Floating Catalyst CVD Method for Controllable Synthesis of Single- and Double-walled Carbon Nanotubes

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Where am I from?

Main Directions at my Division

- Synthesis, Properties and Applications of Carbon Nanotubes and Non-Carbon Nanostructures
  - Carbon Nanotubes
  - Non-Carbon Nanostructures
- New Materials for Clean Energy Applications
  - Energy storage materials
  - Solar energy materials
- Exploration of Hydrogen Storage Materials
- Fabrication and Applications of High-performance Carbon Materials

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Outline

- **Synthesis of CNTs by Floating Catalyst CVD (SWNTs, DWNTs, MWNTs)**
- **Structural Control of SWNTs and DWNTs**
  - **The effect of sulfur, carrier gas, and carbon feeding rate**
  - **Synthesis of CNTs with narrow diameter distribution**
- **Growth mechanism of SWNTs/DWNTs by FCCVD**
- **Concluding remarks**

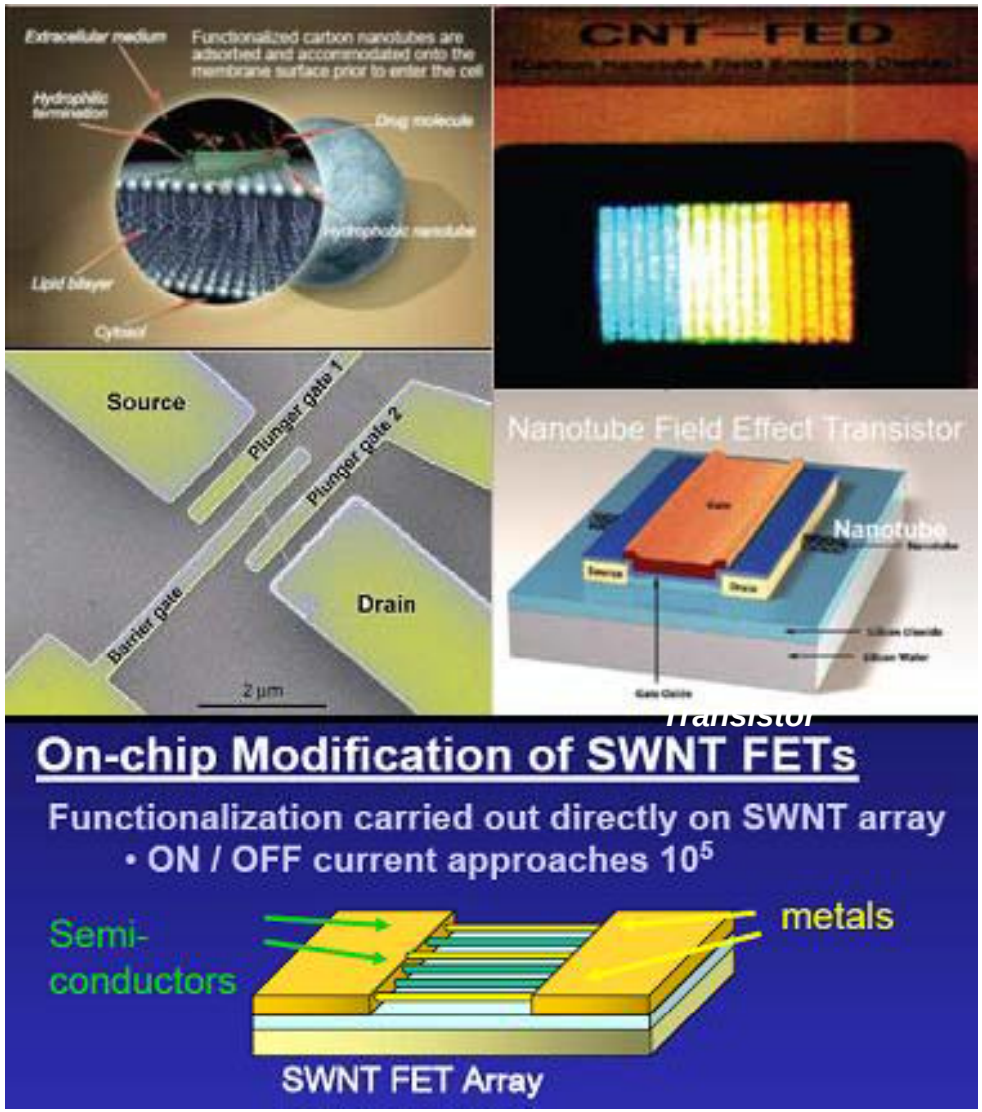
Potential Applications of CNTs

Large Scale

- ✓ Field emitters
- ✓ Energy storage
- ✓ Composites

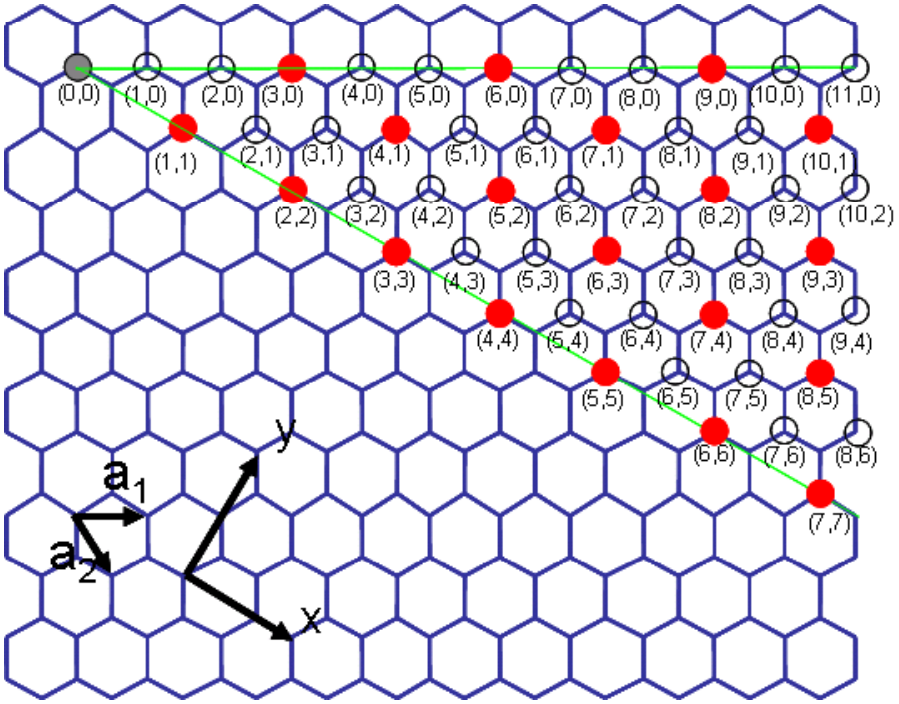
Individual

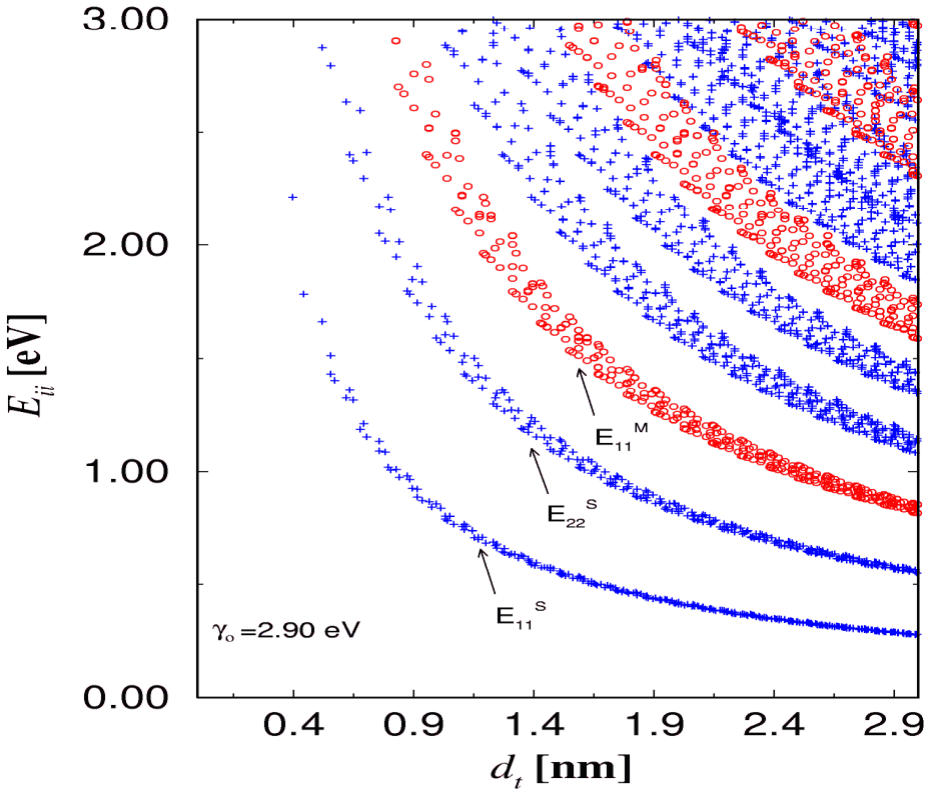
- ✓ Electronic devices
- ✓ STM/AFM tips
- ✓ Sensors



D Tomànek, NT06 Presentation

Electronic Structure --- Structural Control





$$n-m=\begin{cases}3p & \text{metal}\\ 3p\pm1 & \text{semiconductor}\end{cases}$$

$$E_{gap} \propto 1/r$$

R Saito et al., Appl. Phys. Lett. 60(1992) 2204 .
R Saito et al, Phys. Rev. B 61(2000) 2981.

Challenges for CNT Synthesis

- Development of low-cost, large-scale processes for the synthesis of high-quality CNTs
- Control over the structure and electronic properties of CNTs
- Control over the location and orientation of CNTs on a flat substrate
- Development of a thorough understanding of the growth mechanism of CNTs

J Liu, SS Fan and HJ Dai, MRS Bulletin, 2004.

Pioneered Methods for SWNT Synthesis

Arc Discharge Method

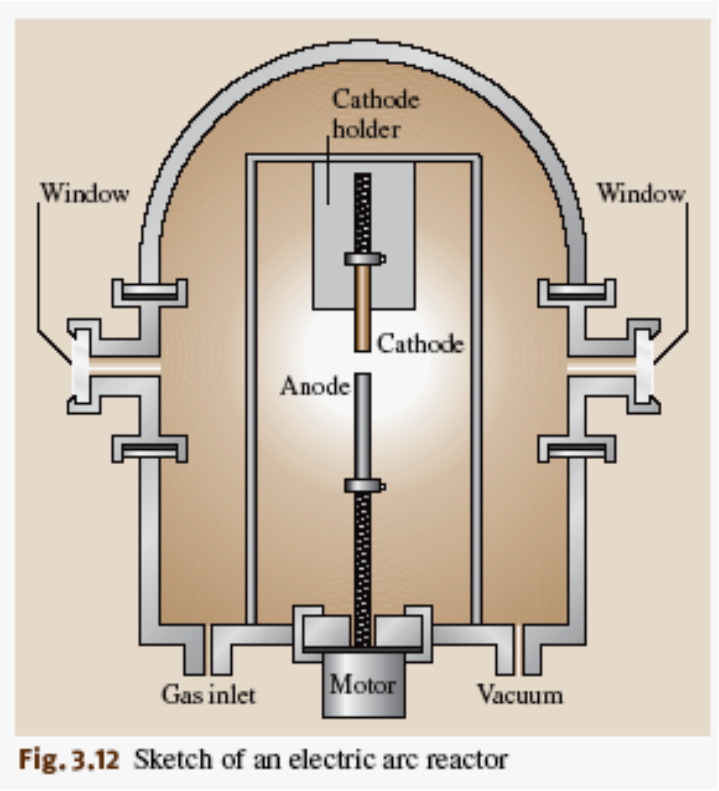
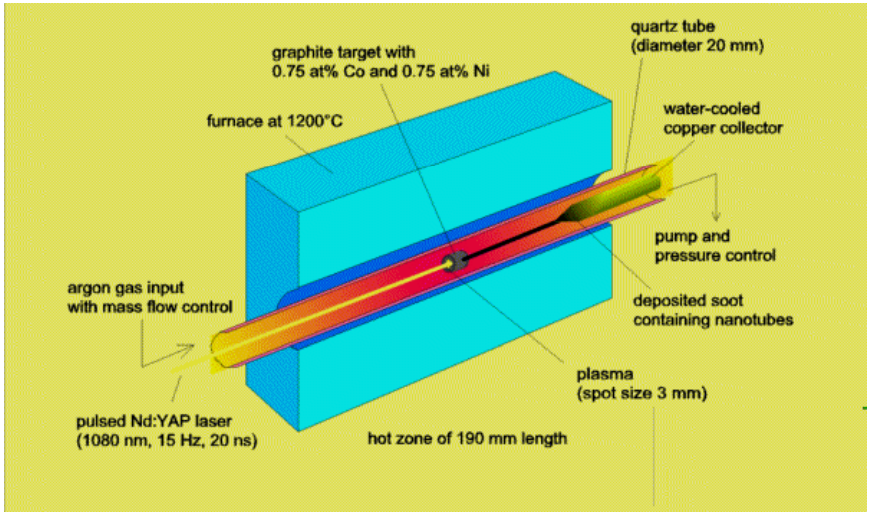


Fig. 3.12 Sketch of an electric arc reactor

Developed by S Iijima

(Nature 1993)

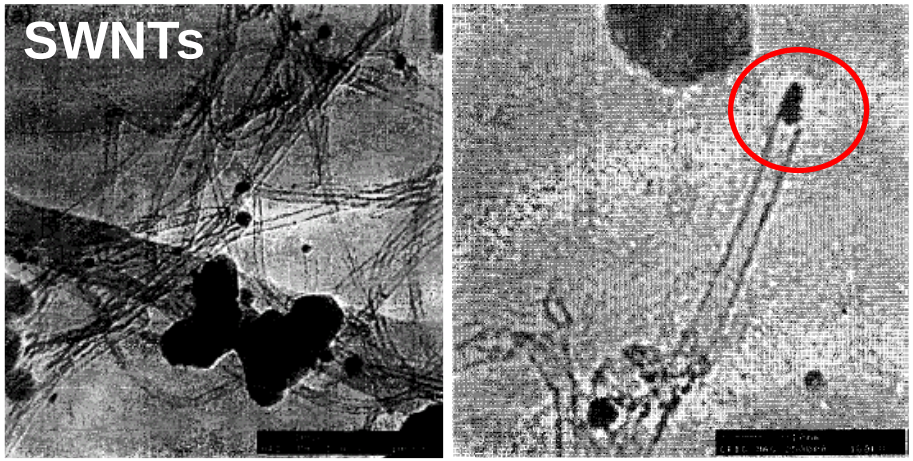
Laser Ablation Method



Developed by RE Smalley group

(A Thess et al, Science 1996)

Growth of SWNTs by CVD method

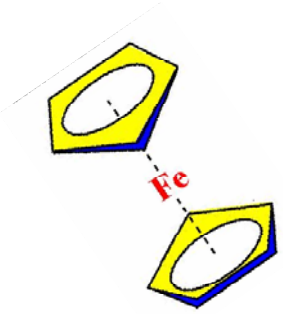


H.J. Dai, et al., Chem. Phys. Lett. 1996

Large scale:

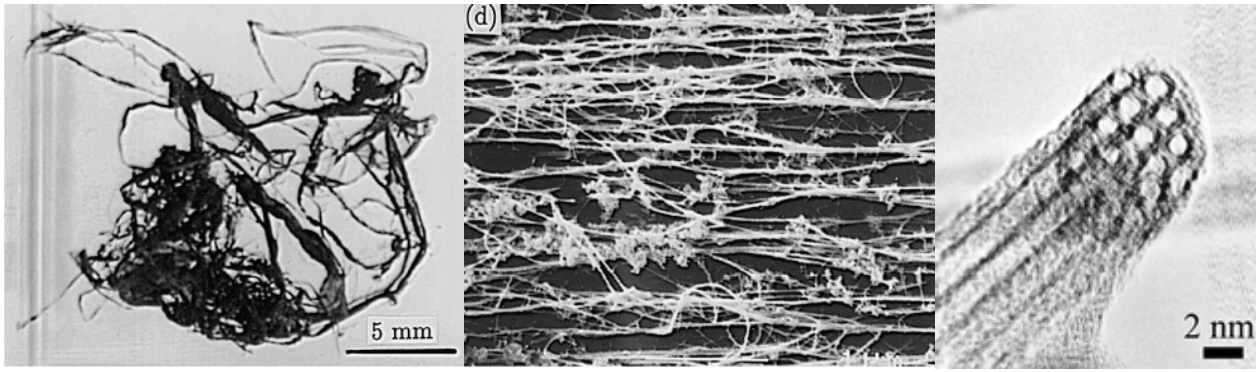
- Carbon supply
- Catalyst supply
- Reaction time
- …

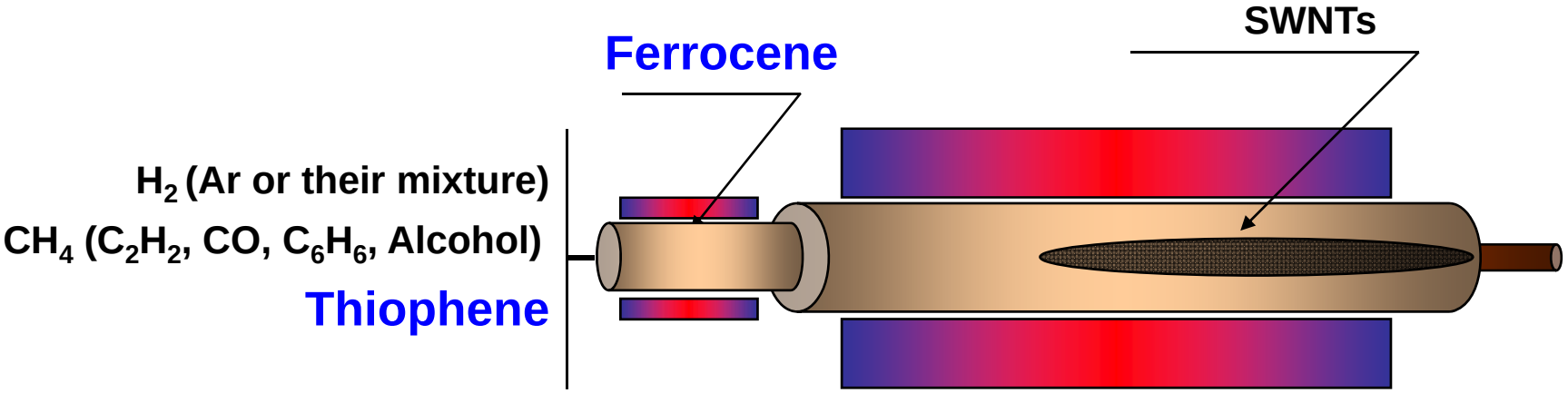
Ferrocene



Floating Catalyst CVD Method (FCCVD)

1998



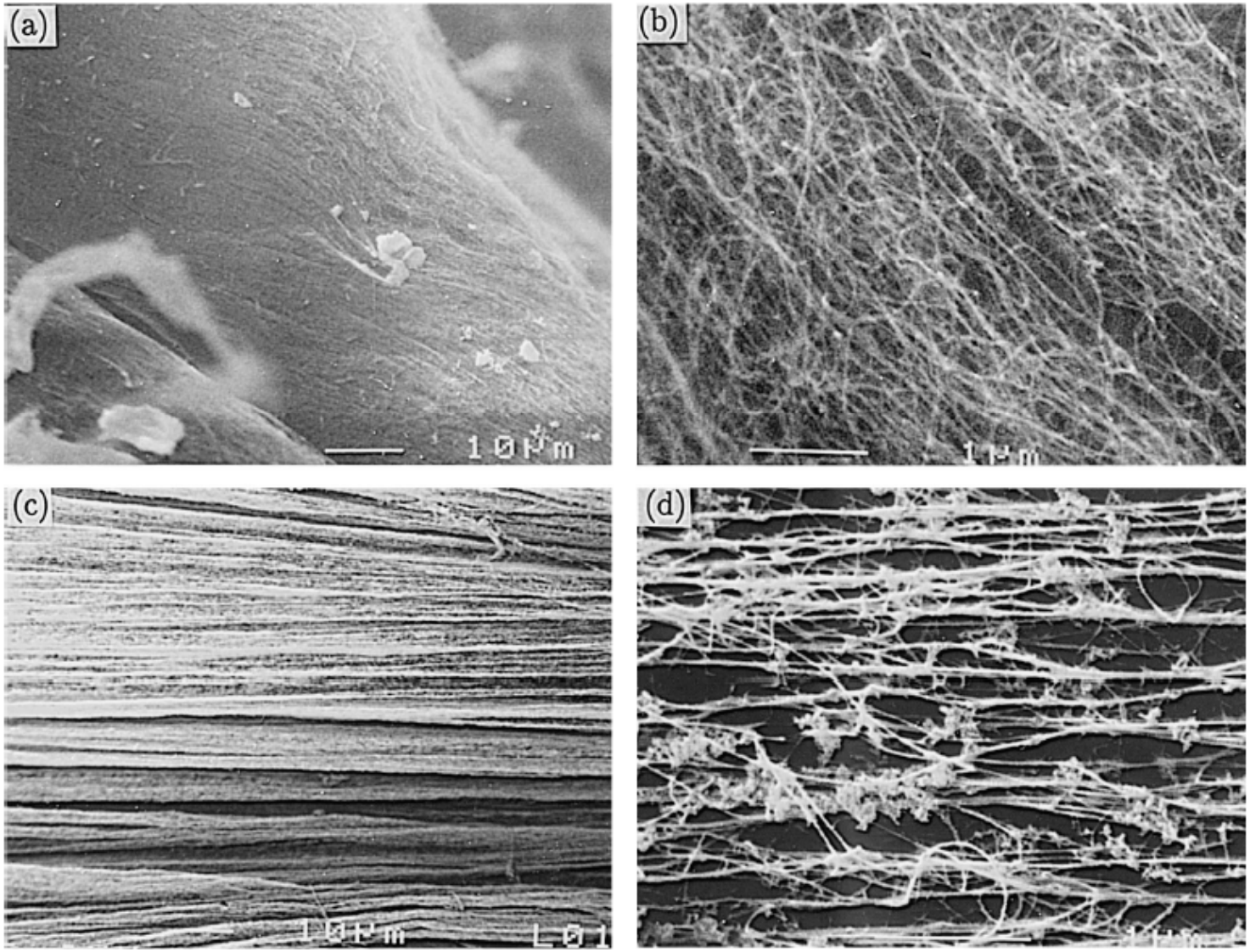


- ✓***Potential for continuous preparation***
- ✓***Possibility of structural control***
- ✓***Low cost, high purity***
- ✓***Simple post-treatment***

HM Cheng et al., Appl. Phys. Lett. 72 (1998) 3282.

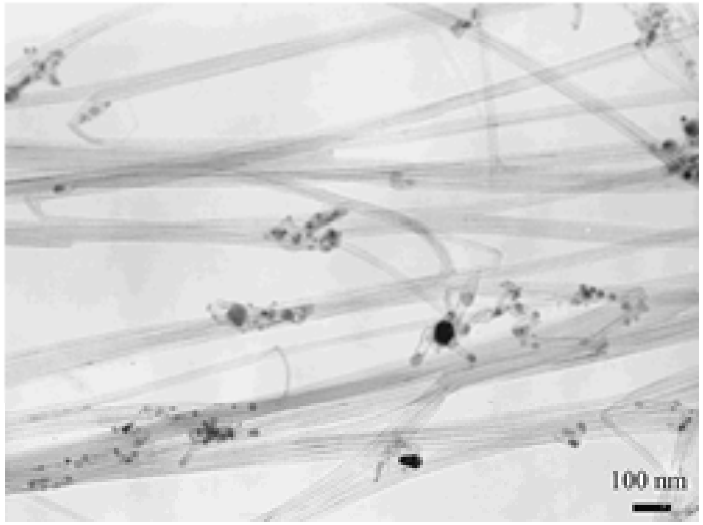
HM Cheng et al., Chem. Phys. Lett. 289 (1998) 602.

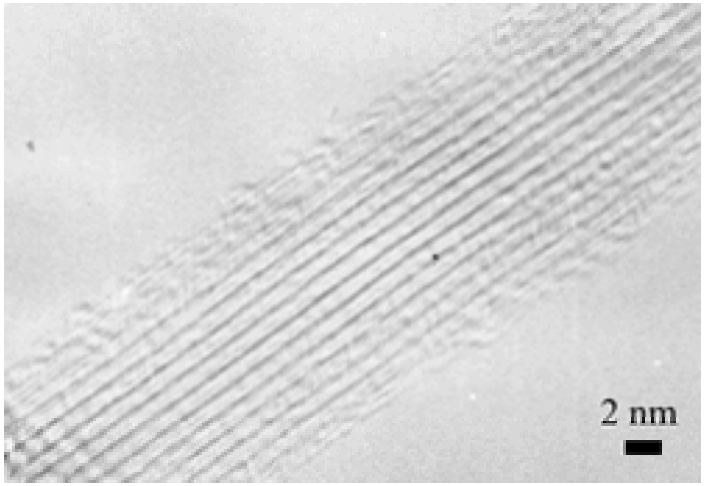
SWNTs by FCCVD

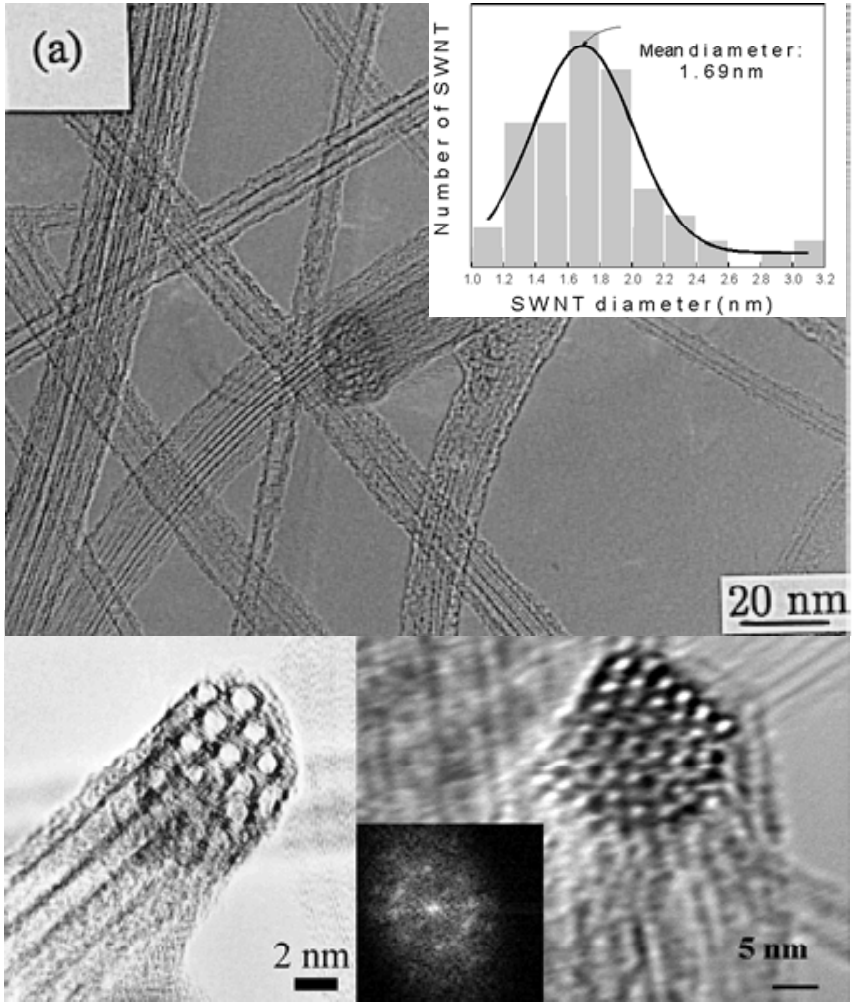


HM Cheng et al., Chem. Phys. Lett.289 (1998) 602.

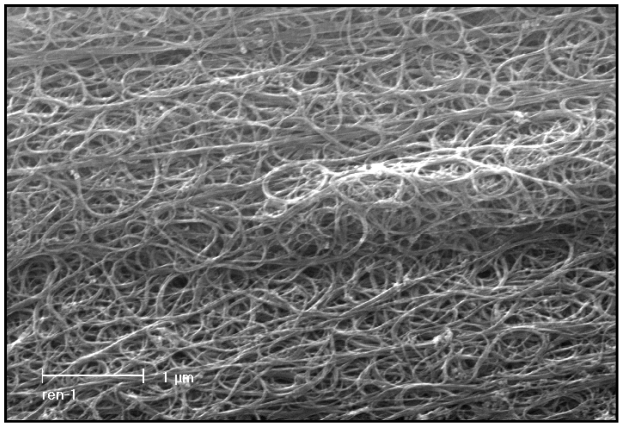
TEM Images of the SWNTs by FCCVD

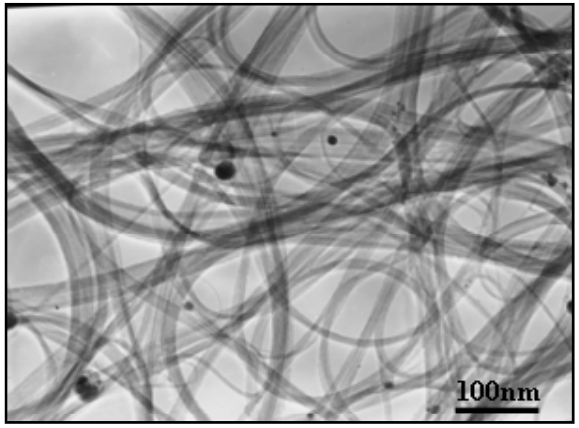


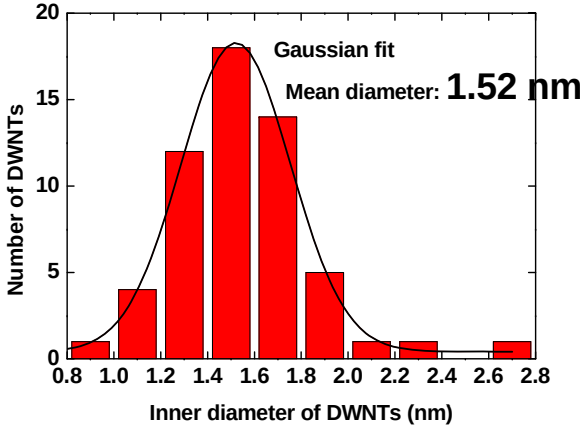


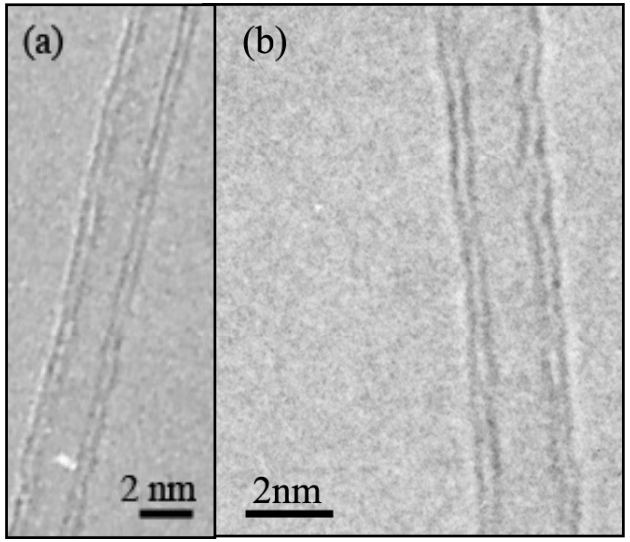


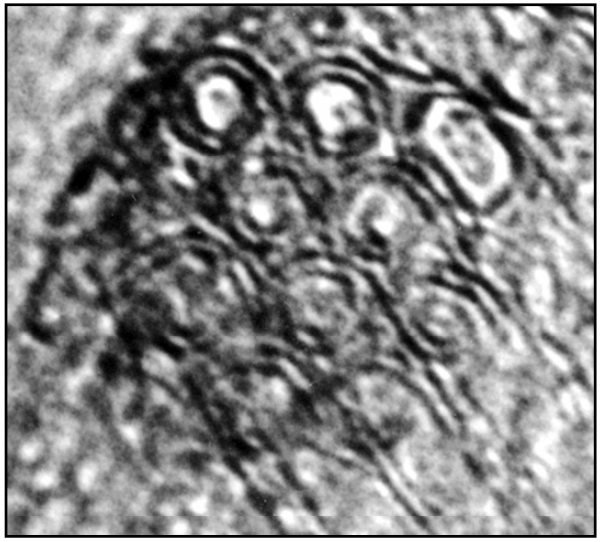
Synthesis of DWNTs by FCCVD

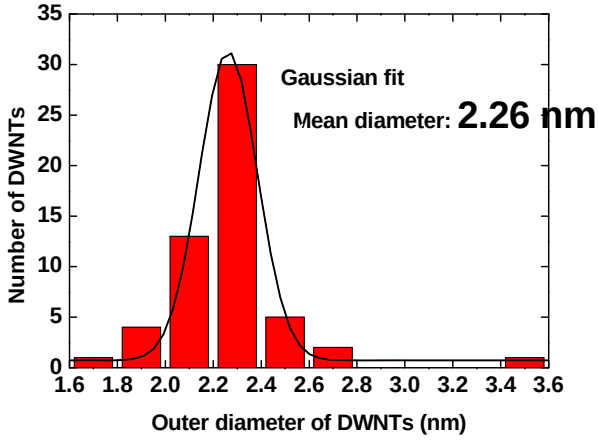










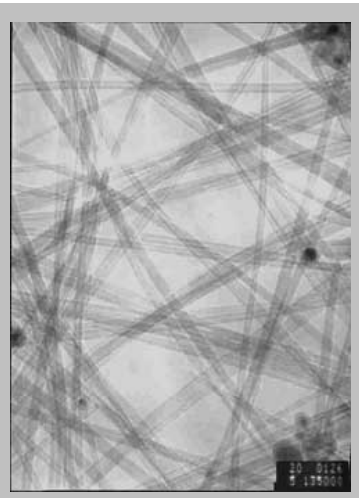


> 70%

WC Ren, HM Cheng et al., Chem. Phys. Lett. 359 (2002) 196.

CNFs/MWNTs with Different Diameter and Wall Thickness

< 10 nm



20-40 nm

50-70nm

70-100 nm

150 nm

- **Carbon feeding rate**
- **Catalyst particle size**
- **Sulfur concentration**

YY Fan, HM Cheng et al., Carbon 38 (2000)789.
YY Fan, HM Cheng et al., Carbon 38 (2000) 921.
YY Fan, HM Cheng et al., J. Mater. Res. 13 (1998) 2342.

Outline

- Synthesis of CNTs by Floating Catalyst CVD (SWNTs, DWNTs, MWNTs)
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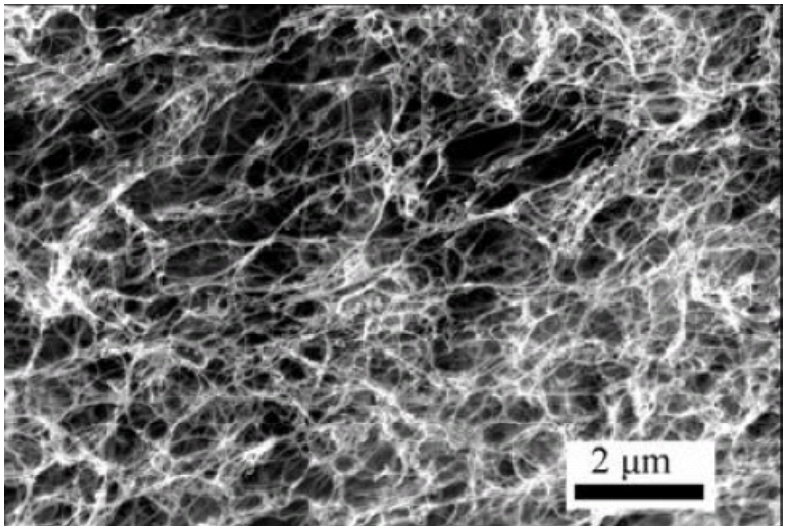
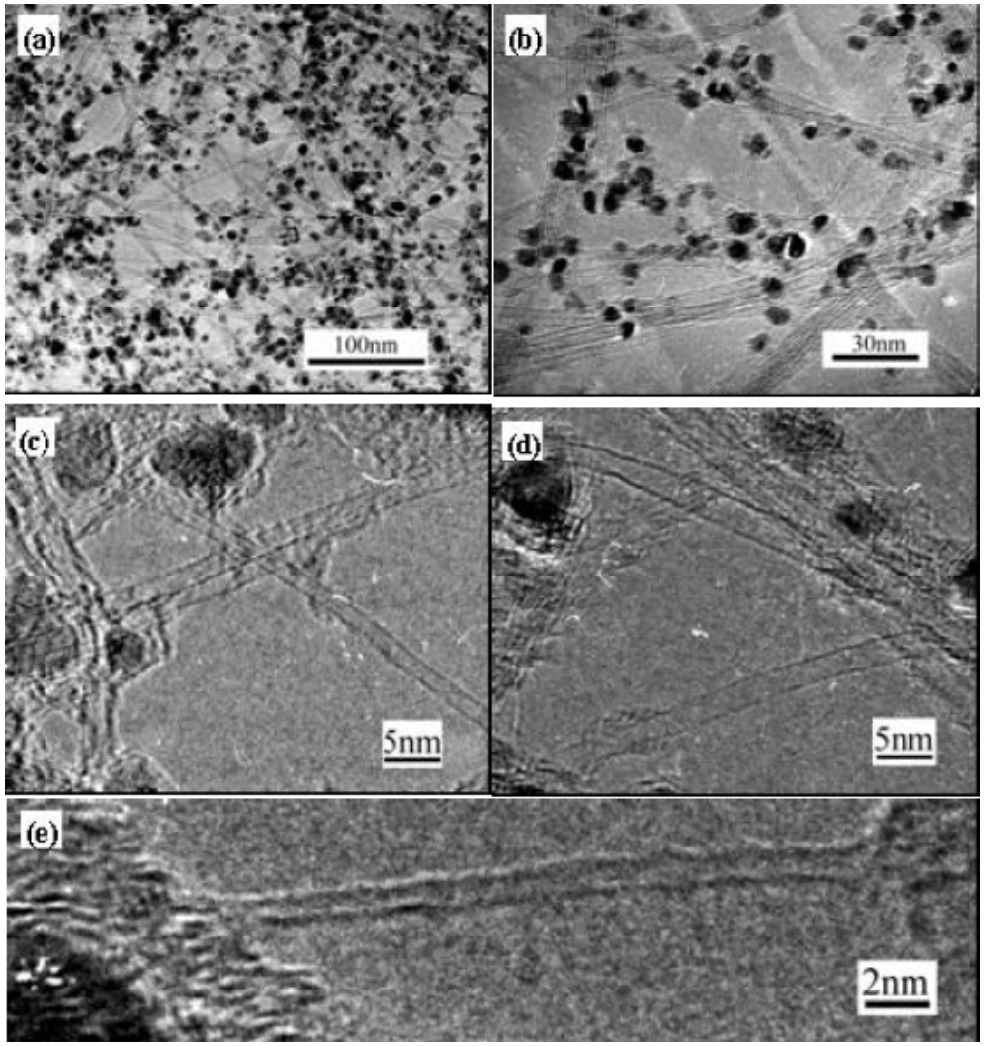
The Effect of Sulfur-- Necessary?

Ferrocene & Argon

Without the addition of sulfur
Without additional carbon

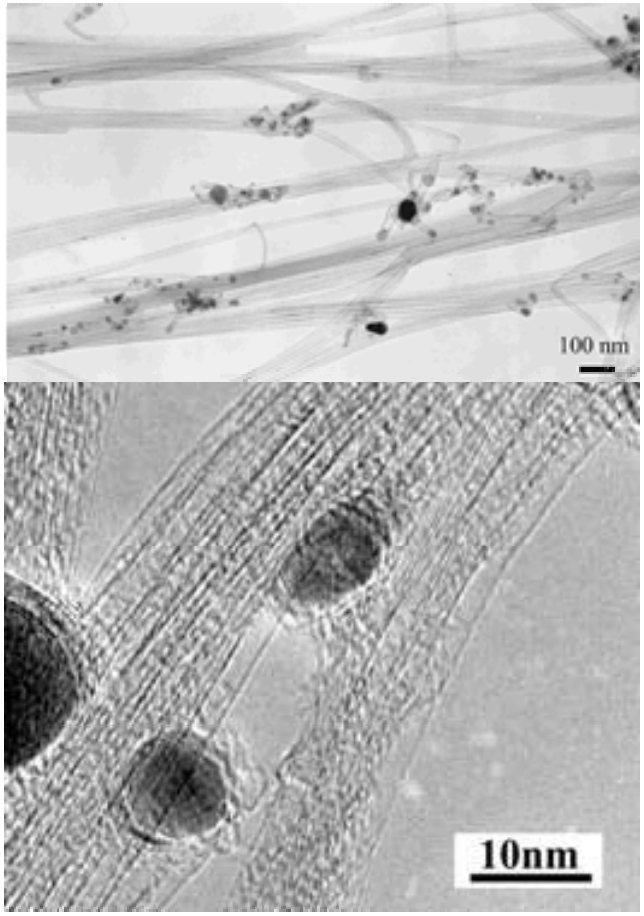




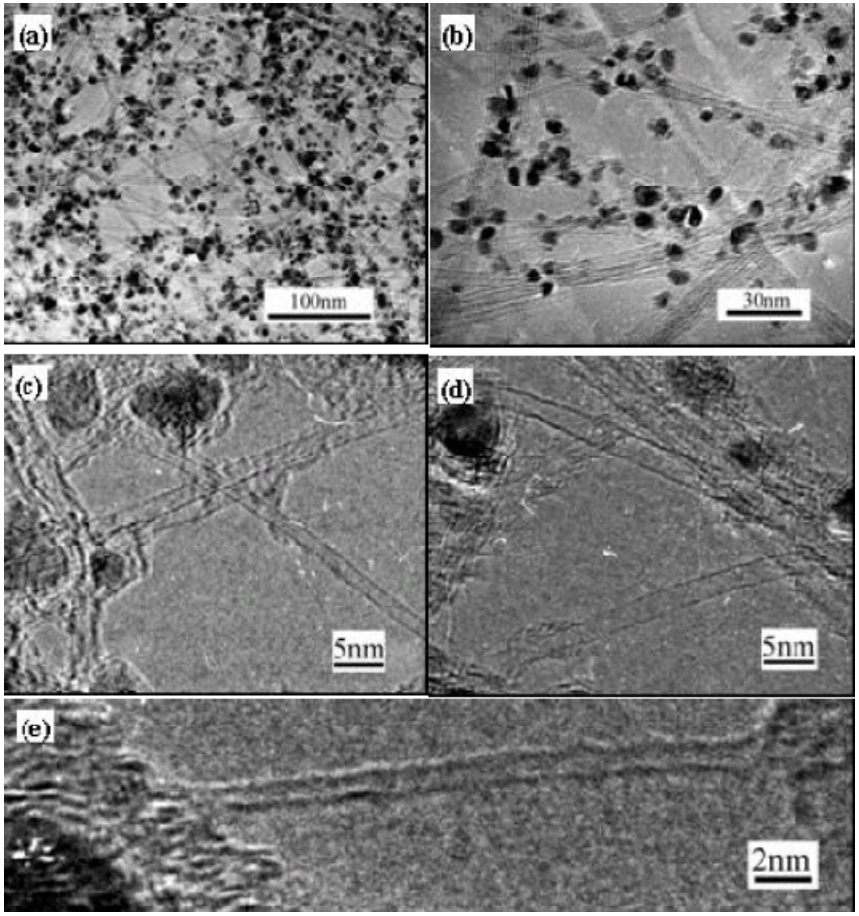
- **Low productivity**

The effect of Sulfur on the Purity and Quality of SWNTs

with sulfur

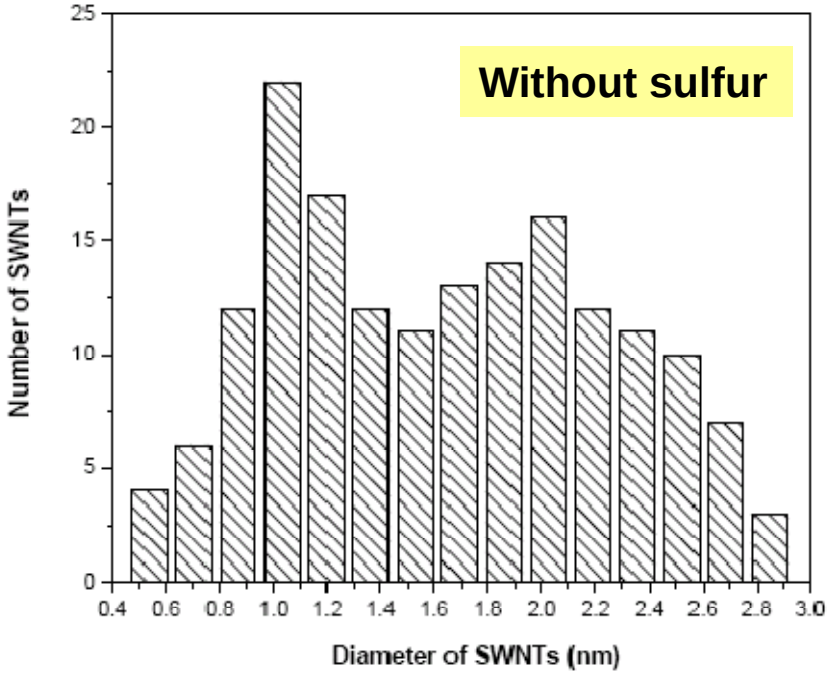


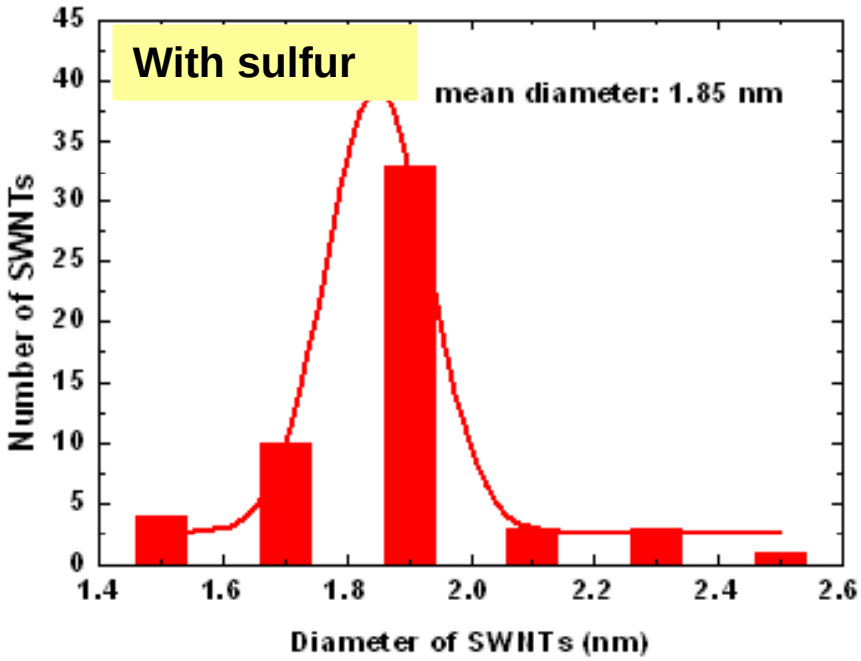
without sulfur



- **Higher purity**
- **Higher quality and narrower distribution**

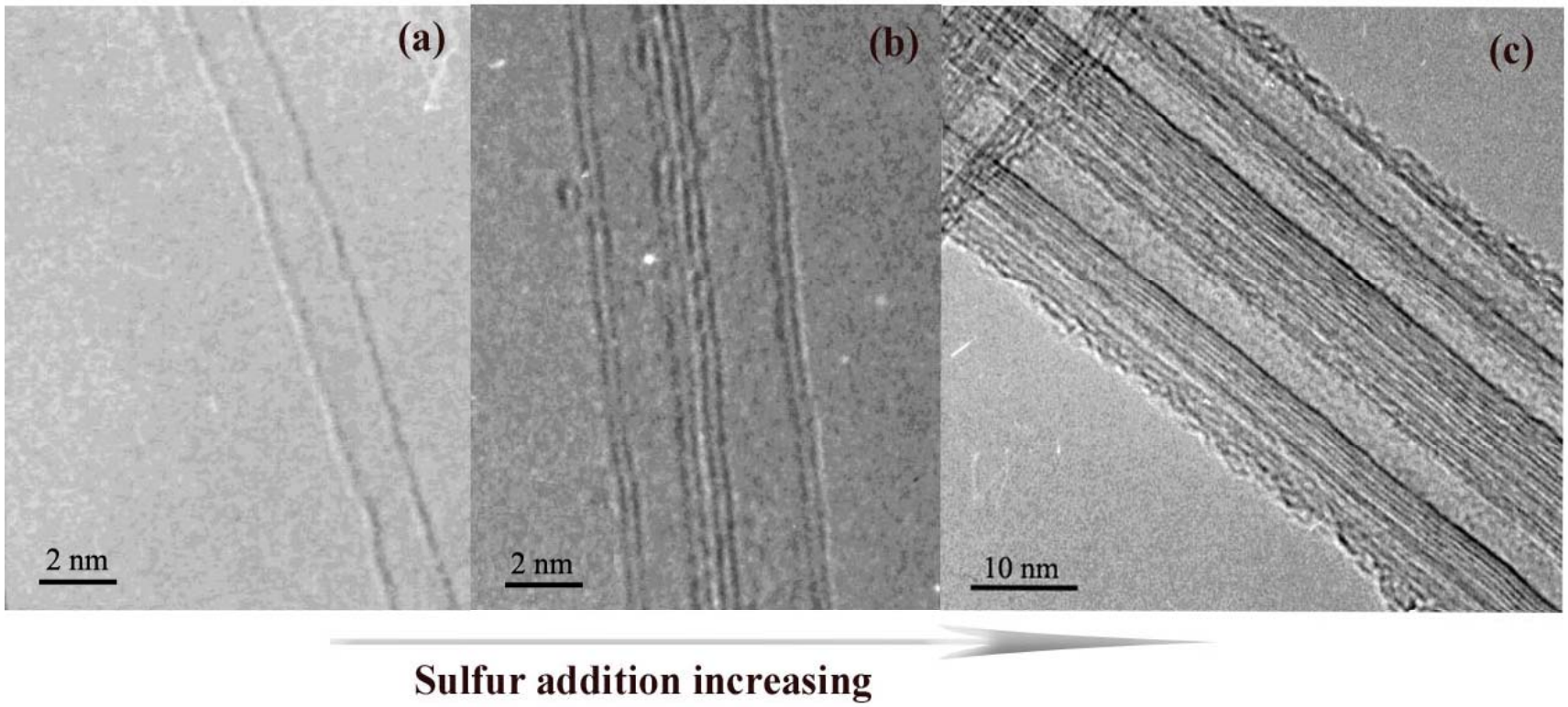
The Effect of Sulfur on the Diameter Distribution of SWNTs





- **Broad diameter distribution!**

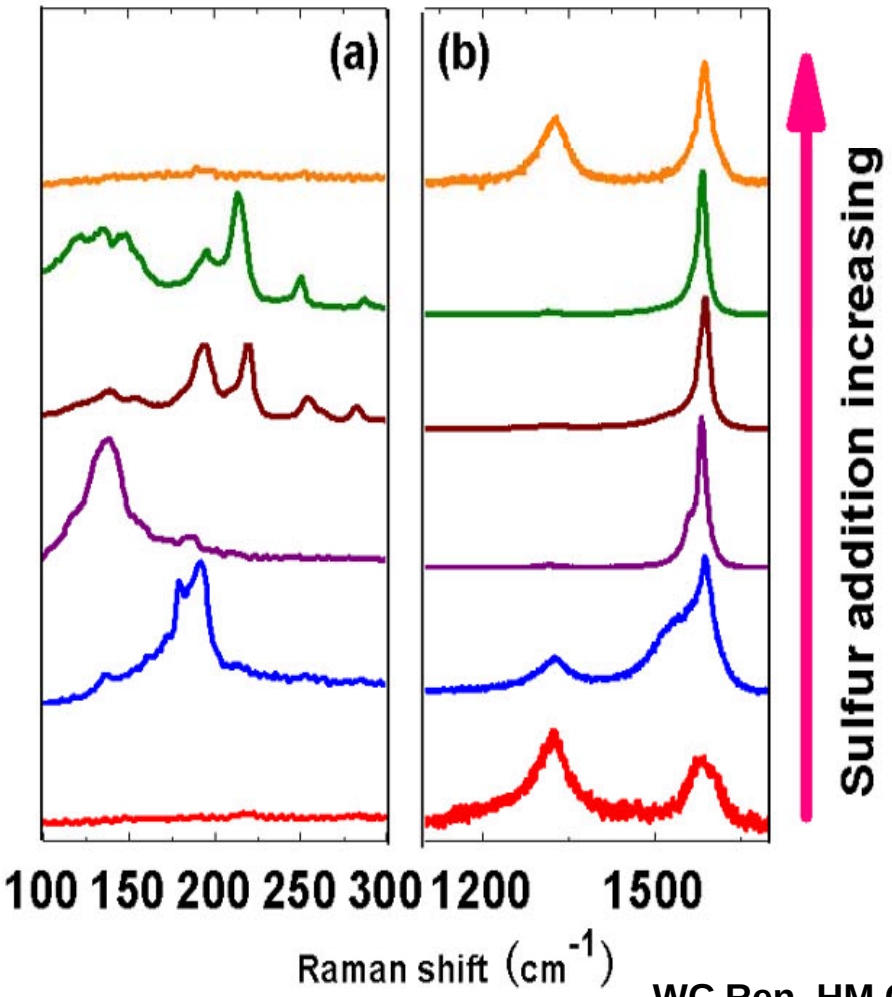
The Effect of Sulfur on Diameter and Shell Number

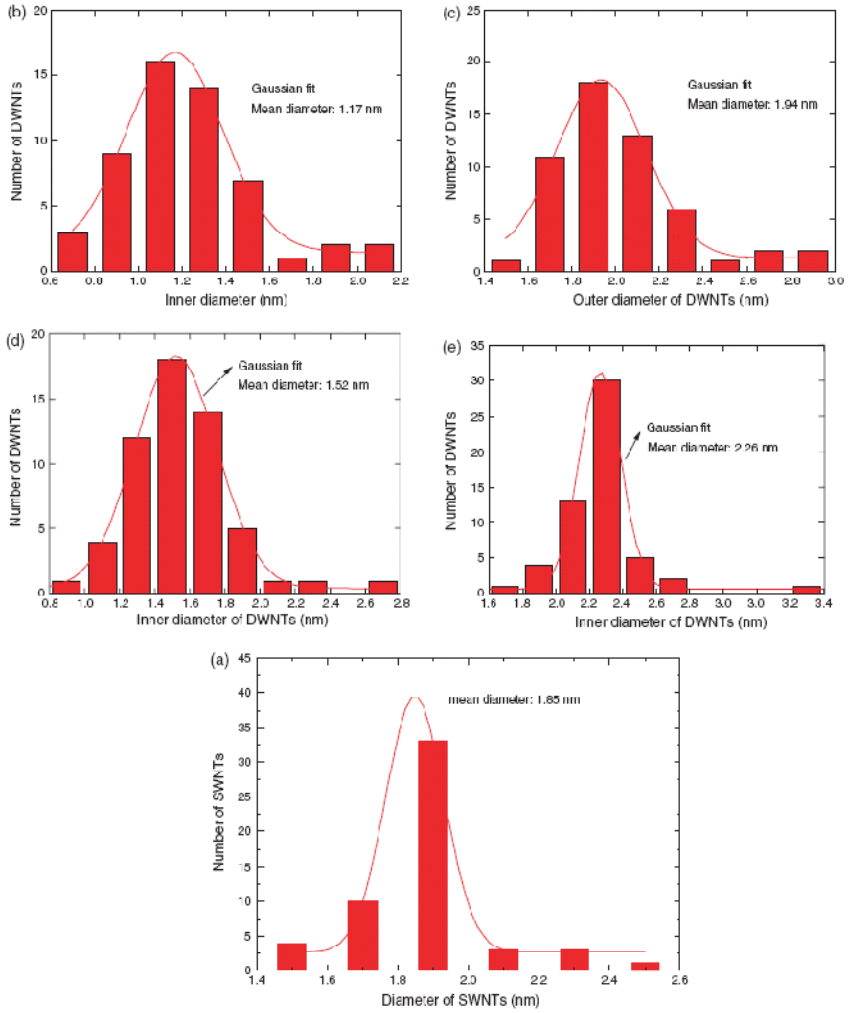


WC Ren, HM Cheng et al., J. Nanosci. Nanotech. 6 (2006) 1339.

Sulfur plays an important role in the structural control (diameter and shell number) of CNTs

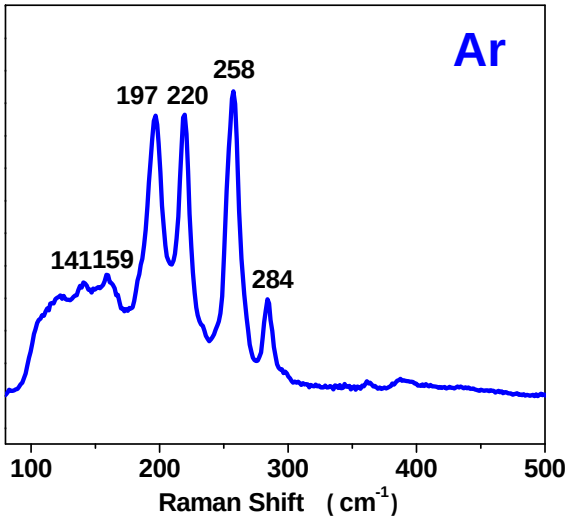
$\omega = A_1/d_t + A_2$

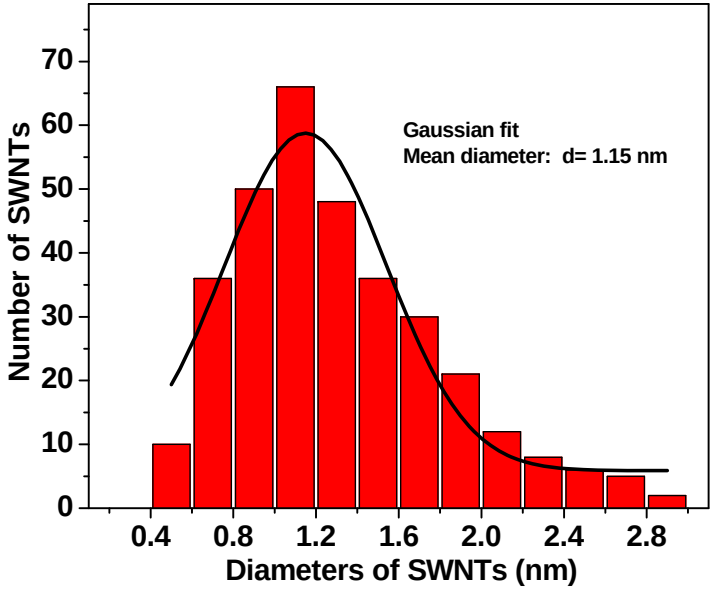


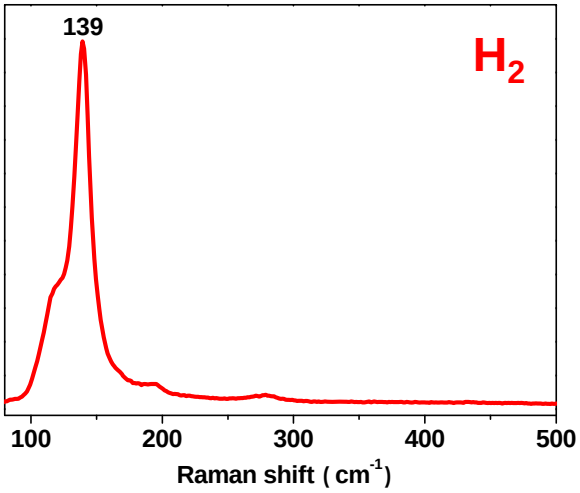


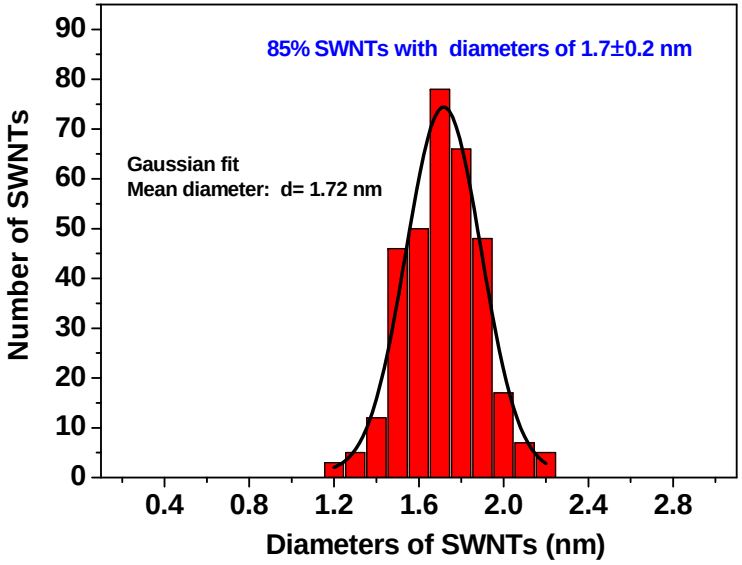
WC Ren, HM Cheng et al., J. Nanosci. Nanotech. 6 (2006) 1339.

Hydrogen is beneficial to the synthesis of Diameter Narrowly-distributed SWNTs



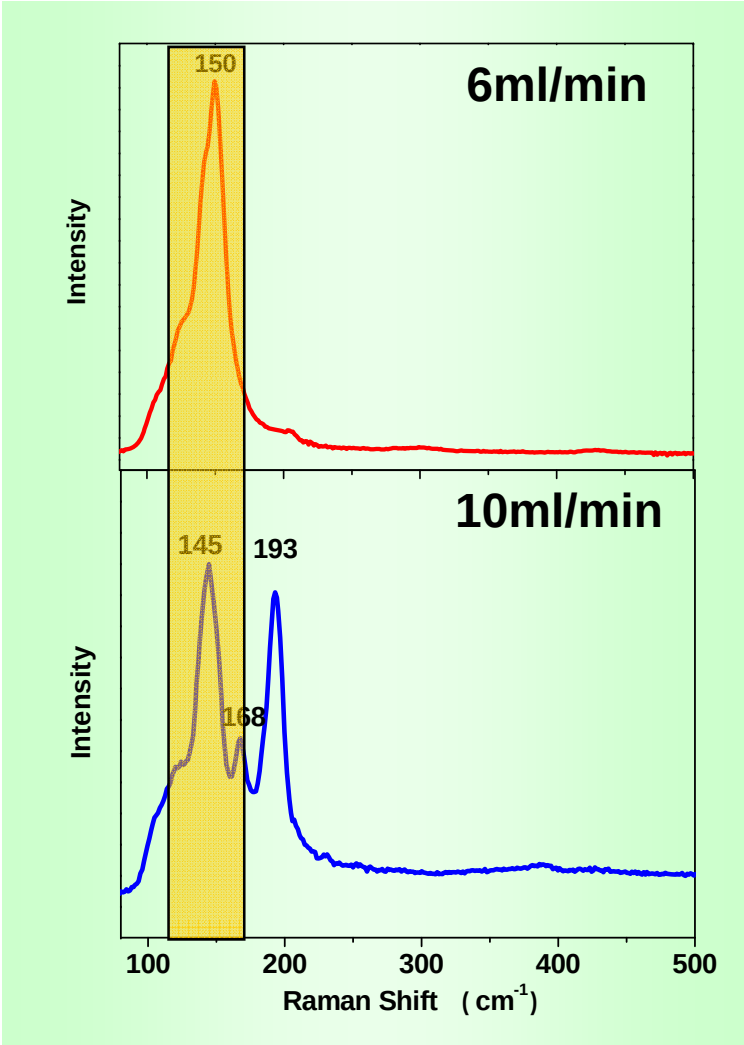


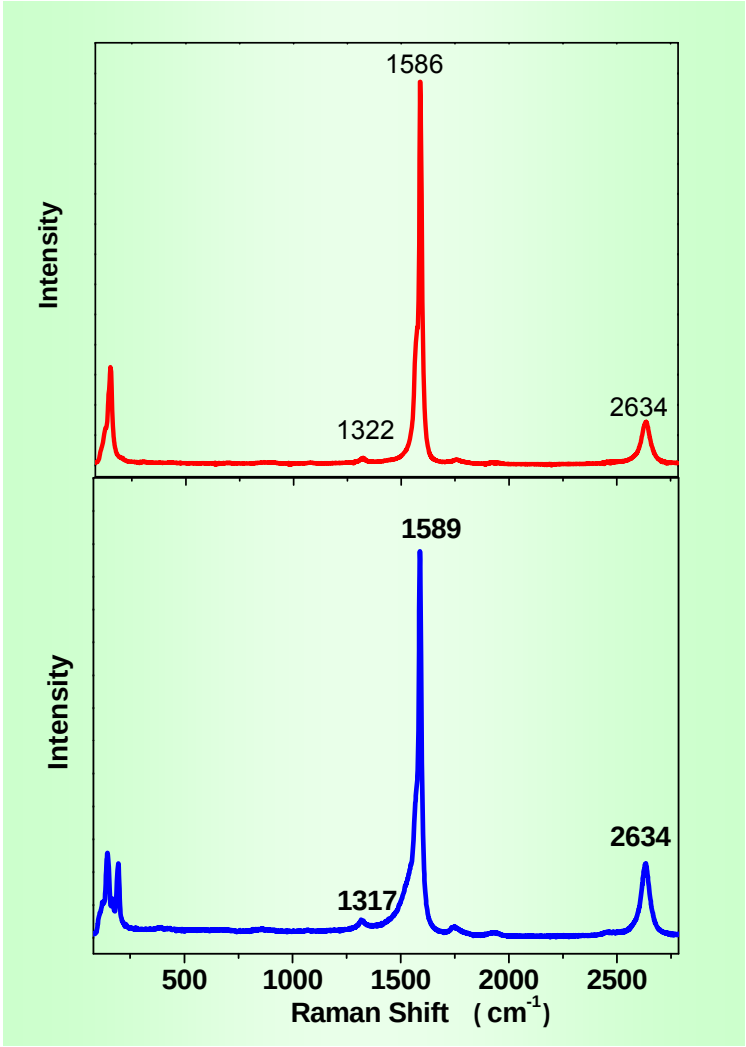




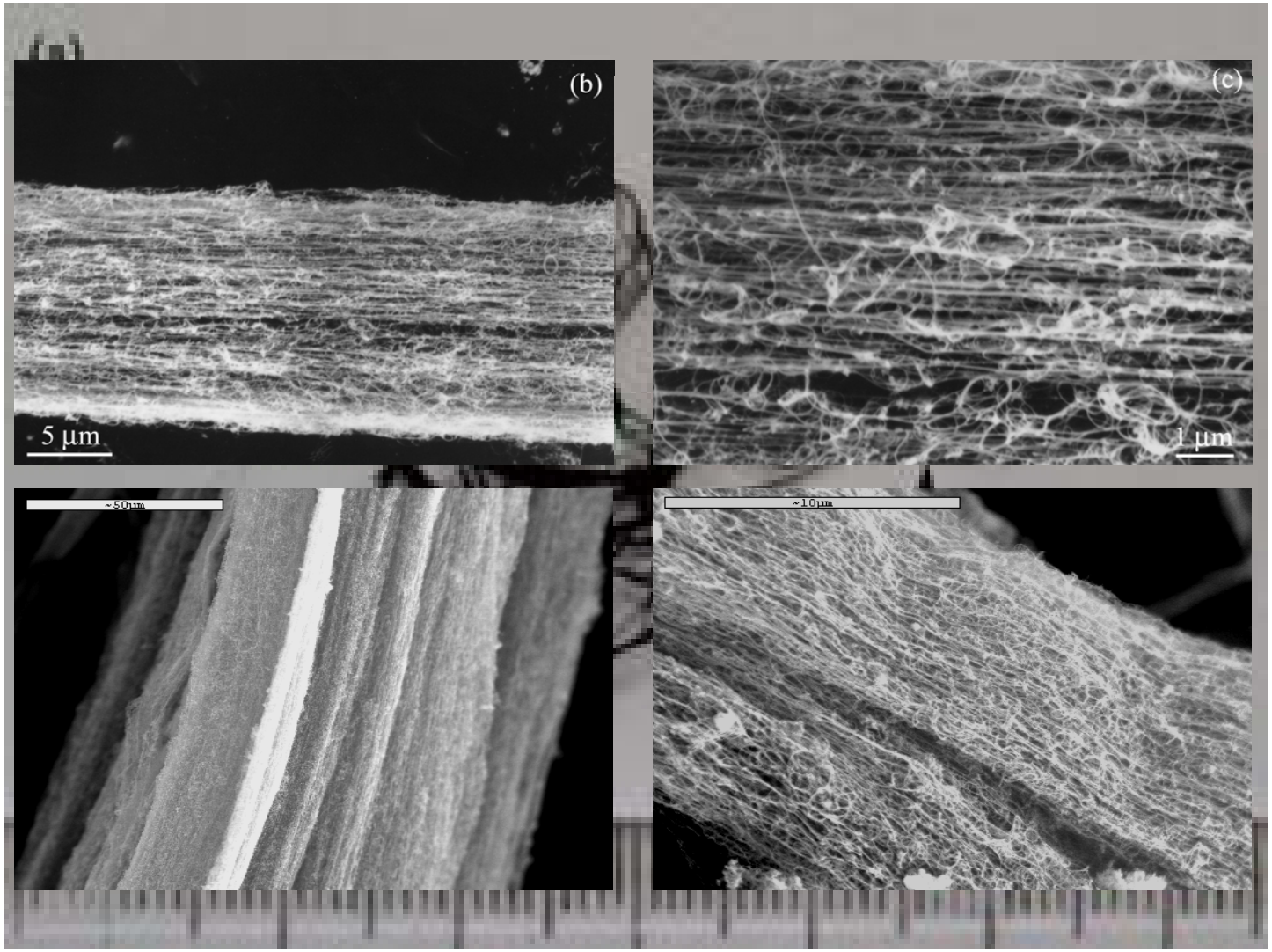
Low carbon feeding rate is beneficial to the synthesis of Narrowly-distributed SWNTs

Carbon source: Methane





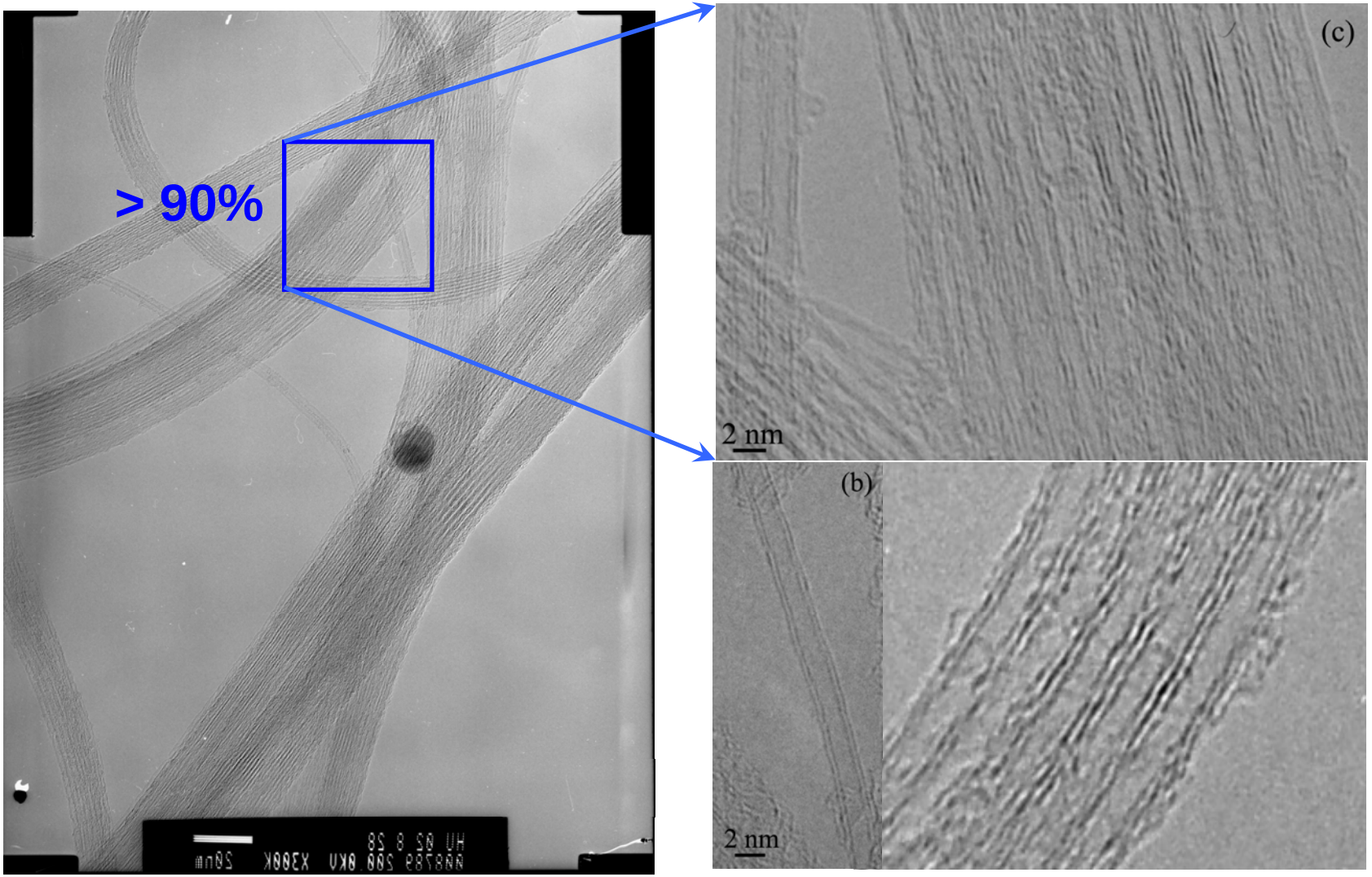
Aligned DWNT ropes by FCCVD



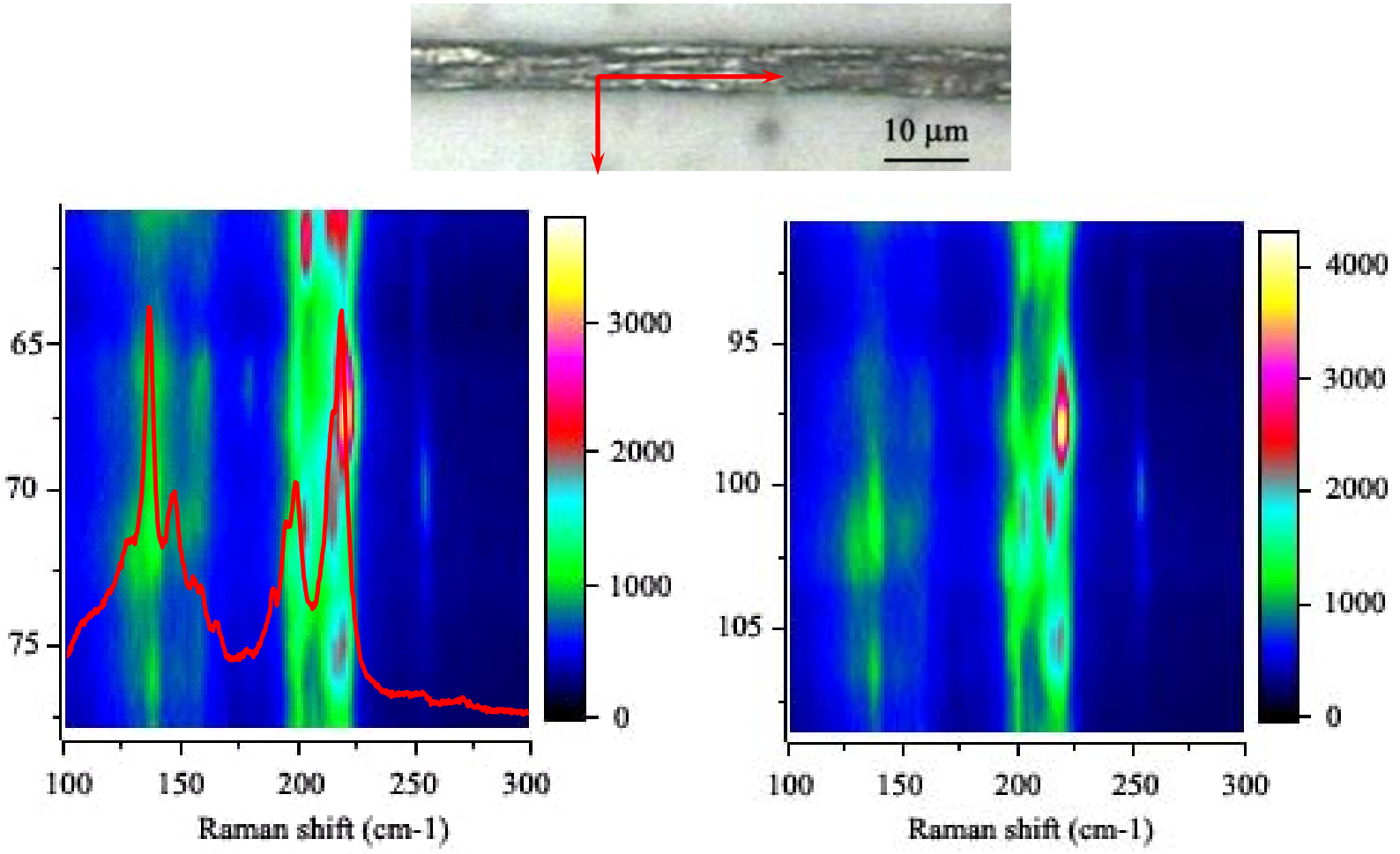
WC Ren, HM Cheng et al., J. Phys. Chem. B 109 (2005) 7169.

Typical HRTEM Images of DWNTs

Outer diameter: 1.7-2.0 nm Inner diameter: 1.0-1.3 nm



RBM Mapping of DWNT Ropes



Narrow diameter distribution

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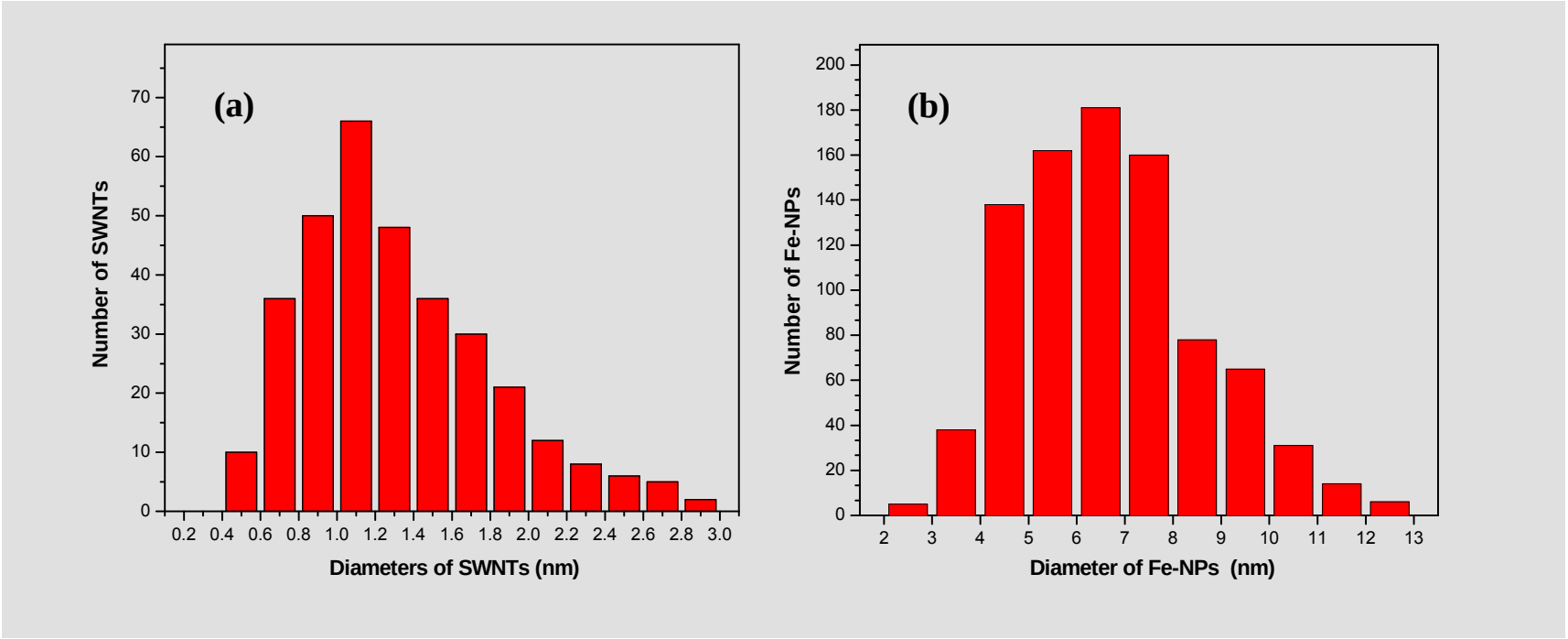
Structural Correlation between SWNTs and the Attached Catalyst Particles

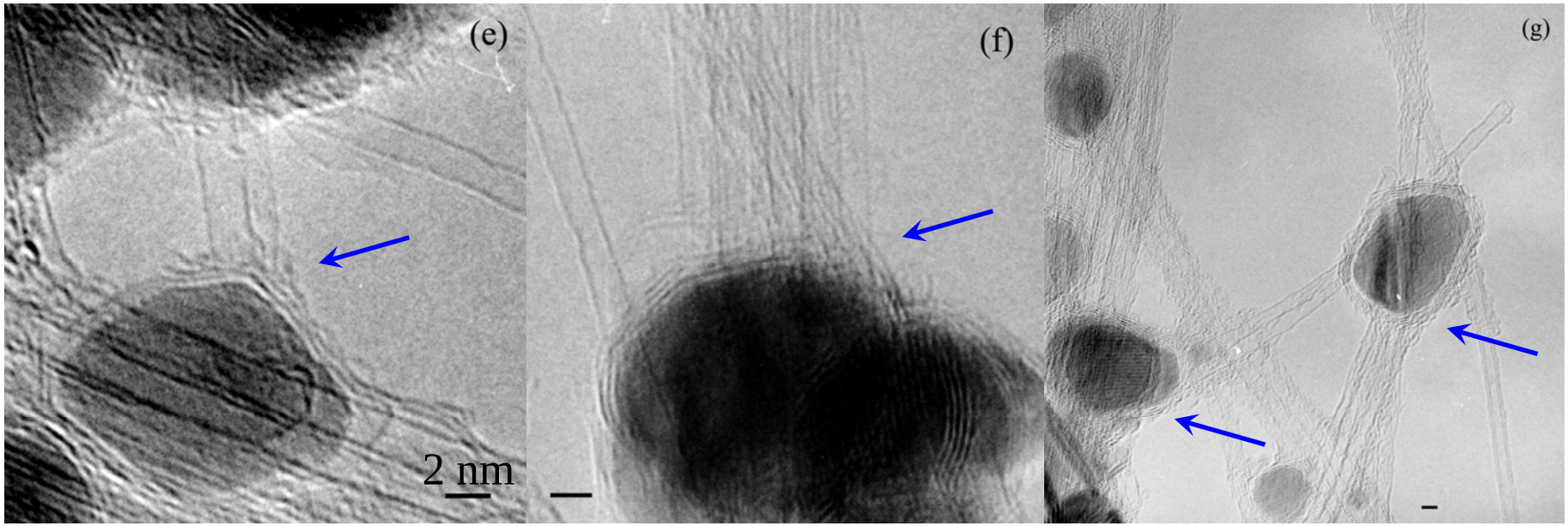


- The size of catalyst particles : > 5nm
- The diameters of SWNTs or DWNTs: < 3 nm (in general)
- SWNTs growth on the localized region of the surface of catalyst

Localized nucleation on big catalyst particles

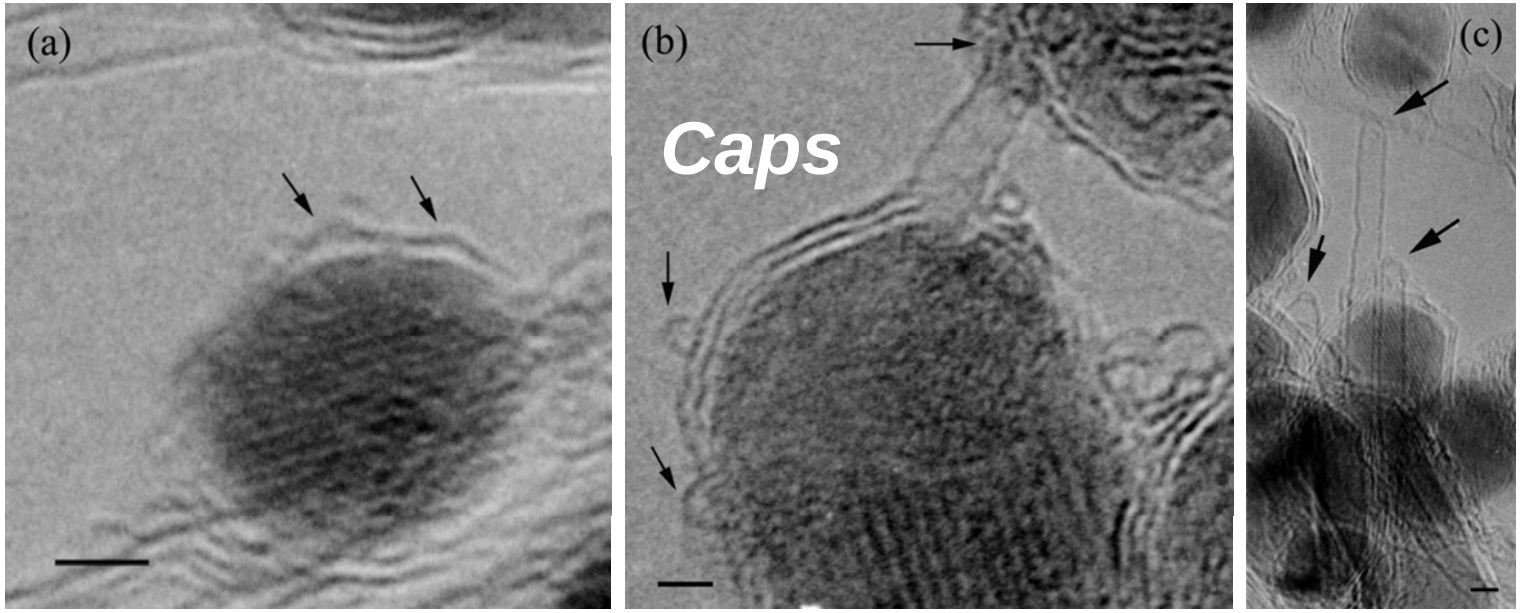
WC Ren, HM Cheng et al., J. Phys. Chem. B 110 (2006) 16941.

Structural Correlation between SWNTs Bundles and the Attached Catalyst Particles



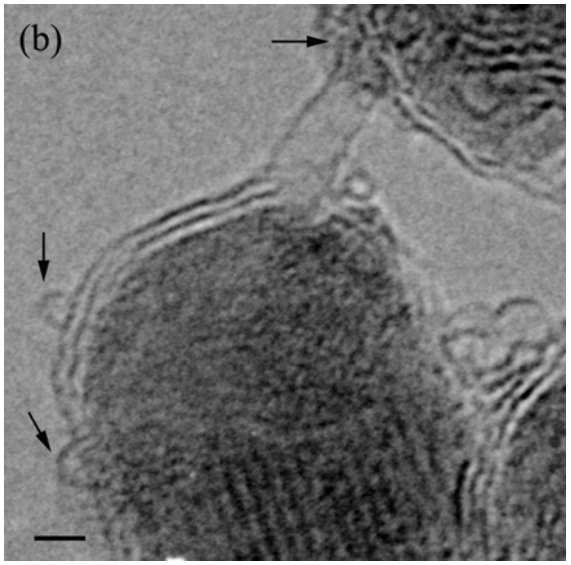
Localized nucleation on big catalyst particles

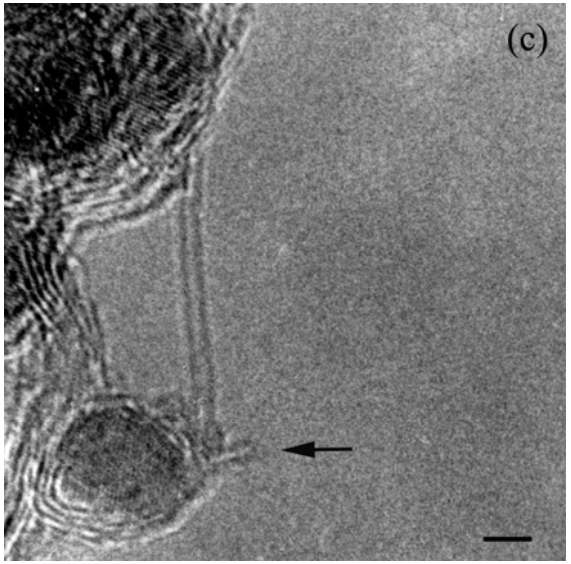
Tip Structure of SWNTs at the Initial Nucleation Stage

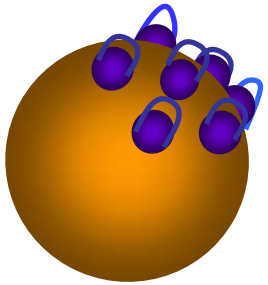


- **Formation of the cap structure**
  - **Bending of graphite islands on the localized zone of the surface of catalyst particles**

Role of Sulfur on the Formation of the Small Caps







VLS growth mechanism

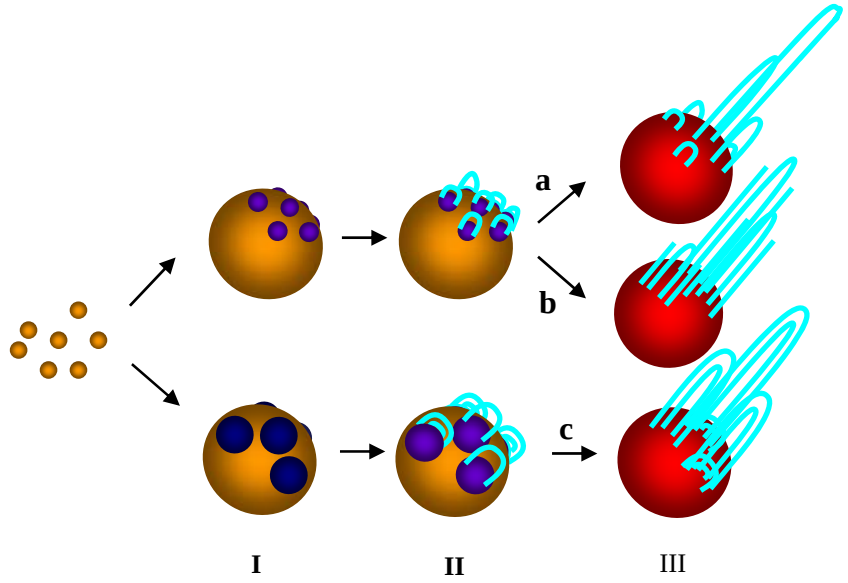
— Precipitation of carbon from the localized liquid zone

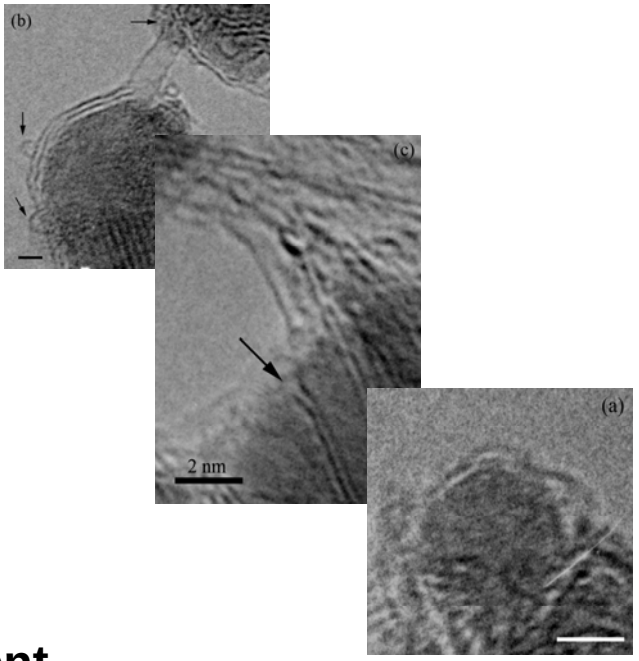
The role of sulfur

- **Decreasing melting point of localized zone**
  - **Key point for the localized nucleation (the diameter of CNTs is closely correlated with the addition amount of sulfur)**
- **Enhancing the decomposition of carbon sources**
  - **Inhibit the continuous extending of graphite islands**
- **Introduction of defects in the graphite islands**
  - **Enhance the bending of graphite islands and consequently nucleation**

Proposed Growth Model

Sulfur-assisted localized nucleation at low temperature





WC Ren, HM Cheng et al., J. Phys. Chem. B 110 (2006) 16941.

Concluding Remarks

- Developed a floating catalyst CVD method for the synthesis of SWNTs and DWNTs
- Attempted the diameter and shell number control of CNTs
- Obtained SWNTs and DWNTs with narrow diameter distribution
- Proposed a localized nucleation model for the growth of SWNTs and DWNTs by FCCVD

Acknowledgment

- Dr. Wencai Ren
- Dr. Feng Li
- Mr. Qingfeng Liu
- Mr. Bilu Liu

- Prof. M Dresselhaus at MIT

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- JSPS for supporting this visit

Thank you very much for your attention!

SYNL

IMR