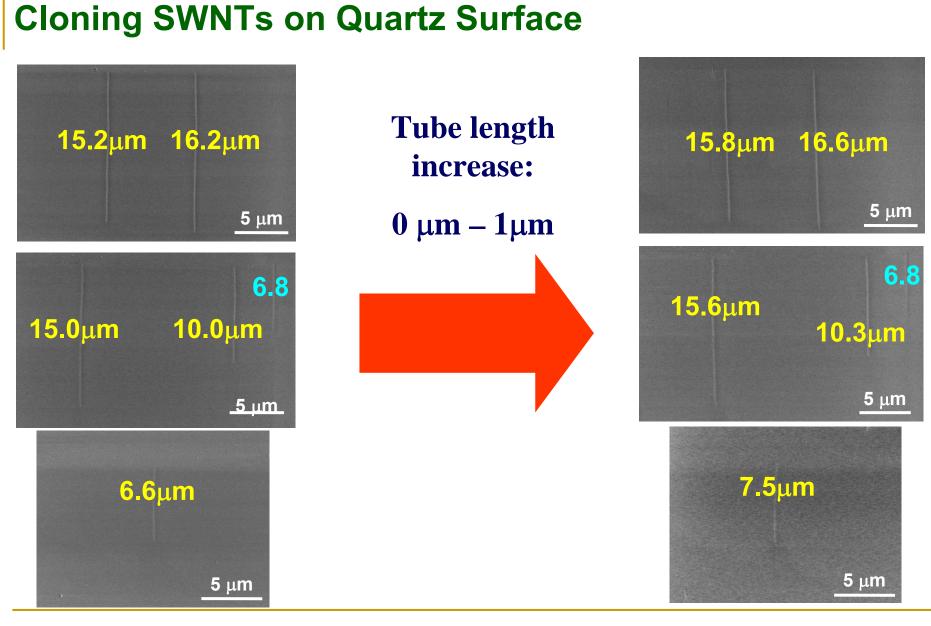
Control of chirality of SWNTs — Cloning growth





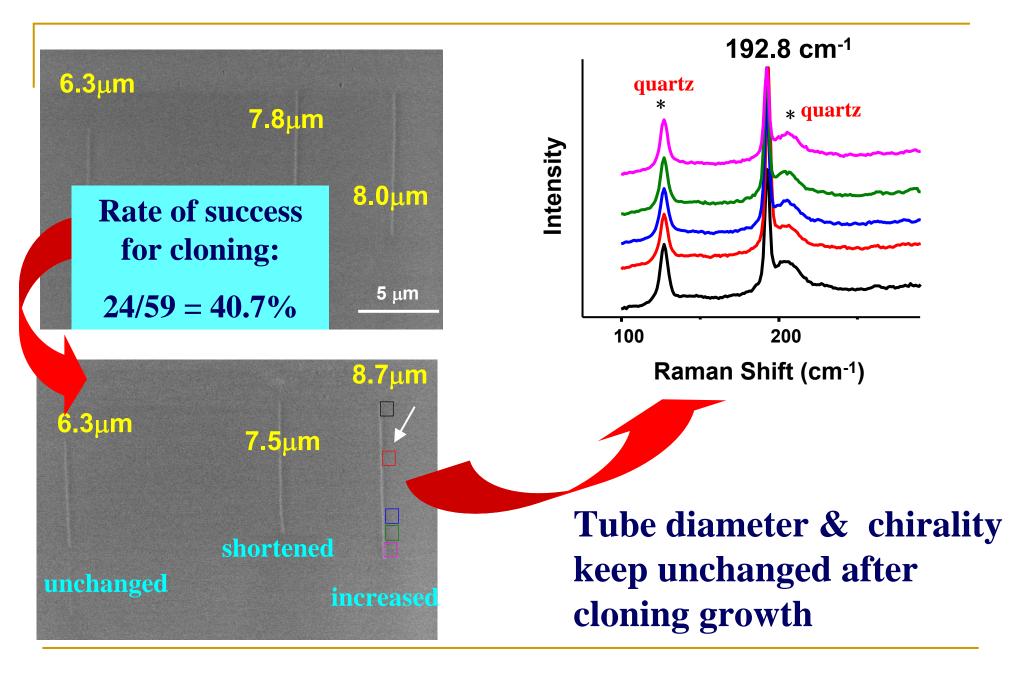
Chinese patent: 2008 1 0222216.7

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



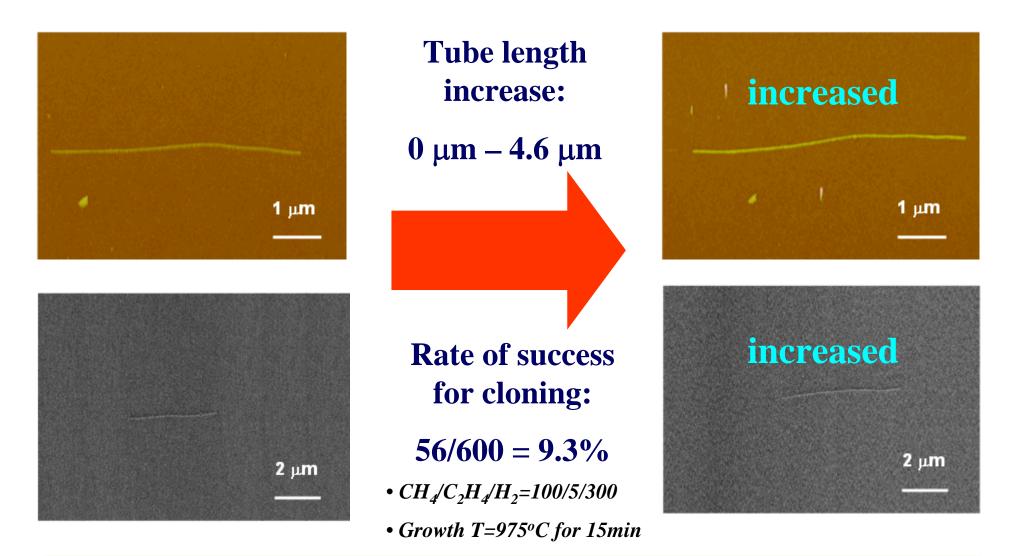
Before growth

After growth



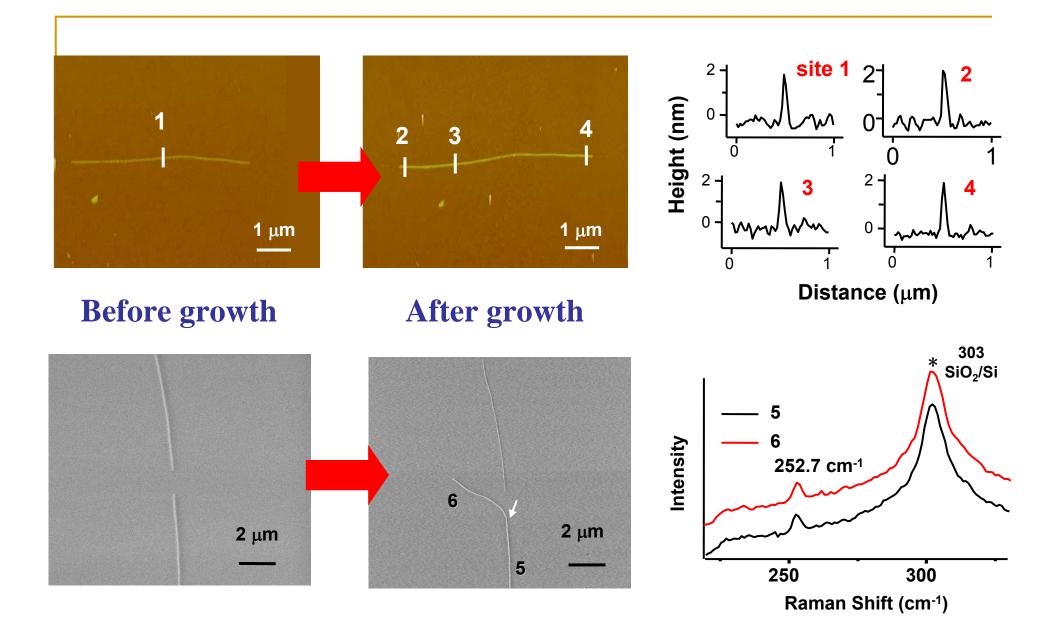
J. Zhang et al., Nano Lett., 2009, 9, 1673

Cloning SWNTs on SiO₂/Si Surface



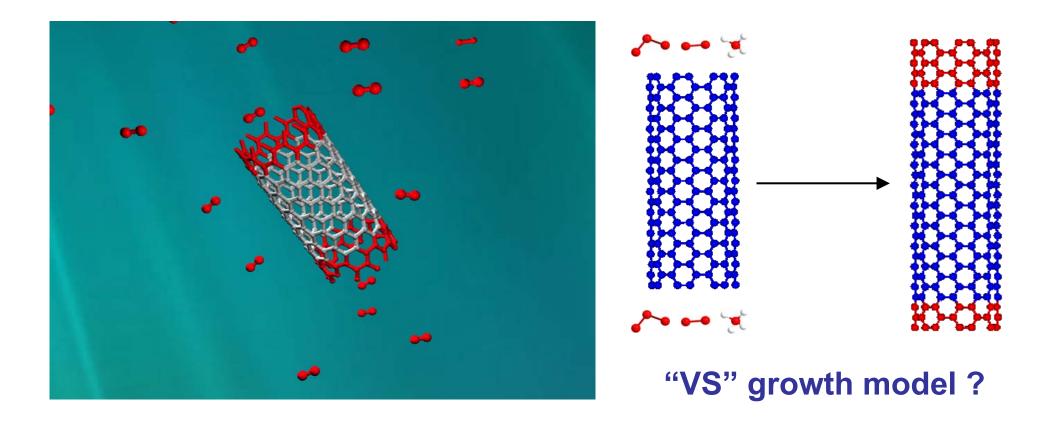
Before growth

After growth



AFM and Raman evidence for the diameter & chirality maintenance

Open-End Growth Mechanism



npe asia materials in association with

home current content archive about editorial committee advisory board register

home » current content » featured highlight » Carbon nanotubes: Perfect clones

featured highlight

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

5 000 Duplicate SWNT-Parent SWNT **Cloning of SWNT**

Fig. 1: Using open-end single-walled nanotubes (SWNTs) as seeds for a cloning growth process may solve current structural control issues

segments of the nanotubes as seeds. These small sections were then heated to 700 °C to remove any impurities.

To grow new nanotube extensions, a stream of gas containing carbon radicals was passed over the seed segments. Using atomic force and scanning electron microscopy, the research team observed new growth of several micrometers in length extending from the seeds. Raman spectroscopy confirmed that the newly grown nanotube segments retained the original seed structure.

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

Instead of requiring an external additive, the growth mechanism discovered by Zhang uses the open ends of the nanotubes themselves as catalysts. The seed segments predetermine the nanotube structure, and any new growth via carbon radicals retains this arrangement.

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

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

Reference

1. Yao, Y.,¹ Feng, C.,¹ Zhang, J.^{1*} & Liu, Z.¹ "Cloning" of single-walled carbon nanotubes via open-end growth mechanism. Nano Lett. 9, 1673–1677 (2009). | <u>article</u> |

Author affiliation

1. Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory for the Physics and Chemistry of Nanodevices. State Key Laboratory for Structural Chemistry of Unstable and Stable Species. College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China *E-mail: jinzhang@pku.edu.cn



nethod to make quantum dot

Nano-C, Inc. Fullerenes, Carbon Nanotubes, PCBM

and Other Derivatives < >

Elicarb™ SW Single-wall carbon nanotubes Commercial supplies

Ads by Google

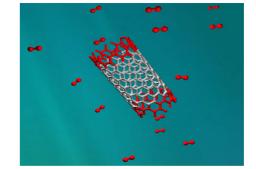
Posted: April 3, 2009

'Cloning' might solve the chirality control issue of nanotube production

(Nanowerk Spotlight) Notwithstanding the tremendous amount of research that has gone into the field of carbon nanotubes, the synthesis of single-walled carbon nanotubes (SWCNTs) with controlled chirality still has not been achieved. Current production methods for carbon nanotubes result in units with different diameter, length, chirality and electronic properties, all packed together in bundles, and often blended with some amount of amorphous carbon. The separation of nanotubes according to desired properties remains a technical challenge. Especially SWCNT sorting is a challenge because the mposition and chemical properties of SWCNTs of different types are very similar conventional separation techniques inefficient.

Using the concept of cloning, scientists in China have discovered an effective method to synthesize any special (n, m) indices SWCNTs

"We found that an open-end single-walled carbon nanotube, which served as seed, could be continual grown via an open-end growth mechanism," Jin Zhang tells Nanowerk. "The new 'cloned' SWCNTs and the parent tubes - the 'seeds' - have the same chirality."



Schematic illustration of a single walled carbon nanotube clone. (Image: Dr. Jin Zhang, Beijing National Laboratory for Molecular Sciences)

These findings by Zhang, a professor of chemistry and molecular engineering at the Beijing National Laboratory for Molecular Sciences, and his colleagues Zhongfan Liu, Yagang Yao, Chaoqun Feng, will be not only helpful to understand the formation mechanism of single walled carbon nanotubes, but also turn the controllable growth of SWCNT with identical chirality into reality

Moreover, this growth mechanism might be an effective way for cloning of graphene from small graphene sheets. Furthermore, large scale cloning of single chirality SWCNT could lead to practical applications.

The scientists reported their findings in the March 13, 2009 online edition of Nano Letters ("Cloning' of Single-Walled Carbon Nanotubes via Open-End Growth Mechanism").

For their technique, Zhang's team first grew ultralong (several tens of micrometers) SWCNTs on SiO₂/Si substrate. The nanotube length is only limited by the substrate size, the hot zone of the furnace, and the growth time. Then, the ultralong SWCNTs were cut into short segments by electron beam lithography (EBL), oxygen plasma ion etching, and lift-off, which could be served as seeds/catalysts and the stencil in the second growth

In a third step, the SWCNT 'clones' were grown from the open-end parent SWCNTs by putting the open-end seeds in a chemical vapor deposition (CVD) furnace to first get rid of -COOH and -OH at the endfunctionalized SWCNTs, which could help expose the active open-end, and then, by introducing CH4 and C_H, carbon source.

"The cloned nanotubes usually grew as much as a few micrometers in length and the longest length of amplified growth was 4.6 µm" says Zhang. "We though that if the second growth is not constrained by the substrate such as the open-end SWCNTs are suspending, the new SWCNTs will grow longer."

While this strategy works in principle, the growth efficiency of cloning and the exact open-end growth mechanism are problems which still need to be solved.

"We have measured more than 600 short seed segments and found the yield of cloning is relatively low, around 9%" says Zhang. "This yield can be greatly improved up to 40% by growing SWCNTs on quartz substrate

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

According to Zhang, the open-end SWCNT catalyst (seed) is more suitable than other reported catalysts for the growth of SWCNTs.

"Firstly, it can not congregate at high growth temperate. The metal catalyst nanoparticles usually congregate at high temperature which will widen the diameter of SWCNTs grown by them. Secondly, carbon radicals will directly add to the open-end and thus the chirality of new cloned SWCNTs will have the same structure as the parent SWCNTs. Thirdly, our results support the idea that nanosize structures might act as a template for the formation of SWCNTs

By Michael Berger. Copyright 2009 Nanowerk LLC



Ads by Google ΛV

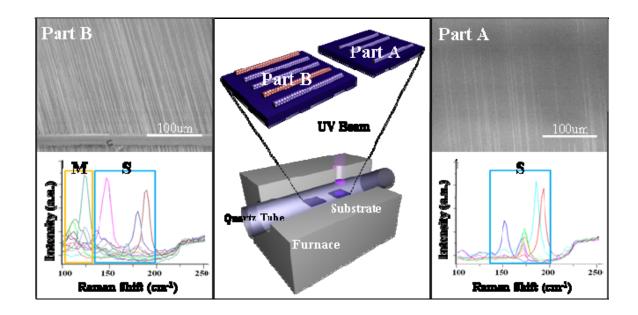
Nano-C. Inc Fullerenes, Carbon Nanotubes, PCBM and Other Derivatives

A-7 Nanonarticle



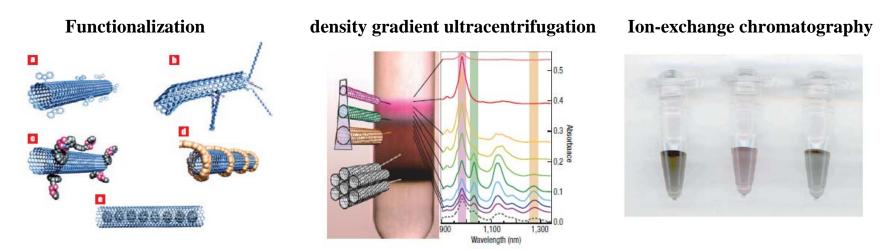
FEI



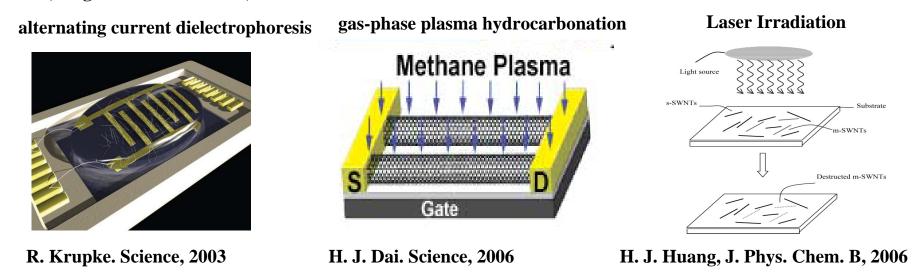


Control of metallic-/semiconducting- of SWNTs —— UV irradiation assistance CVD growth

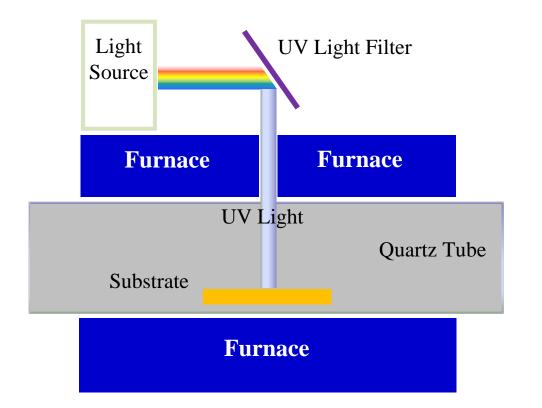
Separation of s-SWNTS and m-SWNTs after growth

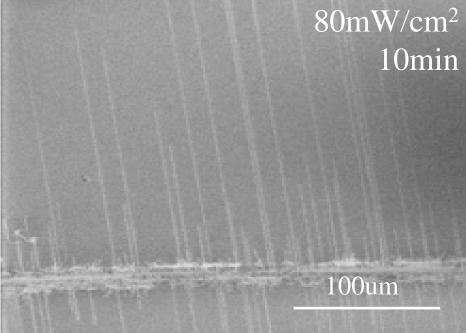


A. Hirsch, Angew. Chem. Int. Ed., 2002 M. S. Arnold, Nature Nanotech., 2006 M. Zheng, Nature Mater., 2003

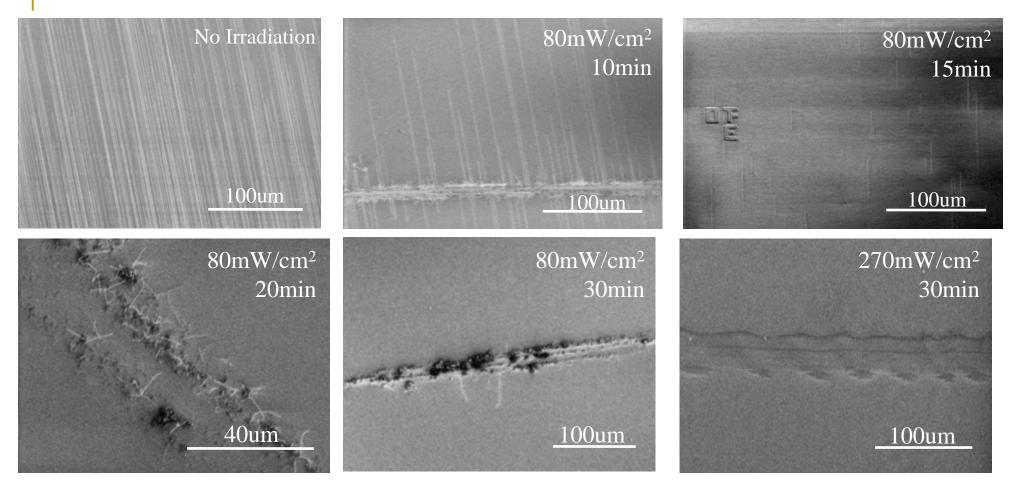


Sketch map of the home-made chemical vapor deposition system

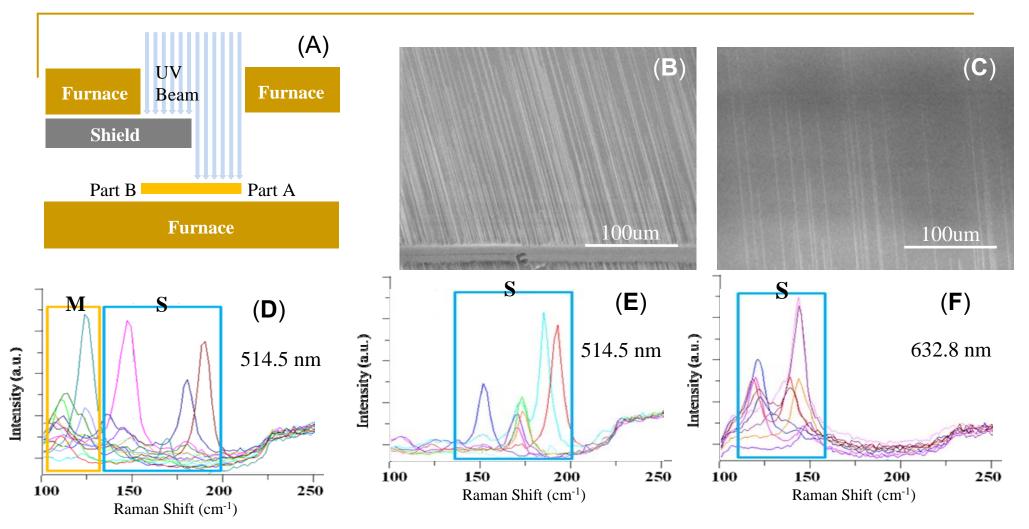




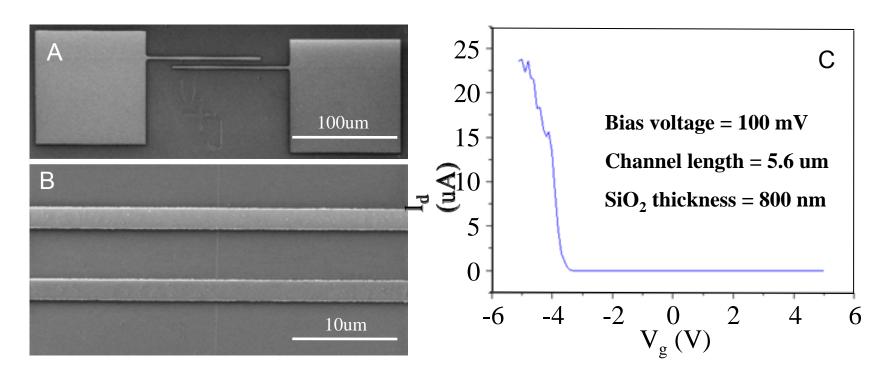
SEM images of SWNTs arrays under different irradiation time



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

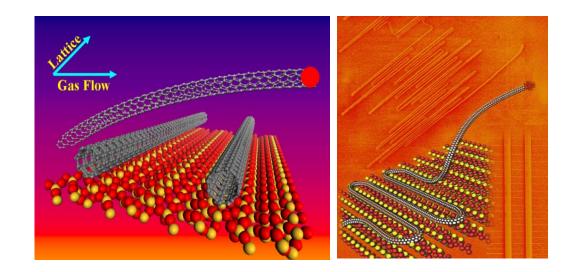


(A) Sketch map of the comparison experiment for SWNT growth with and without UV irradiation. (B)/(C) SEM image of the growth result without/with UV irradiation. (D) Raman spectrum for part B with 514.5 nm excitation. (E)/(F) Raman spectrum for part A with 514.5/632.8 nm excitation. The metallic SWNTs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



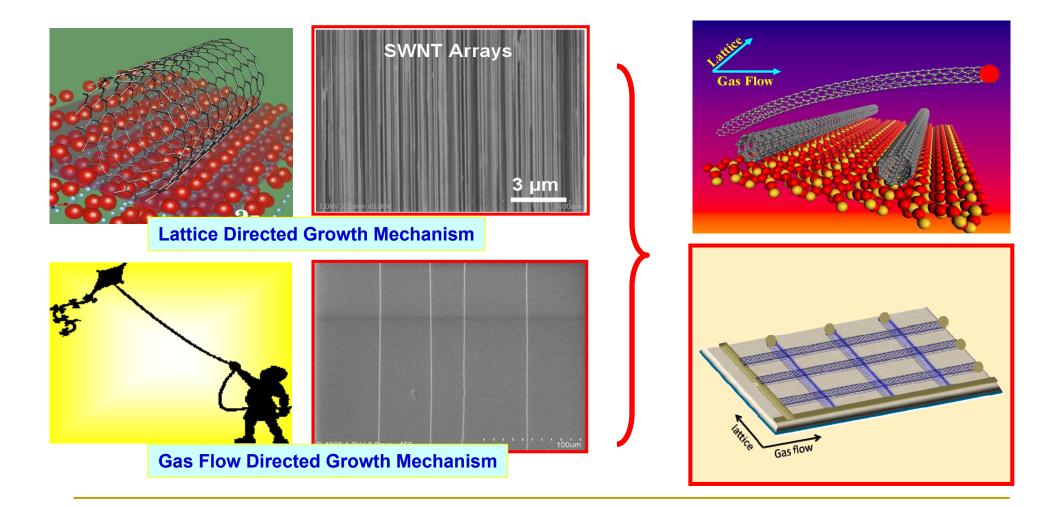
The Raman spectra demonstrated an amazing result that almost 100% SWNTs were semiconducting ones. To further confirm the percentage of the semiconducting SWNTs in this sample, we performed electrical measurement in the single-tube field effect transistors (FET) form. Figure A and B were the low and high magnified SEM images of the single-tube FET structure. Fig. C was the typical I-V curve of a semiconducting SWNT with the on/off ratio over 10⁴. The test parameters of the electrical measurement were inserted in Fig. C. The bias voltage was 100 mV, the channel length was 5.6 um, and the SiO2 thickness was 800 nm. The electrical measurement data showed that 21 out of 22 SWNTs were semiconducting ones.

J. Zhang et al., J. Am. Chem. Soc., 2009, In press

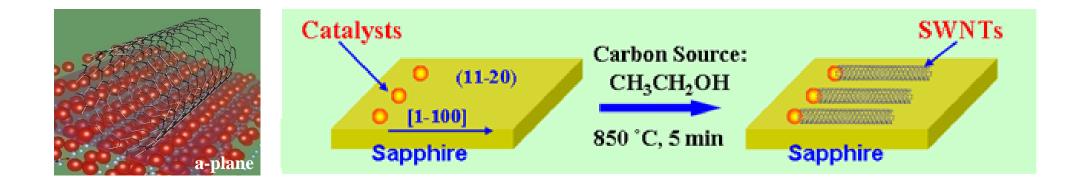


Control of local conformation and architectures — Cooperative growth of floating and lattice oriented growth modes

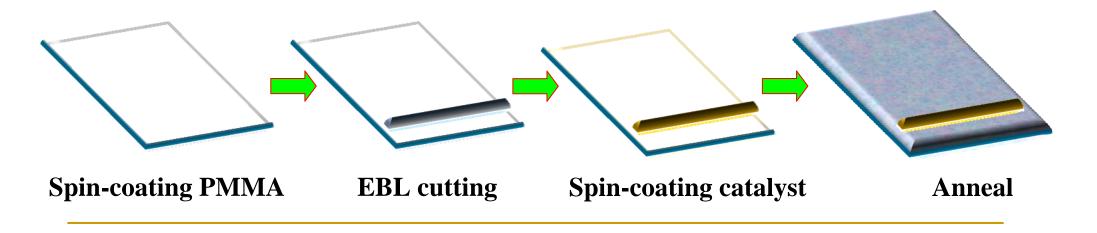
Grow SWNTs Crossbar by Combining the Two Growth Mechanism in One Batch



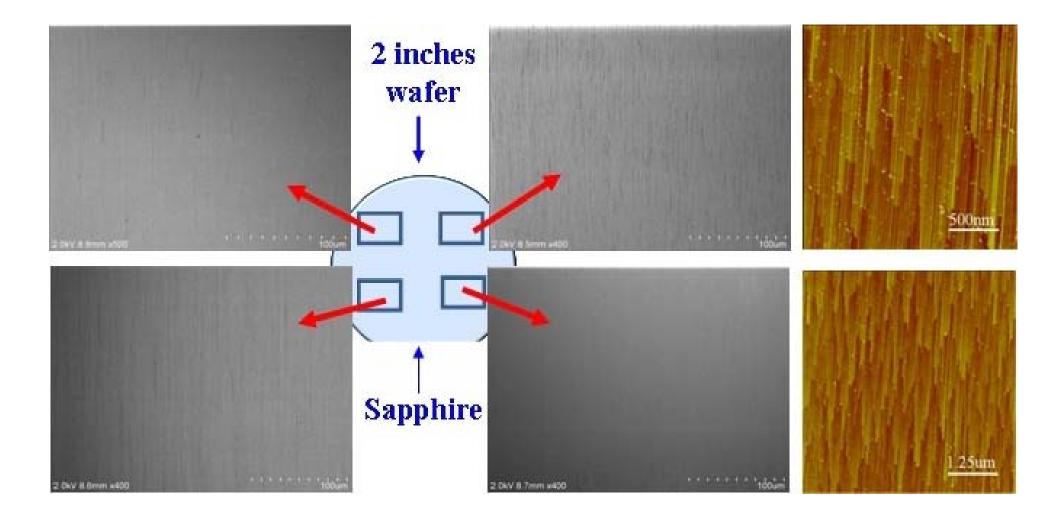
High Density SWNTs Array on Surface



Patterned Catalysts

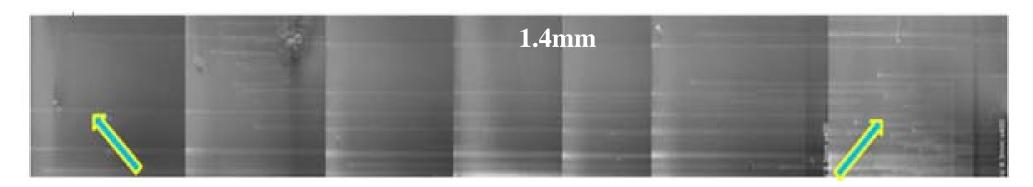


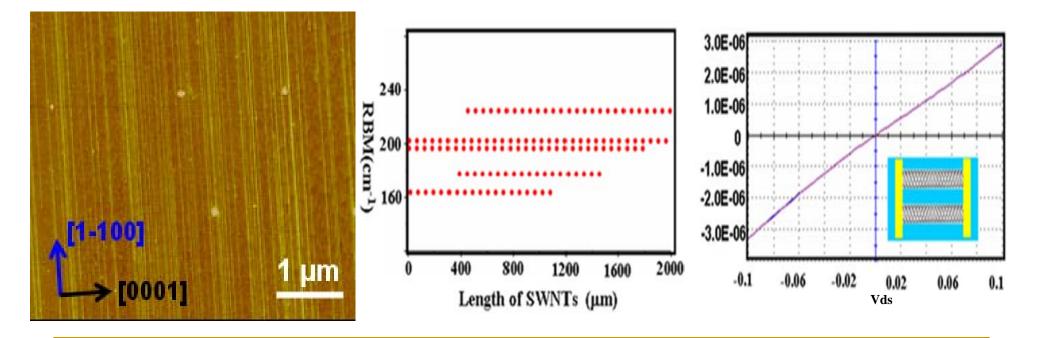
High Density SWNTs Arrays on 2 Inches Wafer



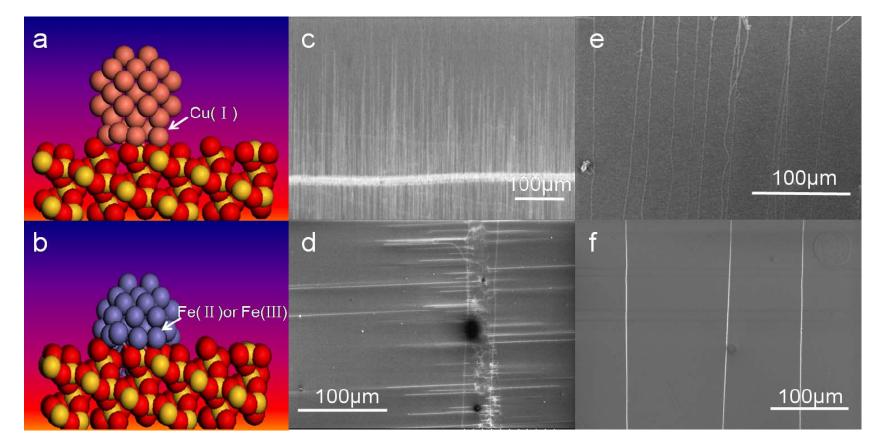
The Density is about 35-40 tubes per micrometer

The length of the High Density SWNTs



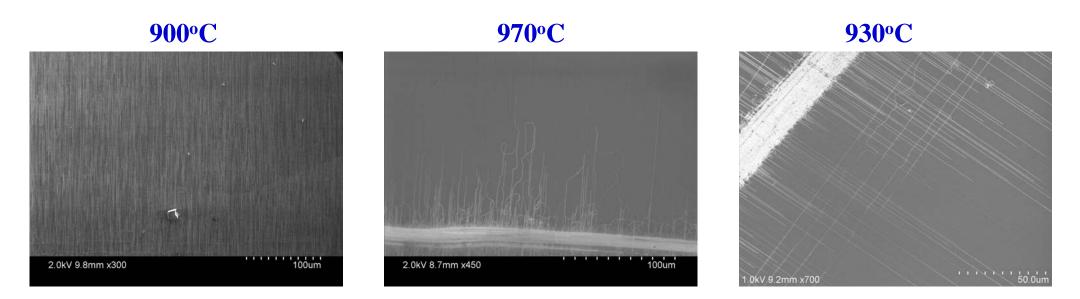


Interaction between Cu, Fe Catlysts and Quartz Surface



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.

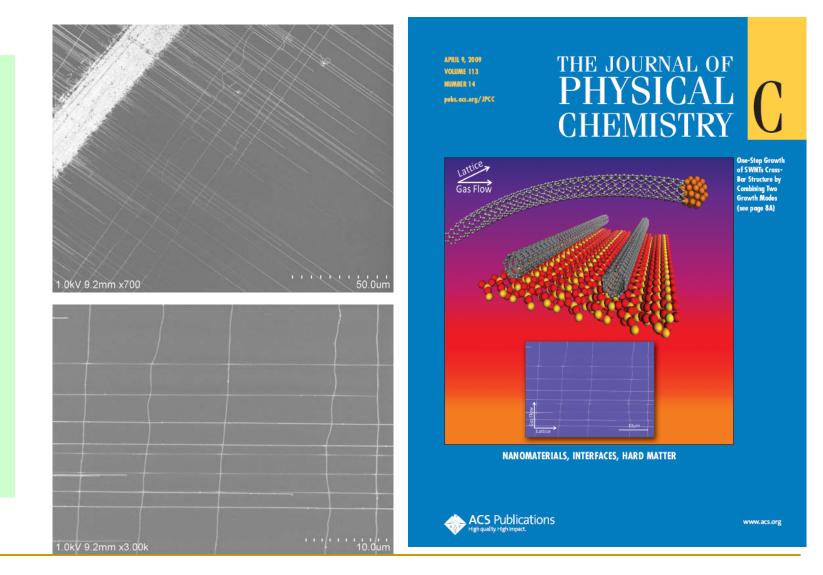
The Effect of Temperature on the Growth of SWNTs on Quartz Surface



- 1. low temperature(900): high density of lattice directed carbon nanotubes, few gas flow directed carbon nanotubes
- 2. optimized temperature(930-950): the density of lattice directed carbon nanotubes is acceptable and it is possible for the growth of gas flow directed carbon nanotubes
- 3. high temperature(970): lattice will be damaged by such high temperature

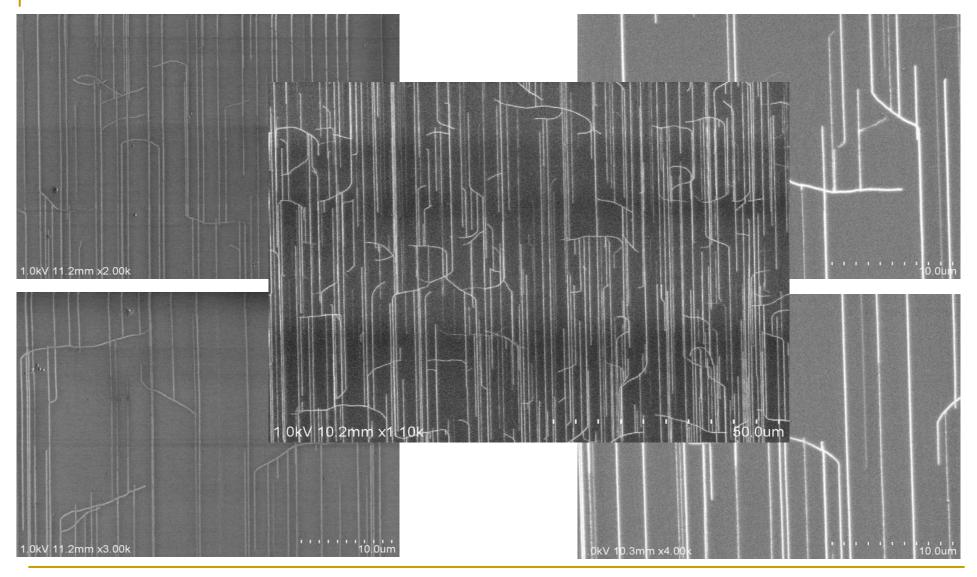
SWNTs Crossbar and Its Potential Application

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.

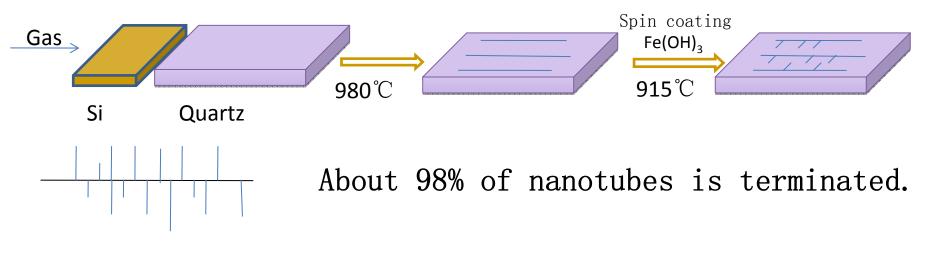


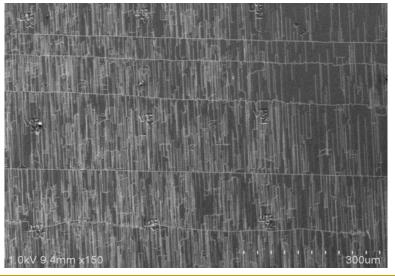
J. Zhang et. al., J. Phys. Chem. C. 2009, 113, 5341-5344 (cover)

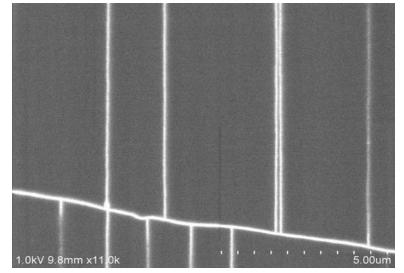
The Phenomenon of the Experiment



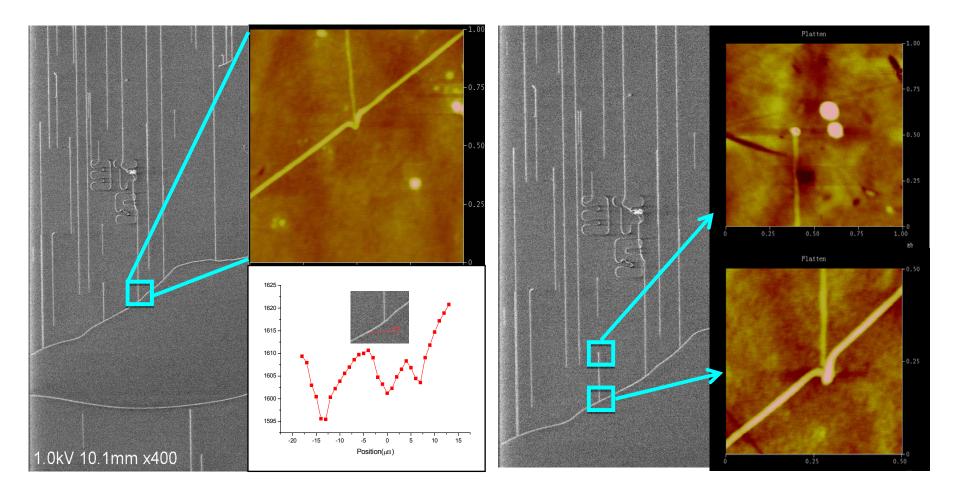
Do Nanotubes Adhere to the Substrate When Grow?







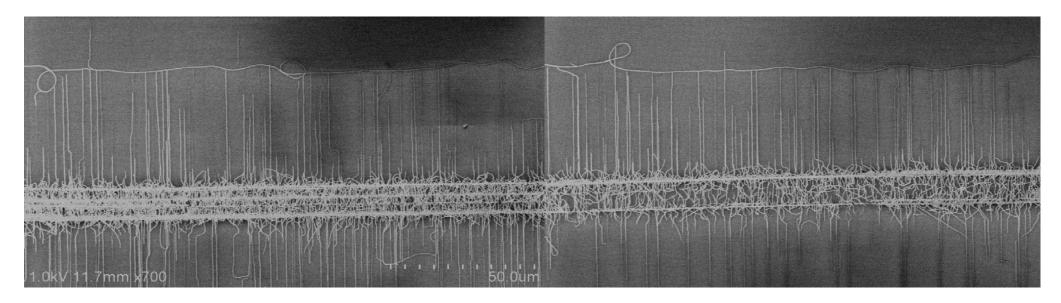
SEM、AFM & Raman Results

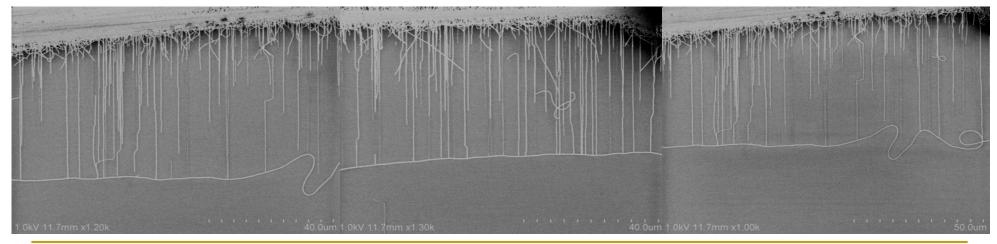


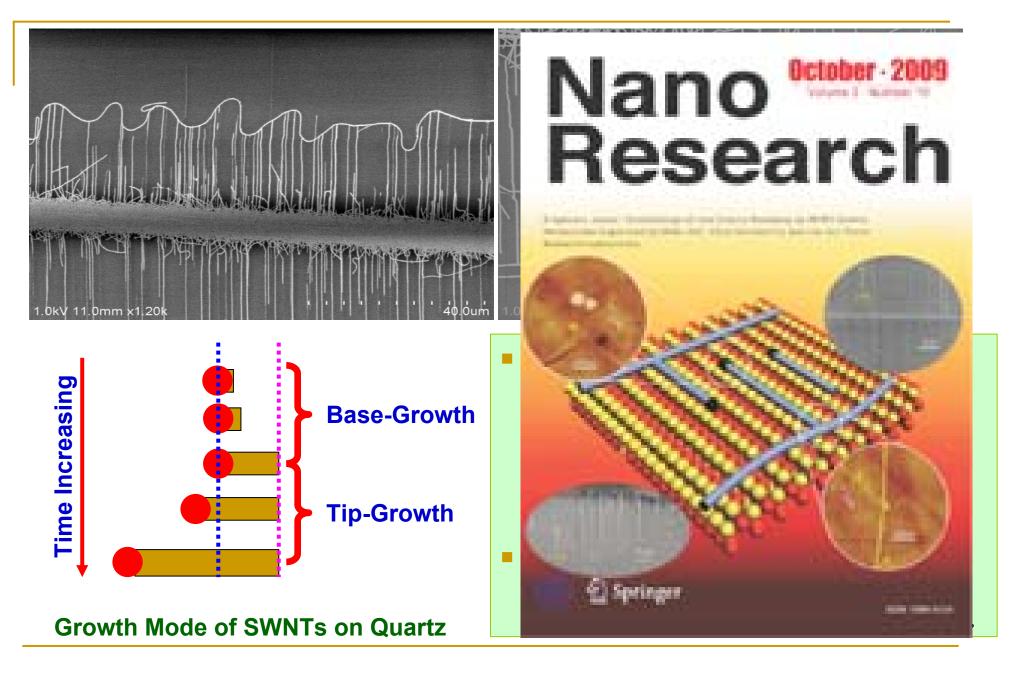
One carbon nanotube hit against another one.

Base-growth Mechanism

Length-controlled Growth of SWCNTs

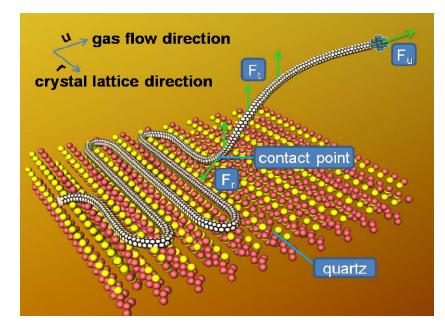






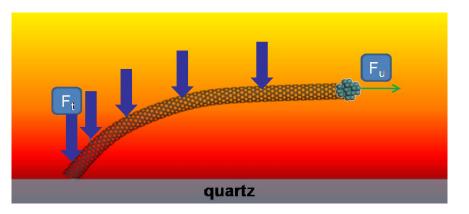
J. Zhang et al., Nano Research., 2009, 2(10), 768-773. (Cover paper)

Control of Local Conformation



- Shear friction force (F_u)
- Thermal buoyancy force (F_t)
- Lattice-alignment force (F_r)

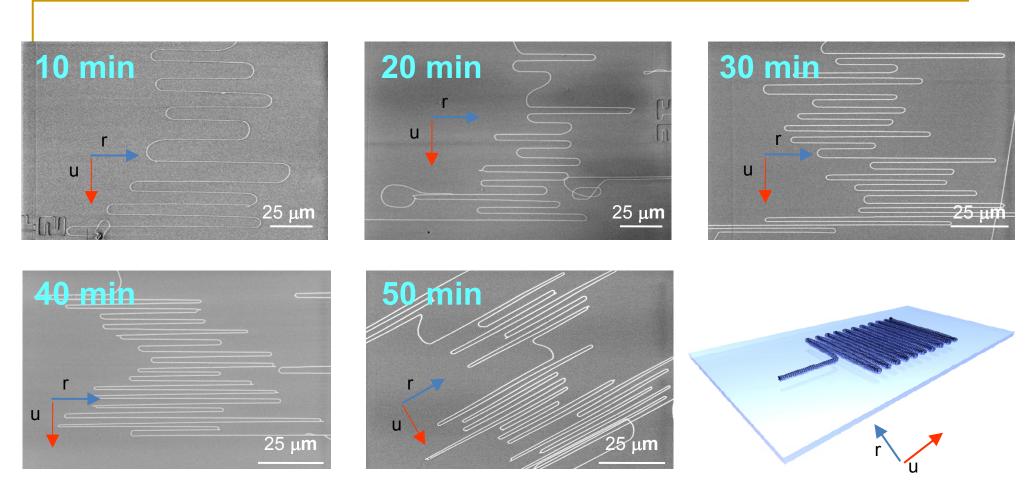
Cooling down process



Cooperation of floating and latticeoriented modes

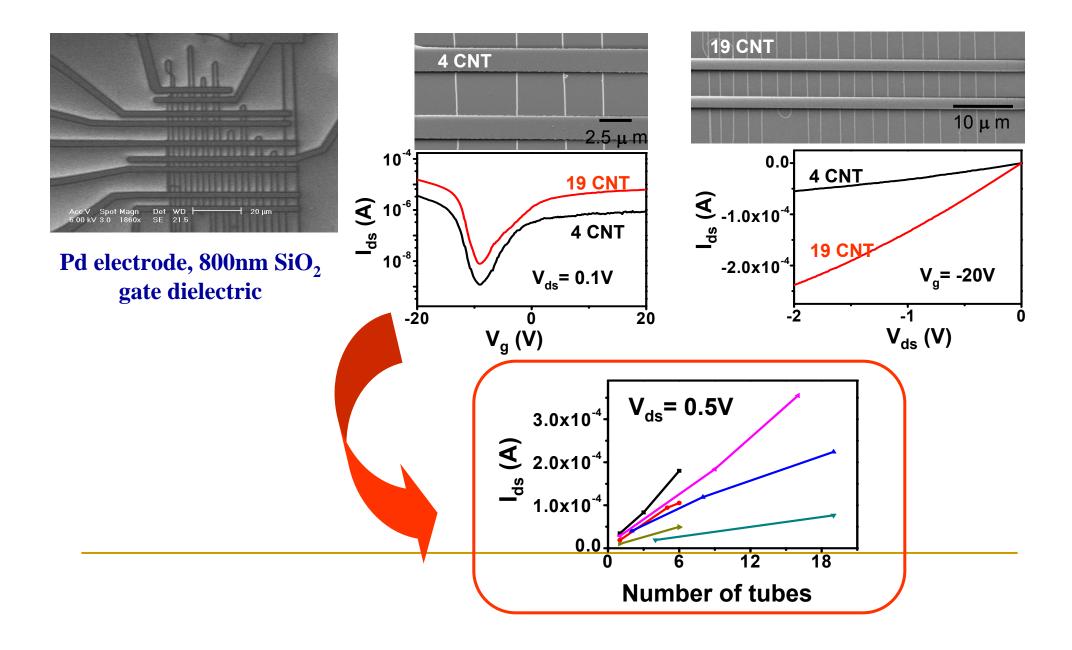
- (1) Activate the floating mode by growing at high temperature (975°C);
- (2) Stop the growth and switch to cooling process;
- (3) Activate the lattice-oriented mode by slowing down the falling speed.

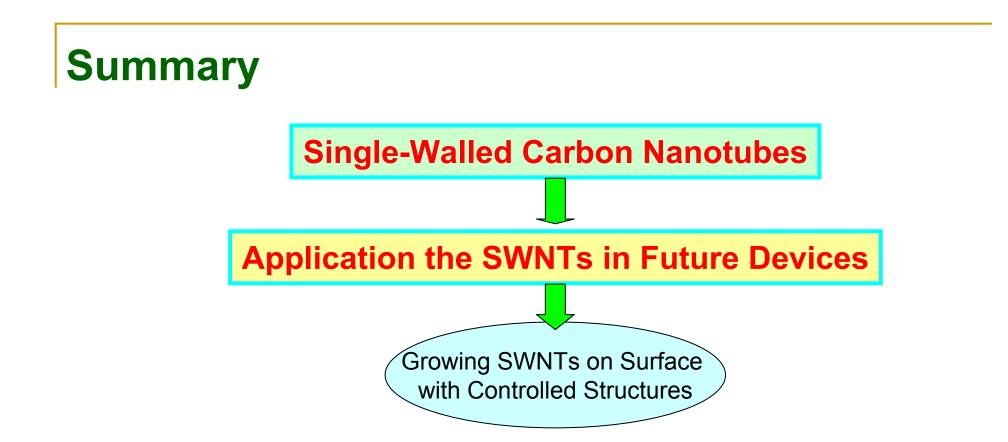
J. Zhang et al., Adv. Mater., 2009, in press (Inside Front Cover)



When setting gas flow direction perpendicular to the lattice orienting direction and cooling down the system from 975°C to 775°C at low speed (4-20°C/min), we found that, the slower the cooling speed, the higher the tube packing density.

High Performance SWNT-FET with Identical Chirality





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.

