



# Pressure-Induced Single-Walled Carbon Nanotube ( $n, m$ ) Selectivity on Co-Mo catalysts

*presented by*

**Yuan Chen**

**[chenyuan@ntu.edu.sg](mailto:chenyuan@ntu.edu.sg)**

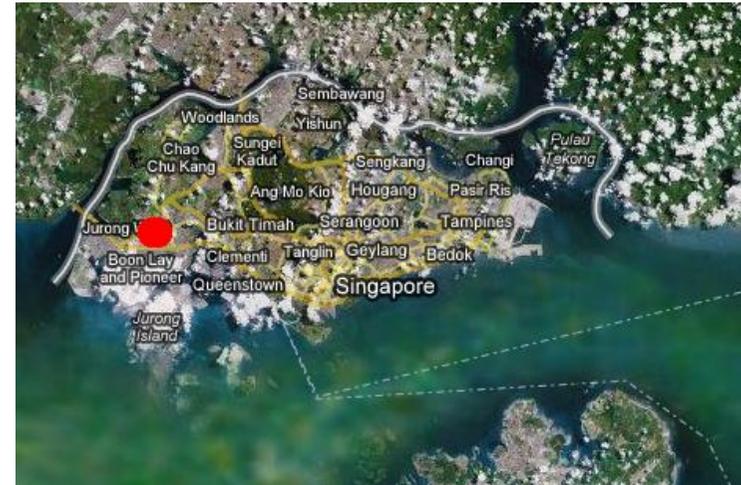
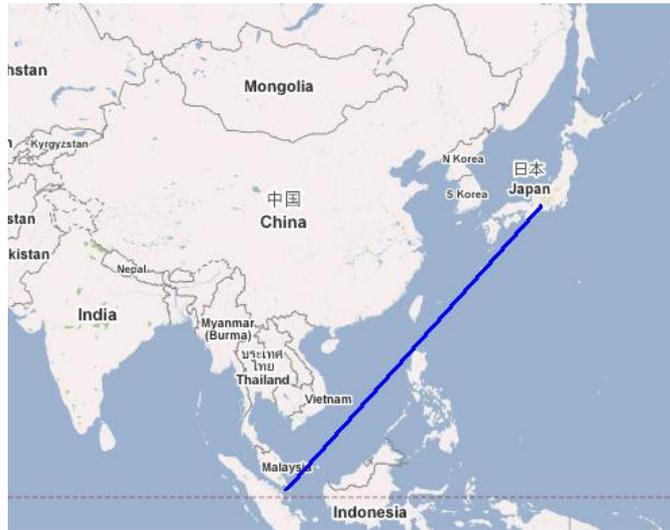
**[www.ntu.edu.sg/home/chenyuan](http://www.ntu.edu.sg/home/chenyuan)**

School of Chemical and Biomedical Engineering

March 2008

# SCBE, NTU @ Singapore

- School of Chemical and Biomedical Engineering Since 2004
- Nanyang Technological University, Singapore



City state of 700 km<sup>2</sup> with about 4.7 million people

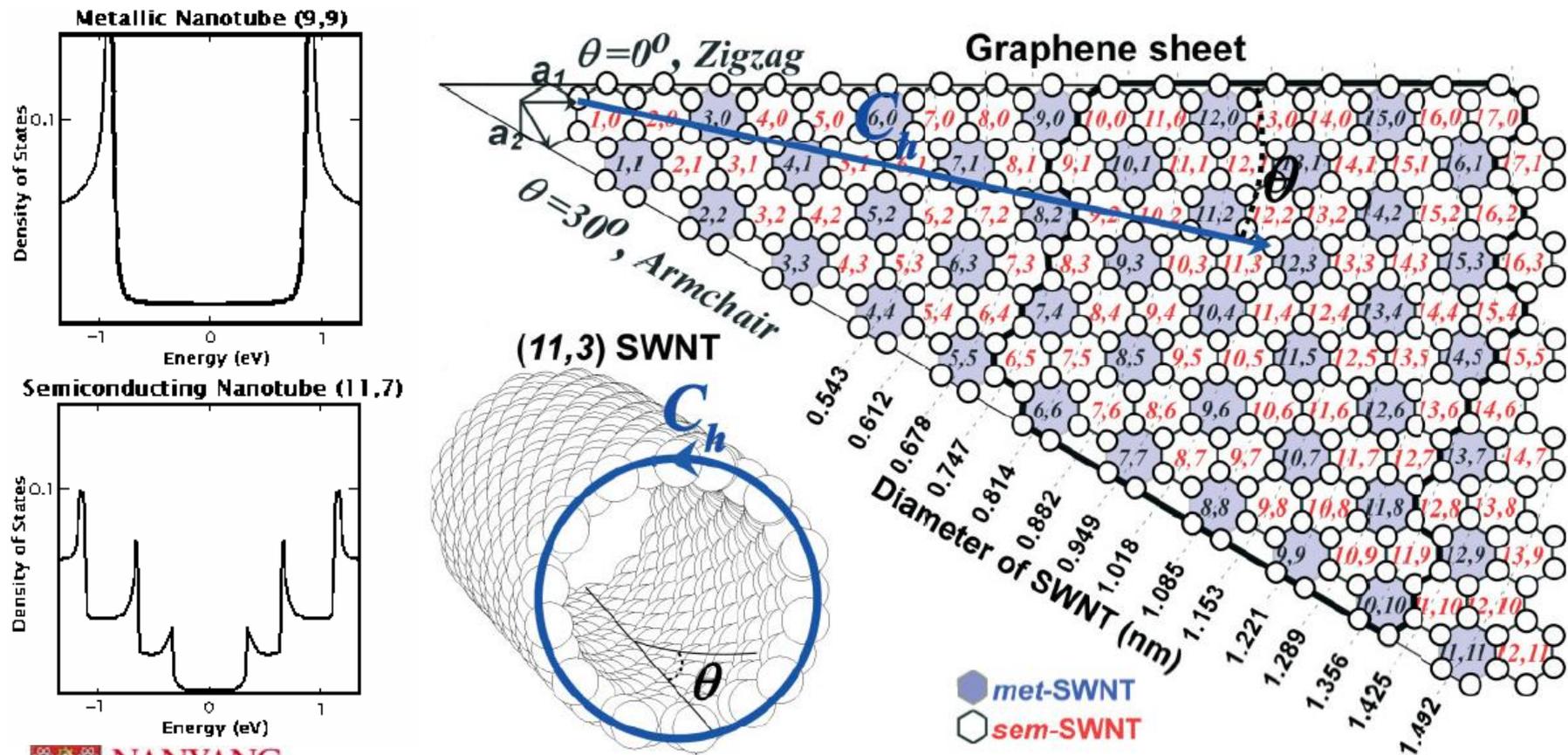
# Research scope

- 1 Growth of SWNT on Co-MCM-41
- 2 How synthesis conditions affect SWNT diameters?
- 3 Correlation between diameters of SWNT and cobalt cluster sizes in Co-MCM-41
- 4 Mechanism of cluster size control during SWNT growth
- 5 Chirality selectivity under different carbon precursors
- 6 Pressure inducted chirality selectivity
- 7 Purification of SWNTs from Co-MCM-41
- 8 Enrichment of (6,5) and (8,3) tubes using co-surfactant extraction



# Chirality of SWNTs

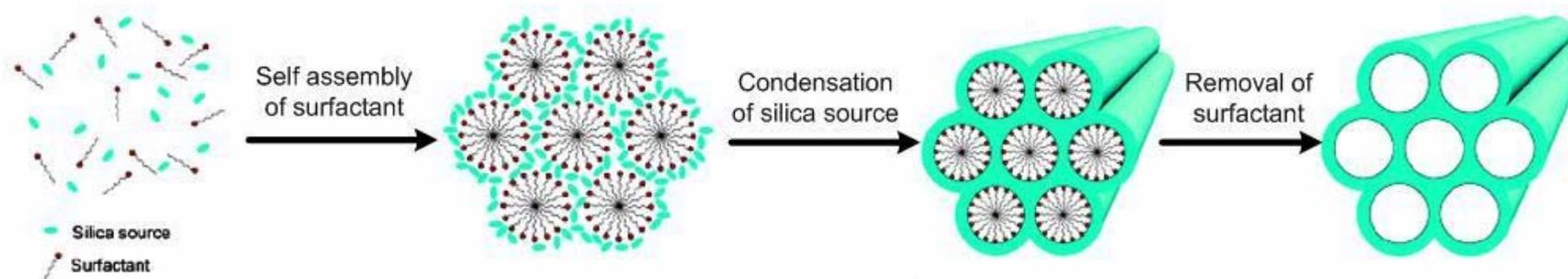
- SWNT electronic properties depend on chiral indices ( $n,m$ ).
- Control synthesis and enrichment processes to produce desired ( $n,m$ ) structure



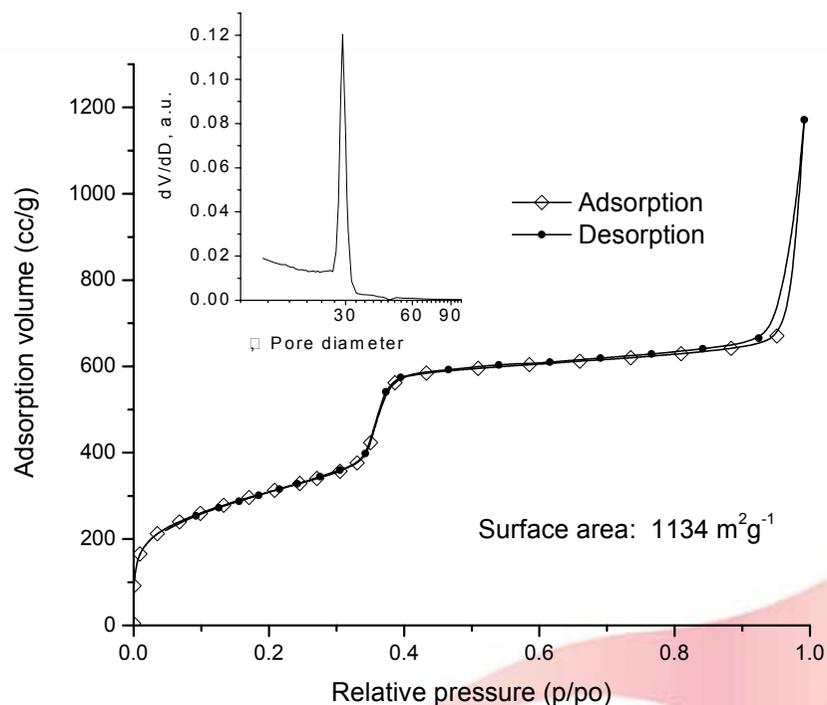
1

# What is MCM-41?

Hatton, B. et al. *Accounts of Chemical Research*, 2005 38(4) 305-312.

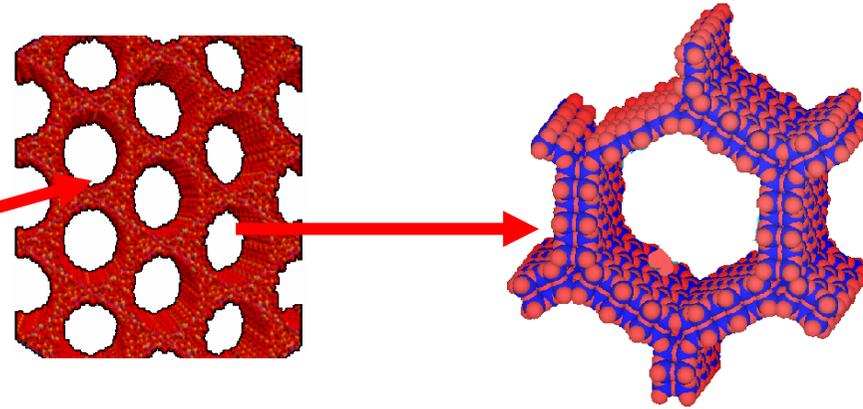
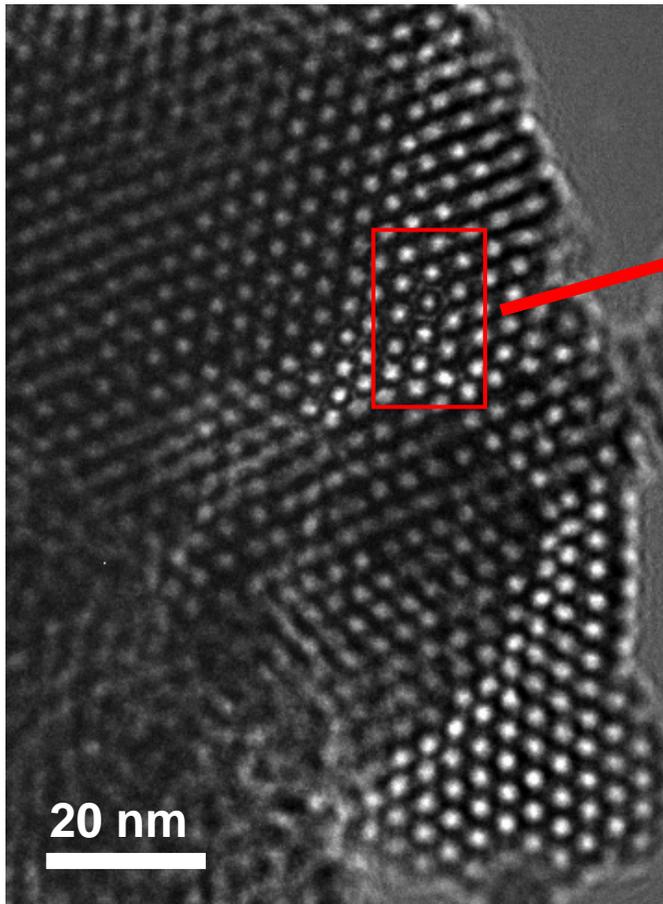


**Mobil composition materials No. 41. Using self-assembled surfactants to control the pore structure of mesoporous molecular sieve.**



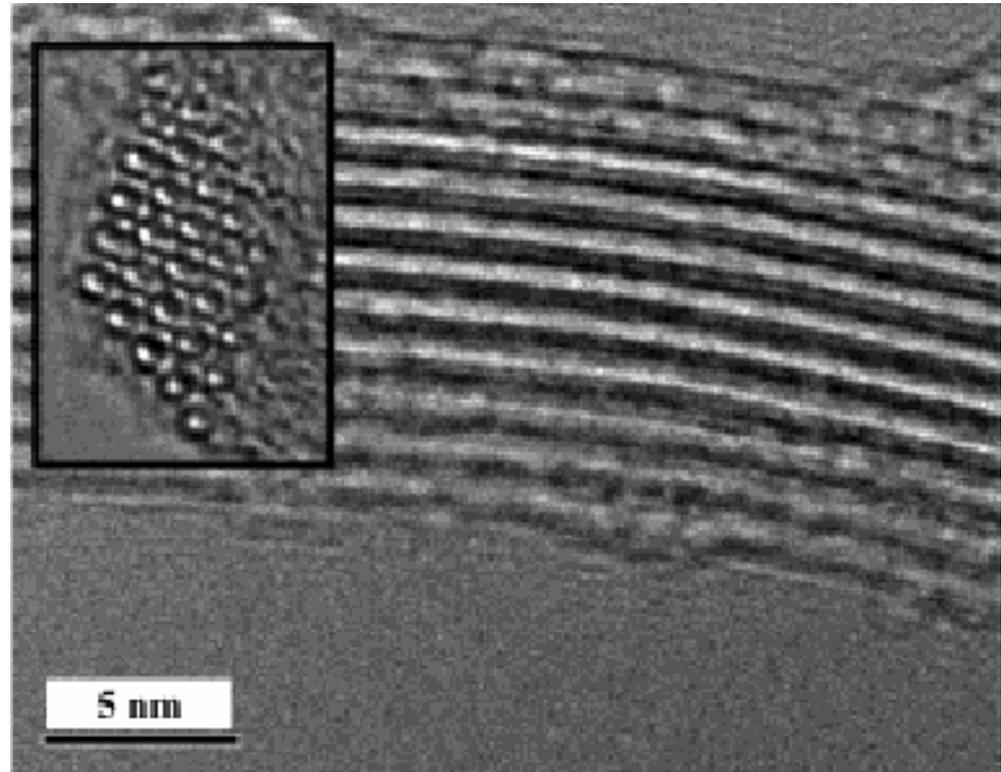
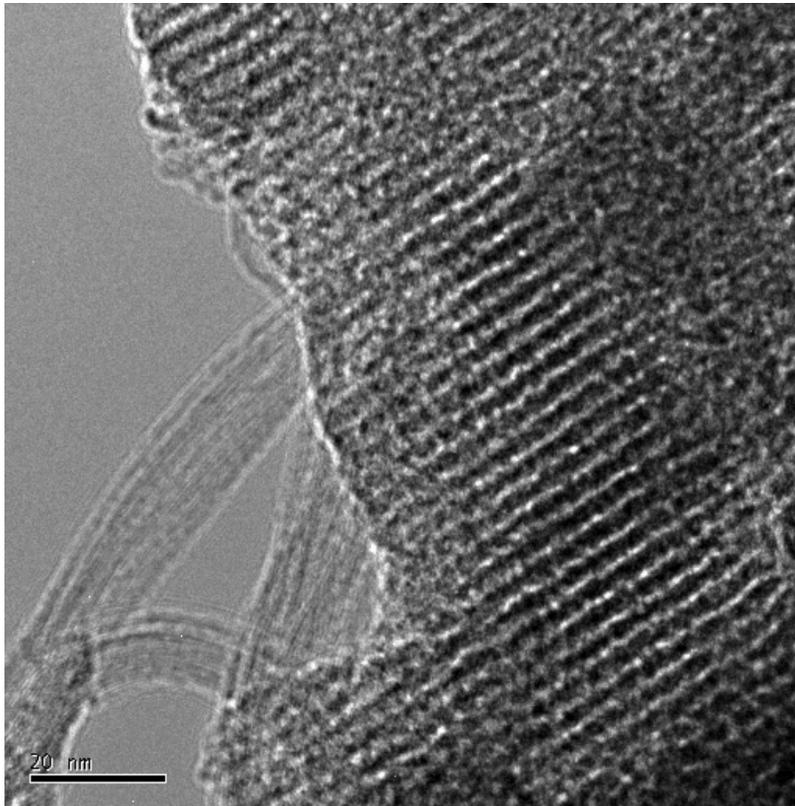
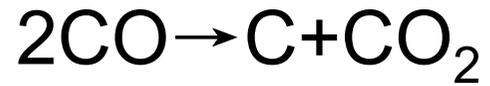
## Co-MCM-41:

Incorporate Co ions in the amorphous wall of MCM-41



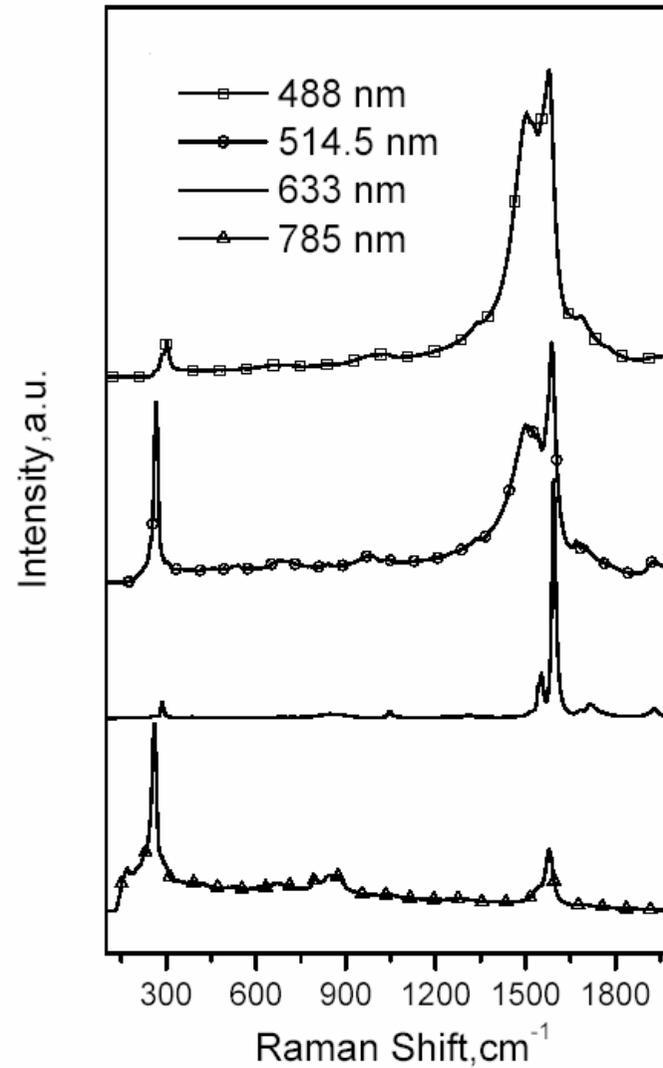
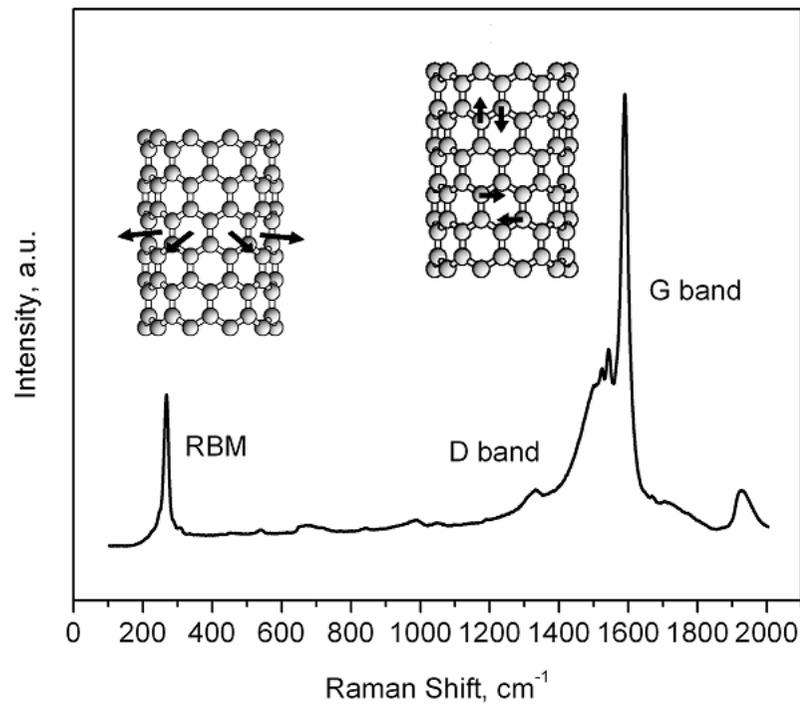
Co-MCM-41 is a mesoporous molecular sieves, cobalt can be incorporated into small amorphous silica rings, forming Si-O-Co bonds, strong bonds allow to control sizes of subnanometer metal clusters .

# TEM images of SWNT with narrow diameter distribution



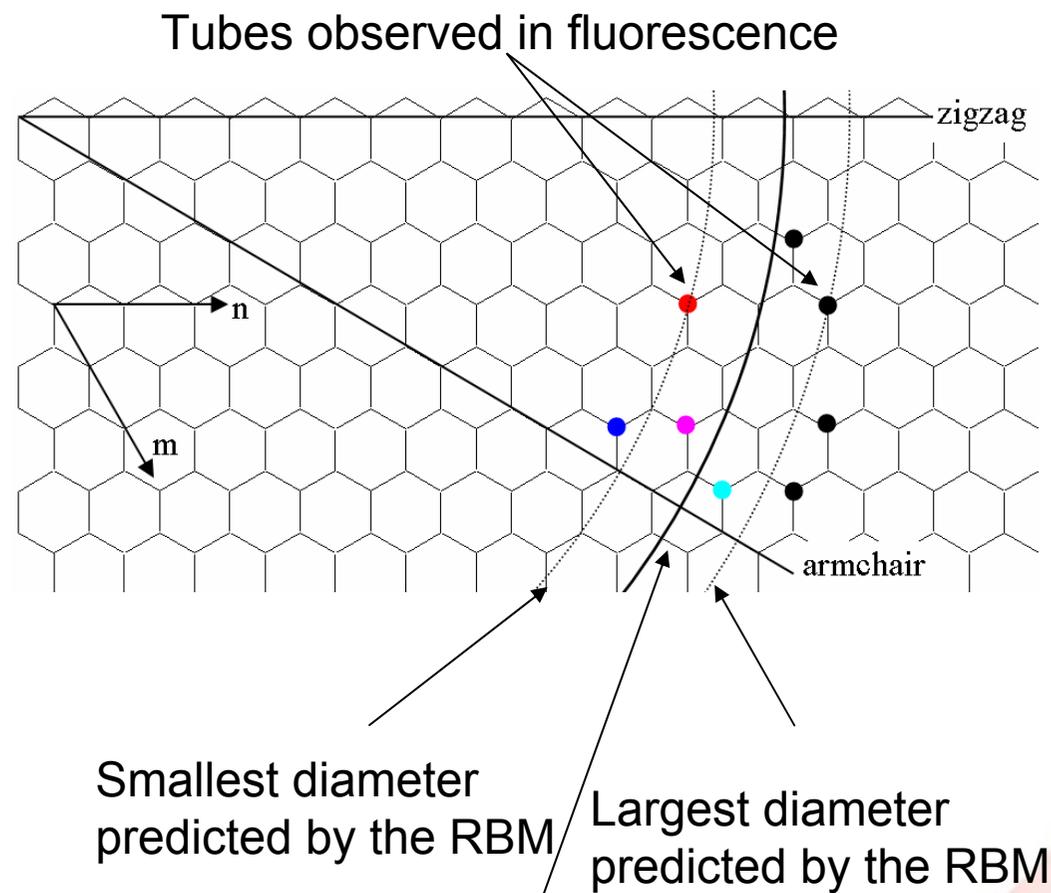
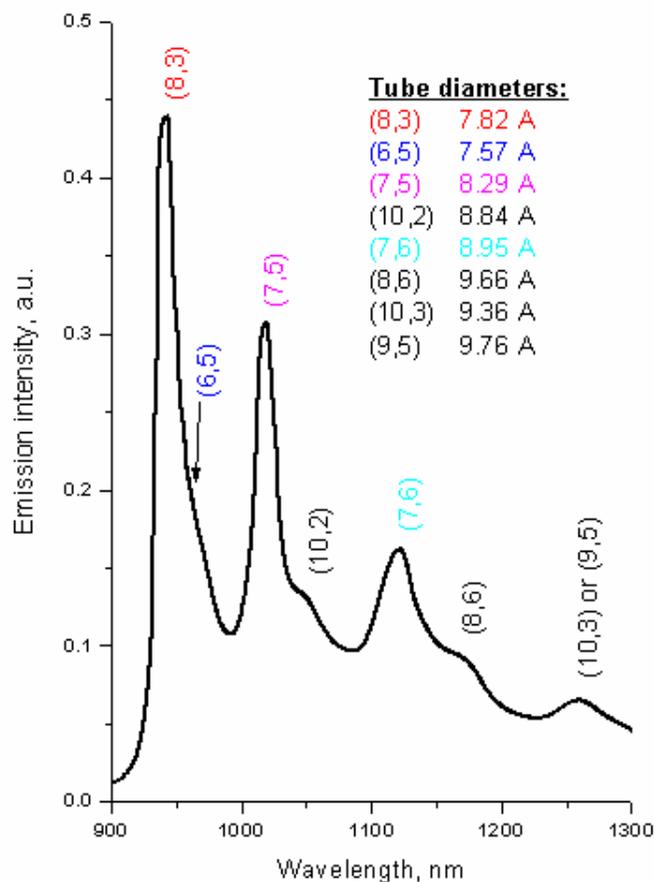
# Raman Spectroscopy

## Narrow peaks in RBM & small D band



# Narrow Diameter Distribution of SWNT

## 0.9 nm $\pm$ 0.05 nm



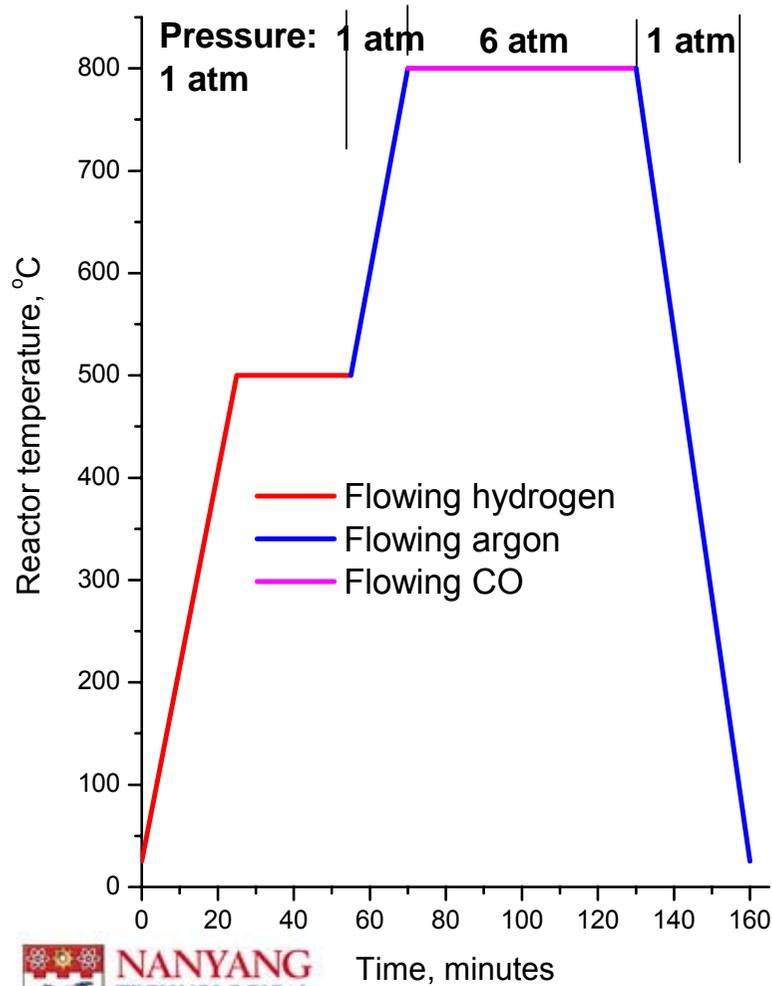
Courtesy of Prof. Bruce Weisman from Rice University (excitation  $\lambda=671\text{nm}$ )



*Journal of Physical Chemistry B*, 2004 108(2) 503

2

## Synthesis Conditions affect SWNT structure



### Reaction conditions:



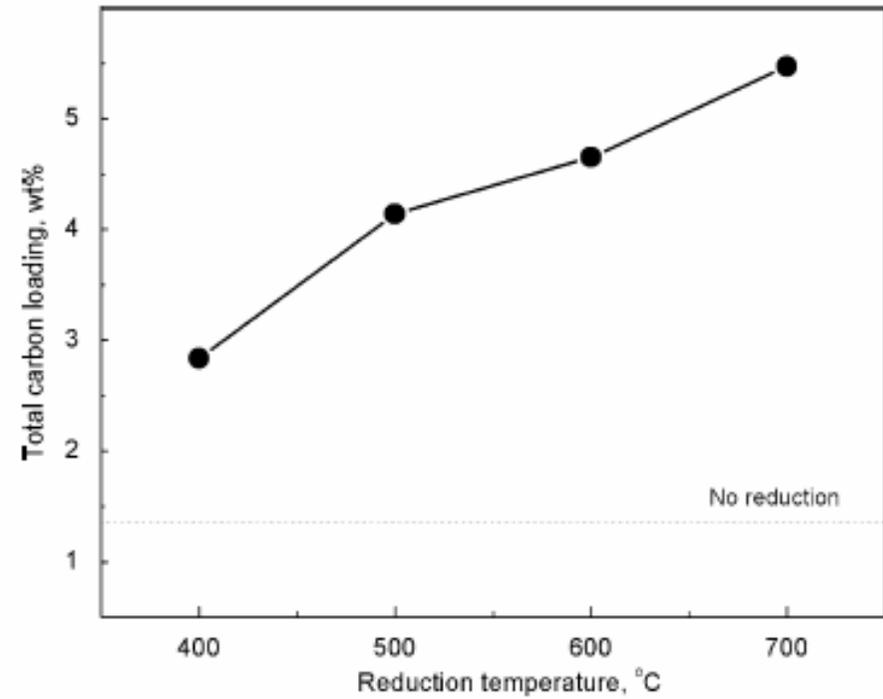
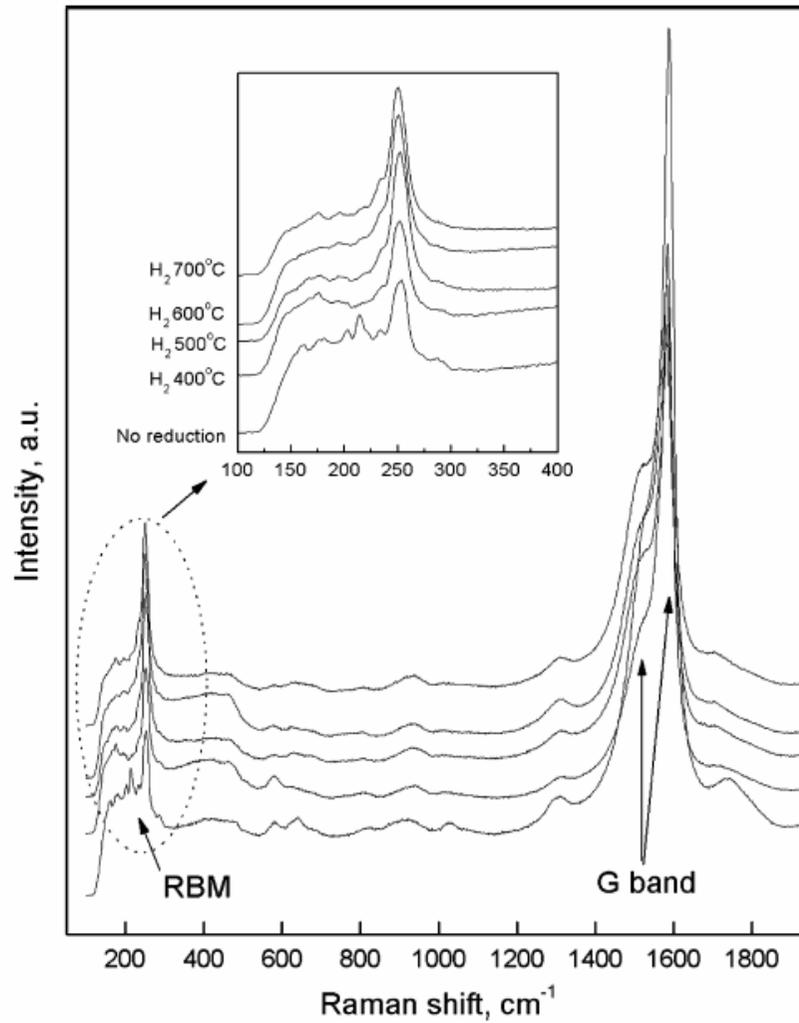
- Pre-reduction at 500°C
- Reaction Temperature: 800°C
- CO disproportionation pressure:  
2-6 atm

1. Pre-reduction temp.
2. Reaction temp.
3. CO Pressure
4. Reaction time

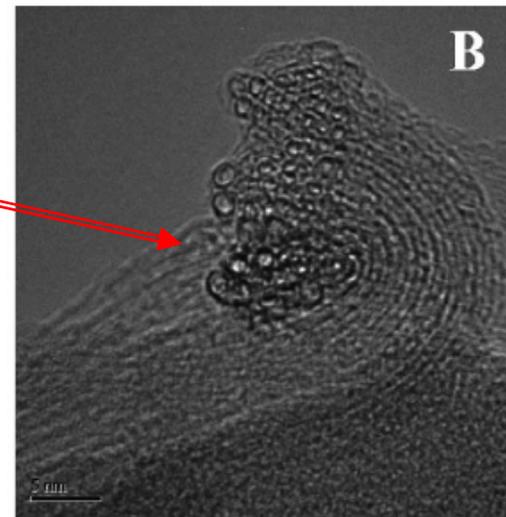
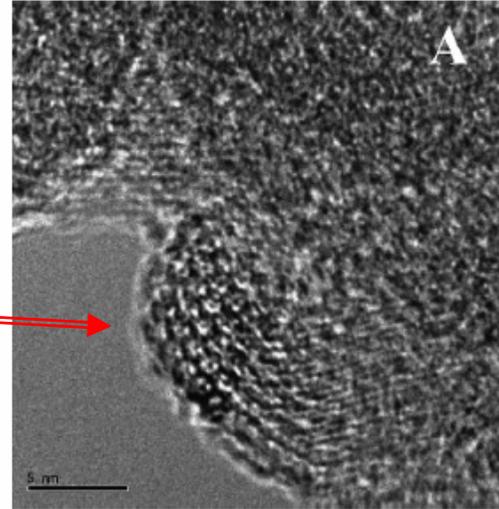
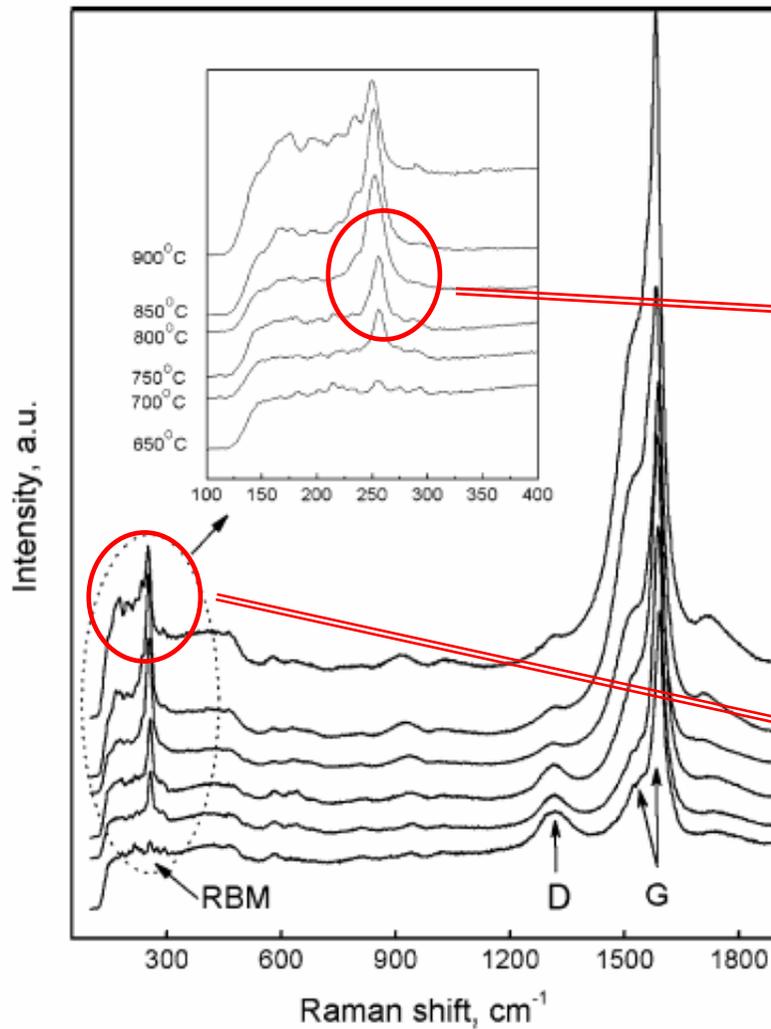
*Journal of Catalysis, 2004 225(2) 453*

*Journal of Catalysis, 2004 226(2) 351*

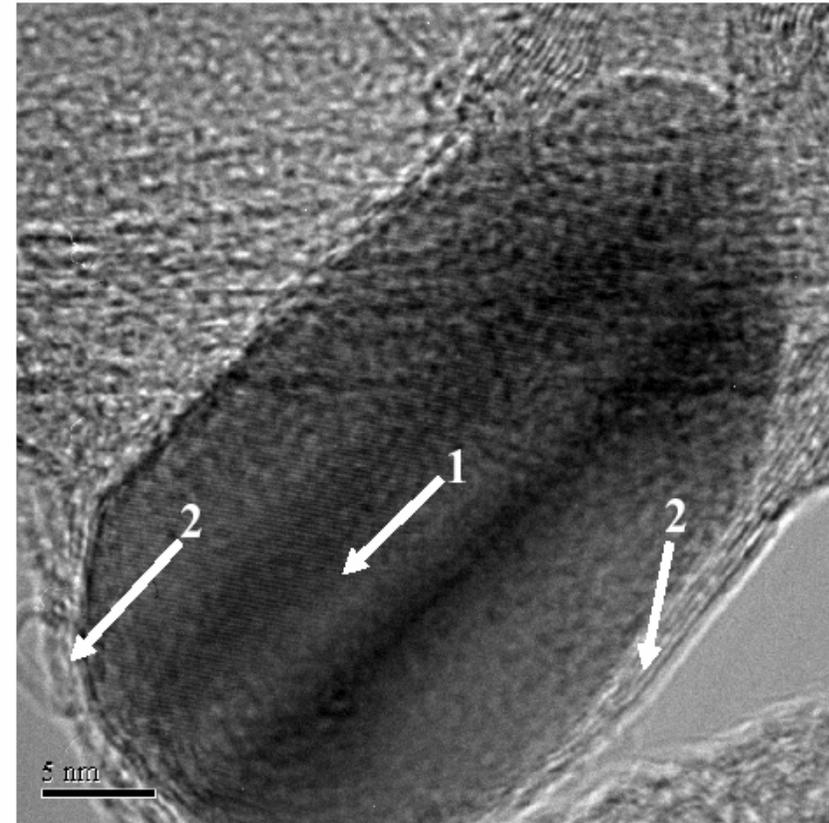
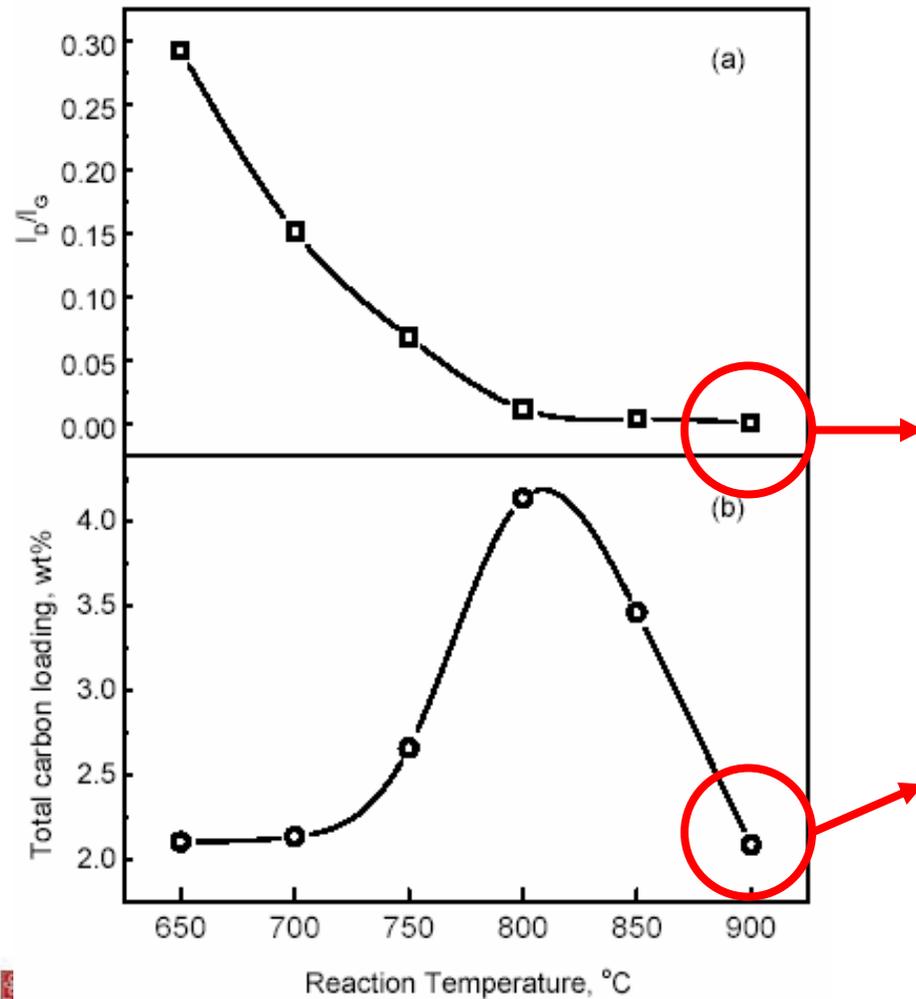
# Pre-reduction temperature



# Reaction temperature – affects tube diameter and carbon loading

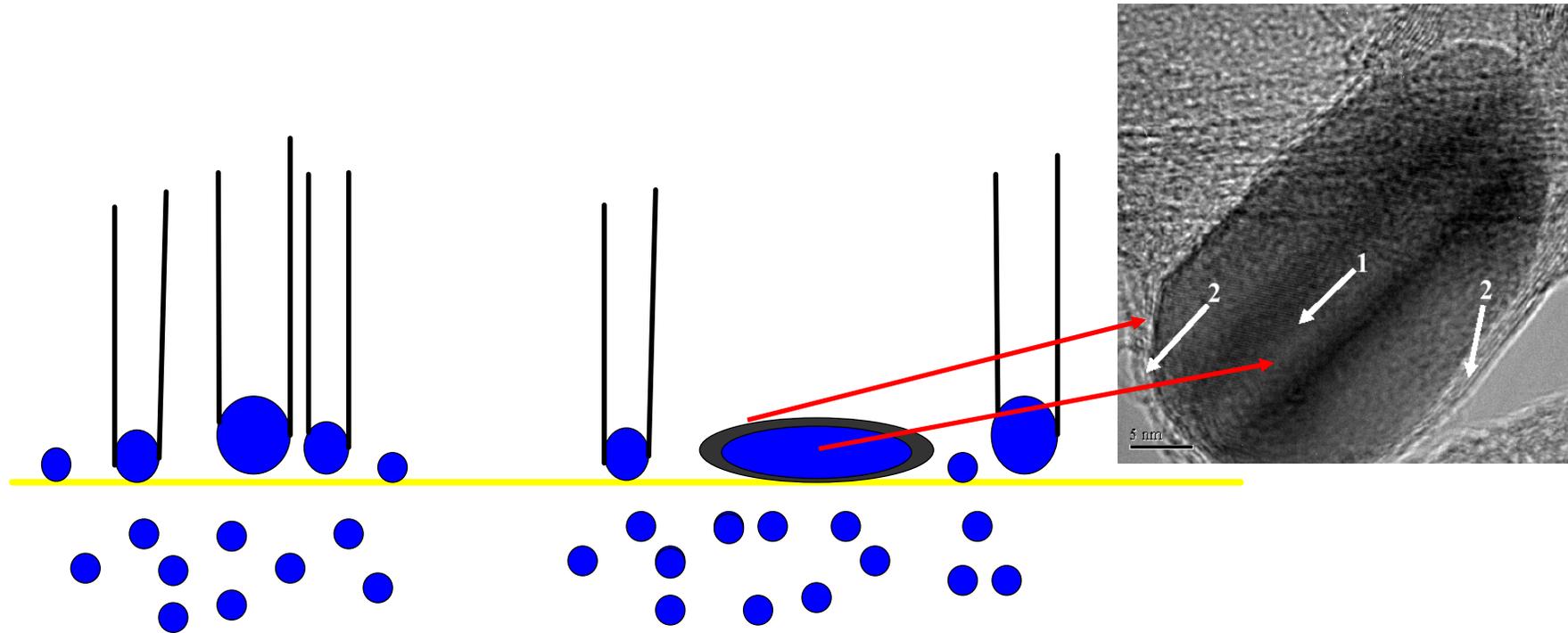


# Reaction temperature – affects tube diameter and carbon loading



3

## Correlation between tube and Co clusters

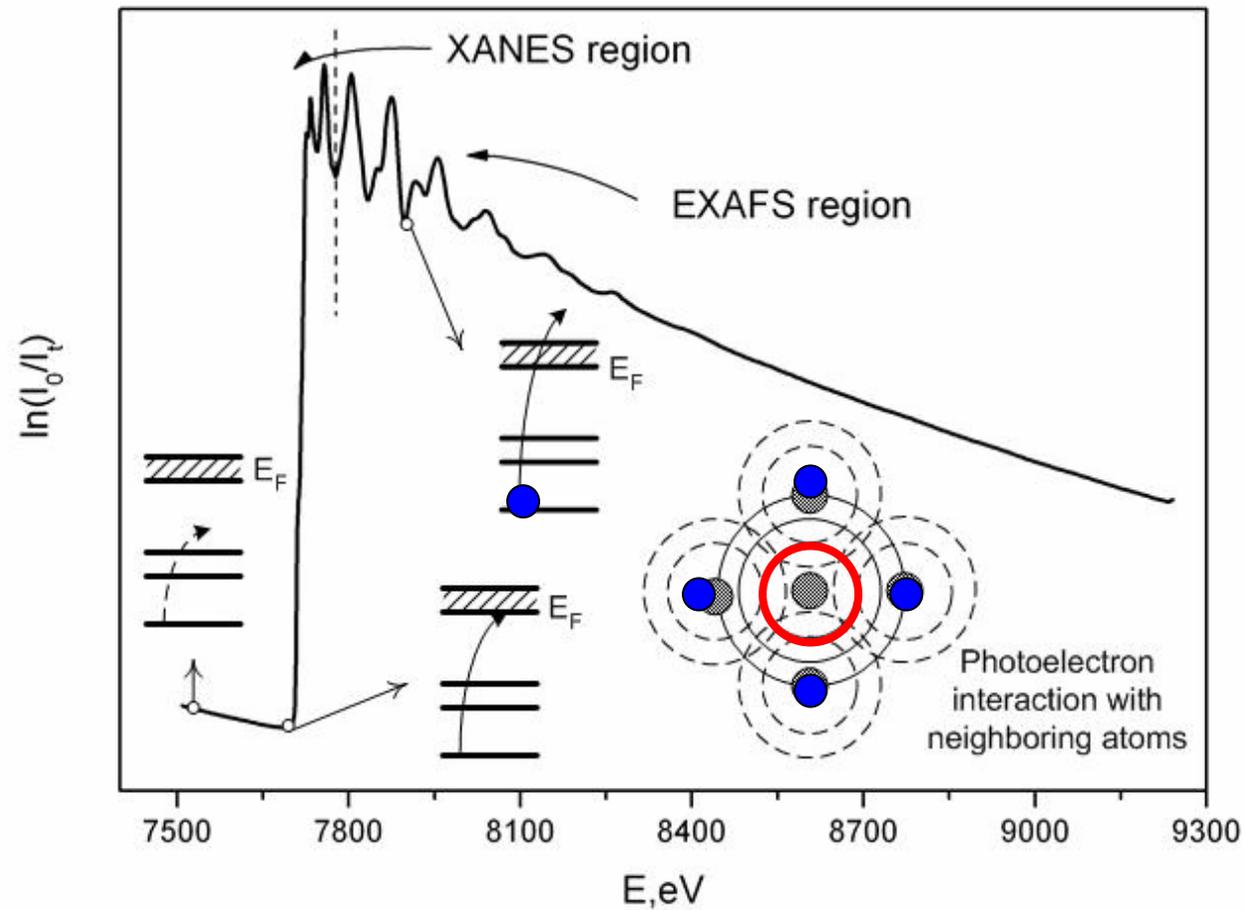


650° C, few Co clusters available for SWNT growth

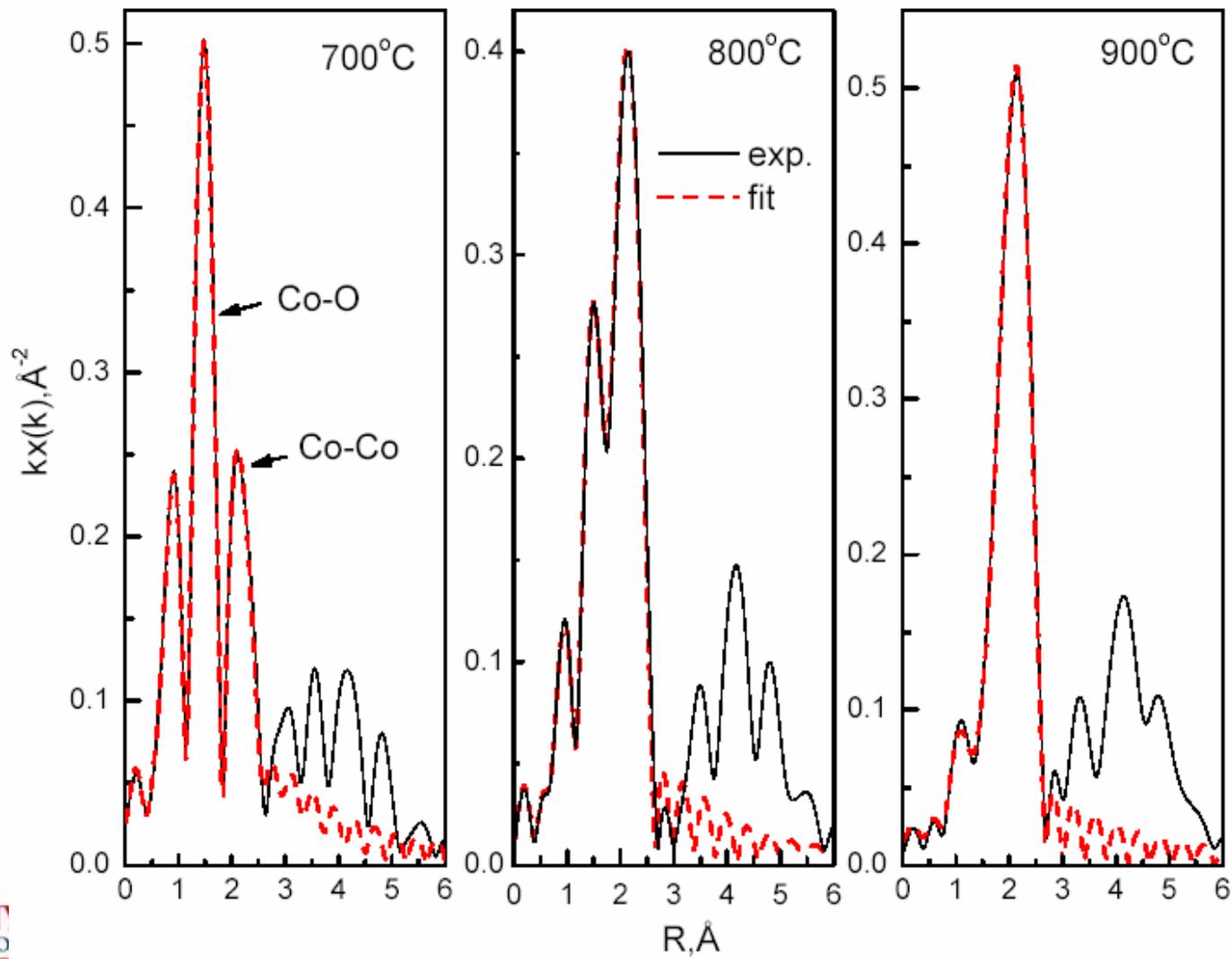
800° C, more cobalt clusters reach the optimal size for SWNT growth

900° C, cobalt cluster nucleation surpasses the rate of initiation of SWNT growth

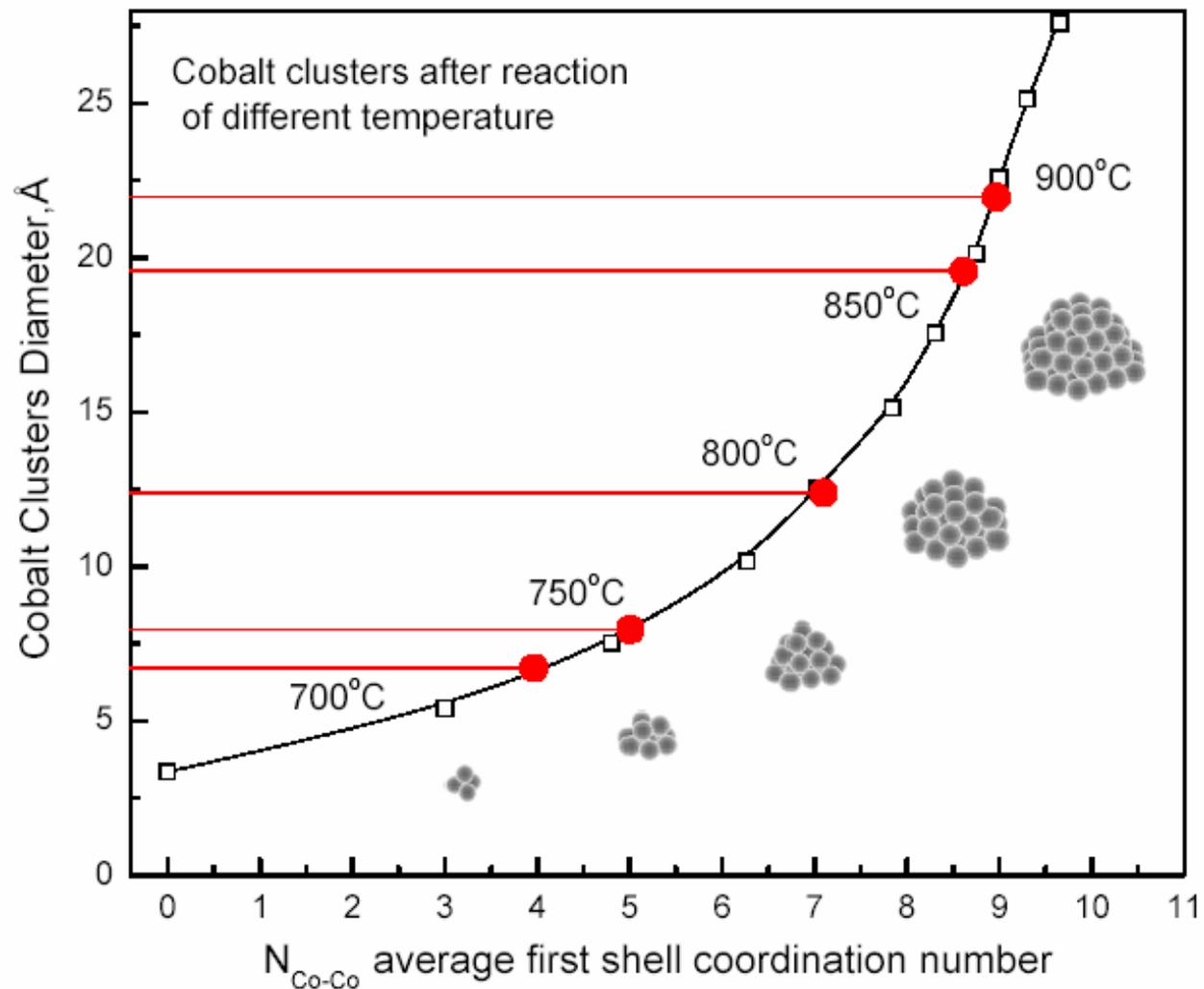
# X-ray absorption spectroscopy: characterize local environment of Co



# EXAFS spectra in R-space



# Average Cobalt clusters size

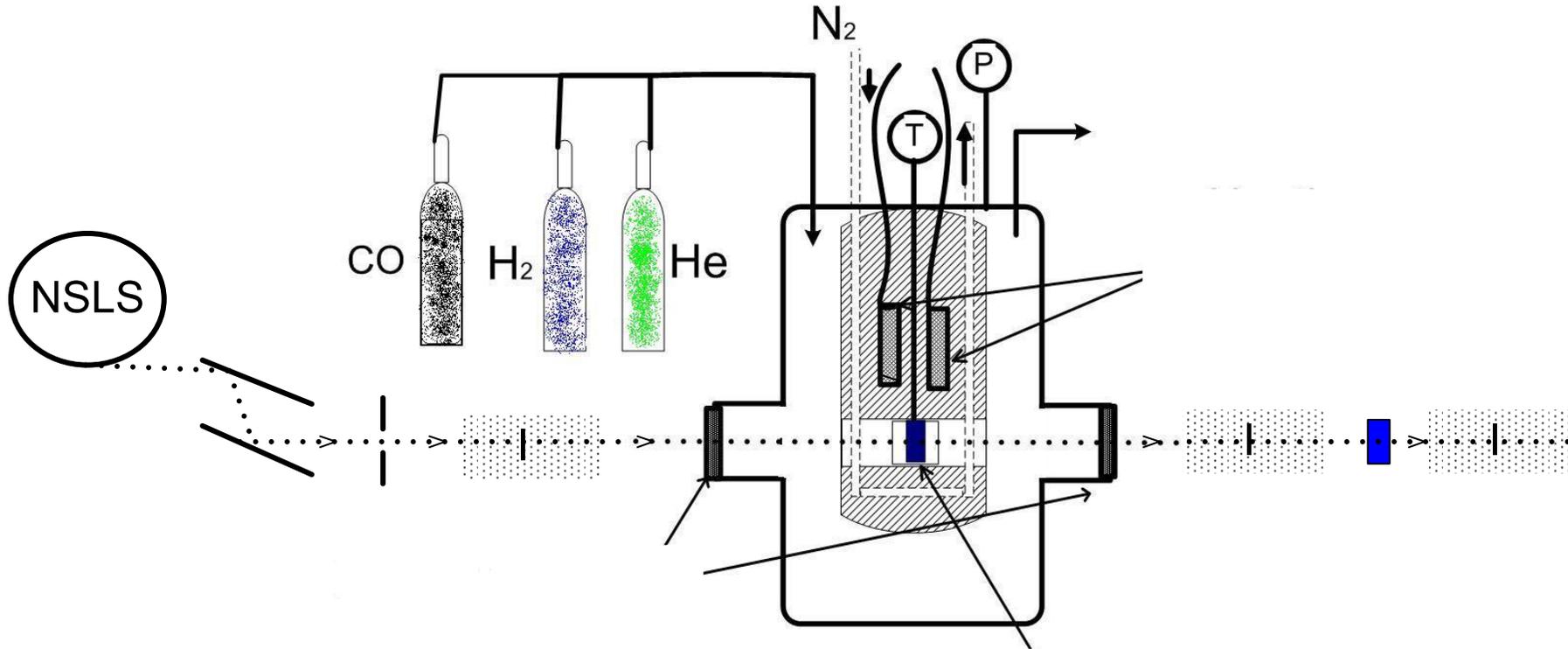


## How Co-MCM-41 work?



- Why Co-MCM-41 need pre-reduction in H<sub>2</sub>?
- What happen during reduction below 500°C in H<sub>2</sub> or He?
- Difference between 500°C and 700°C reduction in H<sub>2</sub>?
- After prereduction at 500°C, where are reduced Co compounds?
- How the CO affects the nucleation of reduced cobalt on MCM-41 surface?
- How the CO pressure changes the SWNT growth and cobalt clusters nucleation?

# In-situ X-ray Absorption System

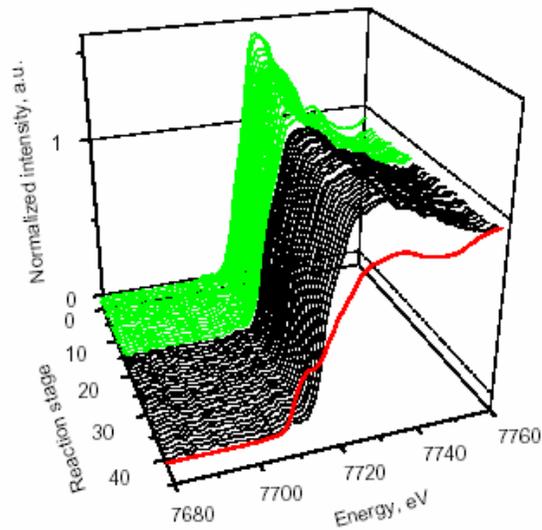


# In-situ X-ray Absorption System

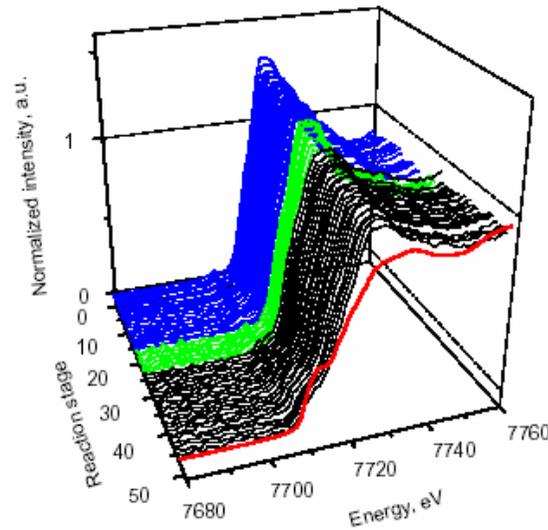


# What does Pre-reduction in H<sub>2</sub> do?

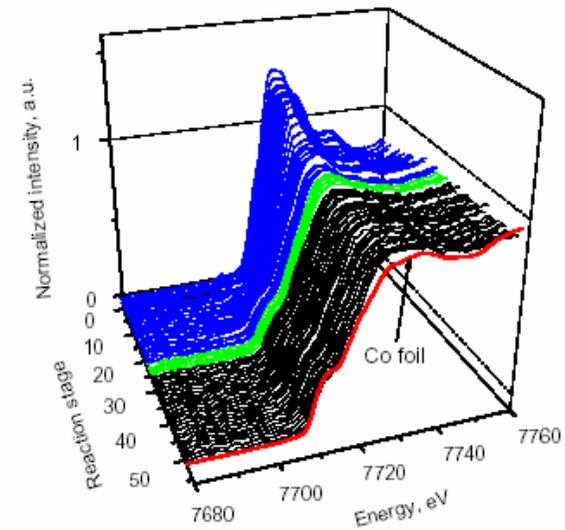
**A**  
No reduction



**B**  
Pre-reduced at 500 °C



**C**  
Pre-reduced at 700 °C



— He atmosphere

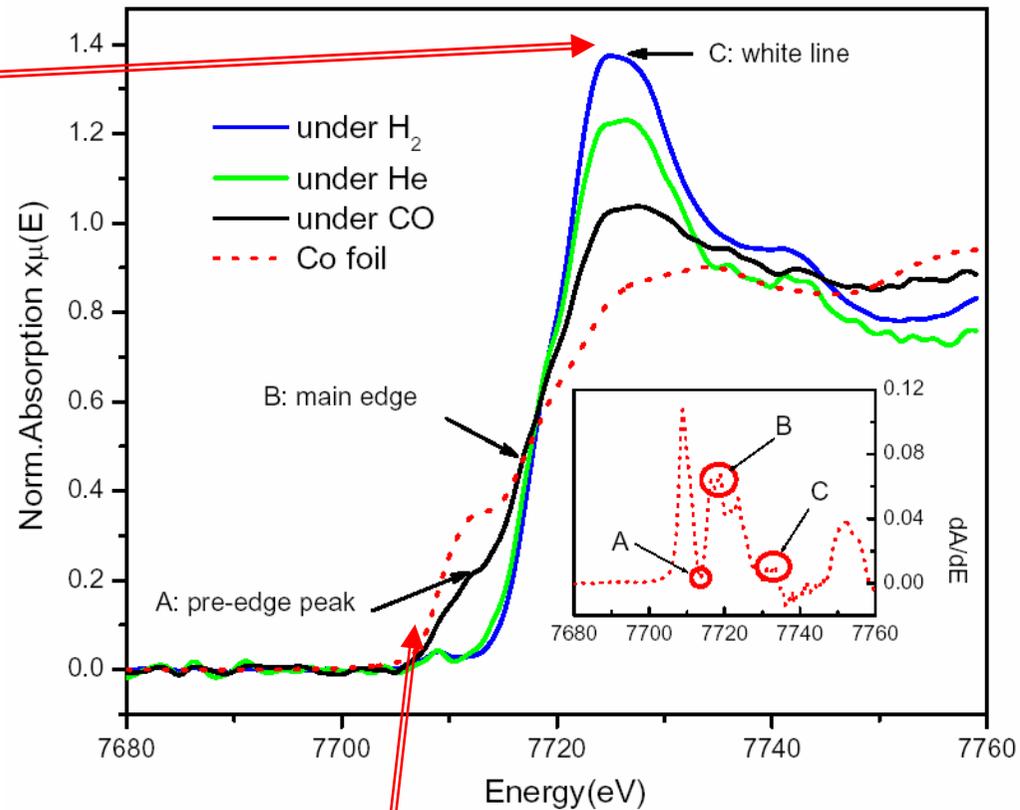
— H<sub>2</sub> atmosphere

— CO atmosphere

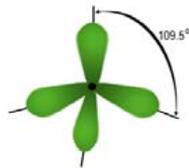
# Spectral features near Co K edge

The density of unoccupied states above Fermi level

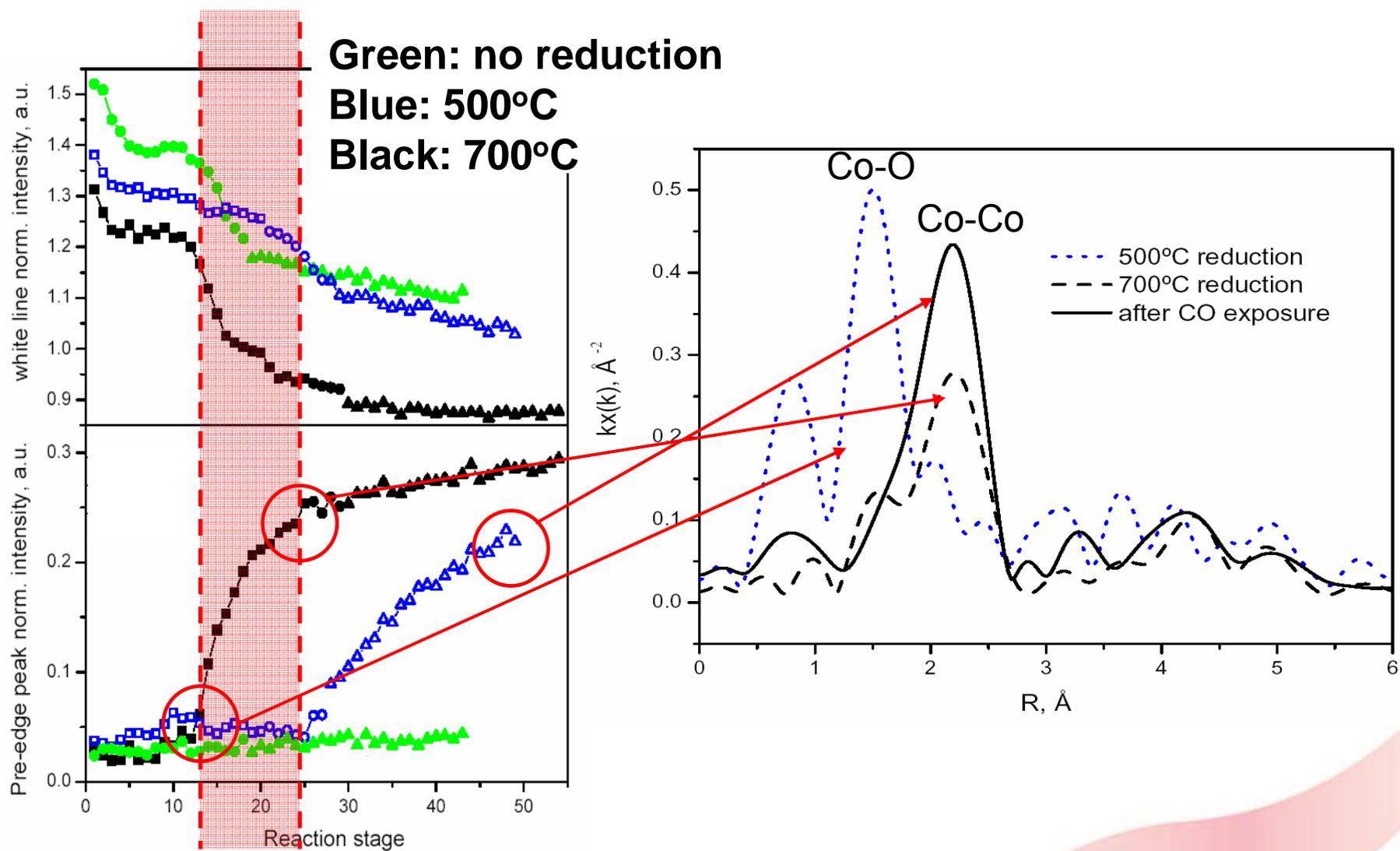
Using white line intensity and pre-edge peak intensity to monitor the changes of cobalt state in Co-MCM-41 during reaction



Dipole forbidden transitions (local environment)

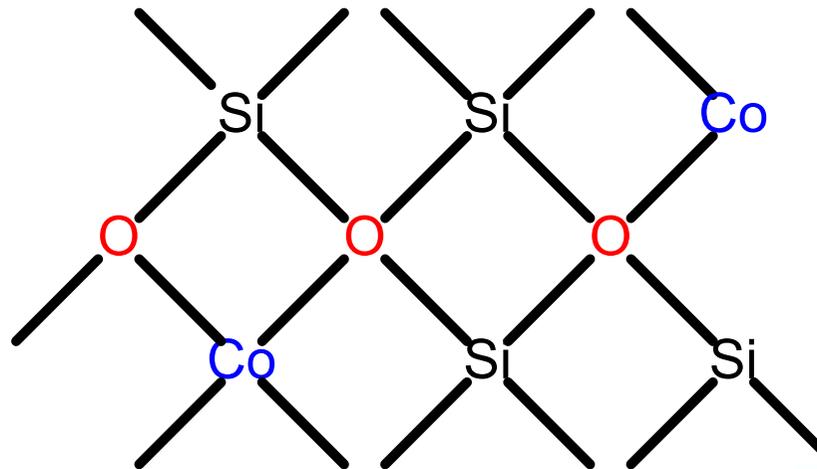
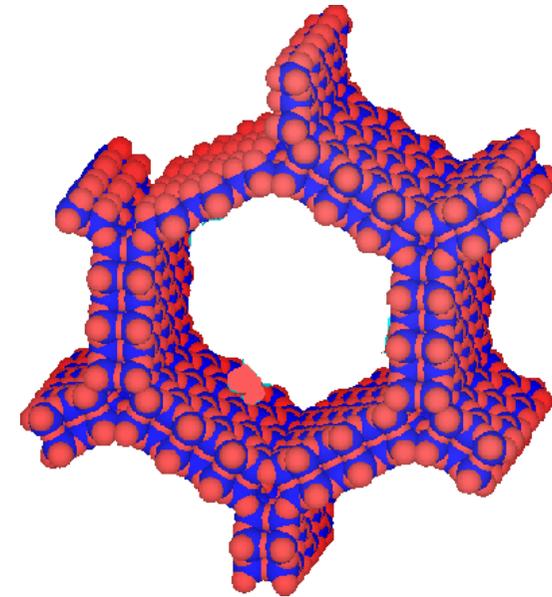


# Sample of mechanism analysis



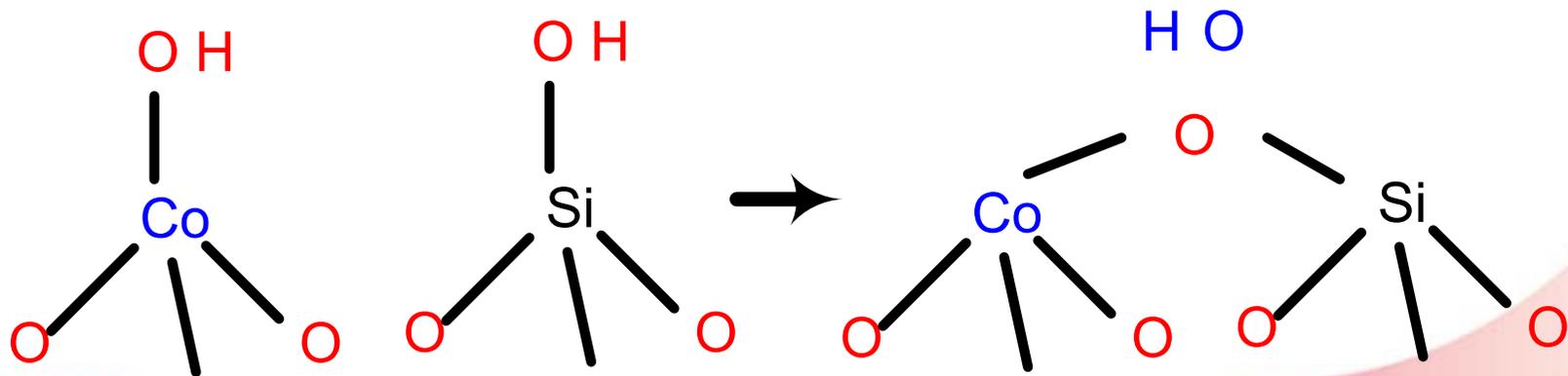
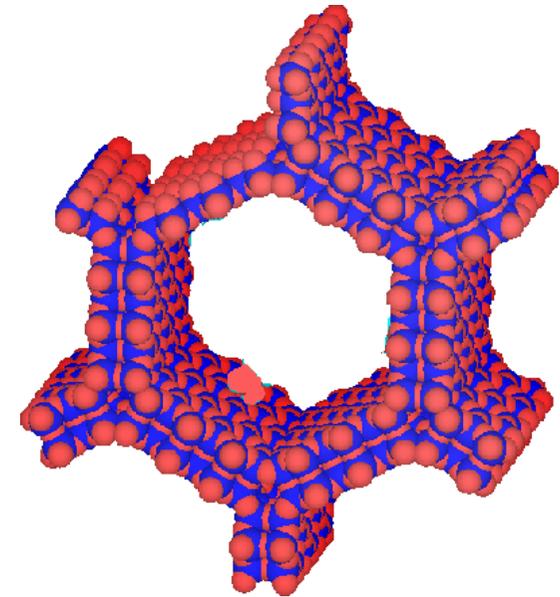
# Pre-reduction in H<sub>2</sub>

- prereduction below 700 ° C does not reduce the cobalt ions to metallic cobalt
- removes hydroxyl groups and oxygen ions creating oxygen vacancies and/or a partially reduced cobalt species
- increase the density of electrons at the Fermi level weakening the interaction of Co<sup>2+</sup> with the silica framework



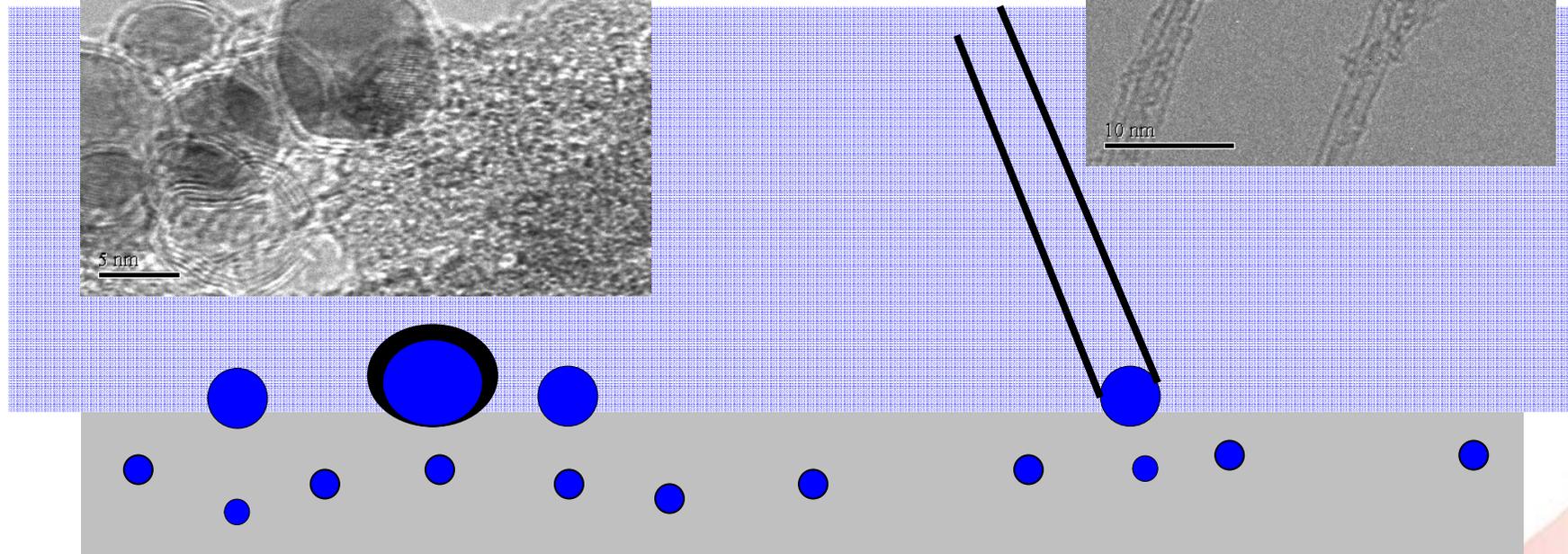
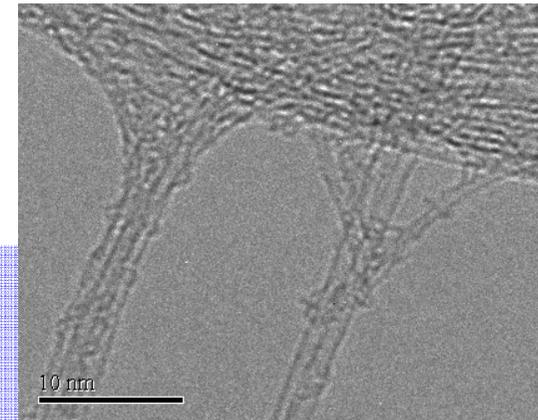
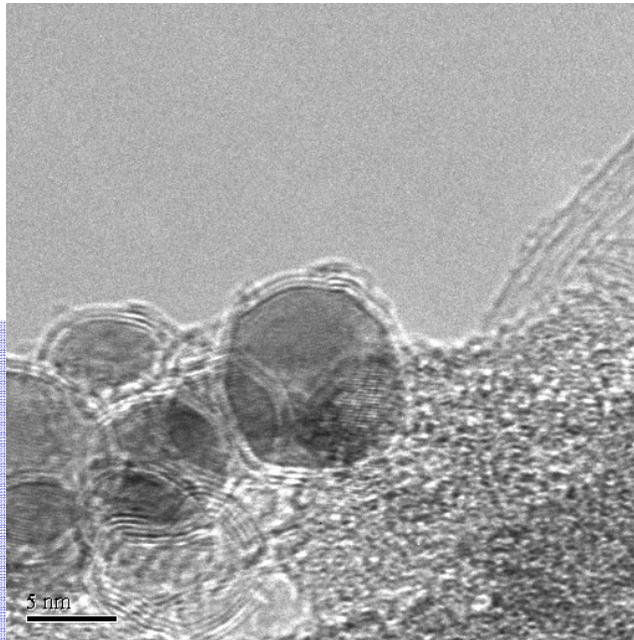
# Pre-reduction in H<sub>2</sub>

- prereduction below 700 ° C does not reduce the cobalt ions to metallic cobalt
- removes hydroxyl groups and oxygen ions creating oxygen vacancies and/or a partially reduced cobalt species
- increase the density of electrons at the Fermi level weakening the interaction of Co<sup>2+</sup> with the silica framework



# Competition between SWNT growth and cluster size growth

*Journal of Physical Chemistry B, 2004 108(40) 15565*

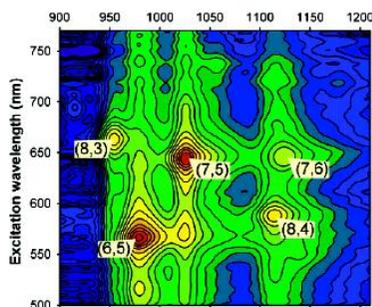


Average 3 nm distance between Co atoms on MCM-41 pore surface to meet another Co atom in 1 wt% Co-MCM-41

# Progress on chirality selective synthesis

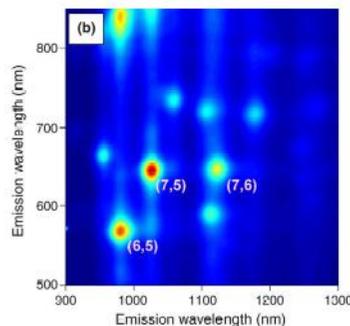
## Bulk samples

- Co-Mo catalyst supported on Silica
- CO as carbon source



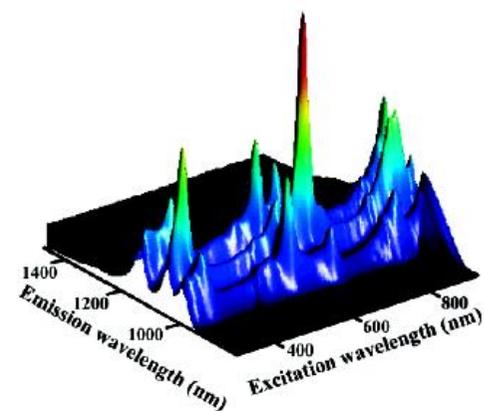
J. Am. Chem. Soc. 2003,  
125, 11186-11187

- Fe/Co catalysts supported on zeolite
- Alcohol as carbon source



Chem. Phys. Lett. 387  
2004, 198-203

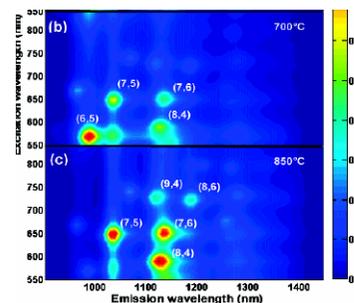
- Co-MCM-41 catalyst
- CO as carbon source



J. Catal. 2004, 225, 453  
J. Am. Chem. Soc. 2006,  
128, 15 511

- FeRu supported on Silica
- Methane as carbon source

J. Am. Chem. Soc. 2007,  
129, 15770-15771



# Control chirality?

- Chirality is related dynamically to catalyst particle-carbon network interactions.
- Thermodynamically? Or Kinetically?
- We hypothesize that chirality selective synthesis of narrow chirality distributed SWNTs can be achieved through precise regulation of both the metallic clusters formation and the carbon decomposition.
- Based on our previous studies, we propose that at a given temperature, an optimized carbon supply rate to the metal clusters is also an important factor in chirality control. The narrowest chirality distribution can only be obtained when the right compromise is reached between the decomposition rate of the carbon source, the diffusion rate of carbon through the particles, and the carbon precipitation rate.



# Strategy in our study

- To alter the chirality selectivity by different carbon precursors, which have distinct decomposition rate and chemical composition. If the narrow chirality selectivity is kinetically controlled, SWCNTs with distinct and narrow  $(n,m)$  distribution should be obtainable.

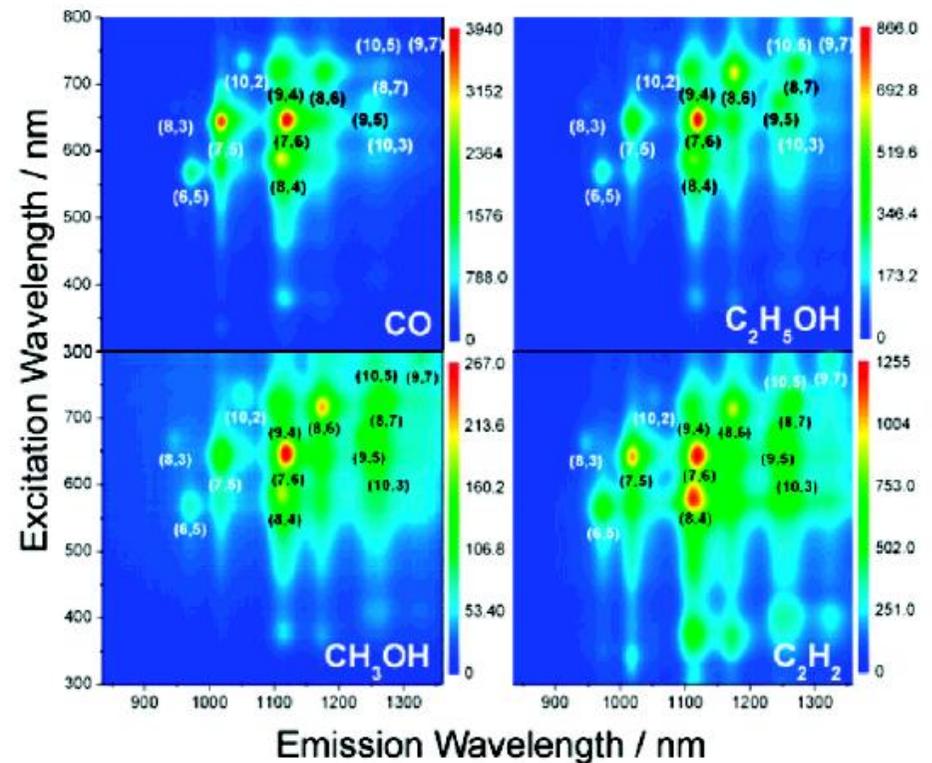
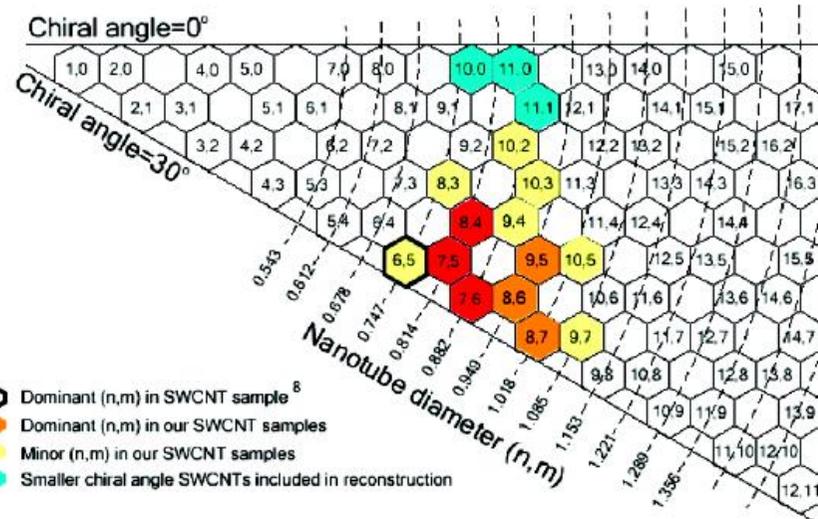
|                                    | Decomposition | Chemical bond | Conditions                         |
|------------------------------------|---------------|---------------|------------------------------------|
| CO                                 | slow          | C=O           | High P (6 bar)                     |
| CH <sub>3</sub> CH <sub>2</sub> OH | fast          | -OH, C-C, C-O | Low P (5mbar), 30 °C               |
| CH <sub>3</sub> OH                 | fast          | -OH, C-O      | Low P (5mbar) 0 °C                 |
| C <sub>2</sub> H <sub>2</sub>      | very fast     | C≡C           | Low P + diluted<br>(5mbar: 1:1000) |



Co-Mo catalyst prereduction 500 °C, growth at 800 °C

# PLE intensity map

- narrowly (n,m) distributed SWNTs can be obtained
- predominantly in the same higher chiral angle region
- different carbon sources lead to different chiral tubes
- Zigzag tubes cannot be detected
- intensity from larger tubes are very weak



# $(n,m)$ abundance characterization

- **Florescence spectroscopy**

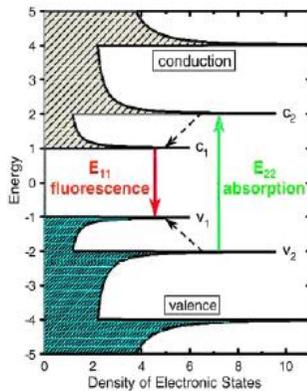
semiconducting tubes, different photoluminance quantum efficiency

- **UV-vis-NIR Absorption spectroscopy**

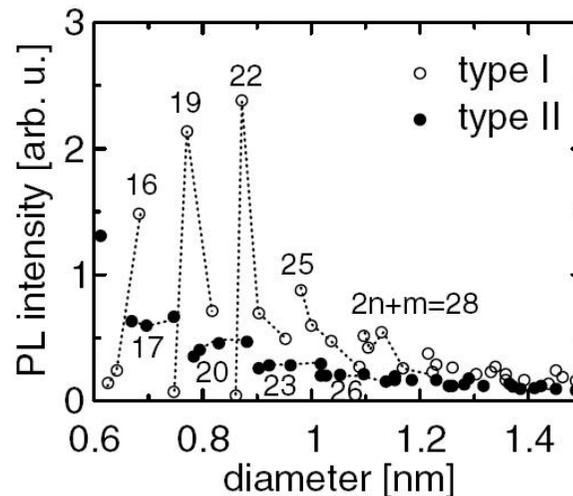
Highly overlap, especially for metallic tubes, absorption extinction coefficient

- **Raman spectroscopy**

Resonant (need tunable laser Raman), Raman cross section



*Science* **2002**, 298,  
(5602), 2361-2366



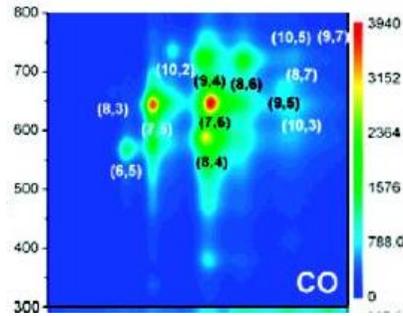
*Carbon* **2006**, 44, (5), 873-879

$$A(n, m) = C \frac{I_{\text{exp}}(n, m)}{I_{\text{cal}}(n, m)}$$

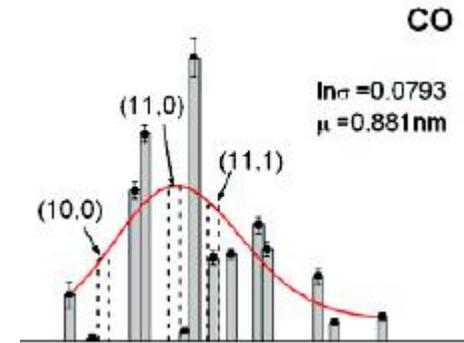
PL quantum efficiency

# NIR spectra fitting method

J. Am. Chem. Soc. 2006, 128, 15 511



$$A(n, m) = C \frac{I_{\text{exp}}(n, m)}{I_{\text{cal}}(n, m)}$$

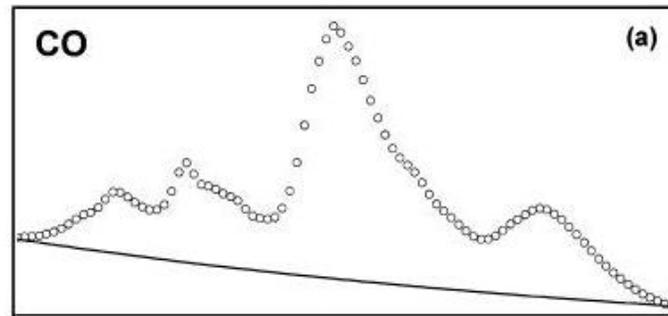
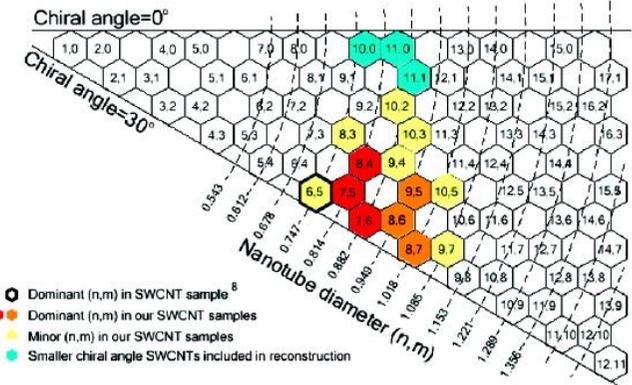


Electron-Phonon Interaction Model

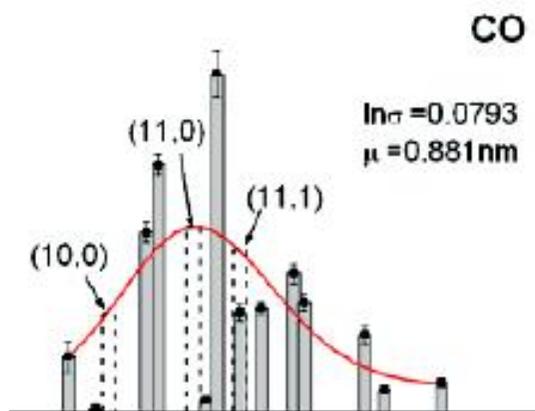
Carbon 2006, 44, (5), 873-879

$$\gamma_e = C_1 + C_2/I_{\text{cal}}^{\text{abs}}(n, m)$$

$$OD(E) = C \sum_{n, m} A(d_t) I_{\text{cal}}^{\text{abs}}(n, m) \frac{\gamma_e}{4(E - E_{11}(n, m))^2 + \gamma_e^2}$$

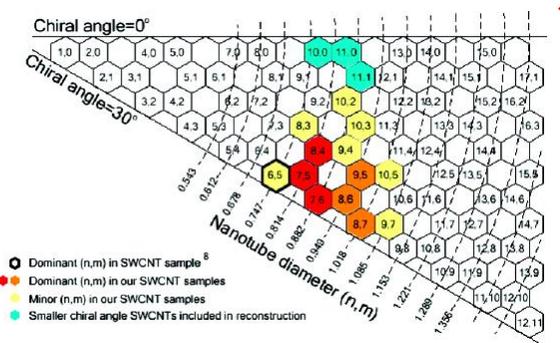


# Reconstruction of NIR spectra

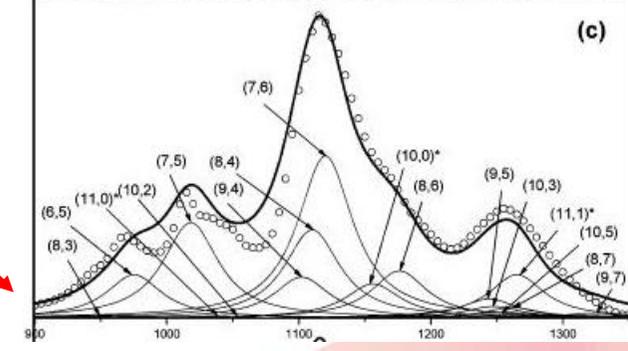
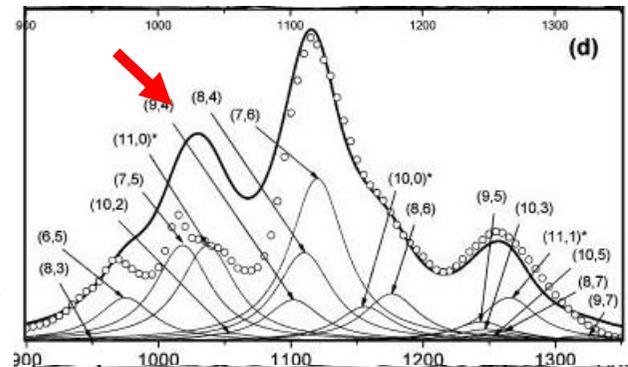
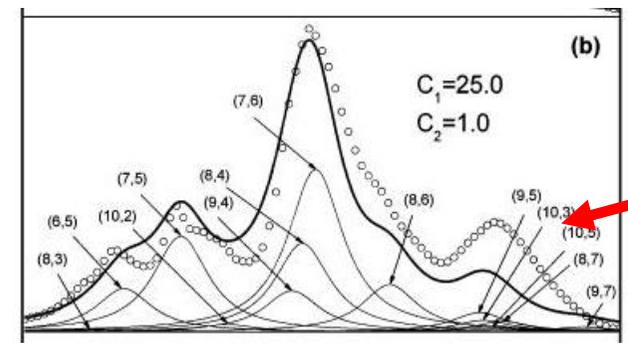


Only tubes identified in PLE

Follow log-normal distribution



Average level of yellow tubes





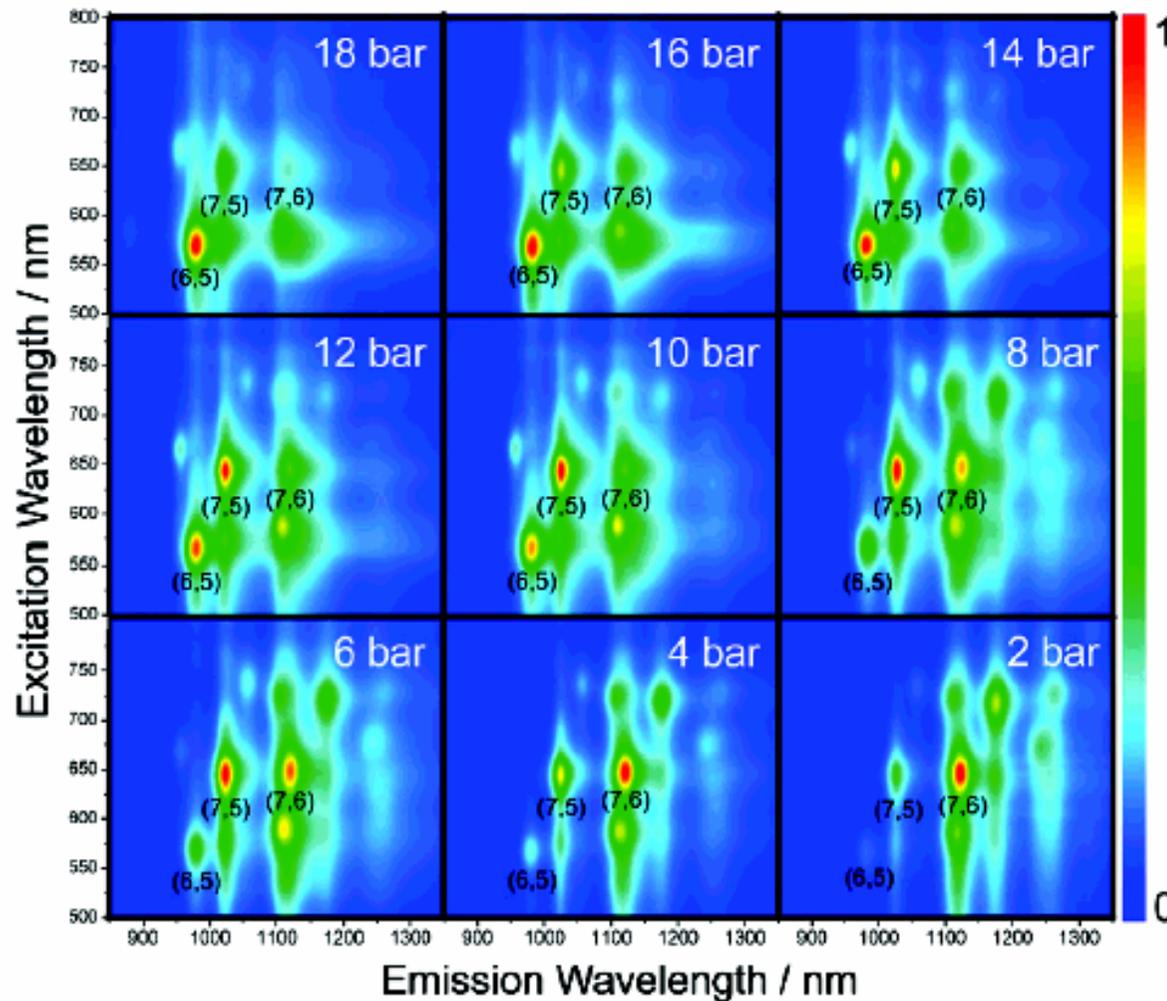
# Findings:

- Successful synthesis of narrow chiral distributed SWCNTs with different carbon precursors
- Selectivity to tubes with higher chiral-angles
- Failure of NIR absorption spectra reconstruction indicates large diameter tubes
- Selectivity is influenced by pressure and precursor chemistry
- The  $(n,m)$  selectivity can be shifted.

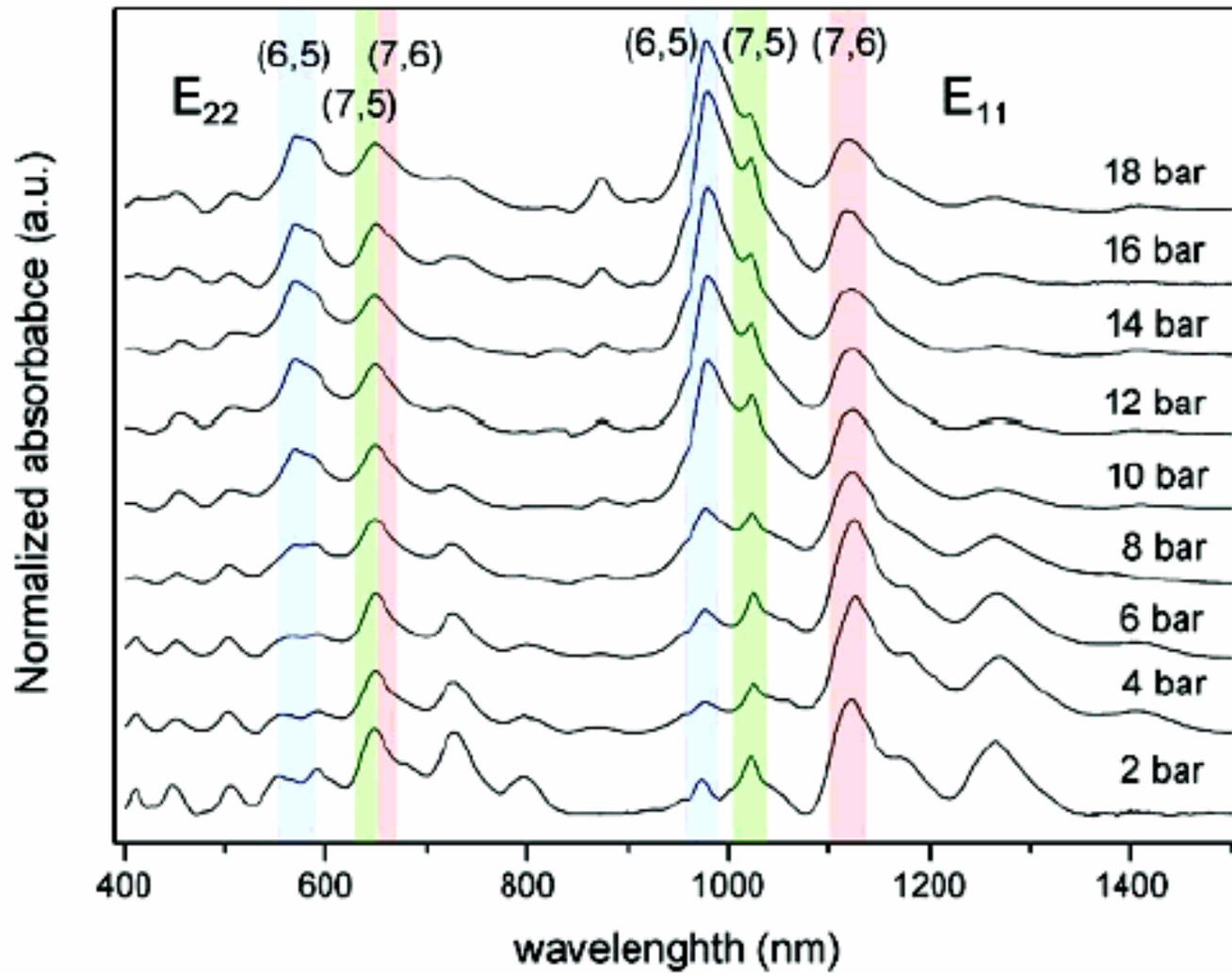


6

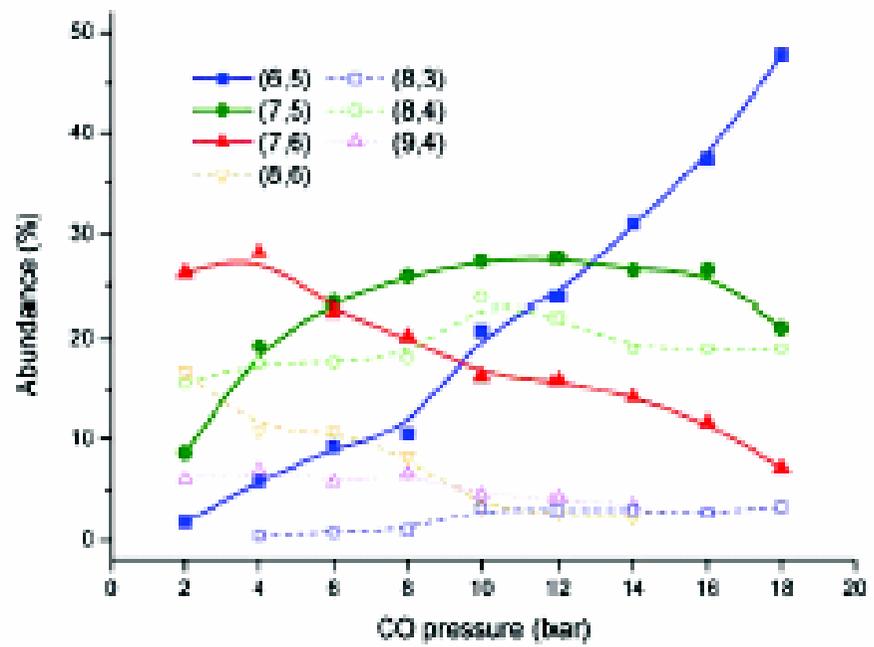
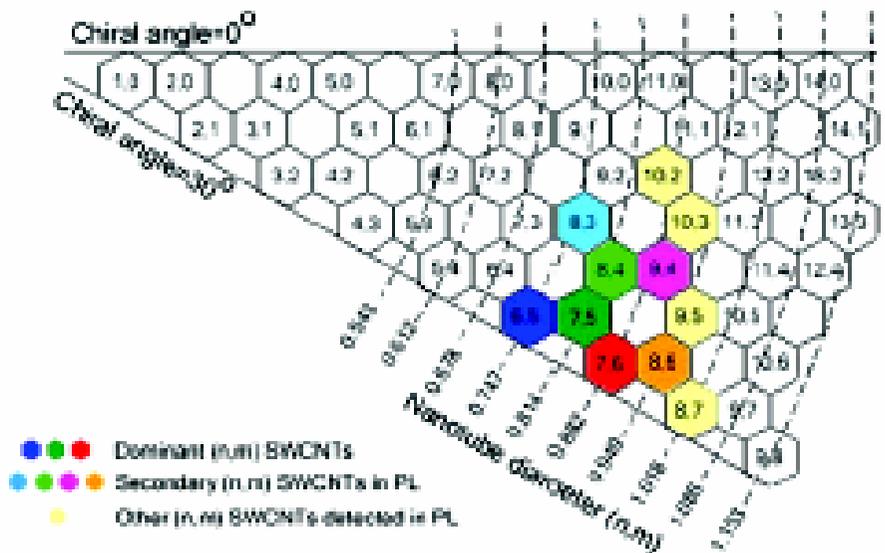
# Pressure induced $(n,m)$ selectivity on Co-Mo using CO



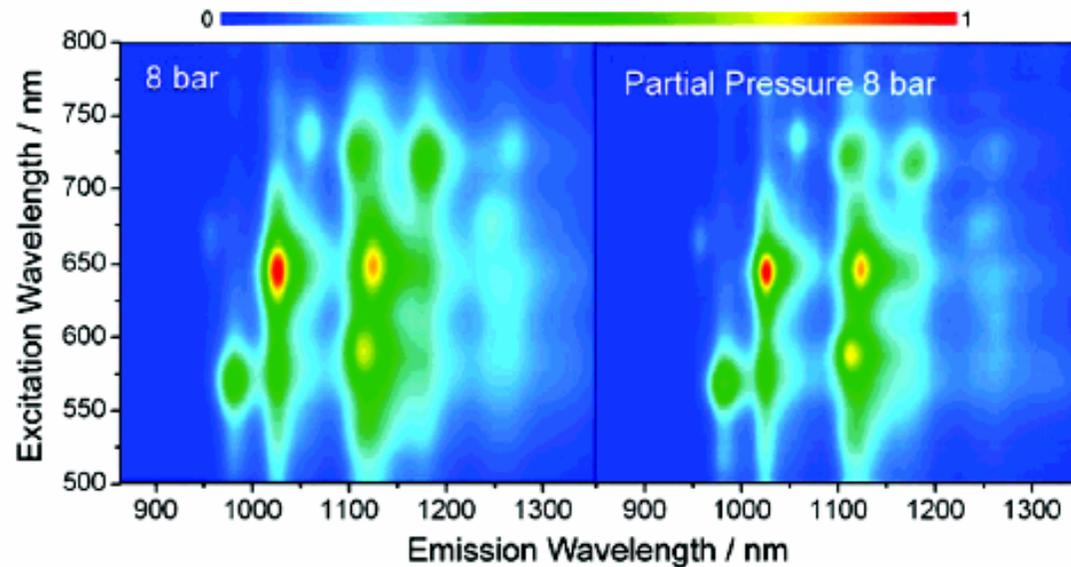
# Pressure effect



# High pressure – high carbon feeding rate?



# Partial pressure vs. total pressure



- CO pressure is a critical factor in SWCNT ( $n,m$ ) control for Co-Mo catalysis
- We can obtain bulk SWCNT samples enriched with three dominant tubes at (6,5), (7,5), and (7,6).

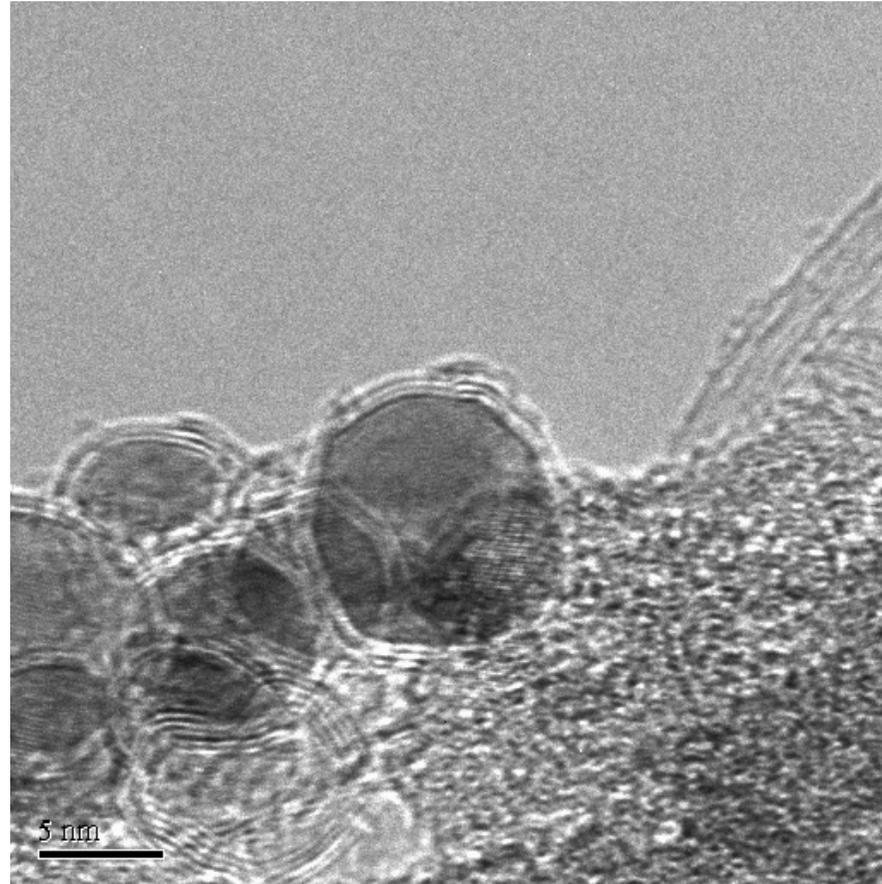
7

# Purification of SWNT from Co-MCM- 41

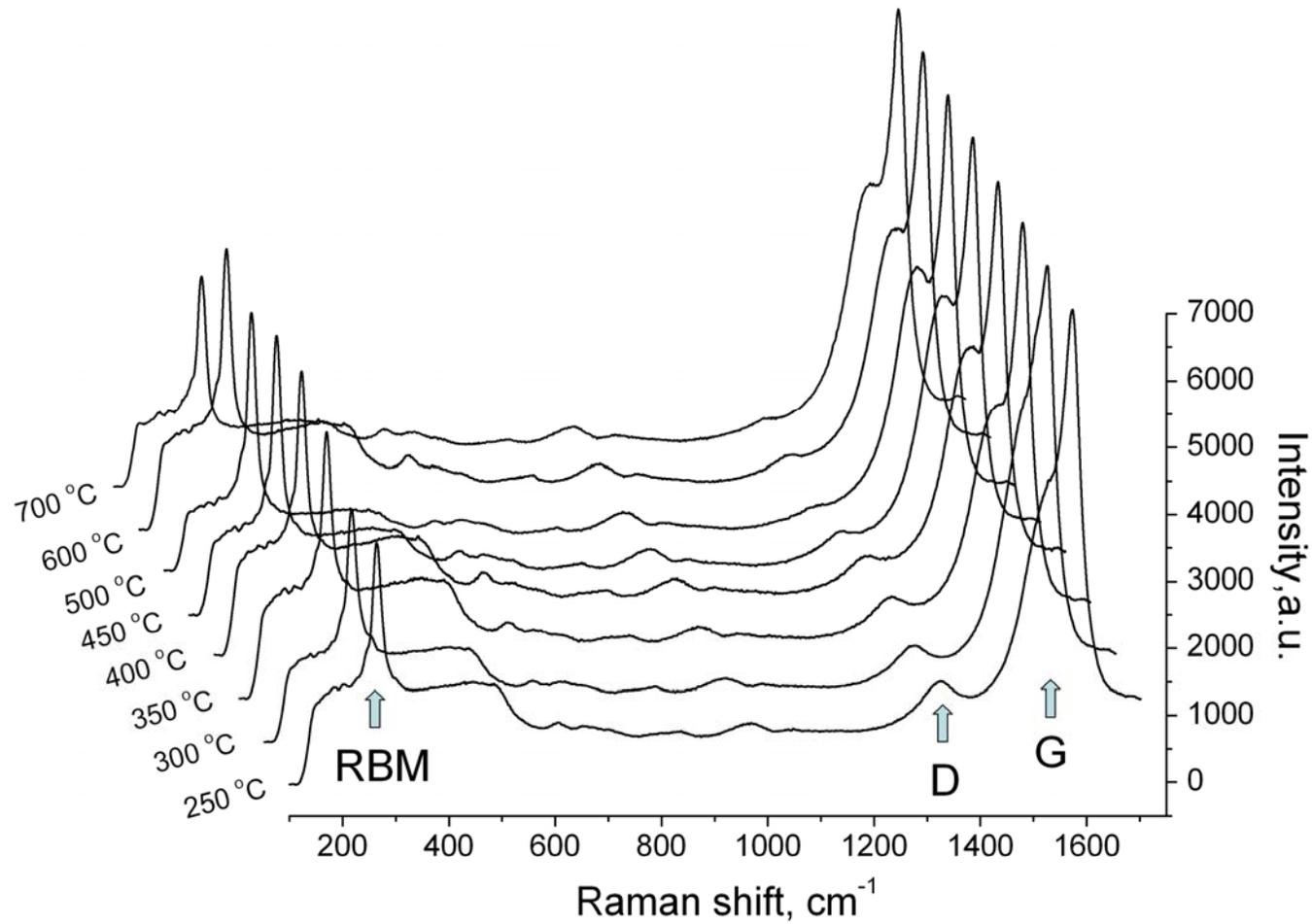
Issues:      Approaches:

- 1) MCM-41 templates  
NaOH to remove silica
- 2) Cobalt residues  
HCl to remove cobalt
- 3) amorphous carbon  
5% O<sub>2</sub> oxidation

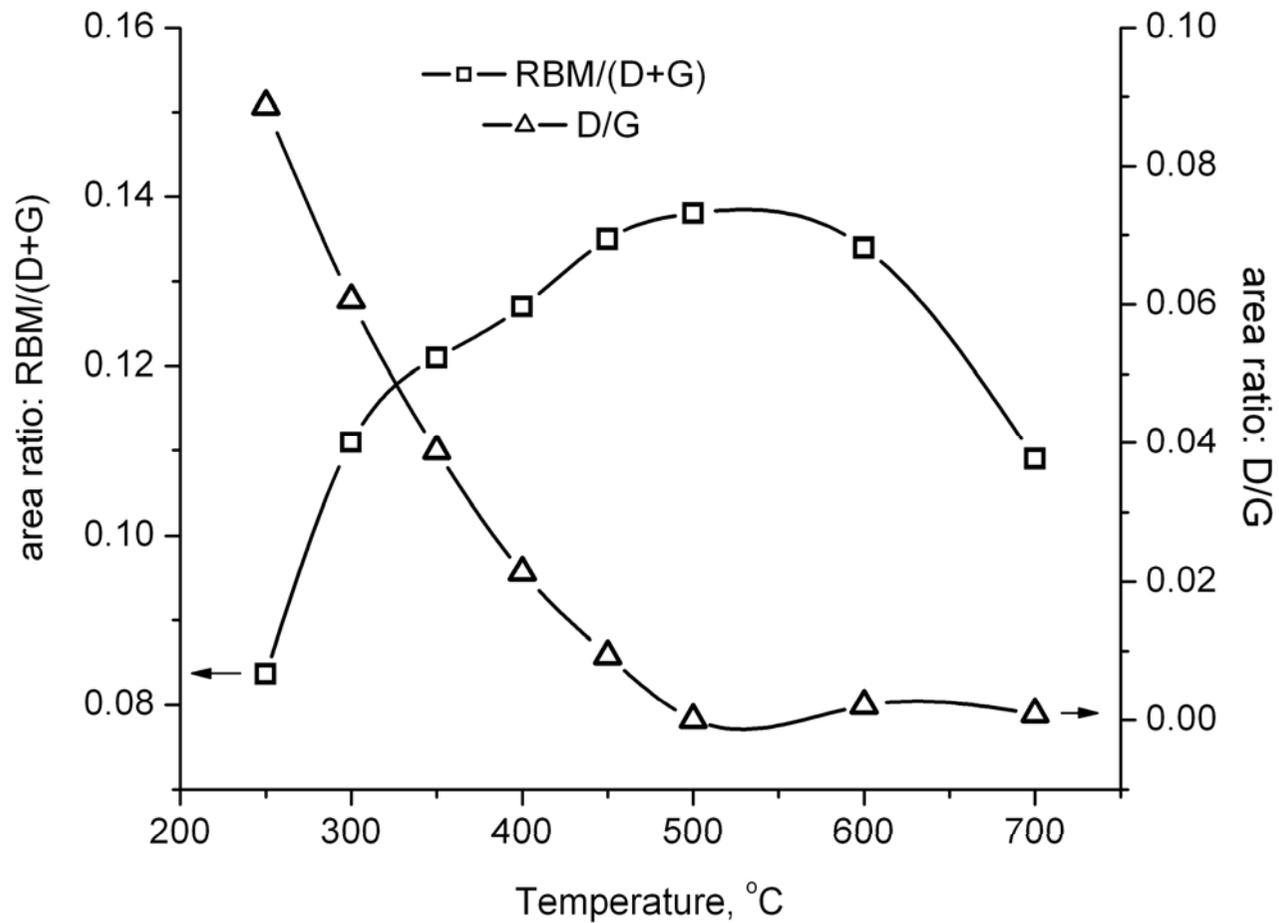
**Preserving SWNT  
Structure**



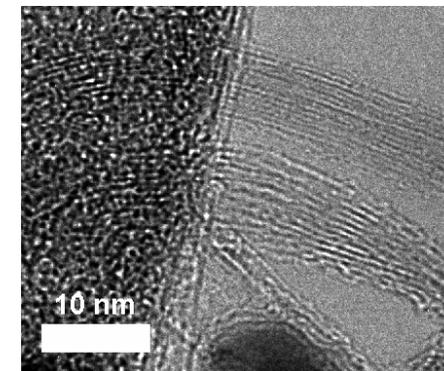
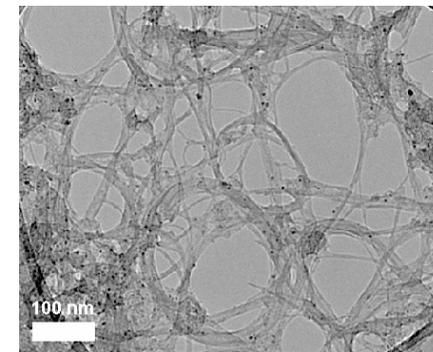
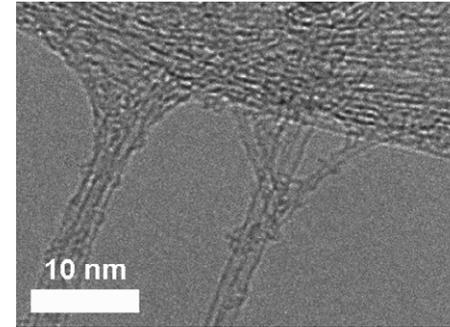
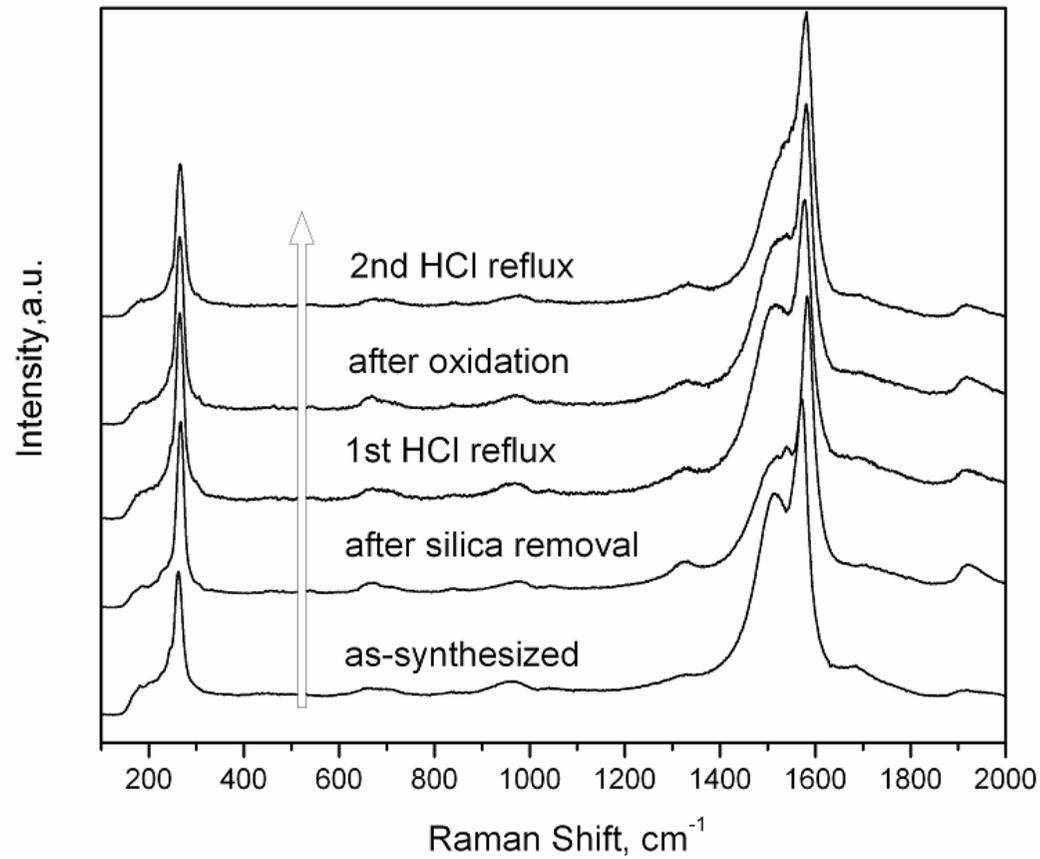
# Amorphous carbon removal



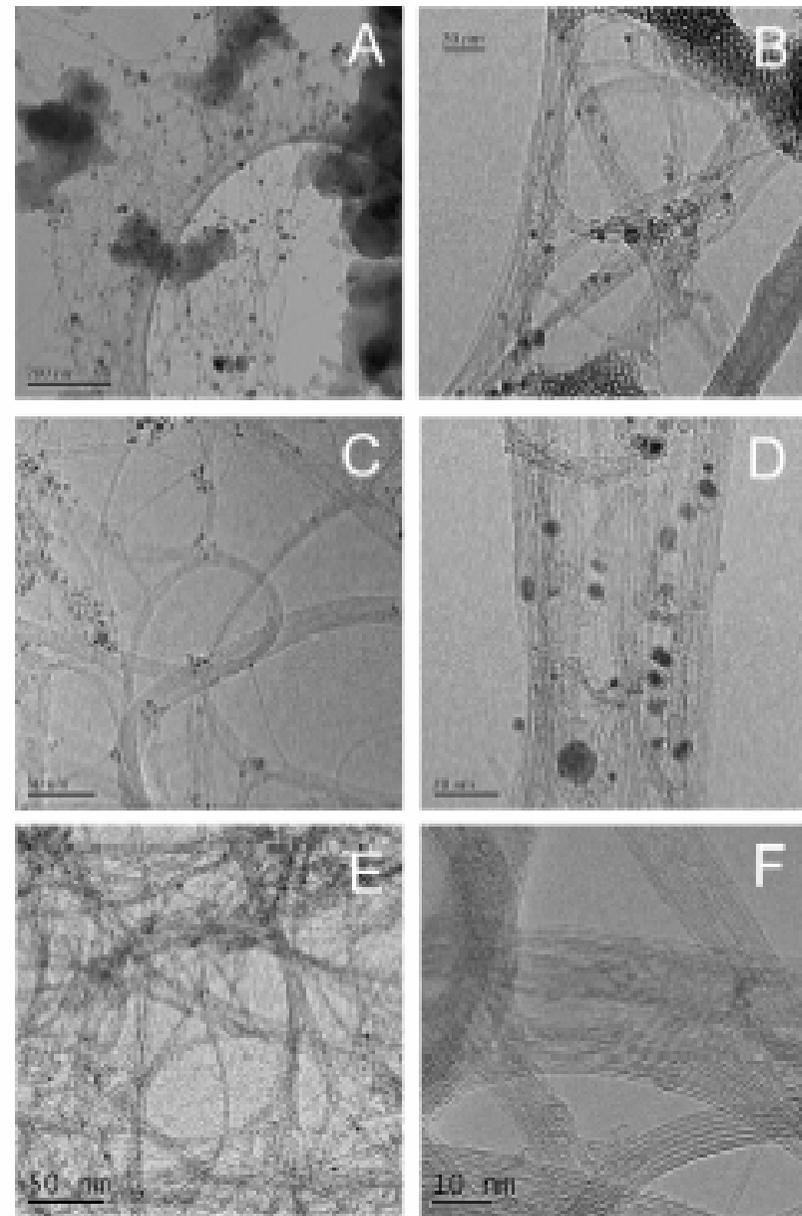
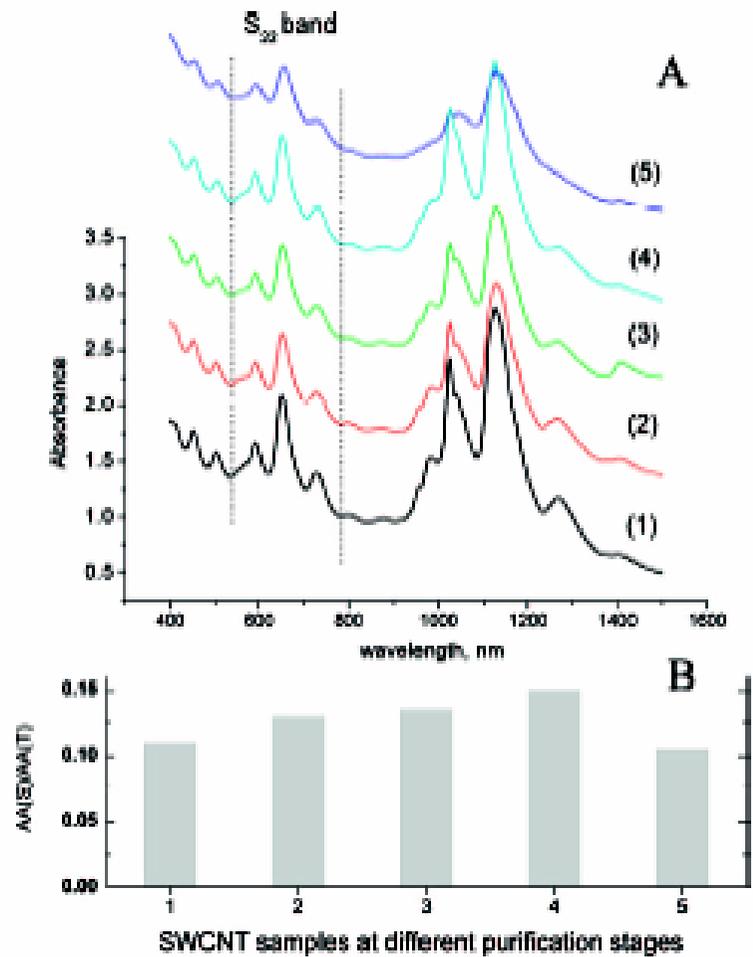
# Amorphous carbon removal



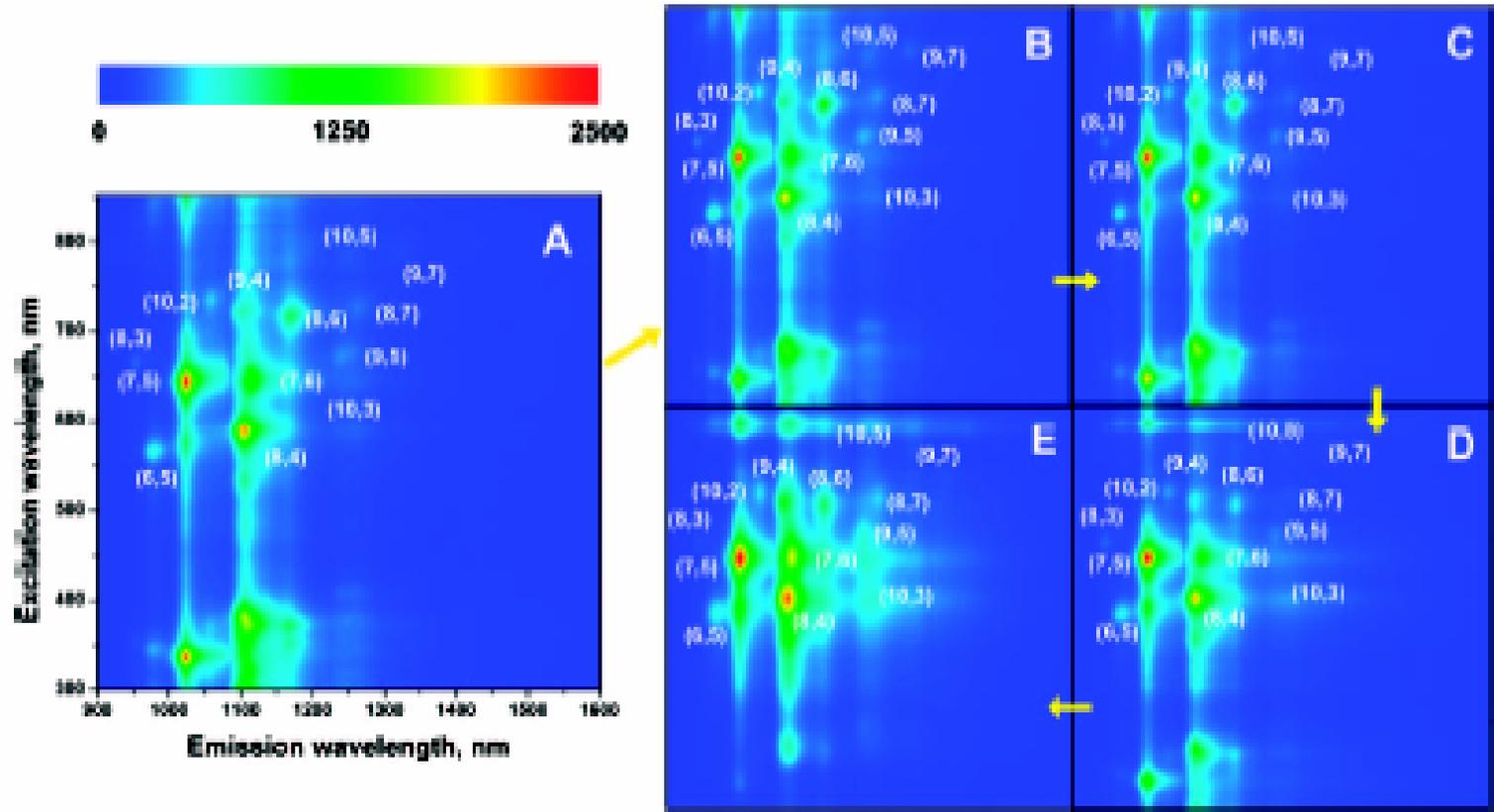
# Purification of SWNT from Co-MCM-41 --- four steps



# TEM & UV-vis-NIR

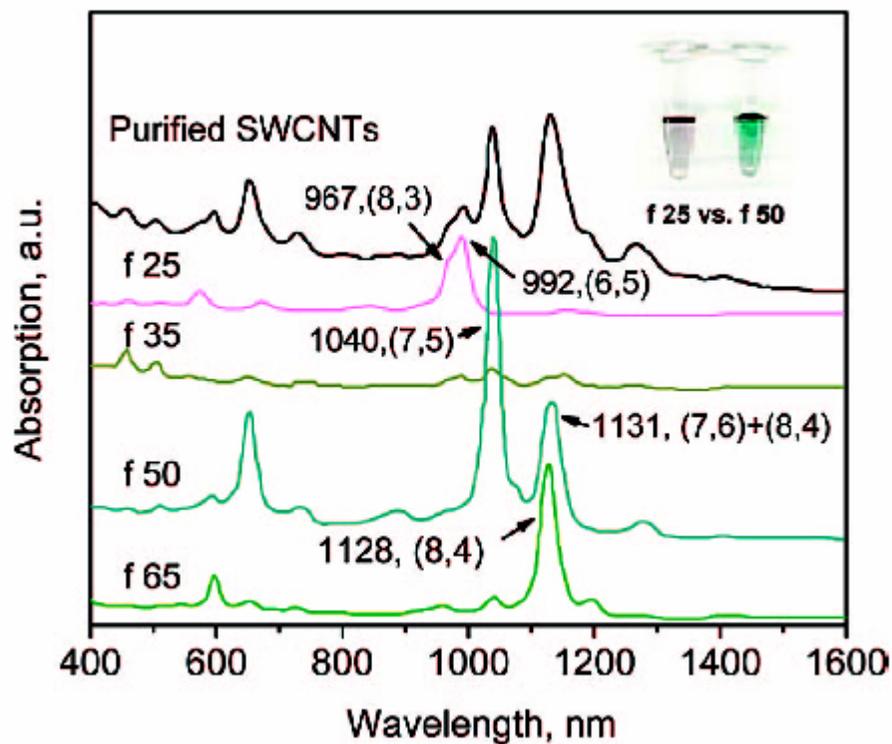


# PL of SWNTs

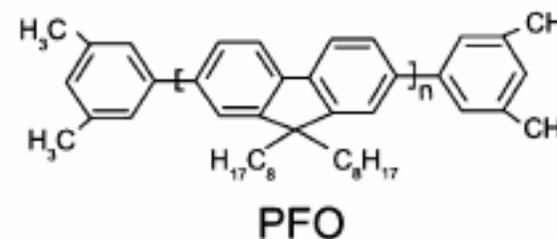
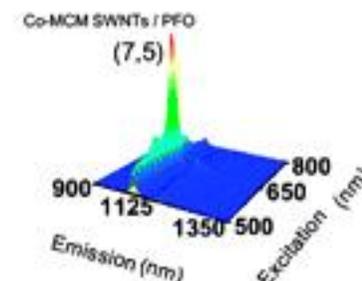
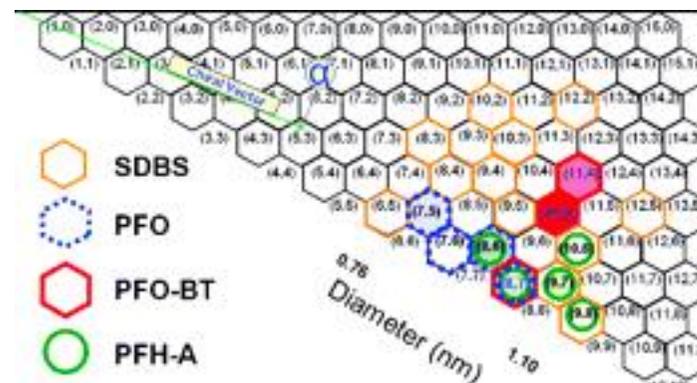


# $(n,m)$ selective enrichment

Results of SWNTs from Co-MCM-41



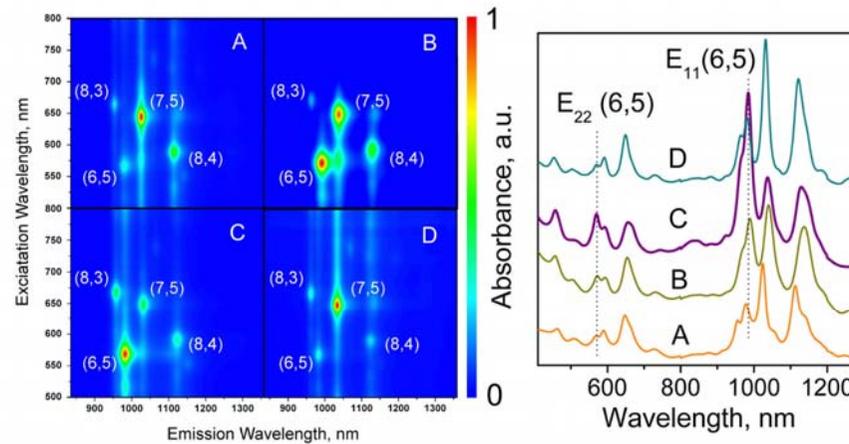
Zheng M., et al., Nature Mat., 2003, 338  
 Zheng M., et al., JACS 2007, 129, 6084



PFO, poly[(9,9-dihexylfluorenyl-2,7-diyl)-co-(9,10-anthracene)]

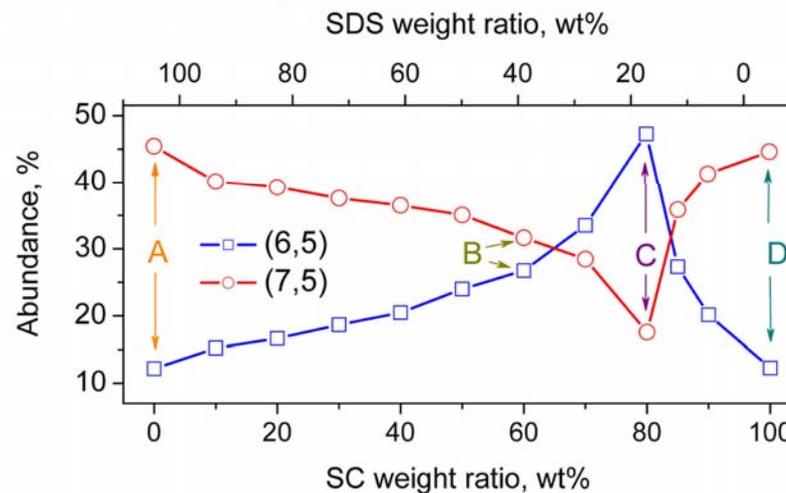


# Selective enrichment via co-surfactants (without gradient fractionation)



Journal of Physical  
Chemistry, B  
2008, 112, 2771-2774

Pure SDS

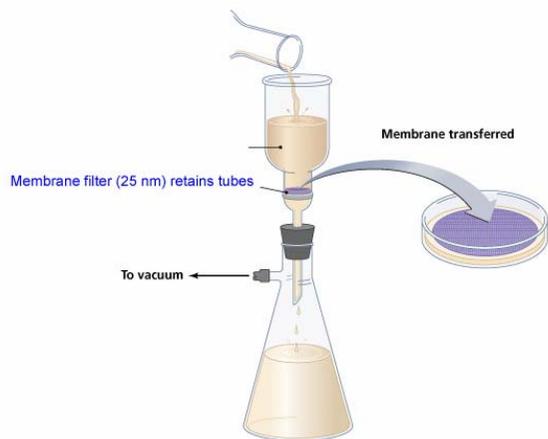


Pure SC



Mixture of (sodium dodecyl sulfate) SDS  
and sodium cholate (SC)

# Confirm the chirality selectivity

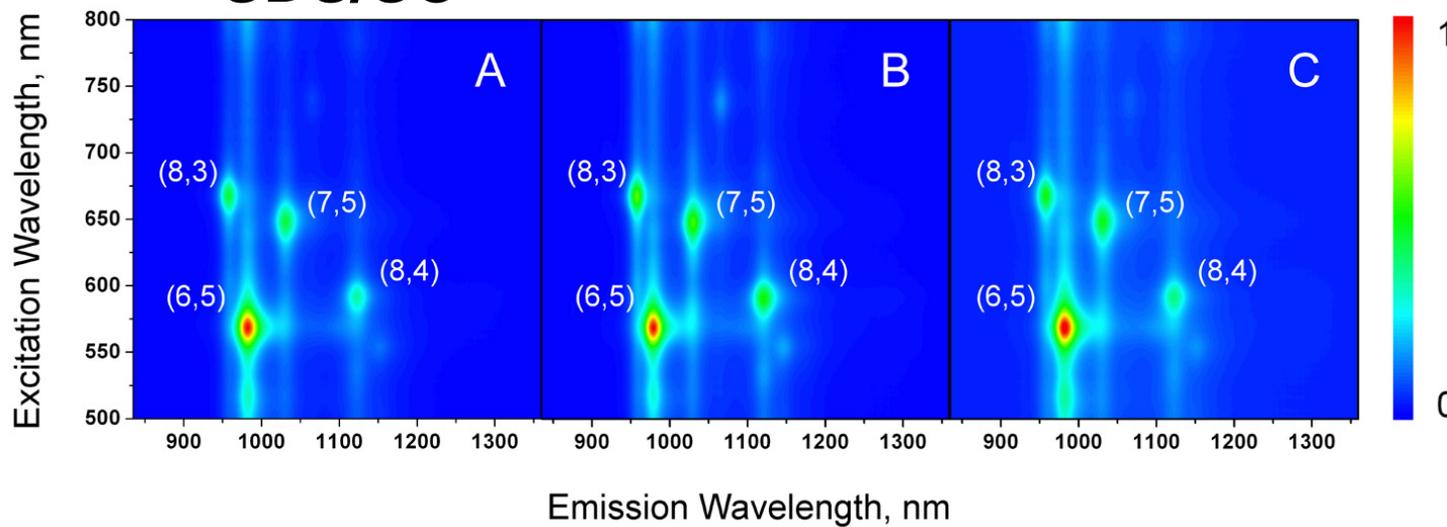


Filtration – Sonication

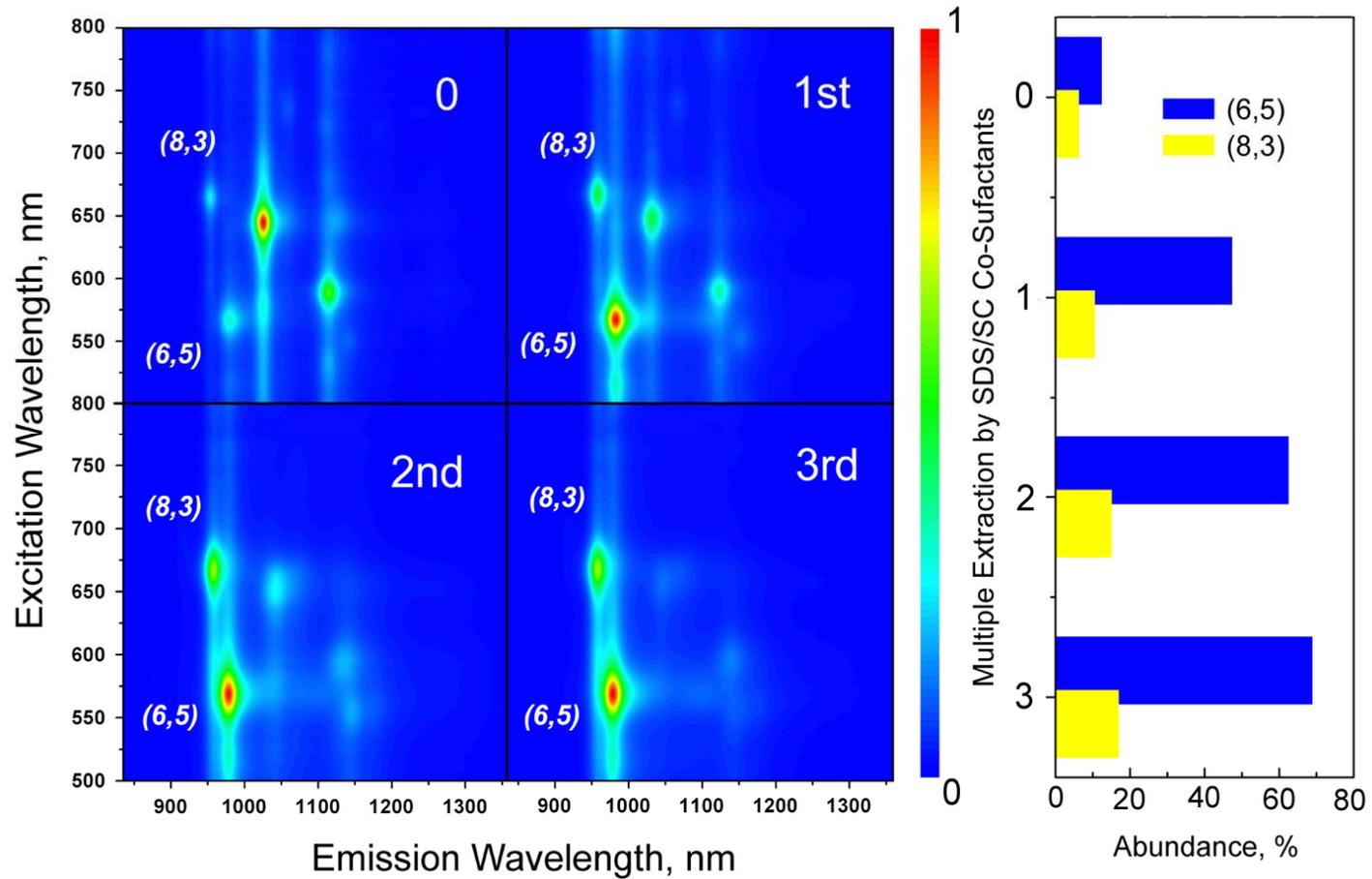
**SDS/SC**

**SDS**

**SC**



# Multiple extraction cycle



# Research scope

- 1 Growth of SWNT on Co-MCM-41
- 2 How synthesis conditions affect SWNT diameters?
- 3 Correlation between diameters of SWNT and cobalt cluster sizes in Co-MCM-41
- 4 Mechanism of cluster size control during SWNT growth
- 5 Chirality selectivity under different carbon precursors
- 6 Pressure inducted chirality selectivity
- 7 Purification of SWNTs from Co-MCM-41
- 8 Enrichment of (6,5) and (8,3) tubes using co-surfactant extraction



# Acknowledgement

Funding from:

- College of Engineering, Start-up Grant, NTU
- Acrf Tier 1, MOE, Singapore

Prof. Lisa Pfefferle (Yale)

Prof. Gary Haller (Yale)

Prof. Dragos Ciuparu (Romania)

Dr. Steven Lim (Yale)

Prof. Lain-Jong Li (NTU)

Dr. Patrick Poa (IMRE)

Bo Wang (NTU)

Li Wei (NTU)

