Tailored
Hybrid
Structures

epm

Paola Ayala

C, B, N and P:

“Low Doping vs. Heteronanotubes"

Workshop Carbon Nanotube Growth, Separation and Spectroscopy

The University of Tokyo, 05.10.2012

OUTLINE

State of the art

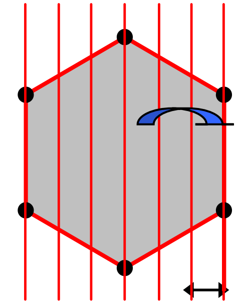
- Morphological characteristics
- Theoretical approaches
- Successful experimental attempts, Experimental data

Our Samples: Experimental Evidence of SW doped CNTs

- Sample morphology: SWNT/MWNT
- Diameter/diameter distribution and defect concentration
- Heteroatom-content, doping environment

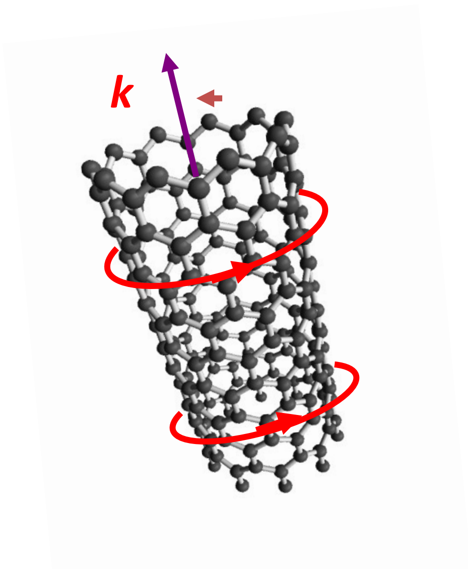
Future Perspectives regarding doped CNTs

Electronic Properties and Structure of SWNTs

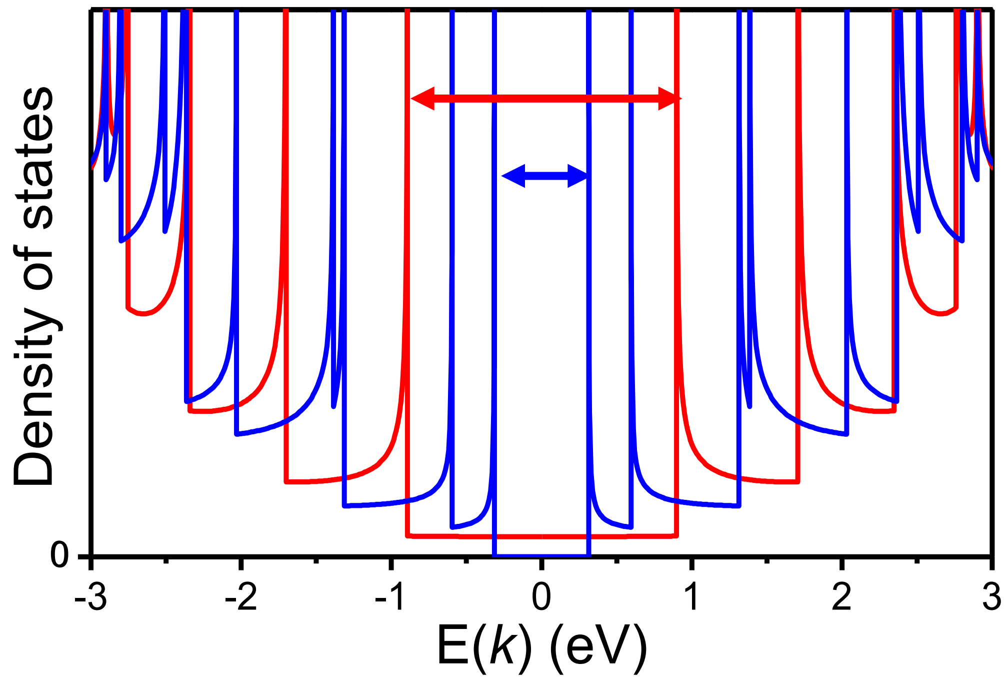


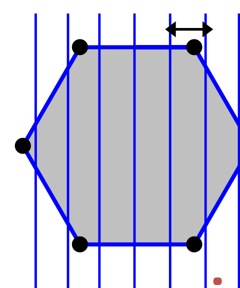
1/3

metal



σ-bands: ~ 50 eV
π-bands: ~ 20 eV



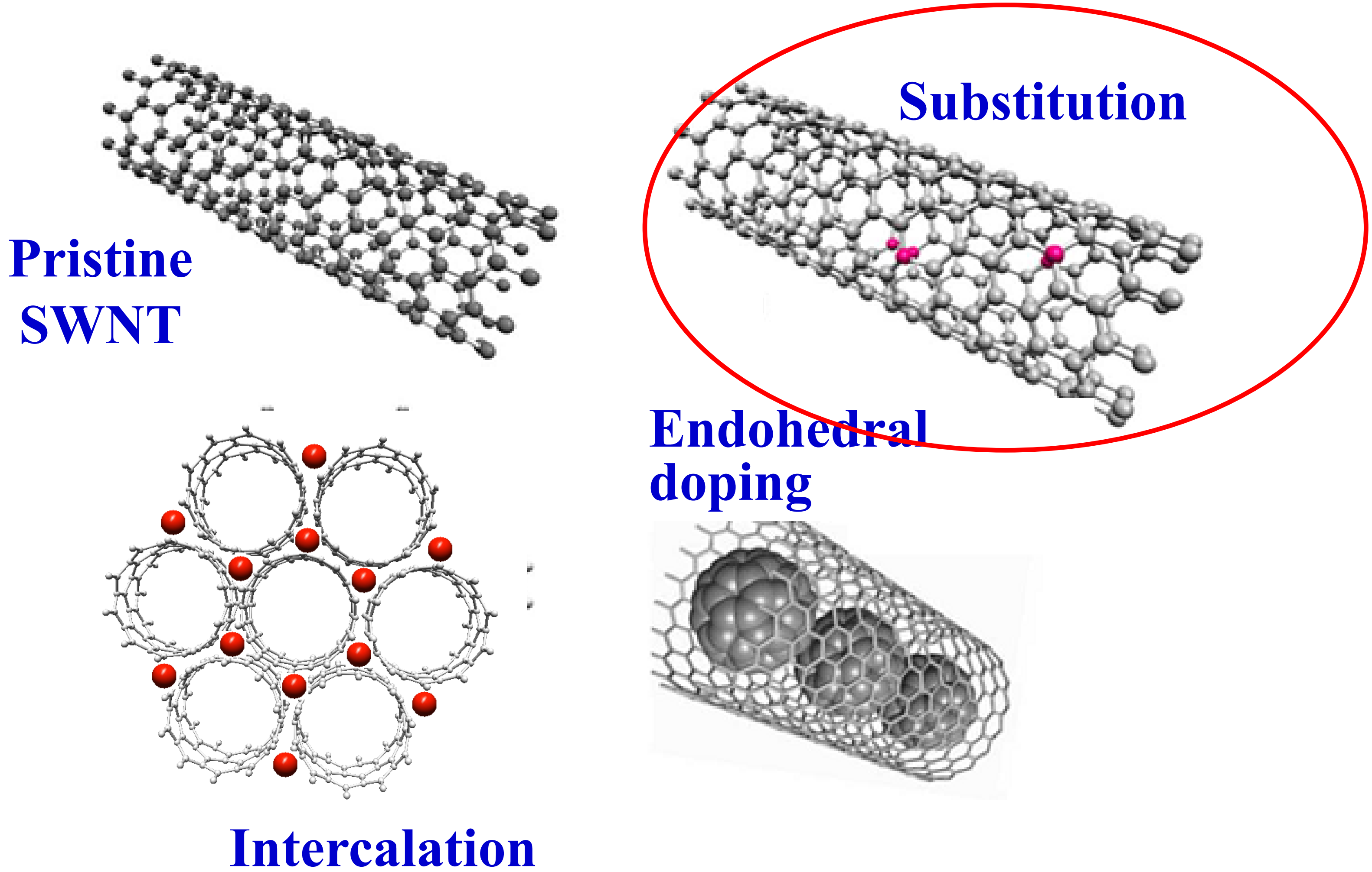


2/3

semiconductor

Electronic properties fully determined by geometry!!!

Modifications to induce changes in the electronic structure…



P.Ayala, et al., Reviews of Modern Physics 82(2010)1843-1885.
P.Ayala, et al., Carbon, 41 (2010) 1853.

Doping with N, B, P?

Different features in MW and SW doped nanotubes.

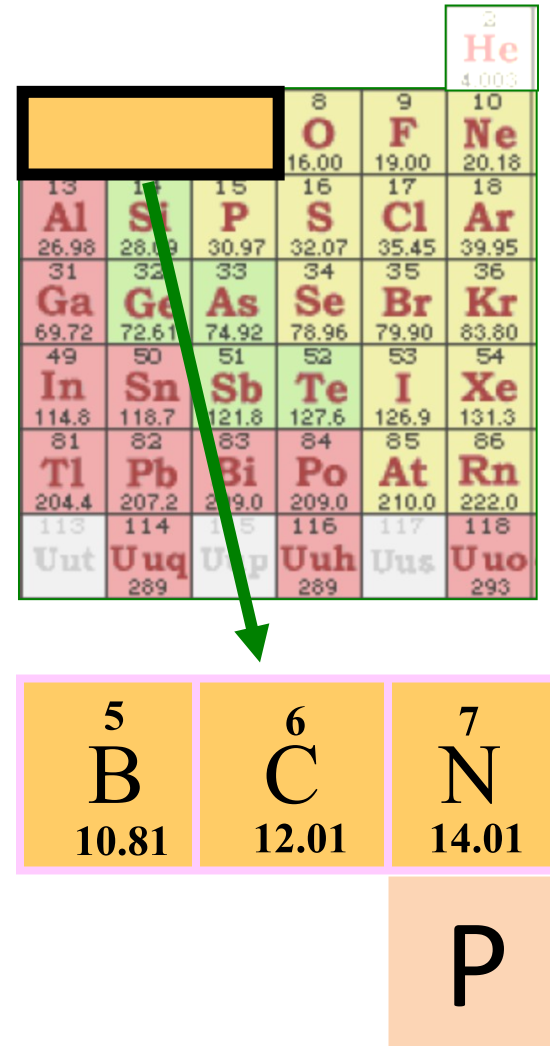
•SWNTs

Sharp localized states above and below the Fermi level (n- or p-type doping), by substitution or removal of C atoms.

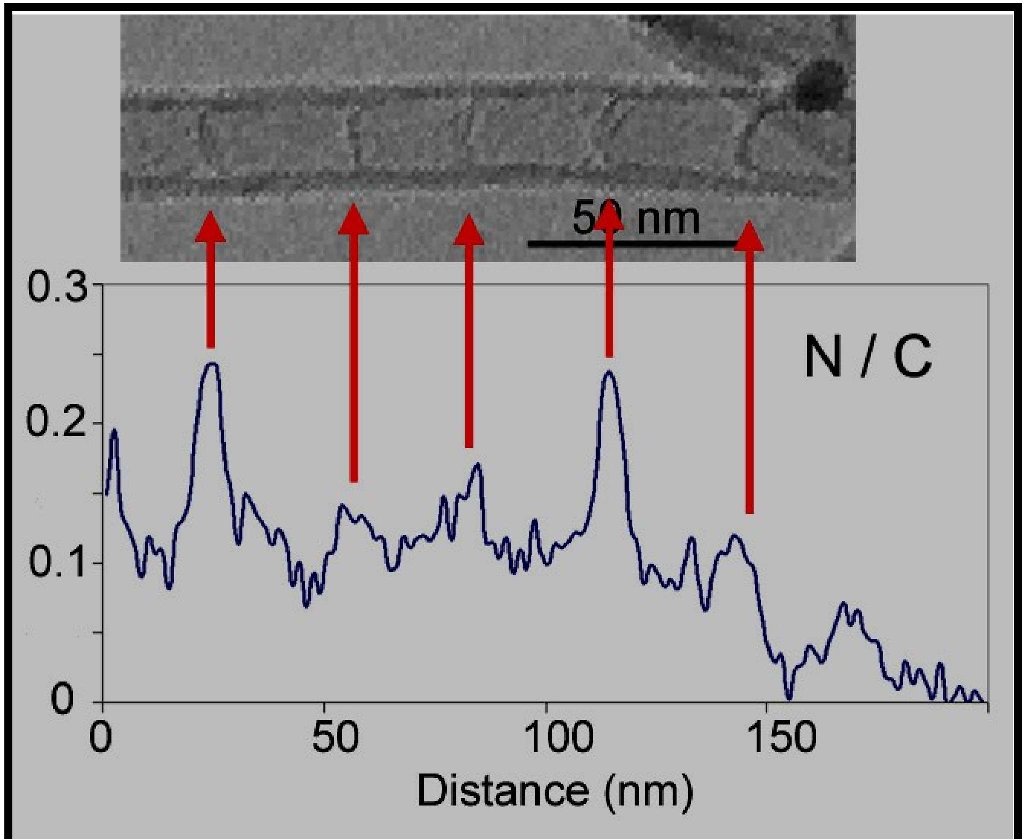
•MWNTs

Gain of electrochemical reactivity,

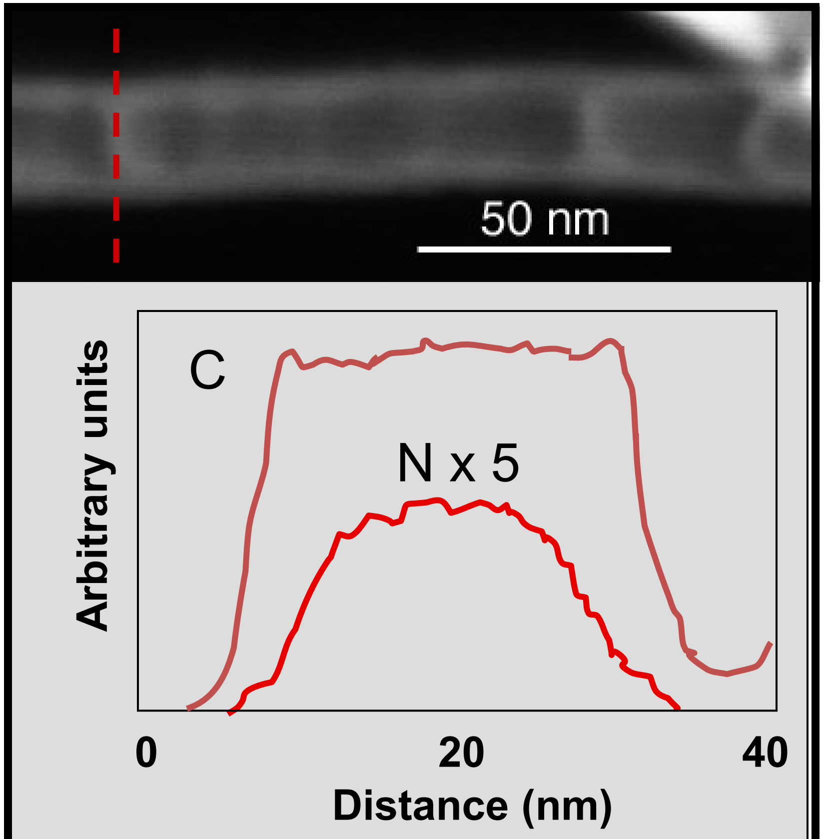
Functionalization for further applications.



How much N can we incorporate Substitutionally?



Profile across the compartment walls



Profile along a compartiment wall

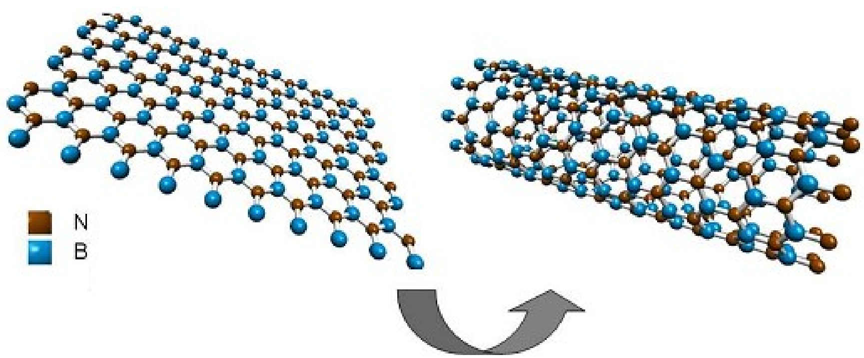
Observations for MW-CNx-CNTs

- N is dominantly localized in the compartiments
- Doping can reach 25 %

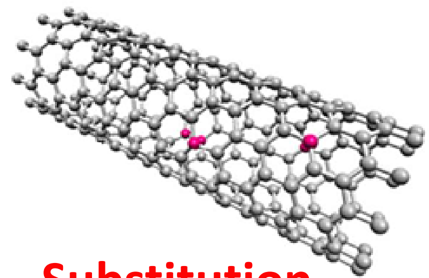
Courtesy: Prof.Christian Colliex. (LPS-Orsay)- CIASEM 2005. Havana

We are dealing here with graphitelike planar structures that resemble the geometry of a honeycomb.

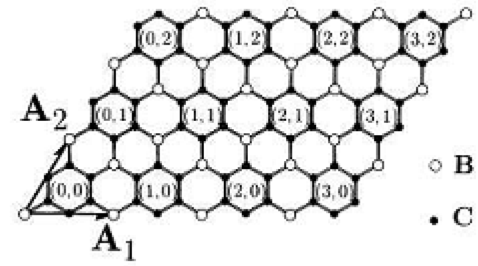
BN-Nanotubes



Boron Doping

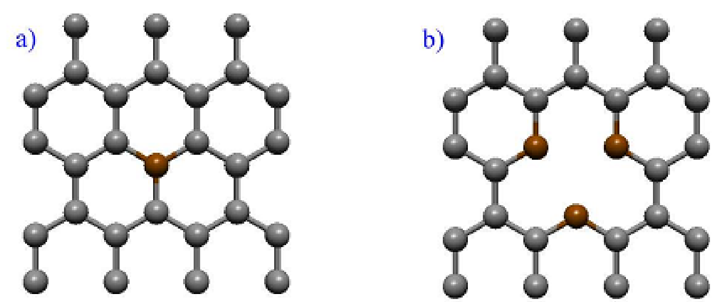


Substitution

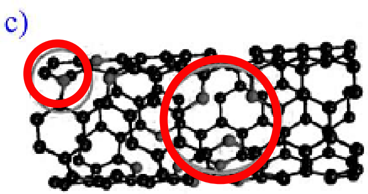


BC_3 Nanodomains

Nitrogen Doping



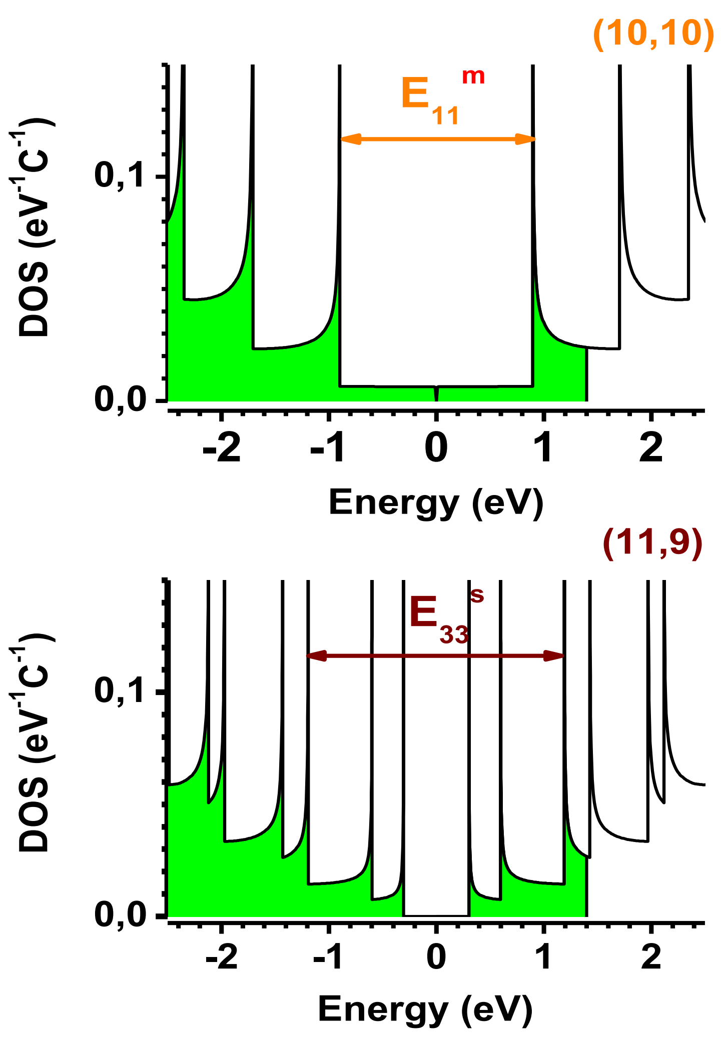
Substitution



Pyridinic

NANOTUBES:

Changing Electronic Properties by substitutional doping



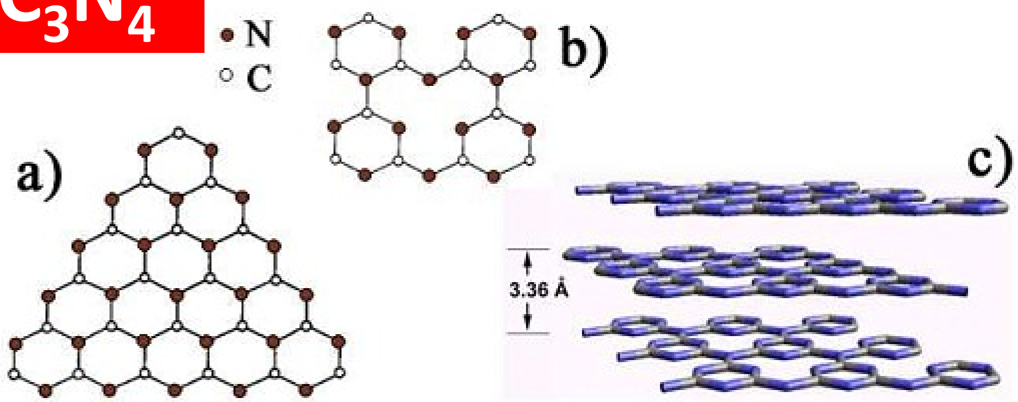
Low doping levels

- Semiconductor Industry
- Rigid band model

High doping levels

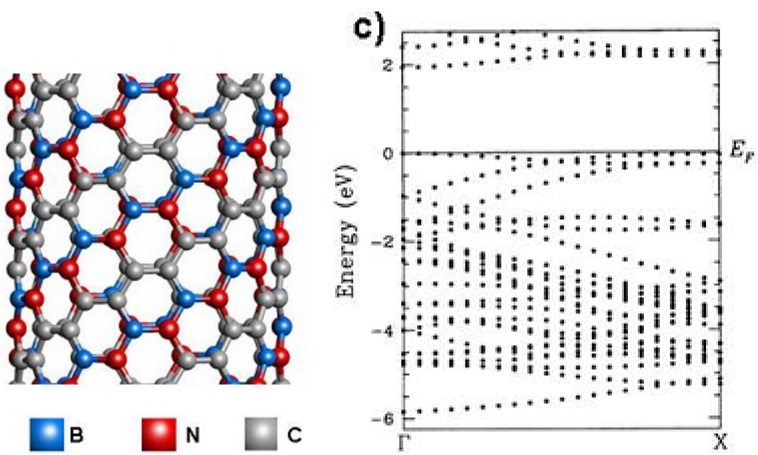
- Chemistry: New stable structures
- Rigid band model not applicable !!!

C_3N_4

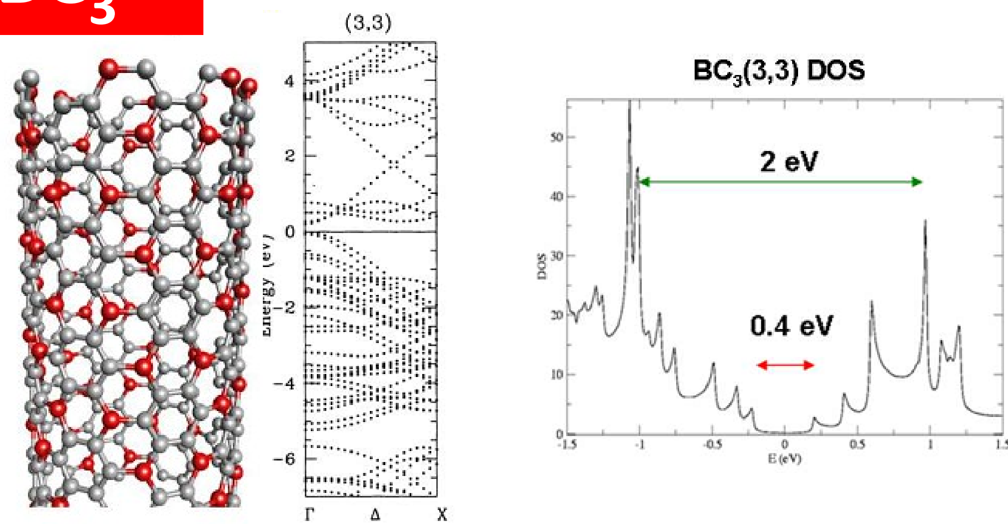


Hexagonal graphitic-like planar structures should be able to generate nanotubules with different stoichiometries based on B, C and N

BC_2N



BC_3

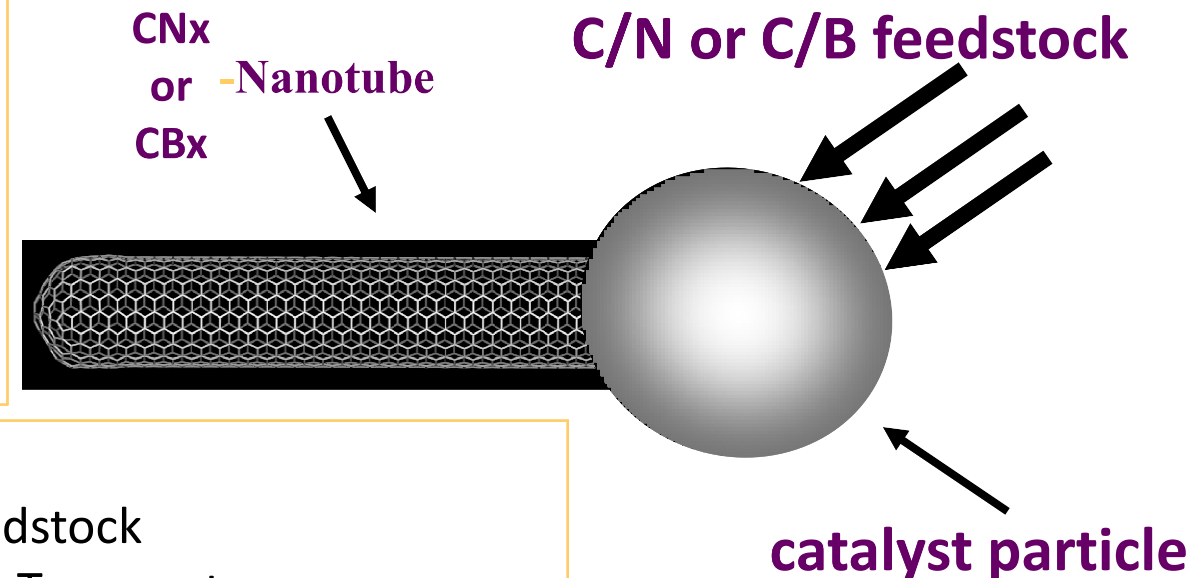


The incorporation of foreign atoms such as B and N can break the stability of a planar structures depending on the site they enter.

CNx and CBx Nanotubes Synthesis

Successful Attempts

- Laser Ablation
- Arc Discharge
- CVD / AA-CVD
- Spray Pyrolysis
- Ball Milling (CBx)
- Substitution Reactions (BC_3)



Parameters to control:

- Vapor pressure C/N Feedstock
- Feedstock Self-Pyrolysis Temperature
- Catalyst Composition and Activity
- Catalyst pre-treatment

A pure C/N feedstock is needed to determine the N incorporation profile within the tubes.

Benzylamine (2%at.)

Acetonitrile (6%at.)

Triisopropyl Borate (4% at.)

Substitutionally doped SWNTs: Challenges

Is it possible to have substitutional doping?

What is the best synthesis method?

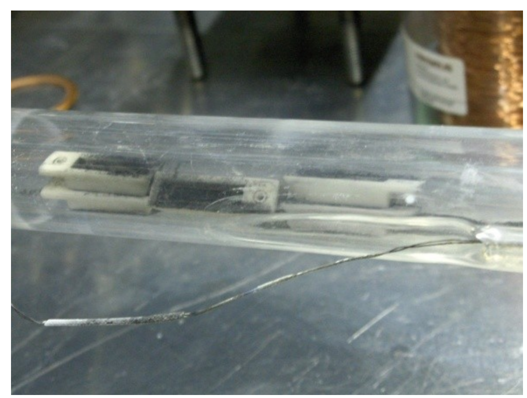
Low substitutional doping

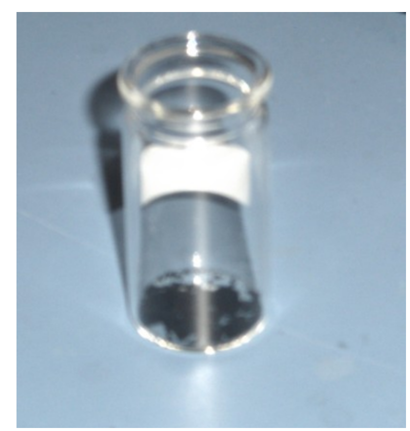
What kind of precursor is ideal?

Characterize efficiently low doping levels

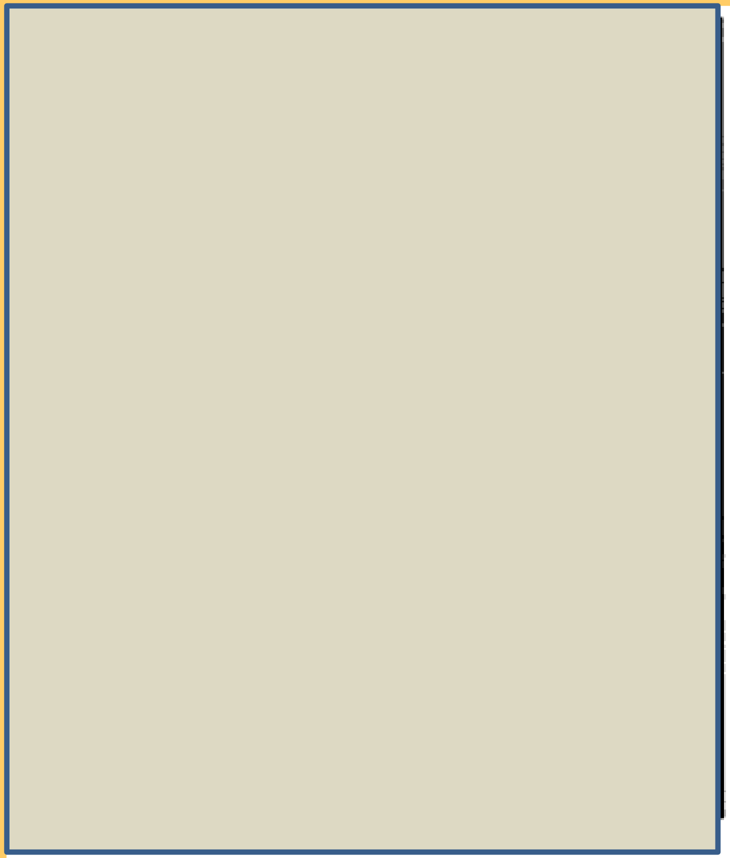
Sample Characterization

- Morphology:
  SEM(Bulk)/TEM (Local)
- Diameter and defect concentration:
  Raman Spectroscopy (Bulk sensitive)
- Doping level
  TEM-EELS (?)
  XPS



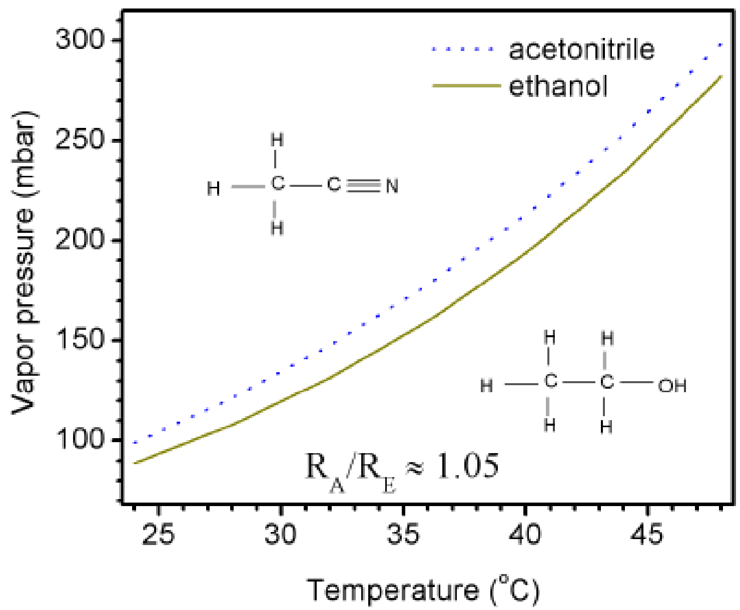


The Reaction Atmosphere



The honeycomb lattice

- Is N incorporation really energetically disfavored?
- Is it possible to synthesize N and B-doped SWNTs?



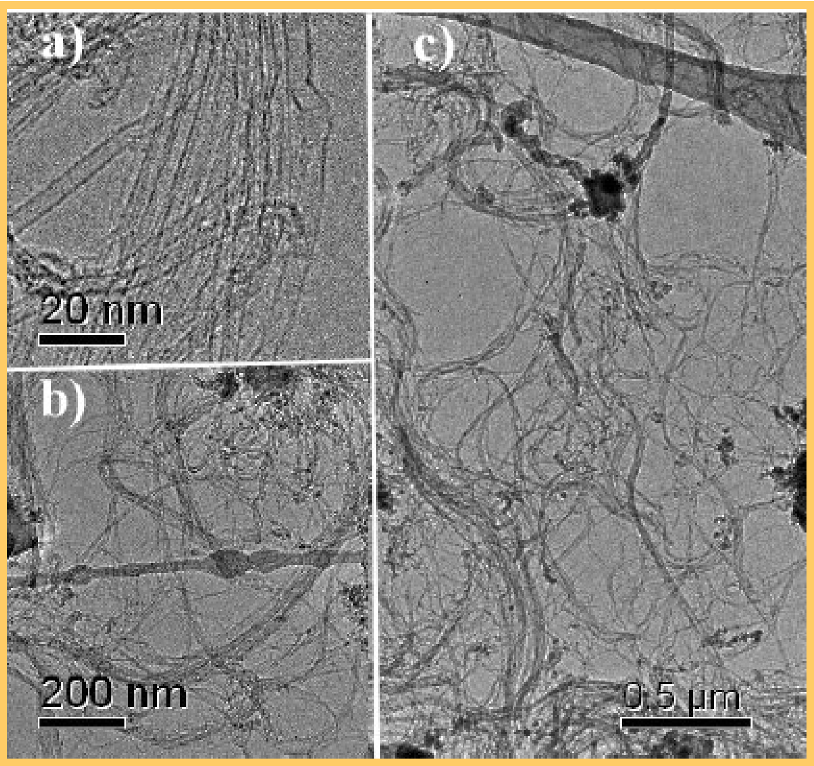
P. Ayala, et al. J. Chem Physics 127 (2007) 184709

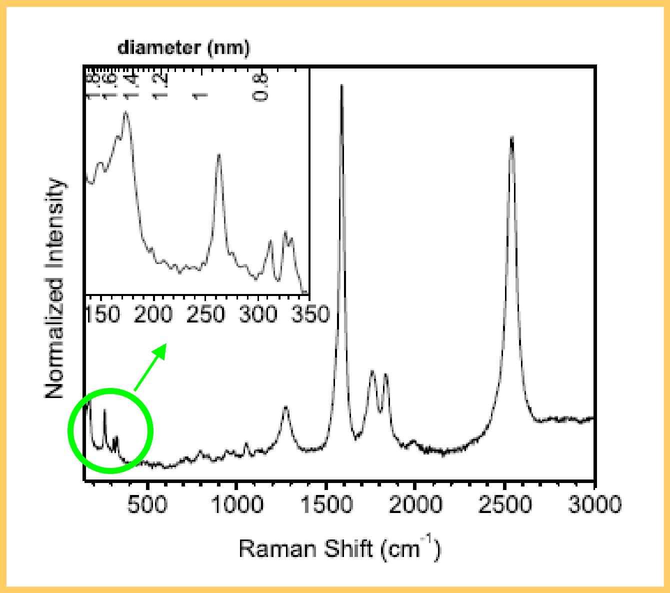
P. Ayala, et al.. Chem Mater 19(2007) 6131

P. Ayala, et al. J. Phys Chem C 101(2007)2879

Effects of the Reaction Atmosphere Composition

Pure Ethanol Nanotubes…





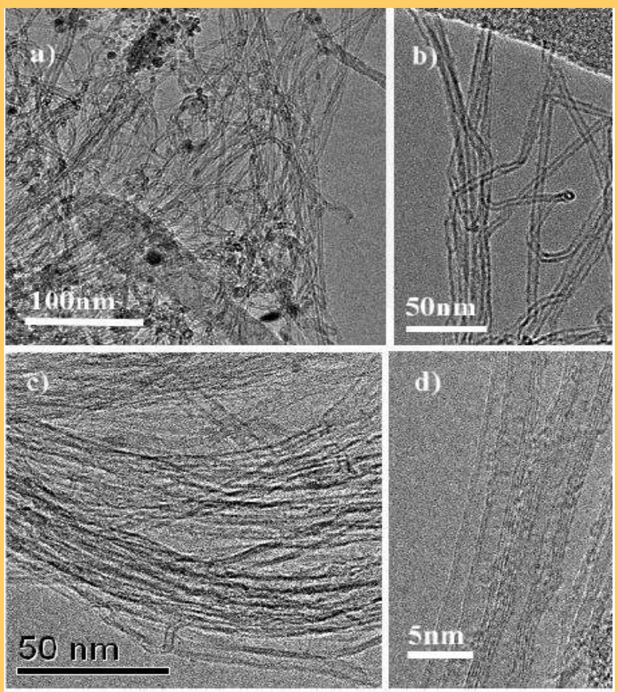
- Growth: Between 800 and 1050°C
- High yield of SWNTs

Raman: 0.8 to 2nm

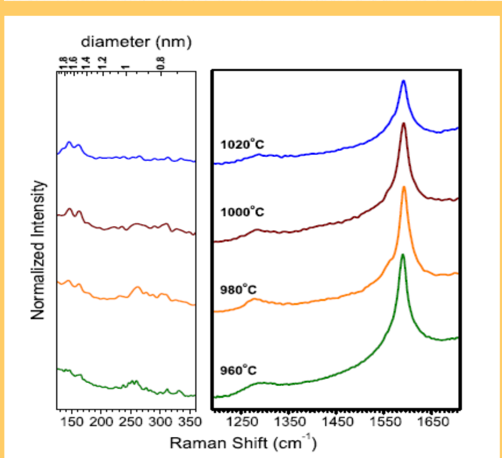
TEM: Bundles

Composed Feedstocks

① Ethanol rich source (10%wt acetonitrile)

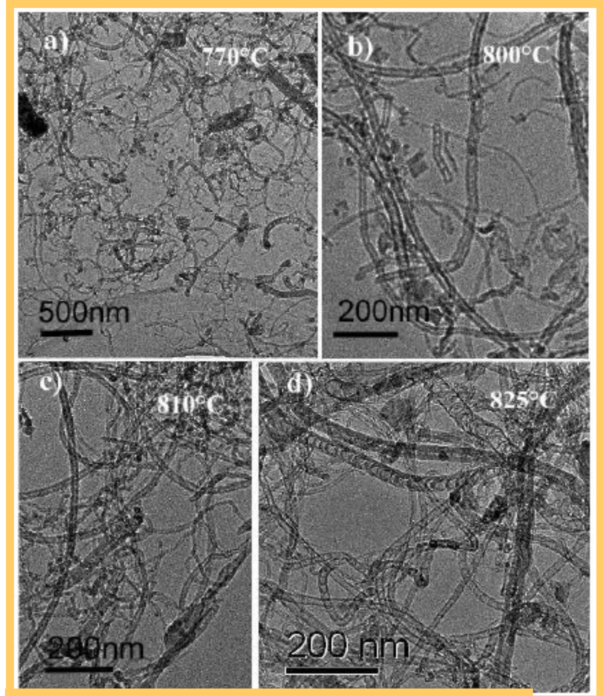


- Onset for NT growth: 880°C
- TEM: SWNTs and low amount of MWNTs

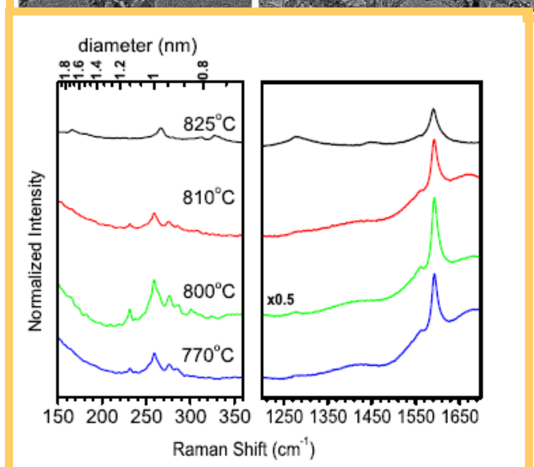


- Constant D/G with temperature
- Onset for MWNTs growth 1020°C

2 Equally contributing composition (1:1 acetonitrile vs ethanol)



- Multiple morphology product independent of synthesis T
- Lower T, ~5% of short (500nm) and thin nanotubes (~1-15nm)

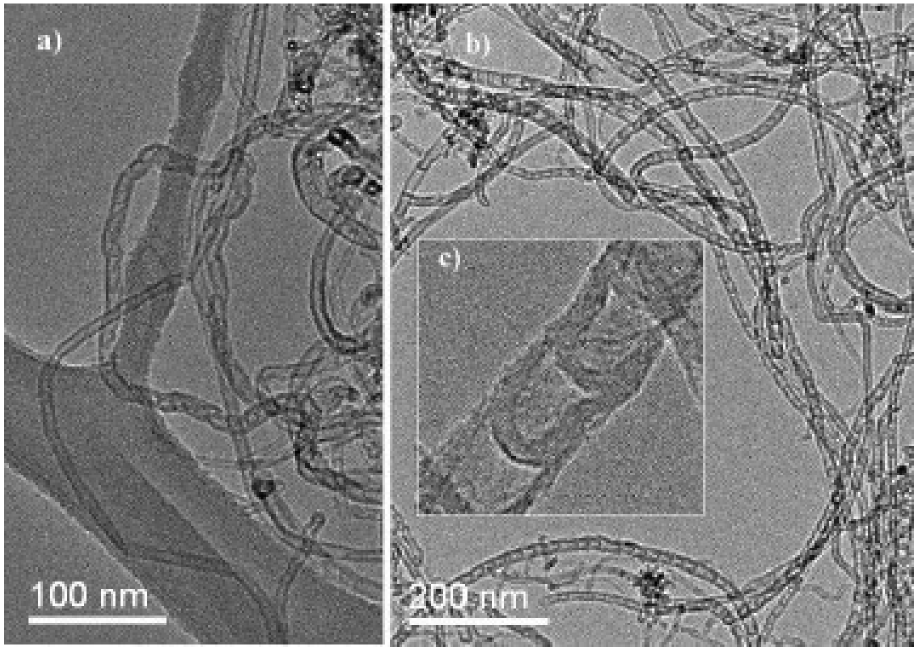


- Highest SWNTs Raman response at 800°C
- Low formation of SWNTs at higher temperatures
- SWNT grow T-window narrows down.

③

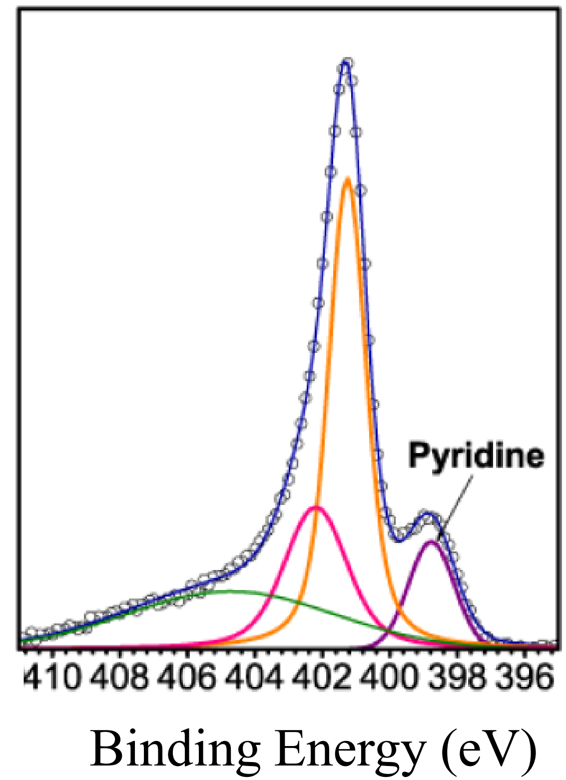
Pure C/N feedstock

Pure acetonitrile feedstock….



- Practically no evidence of SWNTs
- MWNTs grow between 750 and 900^{o}C
- Morphology:

  Defective MWNTs and bamboo-like tubes with diameters between 15 to 20nm.



Max N content:

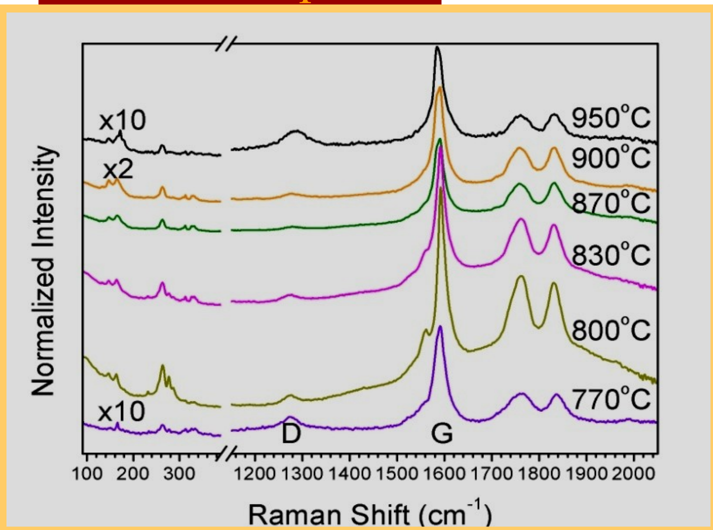
Composed Feedstocks ~1.5 0.2%at.

Pure Acetonitrile Feedstock ~1.7%at

C1s: 284.7eV at all T

Benzylamine CNx-nanotubes

FT-Raman Spectra



•Radial Breathing Mode Response

DWNT /SWNT optimum growth: 800°C to 900°C.

•Highest yield

870°C of DWCNT (320 cm^{-1})

830°C of SWCNT (270 cm^{-1})

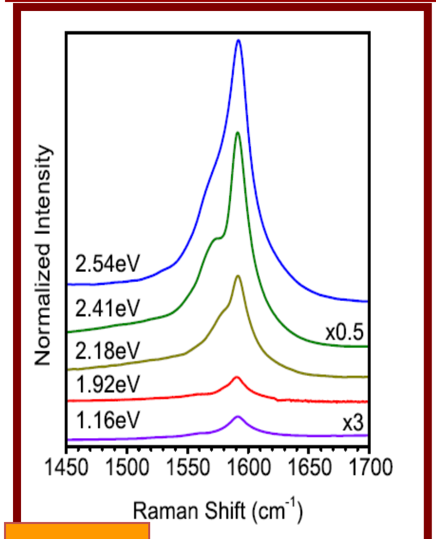
•Relative Nanotube Yield:

Maximum Raman response between 800°C and 870°C

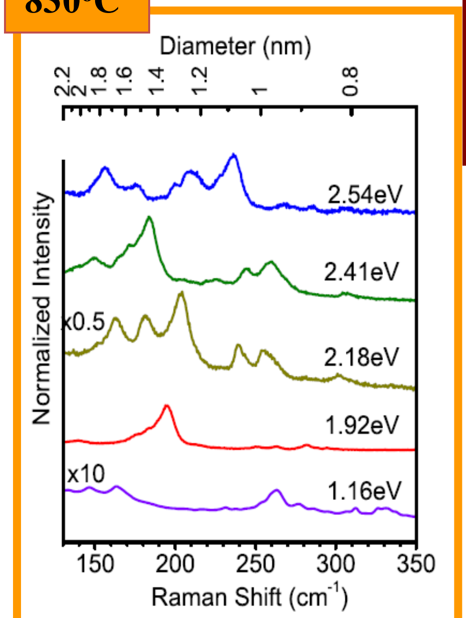
•Relative defect concentration:

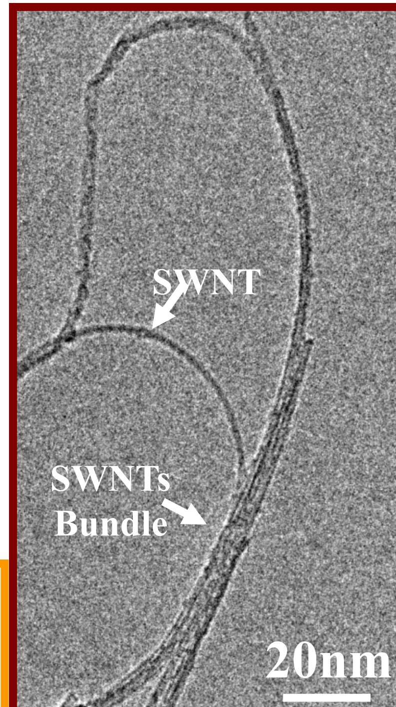
Low D/G ratio down to 1/20

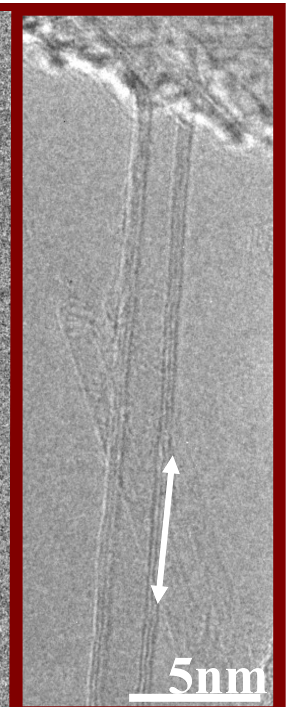
Multifrequency Raman…An insight to diameter distribution

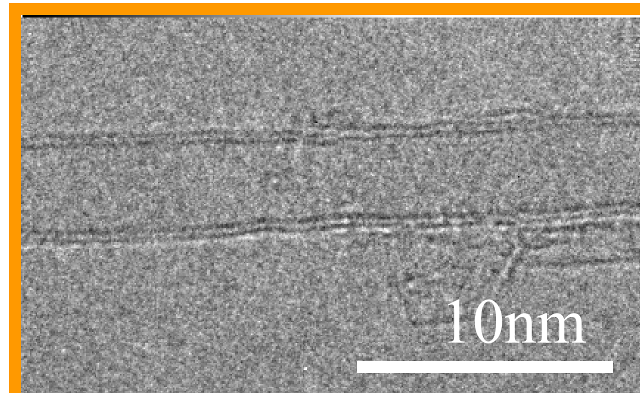


830°C



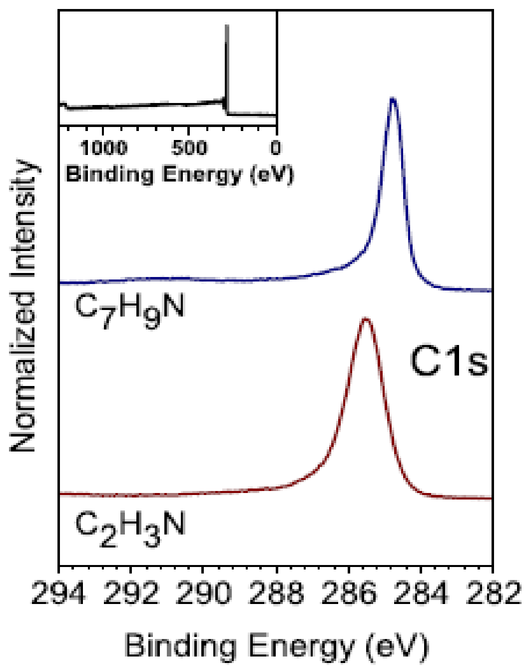






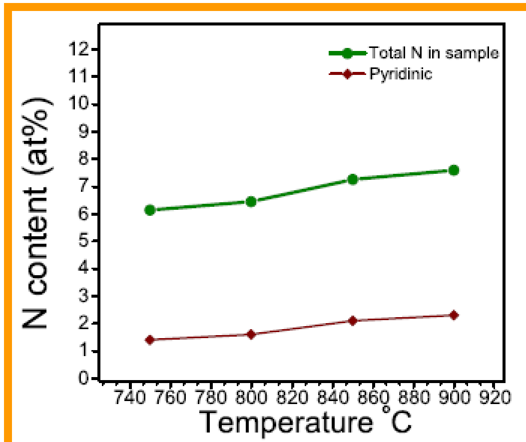
CNx NTs Atomic composition: XPS

C



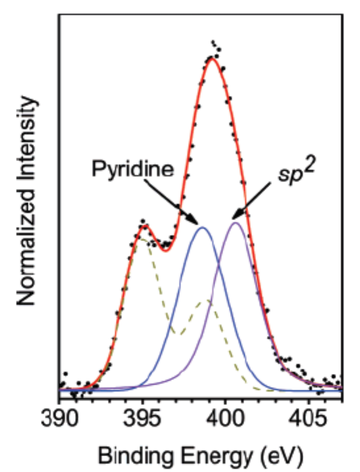
•Broadening of C1s peak at lower nanotube growth temperatures

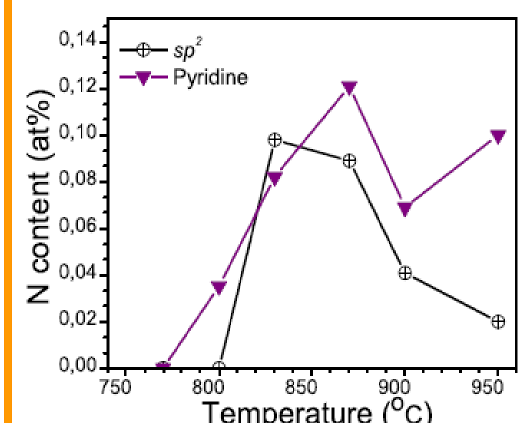
N

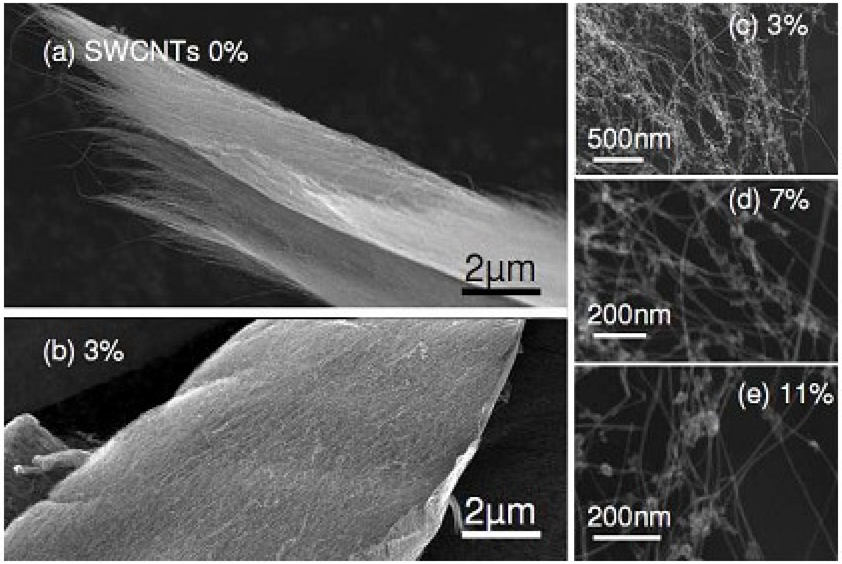


N incorporation profile

• sp^2 and pyridyne compete within SW/DWNT high yield T window

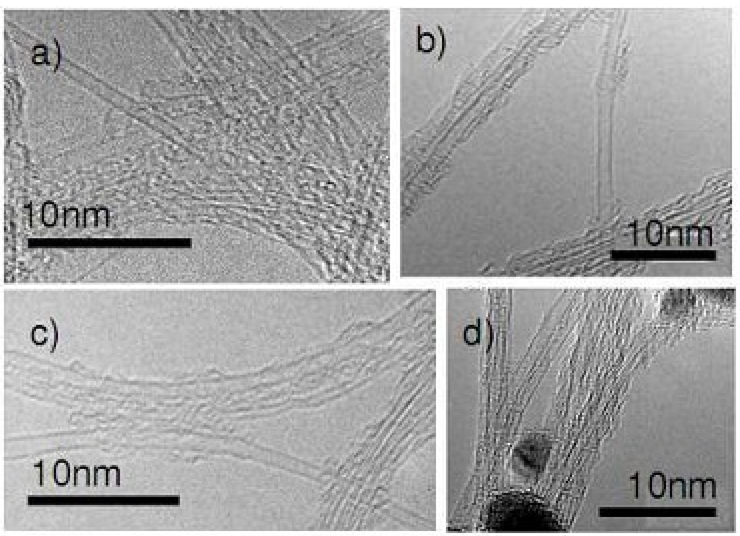


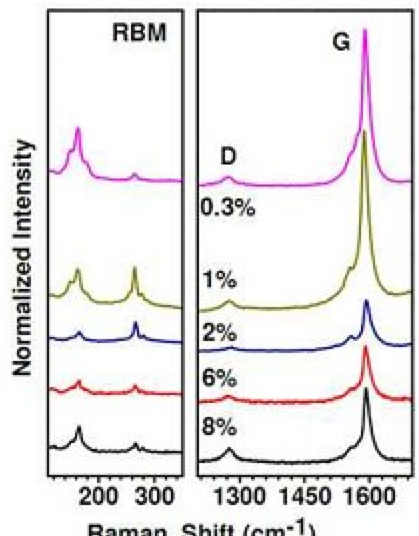




0,3% maximum

Substitutional!!!

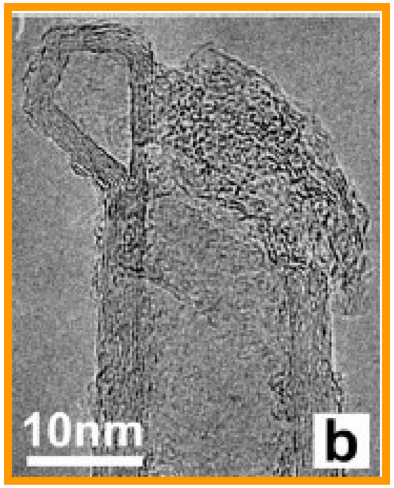




A.L.Elias, P.Ayala, M.Terrones et al.
Journal of Nanoscience and Nanotechnology
Vol.10, 1–6, 2010

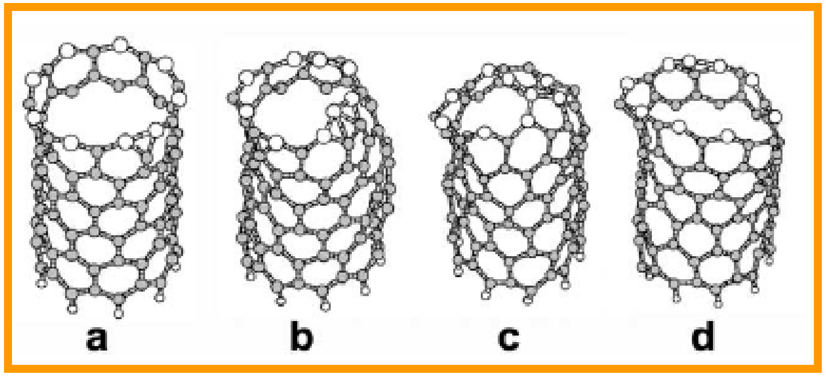
Boron Doped Nanotubes

MWCBx-nanotubes (Illed Caps)



- MW-CBx nanotubes
- Straight
- Illed caps

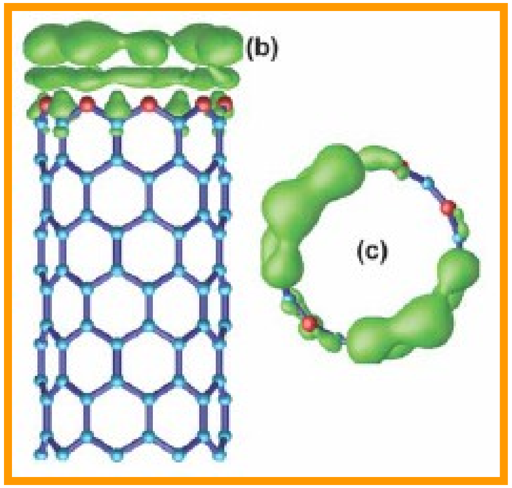
SWCBx-nanotubes



B acts as surfactant inhibiting the closure of NTs

Blase et al. PRB 1998

Atomic Welders

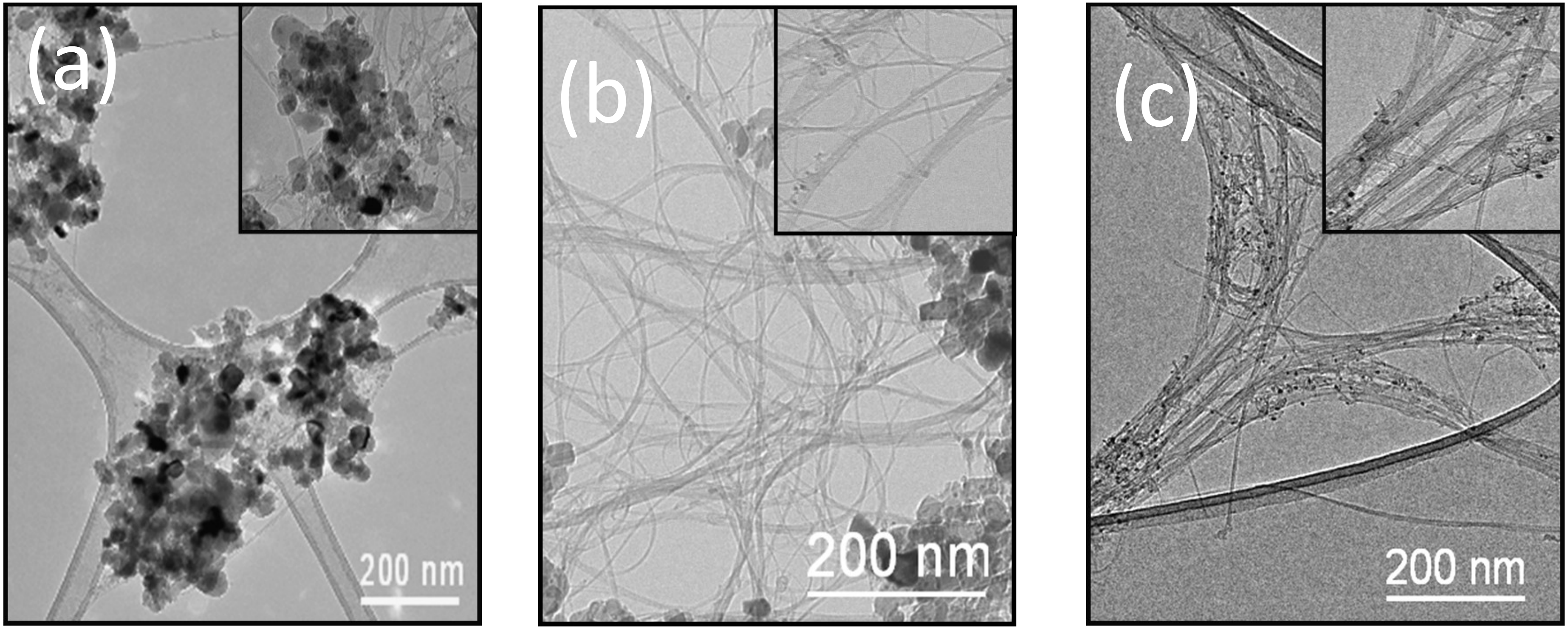


Terrones, M., et al, Materialstoday 7 (2006) 10, 30

- **SW synthesized throug substitution reactions**
- **Doping up to 25%**
- **Arc Discharge-From mixture in target**

Is it possible to use a liquid feedstock for CBx-SWNTs ?

- Problem 1: Experimental Setup
- Problem 2: Precursor and Catayst
- Problem 3: Co-products



Nanotubes fromTriisopropil borate

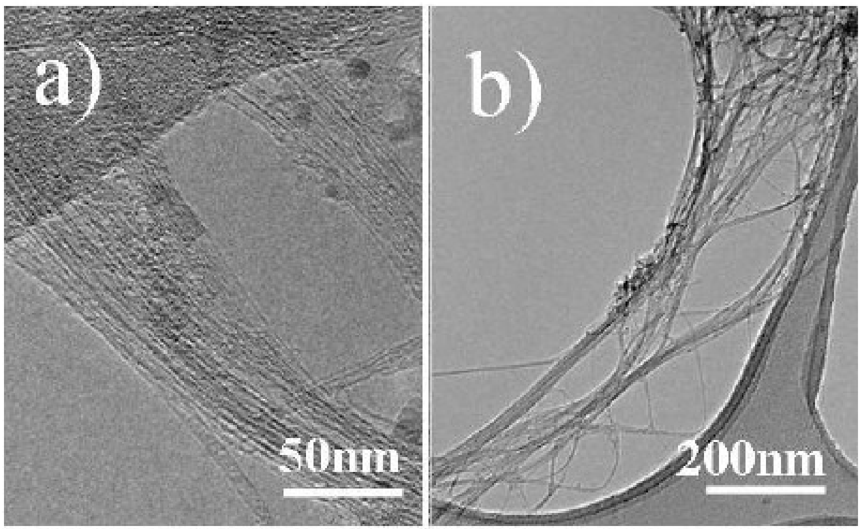
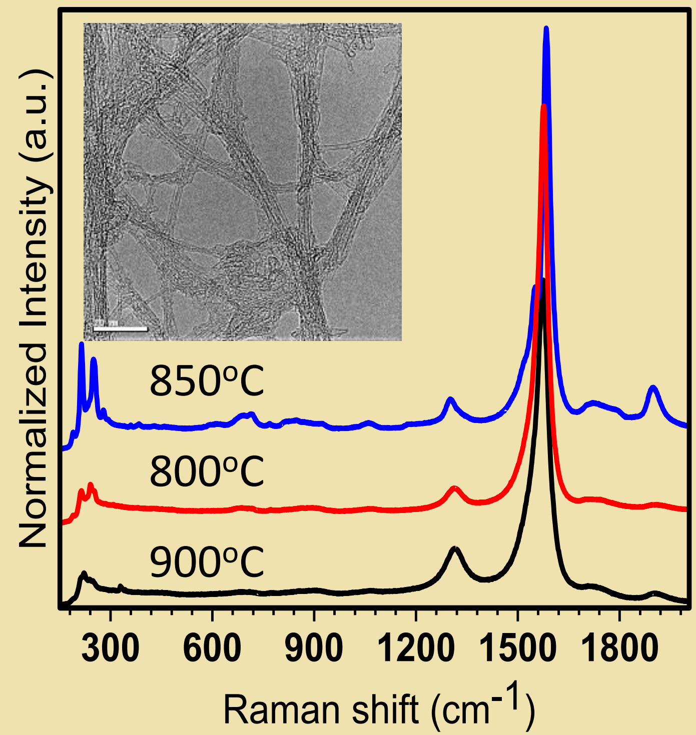
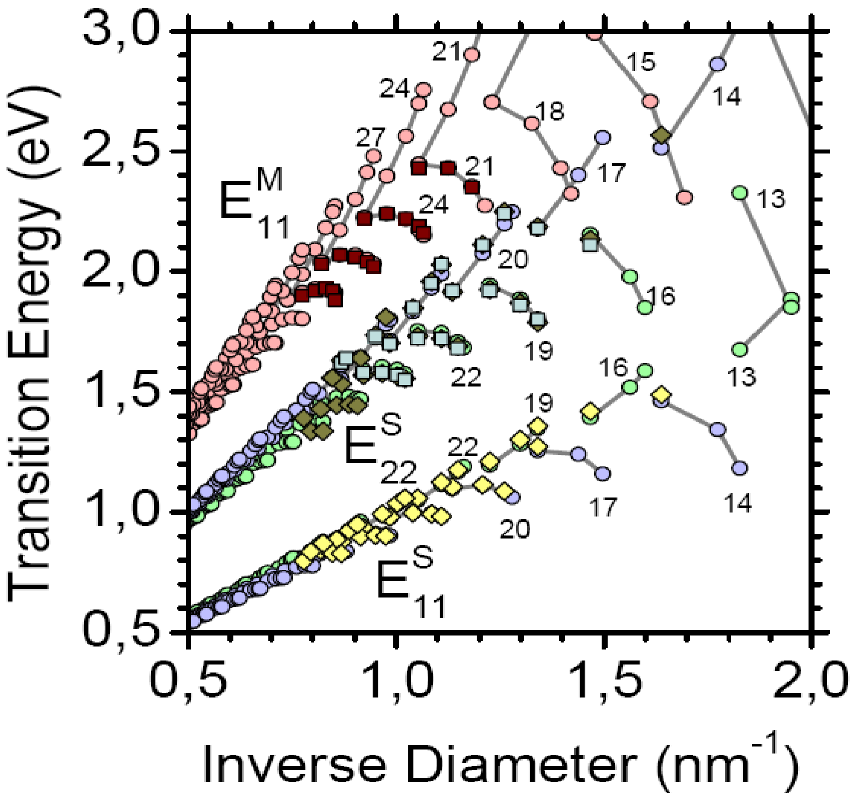


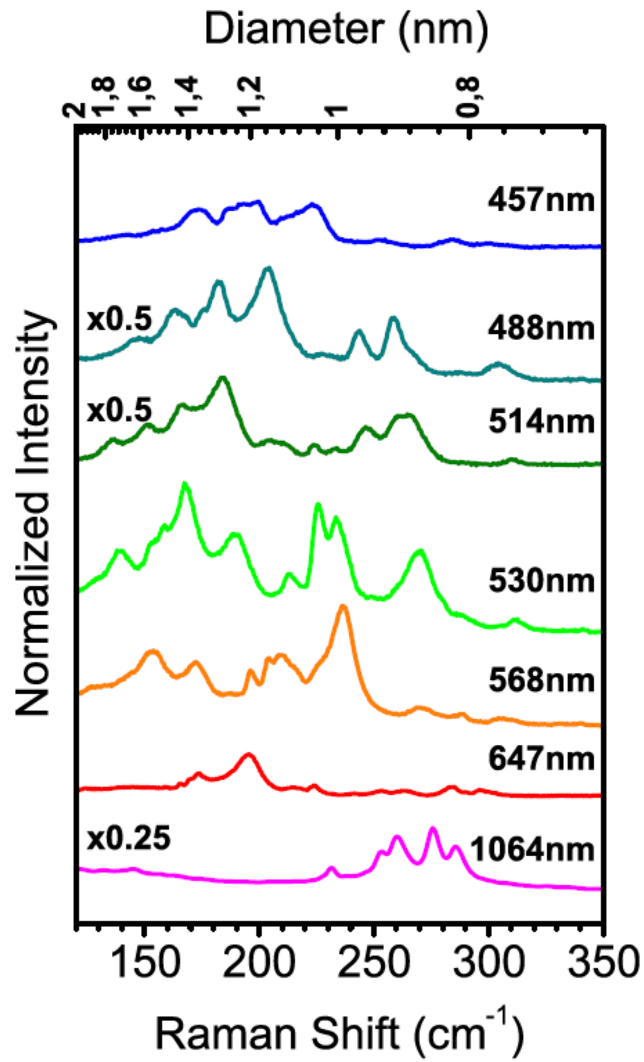
FIG. 2: Low-mag micrographs corresponding to a sample synthesized at 840°C with a supported iron based catalyst.



S. Daothong, J. Parjanne, M. Valkeapää, T. Pichler, **P. Ayala, et al, Phys Stat Sol b 246 (2009) 2518**

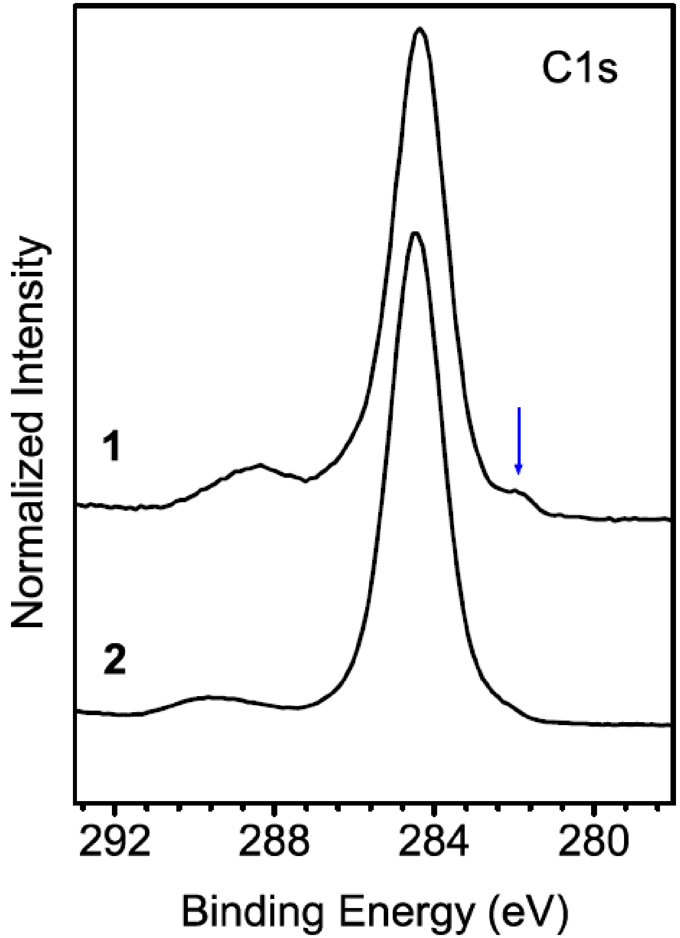
Multifrequency Raman





Multifrequency Raman response in the RBM region with the different laser excitation energies of a samples synthesized at 840^{o}C

XPS:C and B bonding environments



•C1s signal for pure SWNCNTs 284-286 eV

•C1s peak centered in 284.5 eV for B doped SWNTs samples

•Shoulder at 281.5eV (more prominent according to the B neighboring atoms)

Shirasaki et. al.

BC4 →3eV separation

Low doping occurs at lower temperatures!!!

XPS spectra of the carbon C1s binding energy for samples synthesized at 890C and 840C.

P.Ayala, et al. J Mat Chem18(2008)5676

XPS:C and B bonding environments

4 major peaks

• ~191.5-192.1 Substitutional doping (Pachankarla et. al

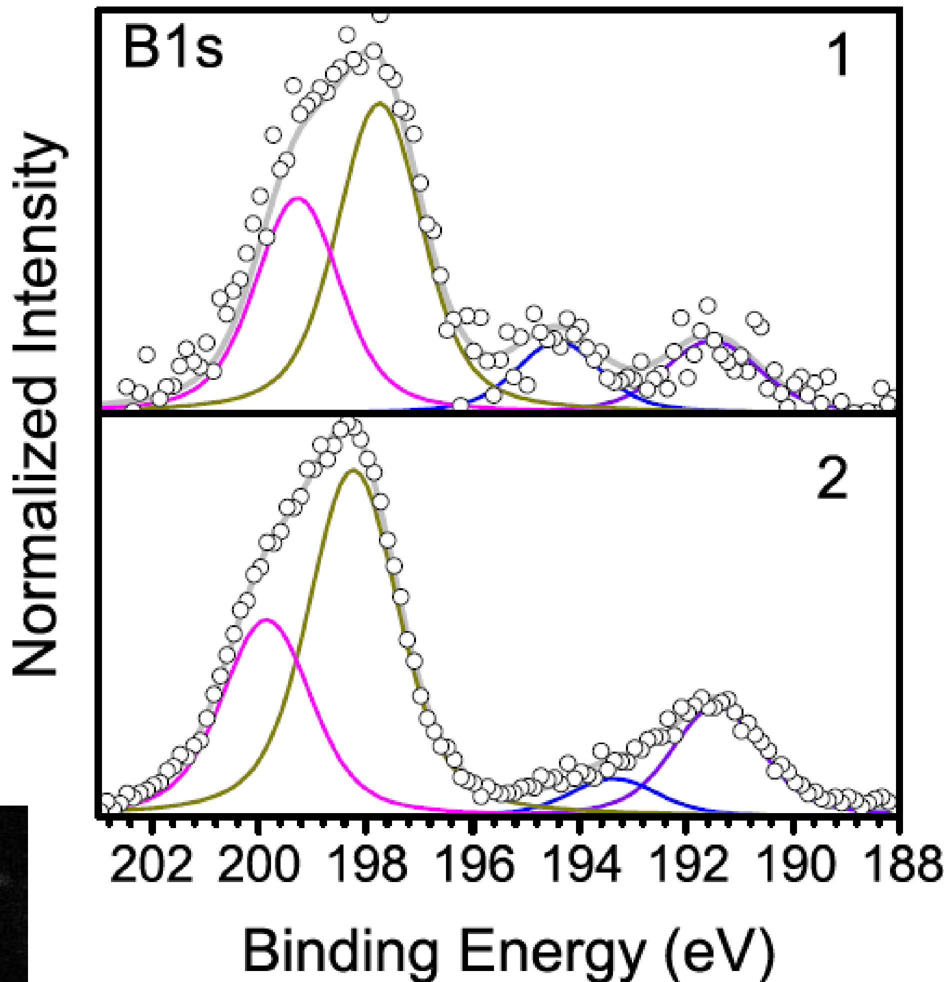
ACSNano, Nov 2007)

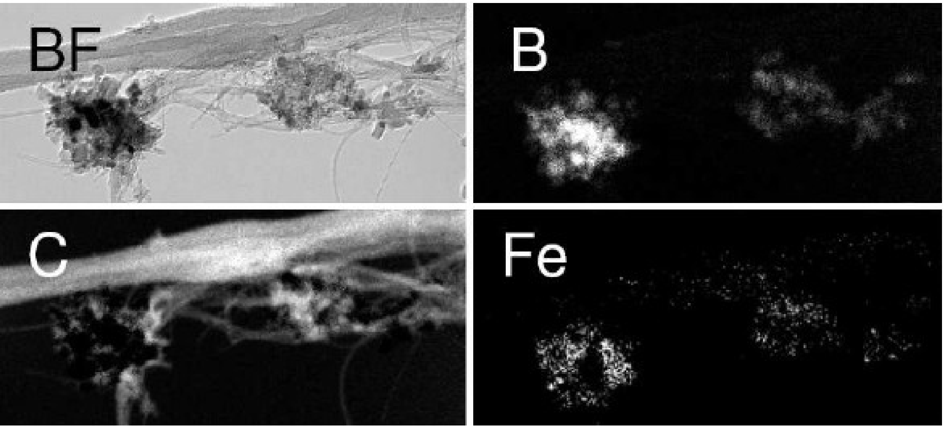
• ~193 Oxide formation

•Major signals

198eV and 199,5ev

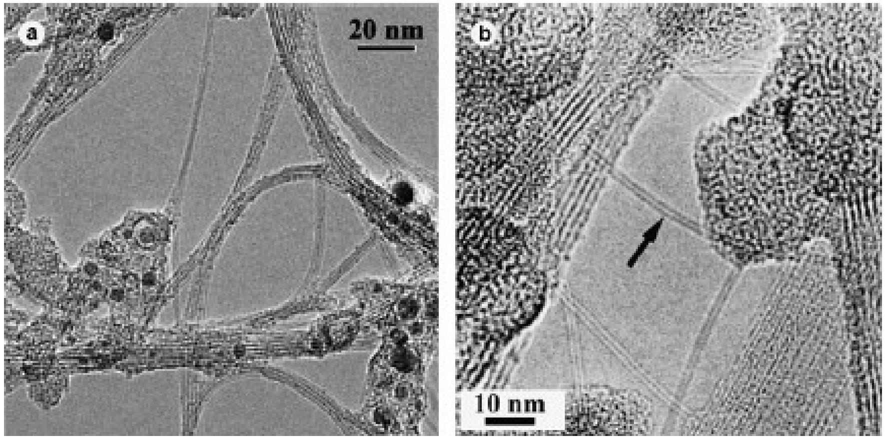
B/Fe containing compounds???

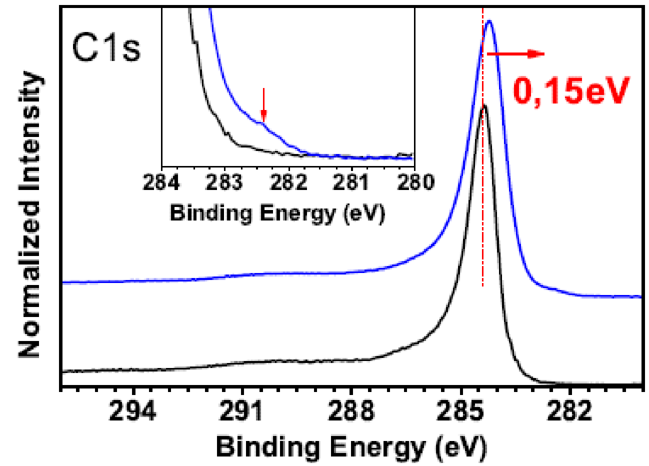




P.Ayala, et al. J Mat Chem18(2008)5676

B-doped SWCNTs with narrow diameter distribution

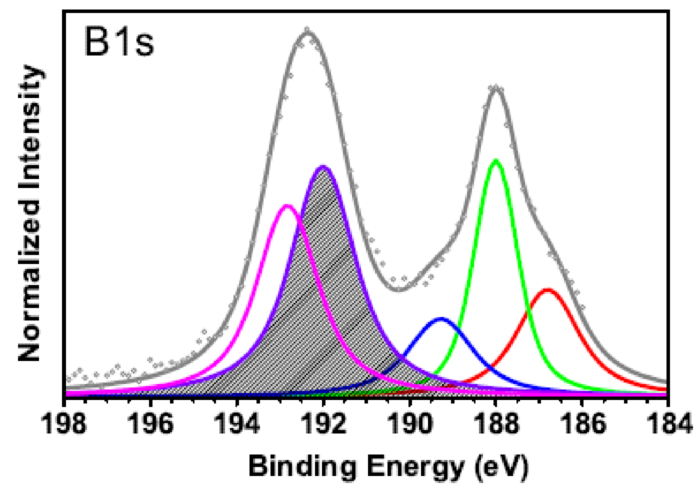




Laser ablation B-doped nanotubes. Micrographs correspond to material produced from targets with nominal boron concentrations of (a) 0at.%, (b) 2.5at.%.

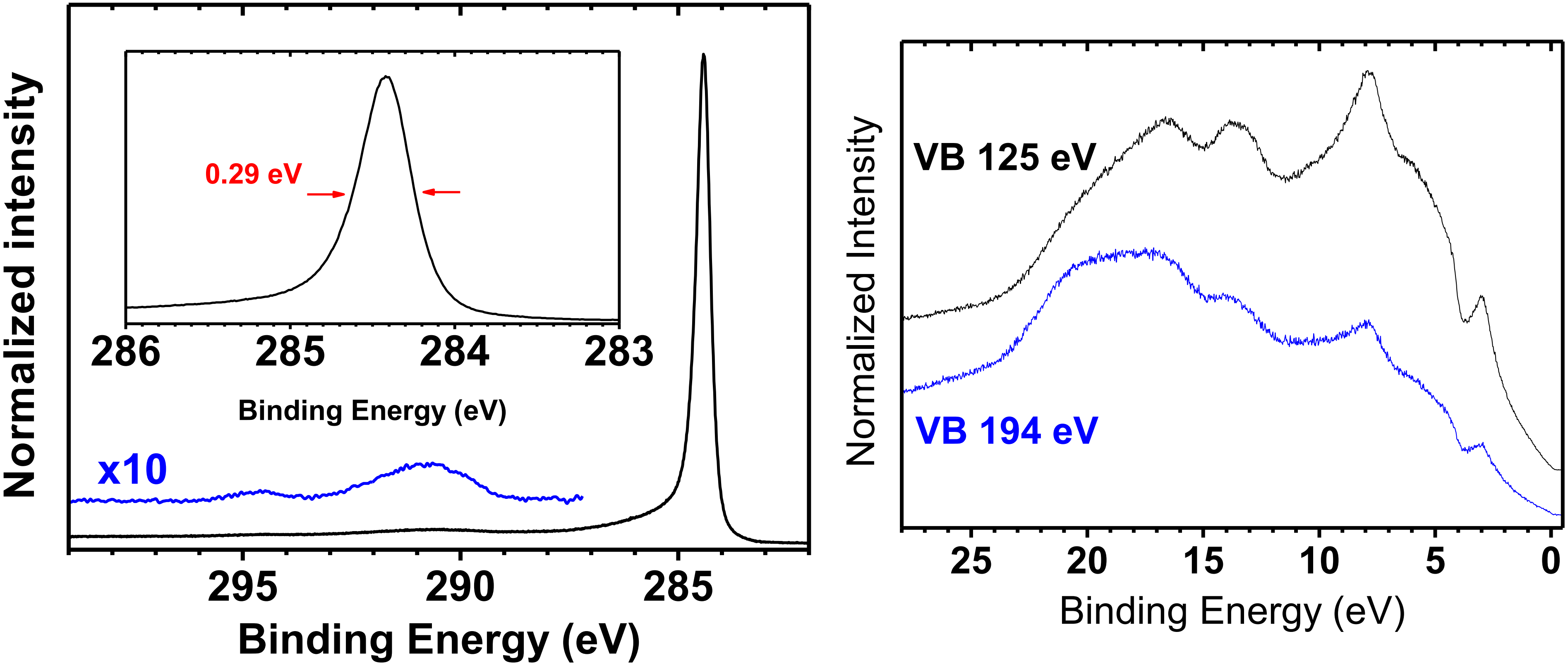
From McGuire et al. Carbon 43(2005) 219.

A. Rao (Clemson University)



P. Ayala et al.
Applied Physics Letters 96 (2010) 18311

Ultra low doping in B-doped SWCNTs



Ultra low doping in B-doped SWCNTs

C1s:

Overall shape

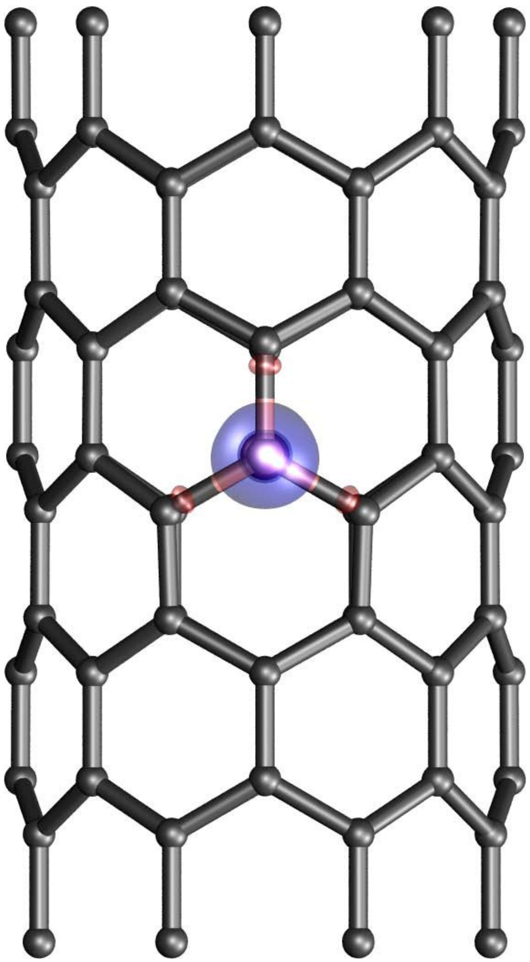
- ***π* resonance at 285.4 eV***

σ* threshold at 291.7 eV

B1s :

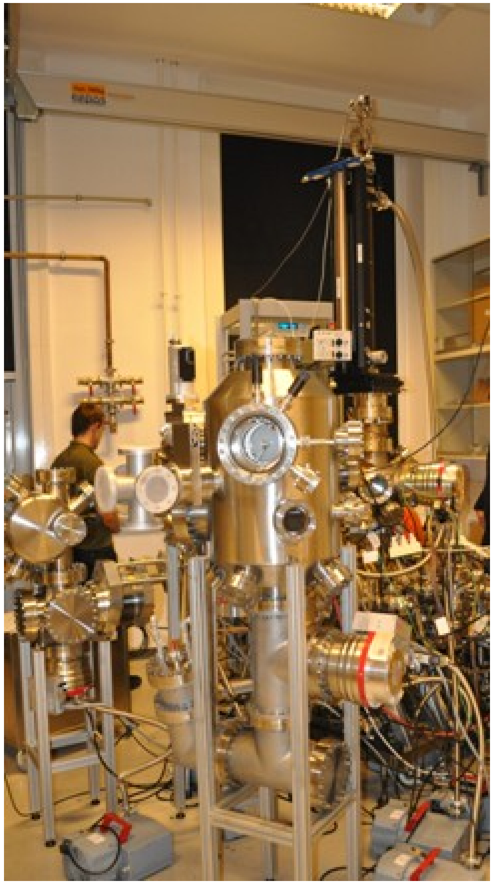
•First identification of heteroatoms in doped purified SWCNTs.

•Boron atomic concentration 0.0005% at.



D.Mowbray, **P.Ayala, T. Pichler, A. Rubio, Materials Express, 1(3) (2011) 225** universität wien

A one-of-its-kind multifunctional spectrometer which includes high resolution photoemission (with XPS and ARPES) has been developed in the group. It is coupled to a multifrequency Raman and a broad range optical (1meV-6eV) setup, including preparation chambers with low temperature (He cryostats) and doping cells for in-situ doping.



Summarizing B and N doped CNTs

- Fesibility to use a pure feedstocks kept at room temperature to produce high quality doped SW nanotubes.
- Pure C/N feedstock, however C to N ratio of source is not reachable.
- Cleanliness of the system is crucial.
- Base pressure influences sample quality
- In absence of N gaseous forms, sp^2 and pyridine compete
- Doping at very low levels (<0.5%)
- Characterize efficiently low doping levels

Techniques Implementation!!!!!

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