Tailoring the electronic properties of low-dimensional carbon hybrids

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universität wien

epm

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OUTLINE

- Introduction/Motivation/Experimental/Applications
- Part 1: Electronic structure of 1D nanostructures:
  Single walled carbon nanotubes (SWCNT):

  a) Pristine SWCNT: nature of the metallic ground state
  b) Electronics and optics with functionalized SWCNT:
  Intercalation, substitution/attachment and filling
- Part 2: Electronic structure of 2D nanostructures:
  Graphene systems:

  a) Graphite revisited: A Key to Graphene and SWCNT
  b) GIC KC_8 revisited: A key to Graphene
  c) Graphane, n-doped graphane: Tuneable gap, acceptor level
  d) Electron dispersion, electron phonon coupling
- Summary and outlook

TODAY

- Introduction/Motivation/Experimental/Applications
- Part 1: Electronic structure of 1D nanostructures:
  Single walled carbon nanotubes (SWCNT):

  a) Pristine SWCNT: nature of the metallic ground state
  b) Electronics and optics with functionalized SWCNT:
  Intercalation, substitution/attachment and filling

Low dimensional quantum solids?

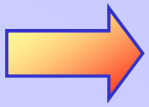
- All solids are of course quantum systems
- 1D and 2D quantum solids:

  - Mesoscopic systems with size quantization

  - Quantum effects already at room temperature

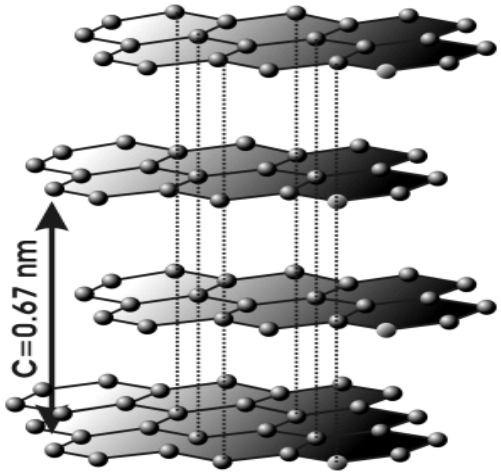
  - Correlation effects crucial:
    electron-hole, electron-electron, electron-phonon

  - Instabilities in 1D and 2D systems!



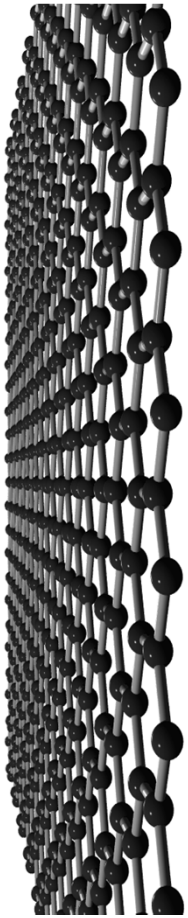
Molecular carbon nanostructures are
archetypical examples of perfect 1D and 2D solids

Dimensionality of sp^2 bonded carbon allotropes

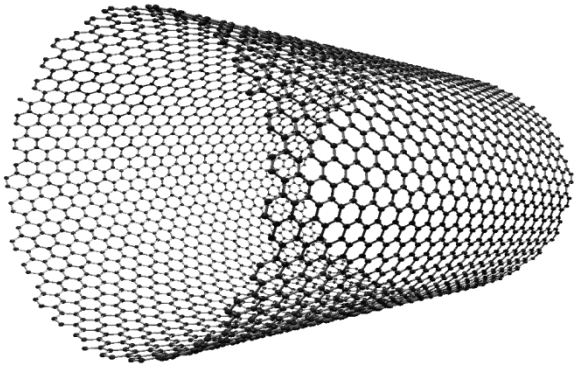


Graphite,
Mittelalter

3D

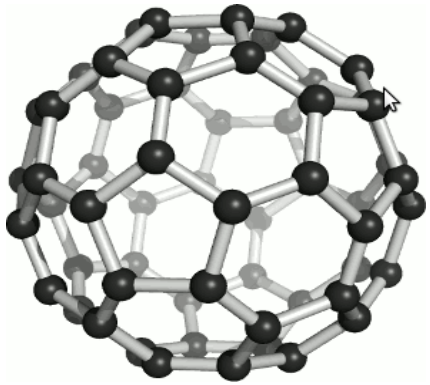


Graphene
2D



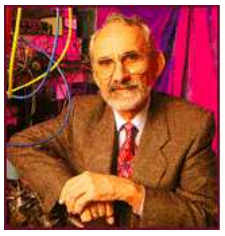
Carbon
nanotubes
Iijima, 1991

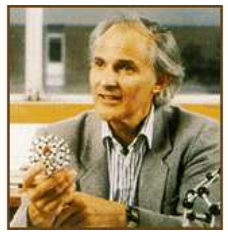
1D

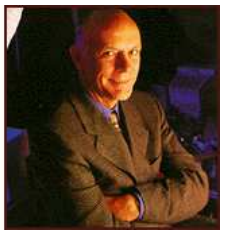


Fullerene
0D

A. Geim, K. Novoselov, 2004
Nobel prize physics, 2010

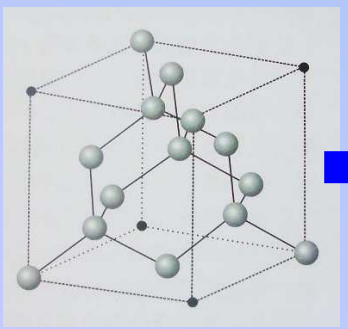




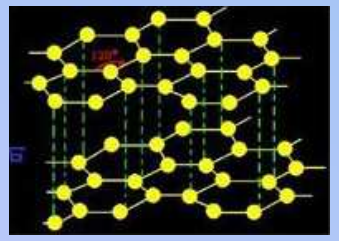


R. Curl, H. Kroto, R. Smalley, 1985
Nobel prize chemistry, 1996

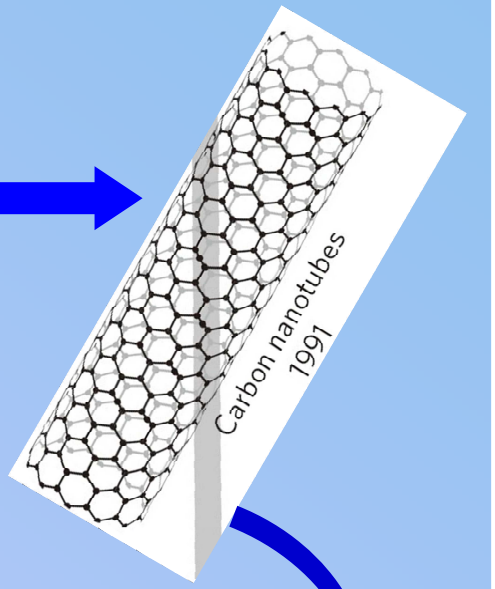
But also .....

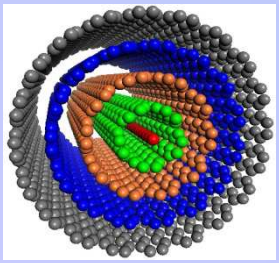


Diamond



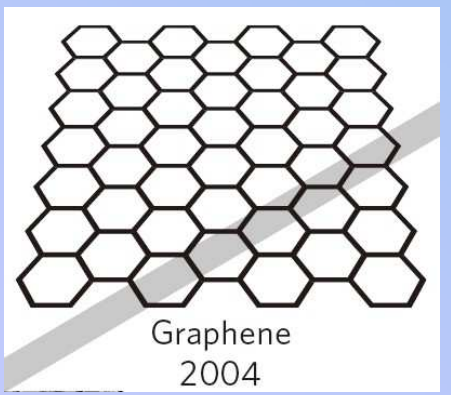
Graphite

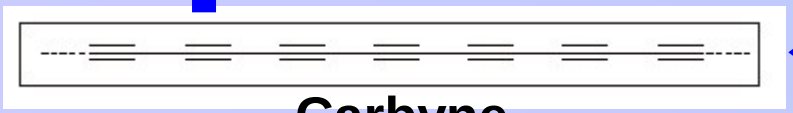




Carbon nanowire

more?





Carbyne

A. Hirsch et al. Nature Materials 9, 868 (2010)

Motivation: Why all carbon nanostructures?

- **Advantages of carbon:**

1. cheap, light

2. structural properties: hard, stiff, flexible, ductile,….

3. biocompatible

4. electronic properties:

insulating ⇨ semiconducting ⇨ semimetallic ⇨ metallic
zero gap semiconductor

diamond	fullerenes, nanotubes	graphite, graphene	nanotubes

⇨ Tunable by functionalisation

Special properties of nanotubes

- Electronic propertieres:

  Geometry of SWCNT : 2/3 are semiconducting 1/3 metallic
  conductivity tunable by functionalisation

  Temendous current carrying capacity: 1 billion A/cm^2
  no electromigration

  Excellent heat conductor: twice as good as diamond

- Mechanical properties:

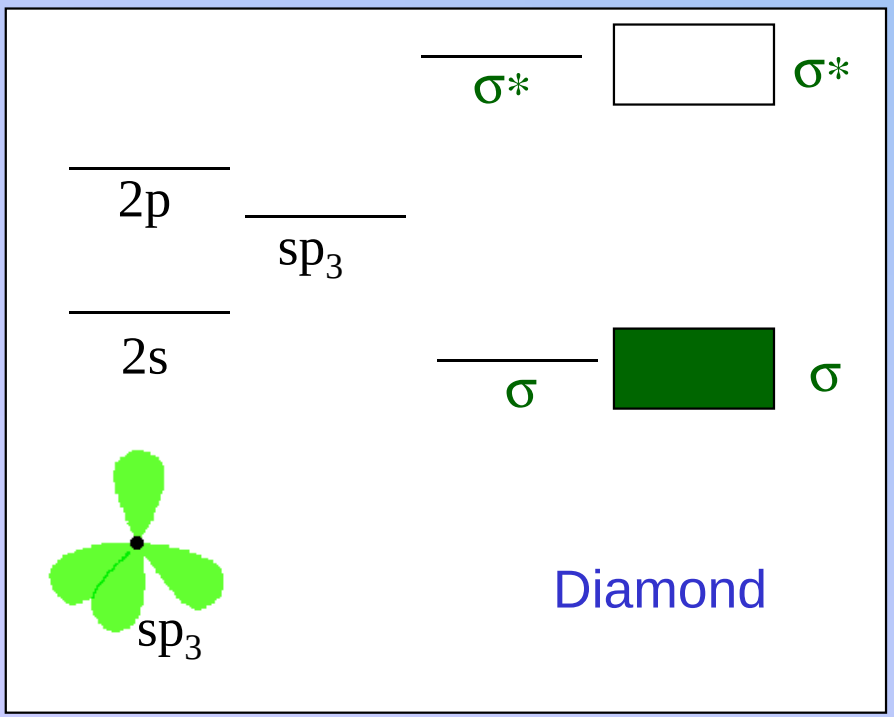
  Strength at least 100 times higher than steel
  Youngs modulus 1 Tpa
  Flexible ⇒ ultimate carbon fibers

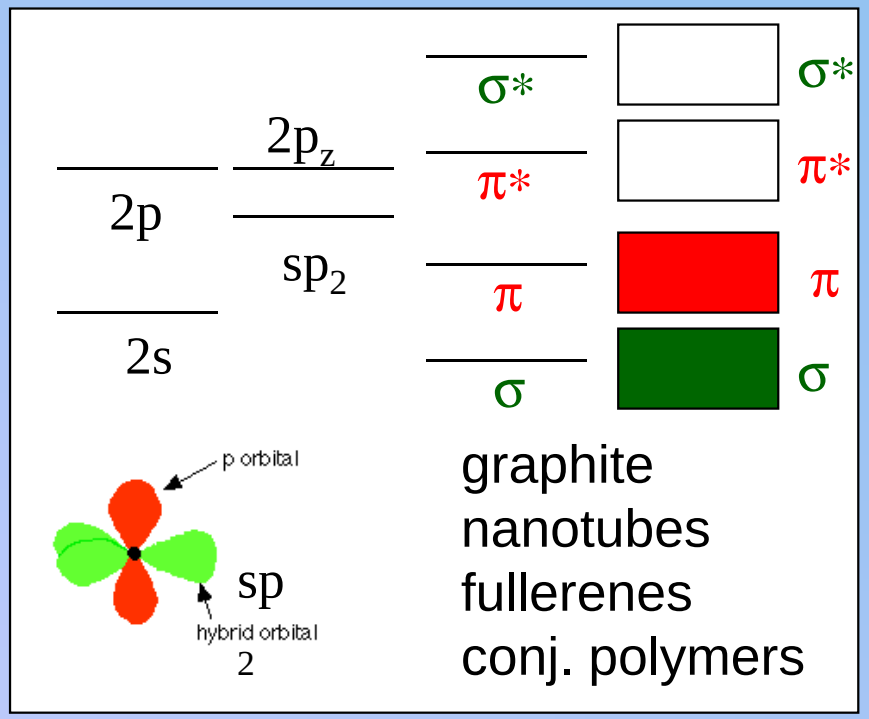
- Geometry:

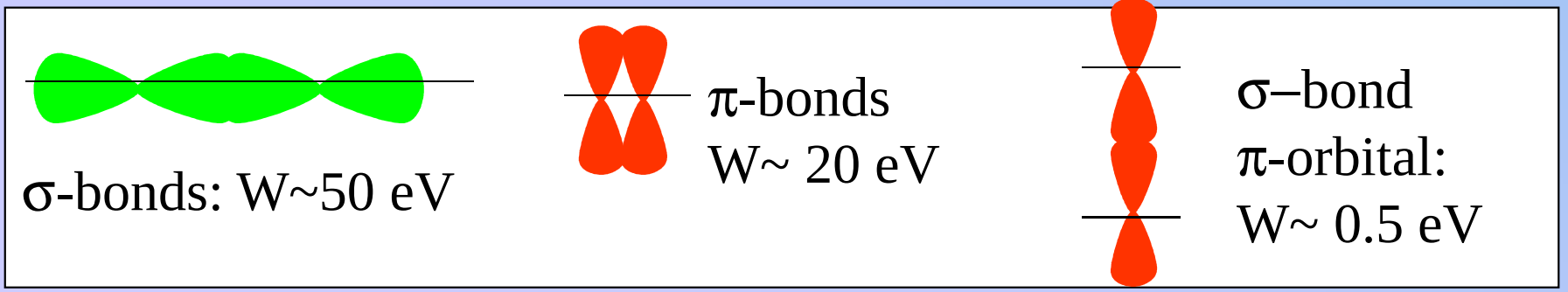
  High aspect ratio of 1000 to 10000, 1 nm diameter
  High surface area

Electronic structure of different carbon allotropes

Two 1s core electrons and 4 valence electrons (two 2s and two 2p)

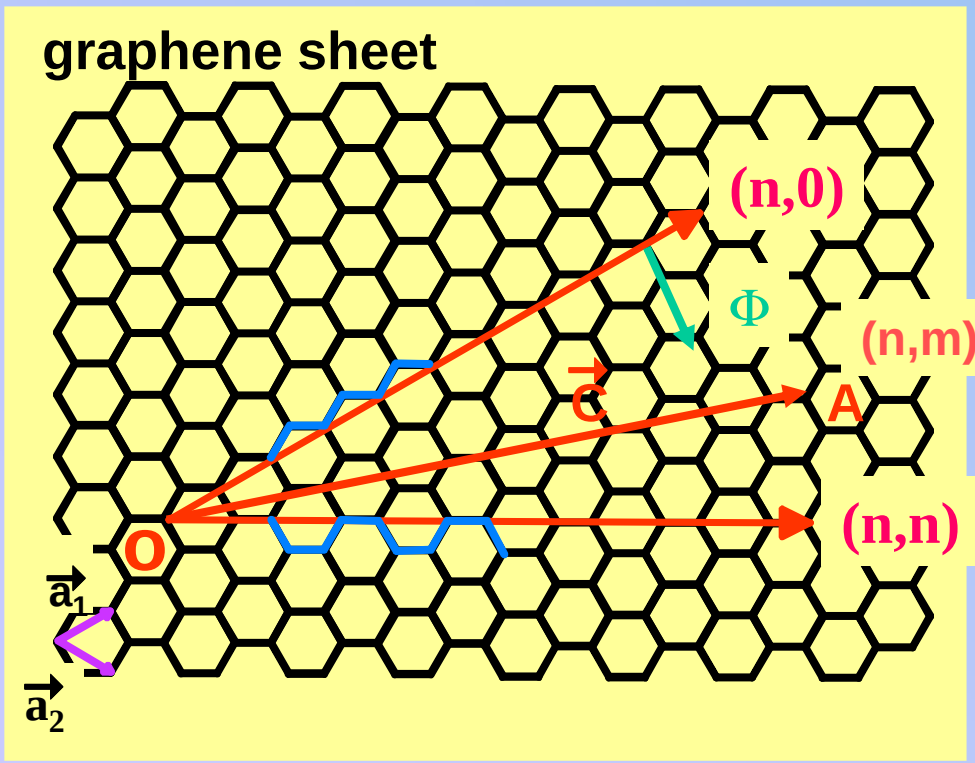


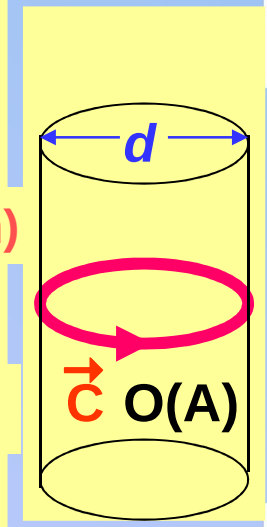


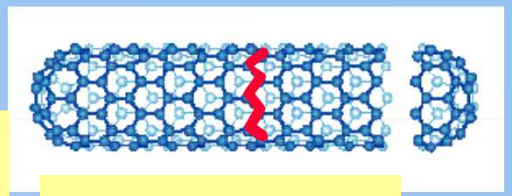


Introduction: formation of single-wall carbon nanotubes

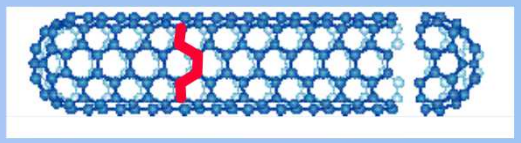
SWCNTs $\vec{C} = n\vec{a}_1 + m\vec{a}_2 = (n,m)$ **Hamada vector**



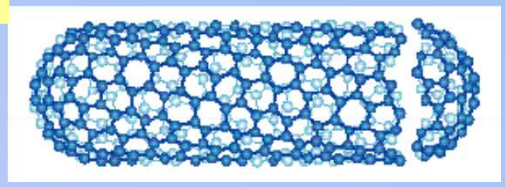




(n,0) zigzag Φ=0



(n,n) armchair Φ=30°



(n,m) chiral 0<Φ<30°

The diameter of SWCNT (n,m):

$d_{n,m}=|C|/\pi=a(n^2+m^2+mn)^{1/2}/\pi$

$a=|a_1|=|a_2|=2.49$ Å

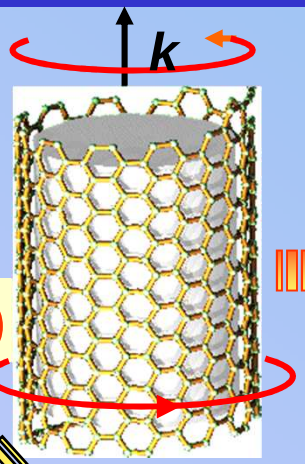
e.g. (10,10) d=1.37nm

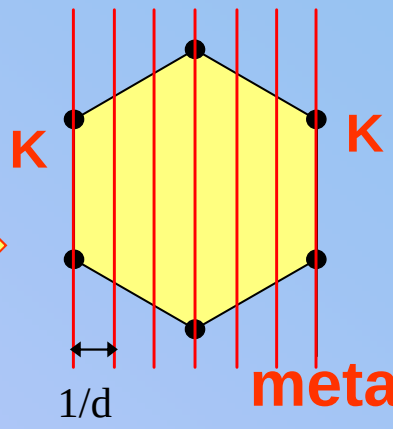
Introduction: electronic properties of SWCNTs

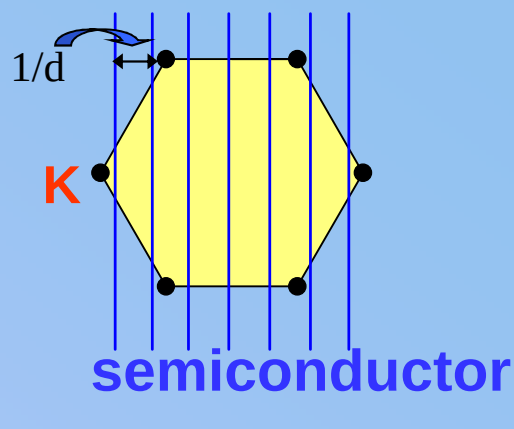
periodic boundaries

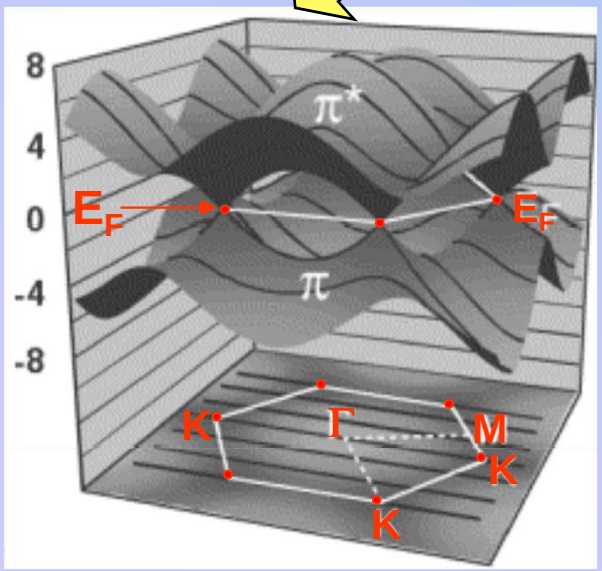
$2\pi d \cdot k_n = 2\pi \cdot n$

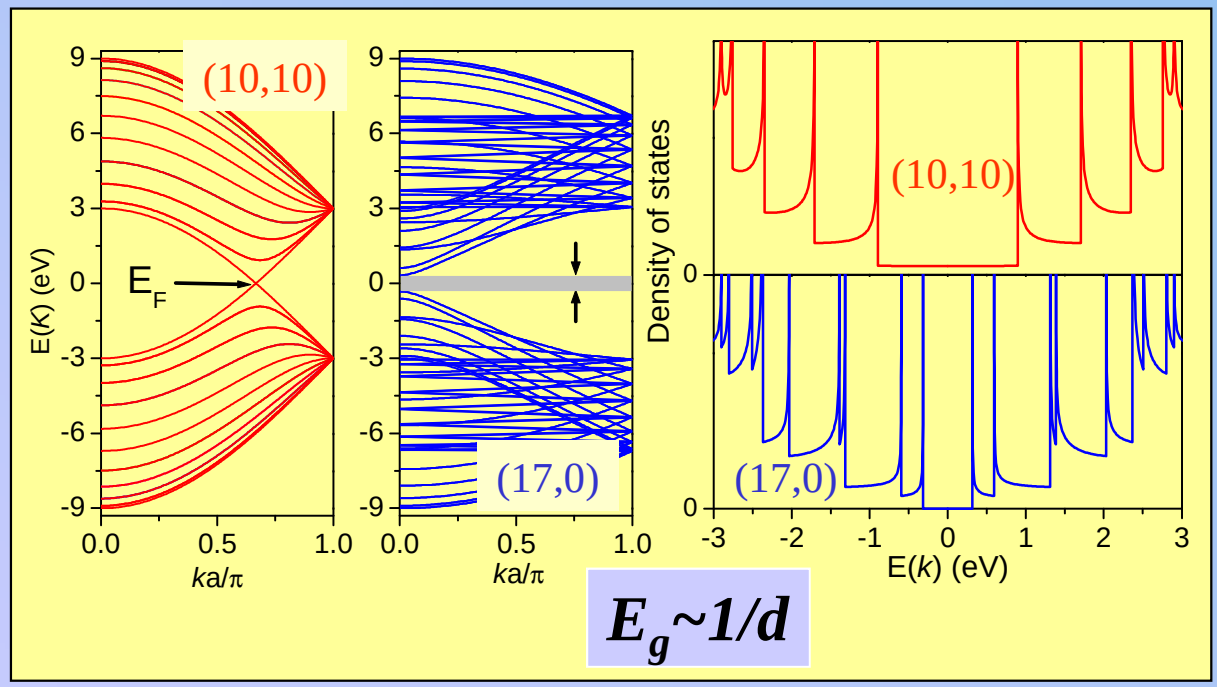
(k_n-quantization)











Electronic properties are determined by the structure of SWCNT

using tight binding approximation

What are we doing on nanotubes ….. ?

Synthesis and purification of SWCNT and DWCNT.
high vacuum CVD!
Electronic/optical properties: EELS, XAS,ARPES,Raman, PL,OAS!
What happens upon functionalization?

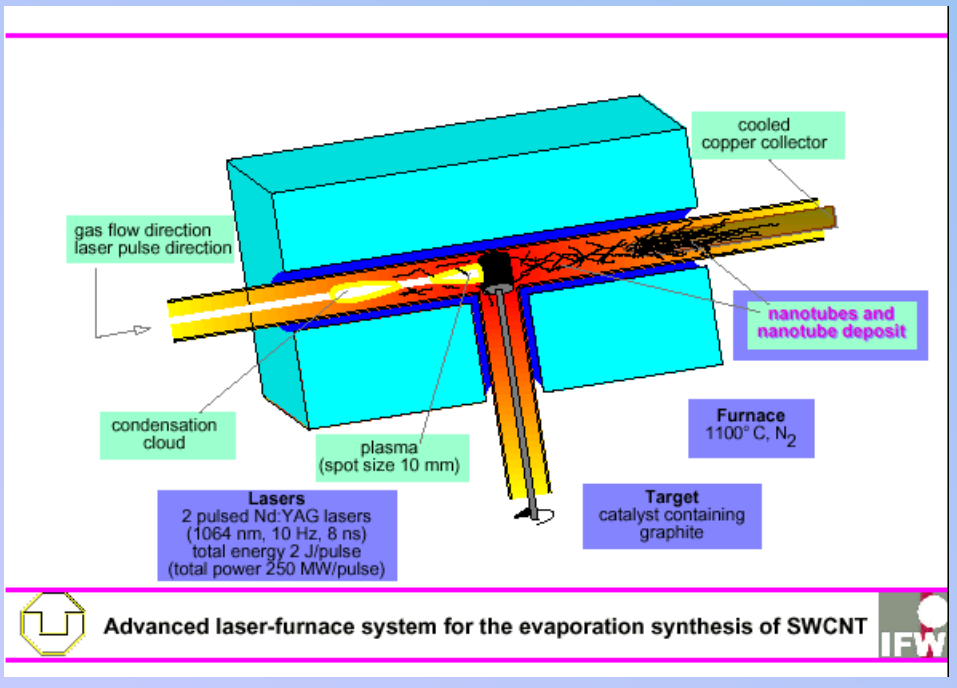
Charge transfer vs. hybridisation: bonding environment, doping level, Fermi level shift and changes in the DOS.

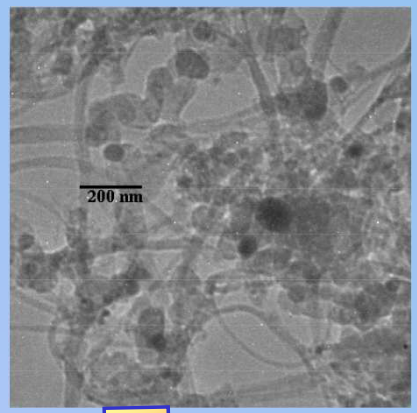
Nature of the metallic ground state:

Normal Fermi liquid or a Tomonaga-Luttinger liquid?
Transition 1D – 3D metal?

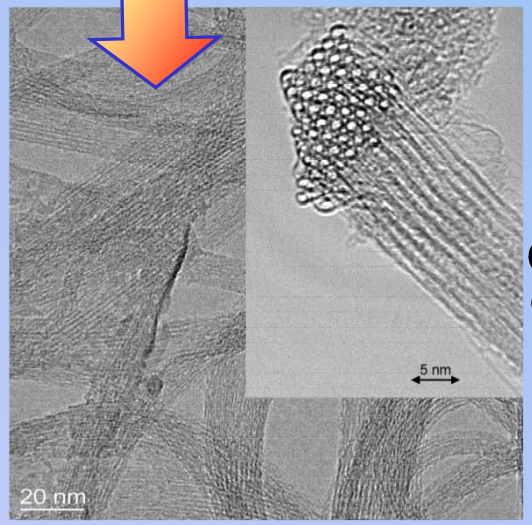
⇨ Electronic structure of functionalized SW(DW)CNT from high energy and optical spectroscopy

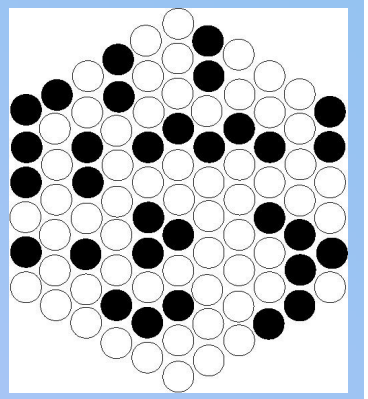
SWCNT from laser ablation/ arc discharge





Purification and opening:
HNO_3, H_2O_2,
Heat treatment





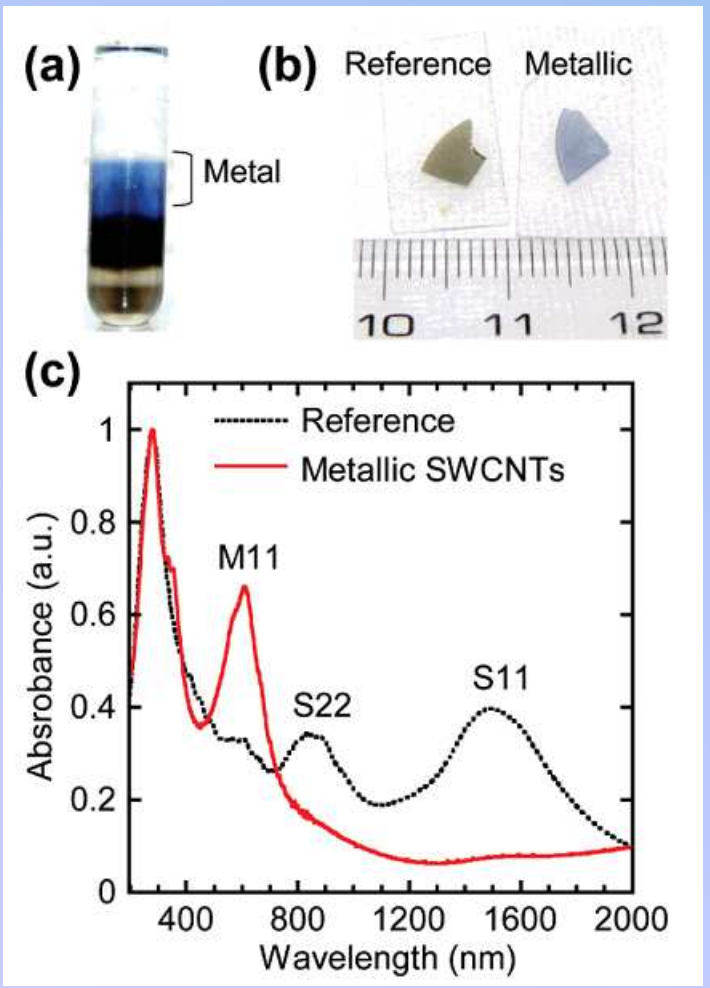
semiconducting
metallic

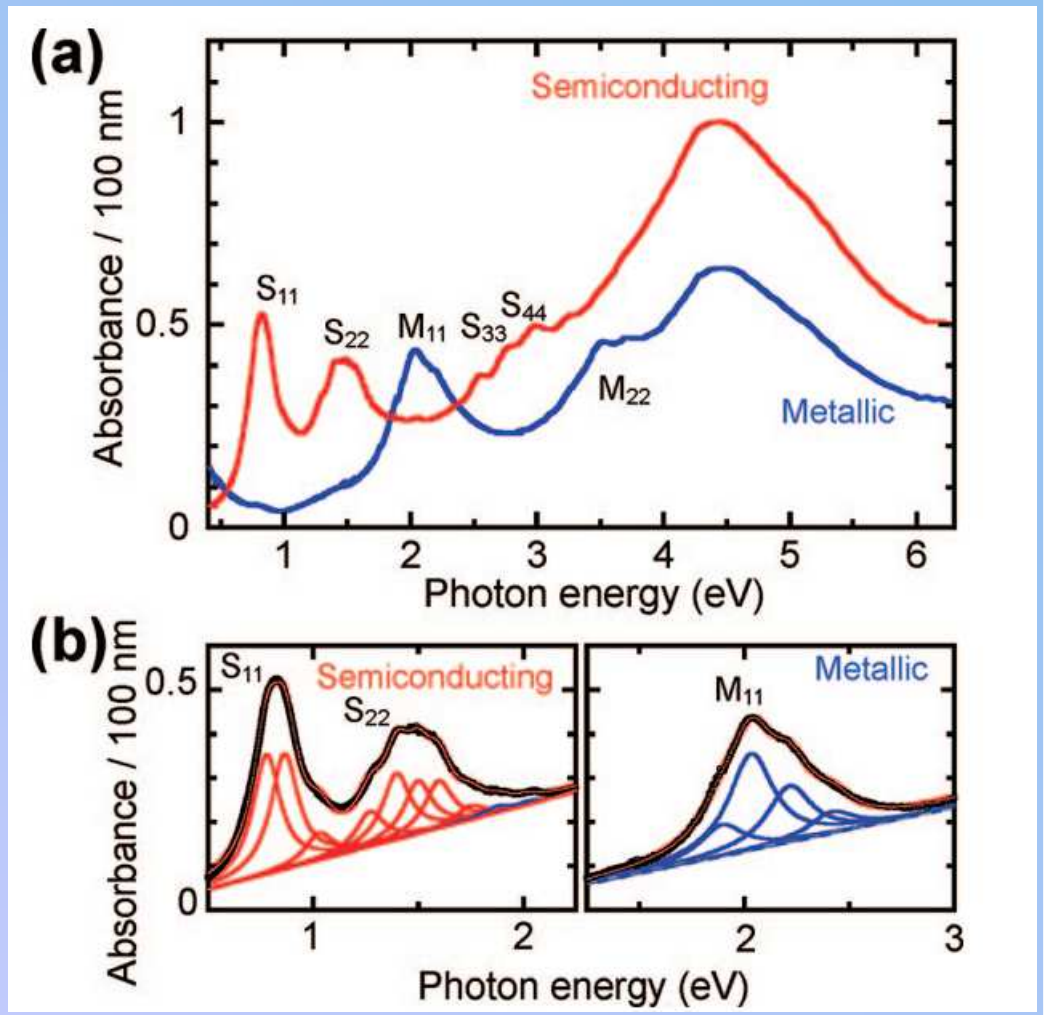
SWCNT yield and diameter distribution vs. T, p, laser pulse, gas, catalyst, …

Optimised: 70 wt% SWCNT, d=1.2-1.4 nm

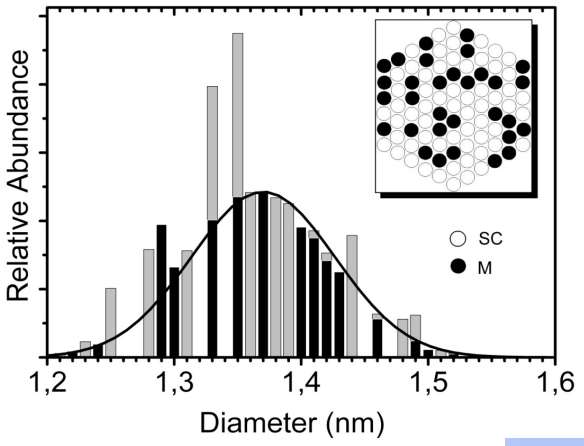
SWCNT with no catalyst and "carbon impurities", d=1.4 +/- 0.12 nm

Optical response of type separated bulk SWCNT

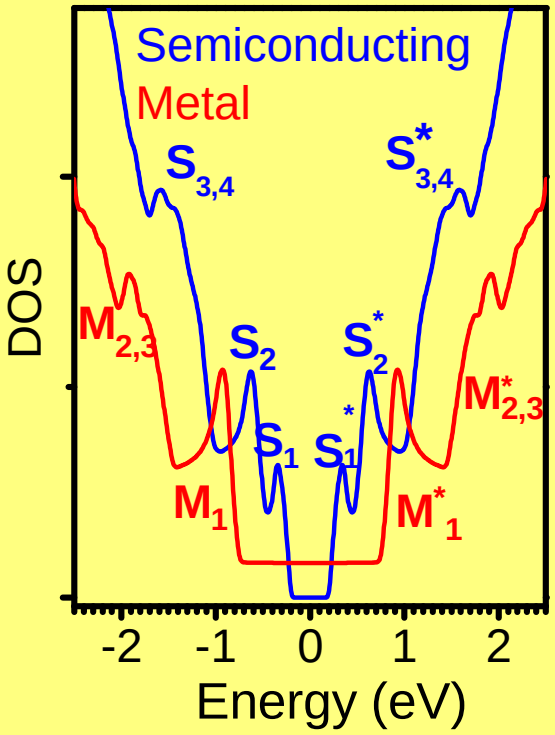


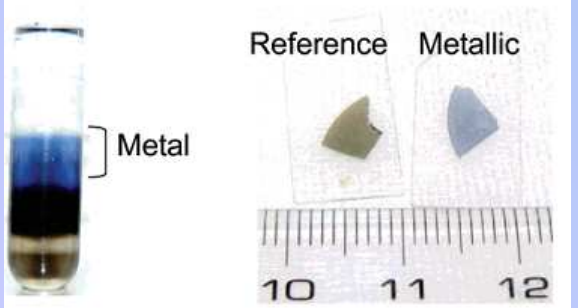


Y. Miyata et al., J. Phys. Chem. C 2008, 112, 3591 (2008)



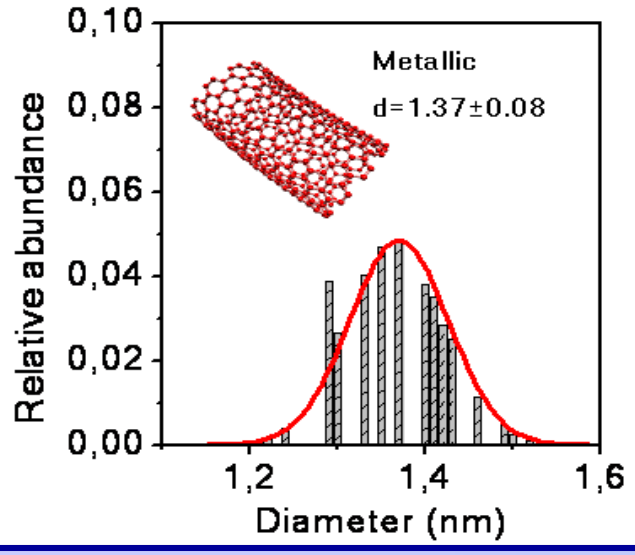
Samples

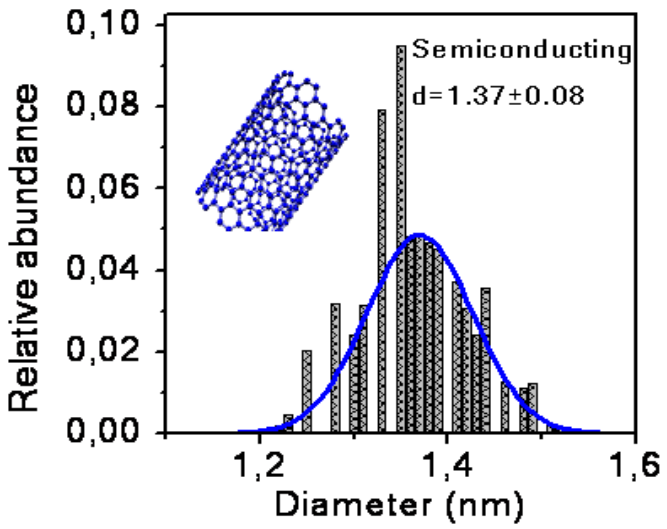




diameter

1.37 ± 0.08nm





Miyata et al.
J Phys. Chem.C 112, 13187 (2008).

Gain from High Energy Spectroscopy

Occupied Density of States

Photoemission Spectroscopy

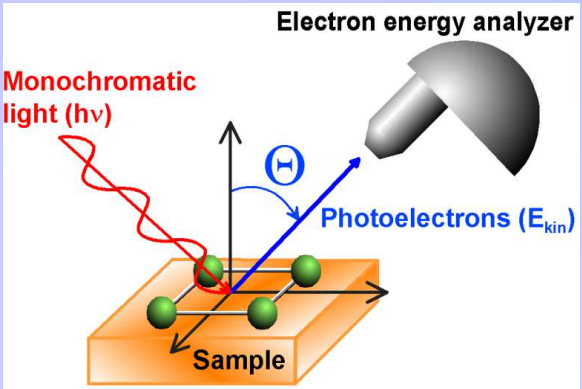
Valence Band

(site selective for RESPES)

Bonding environment

Charge Transfer

Basic Correlation Effects



Unoccupied Density of States

X-ray absorption and EELS

Matrix element weighted DOS

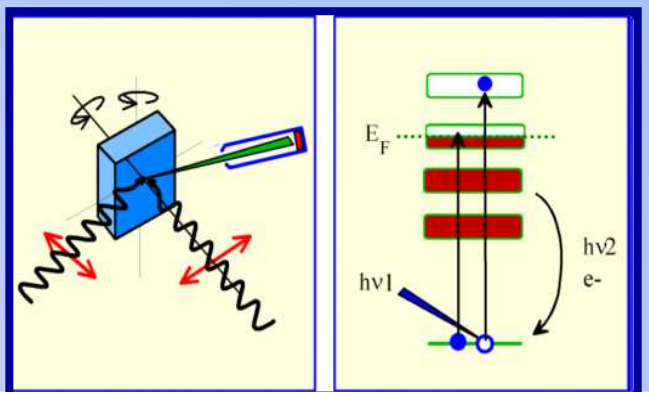
Conduction Band (site selective)

Bonding environment

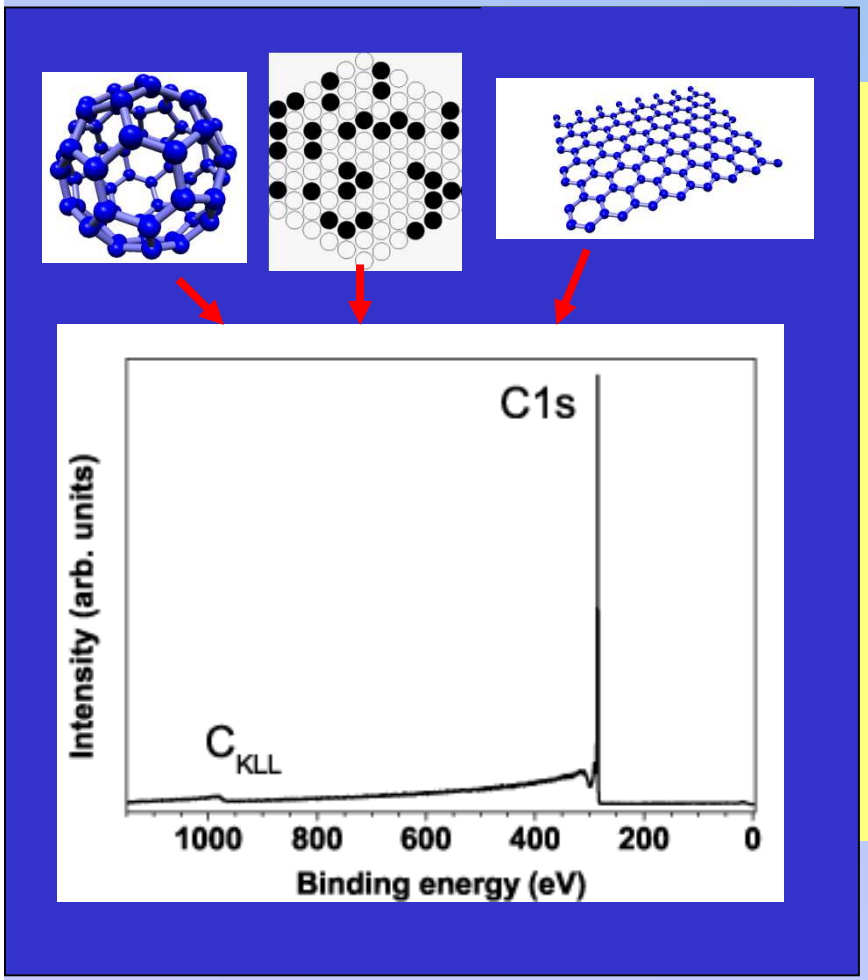
Charge Transfer

Basic Correlation Effects

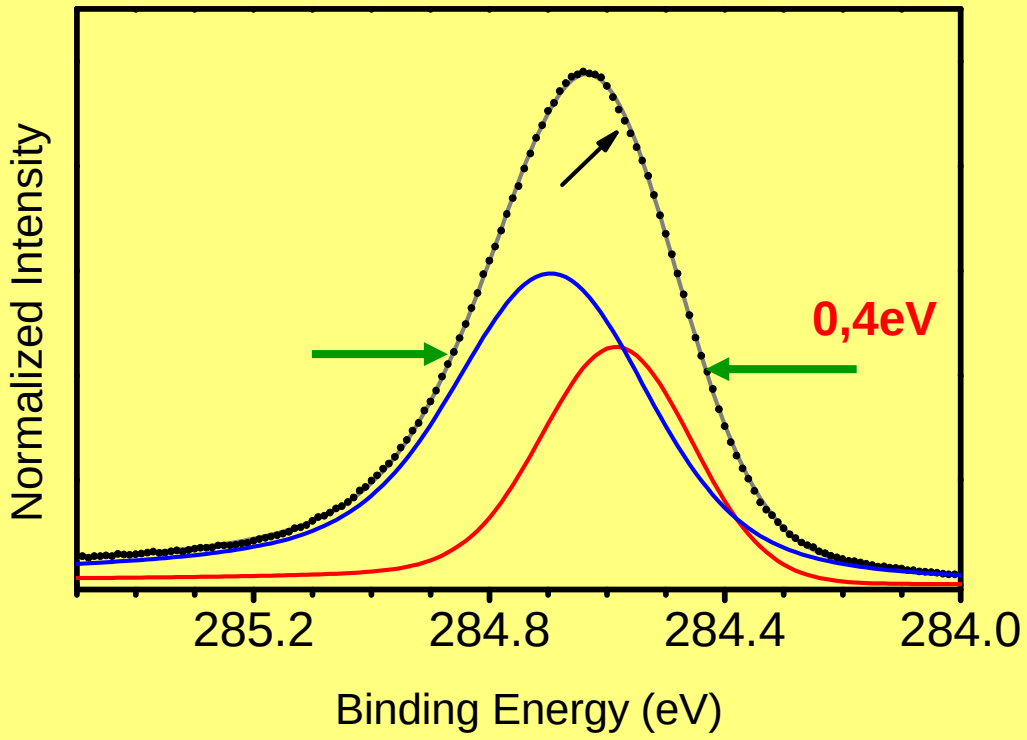
Core Hole Effects!!!



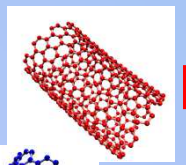
Core Level High resolution XPS



METALLICITY MIXED SWCNT

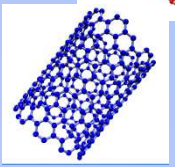


-Doniac-Sunjic lineshape



M

-Voigtian (symetric)



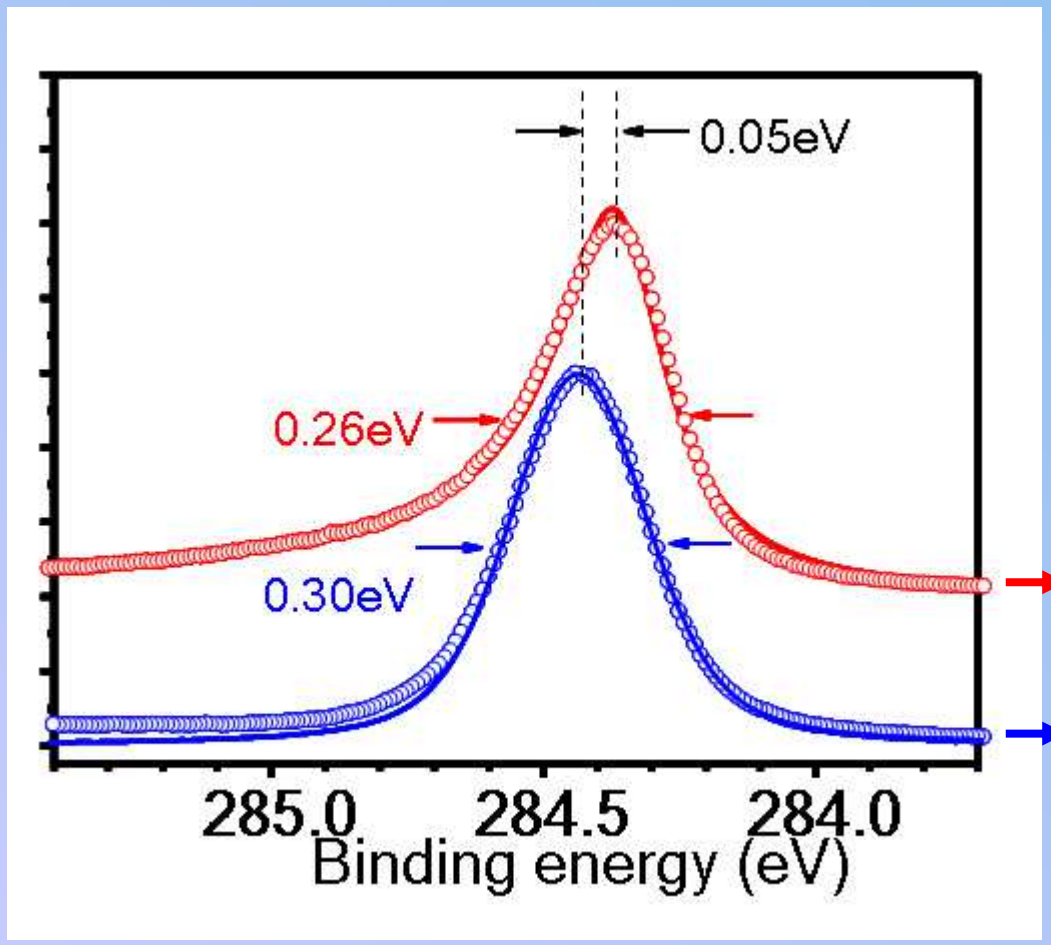
SC

Kramberger et al.
PRB 75 (2007) 235437

High resolution XPS of metallicity sorted SWCNT

Graphite

0,32 eV



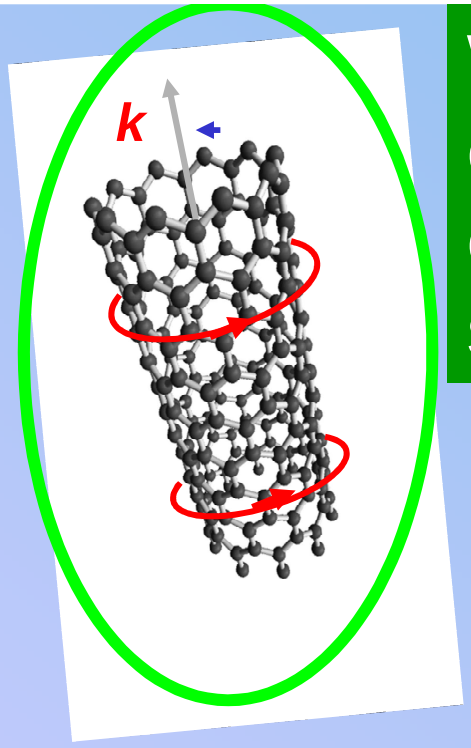
Doniach Sunjic

Voigtian

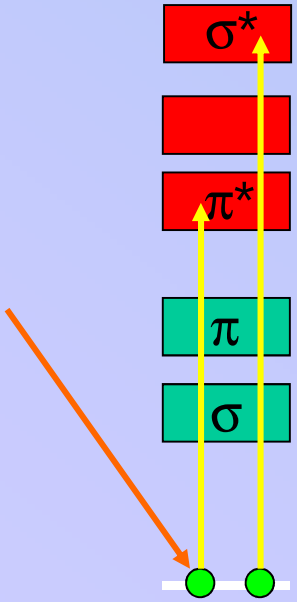
Core hole screening **not** **visibly affected in metallic samples**

Work functions: different in bulk metallic SWCNTs sample

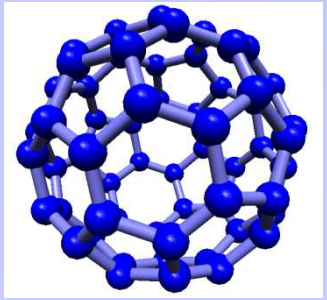
P.Ayala et. al. PRB 80 (2009) 205427

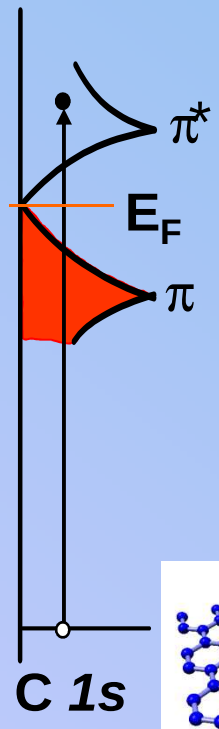


What is the electronic behavior of the 1 D system??

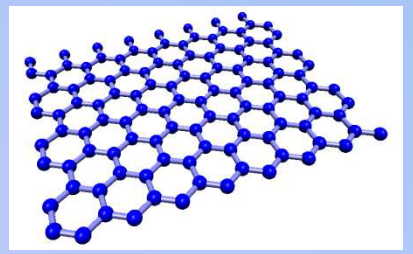


0 D



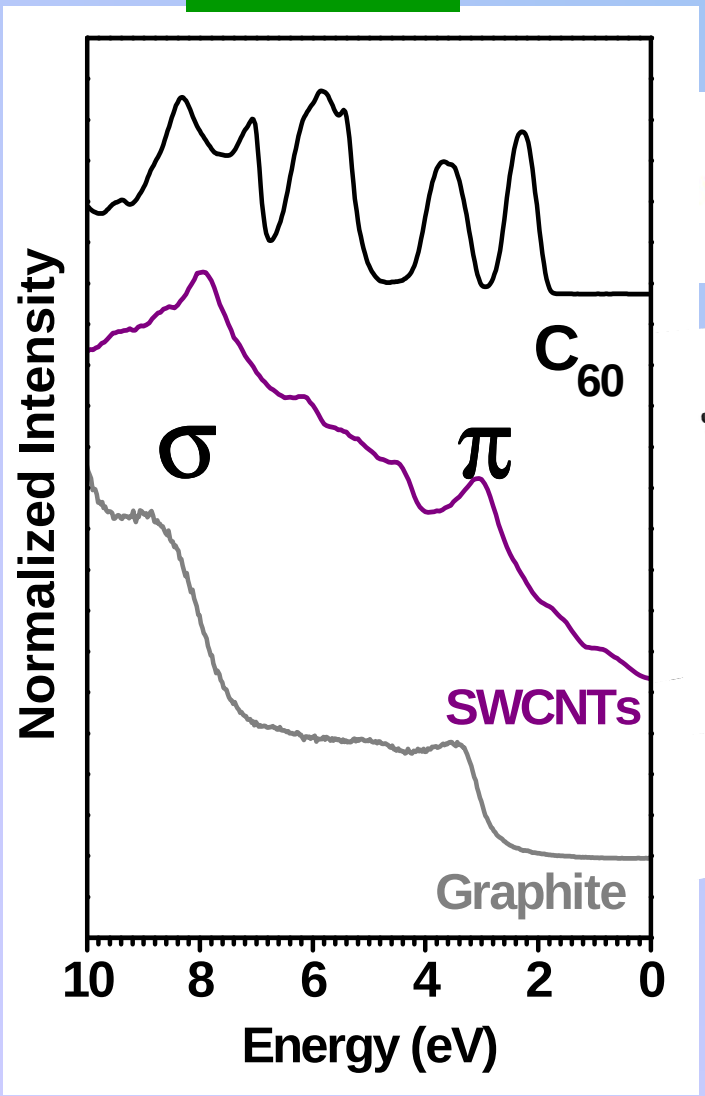


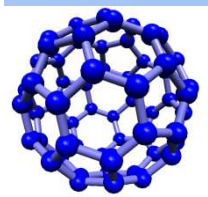
2 D



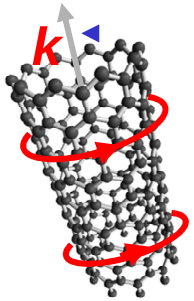
High Energy Spectroscopy studies on sp^2 –hybridized C structures

VB-PES

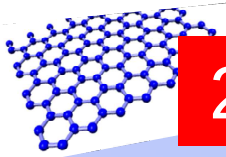




0 D



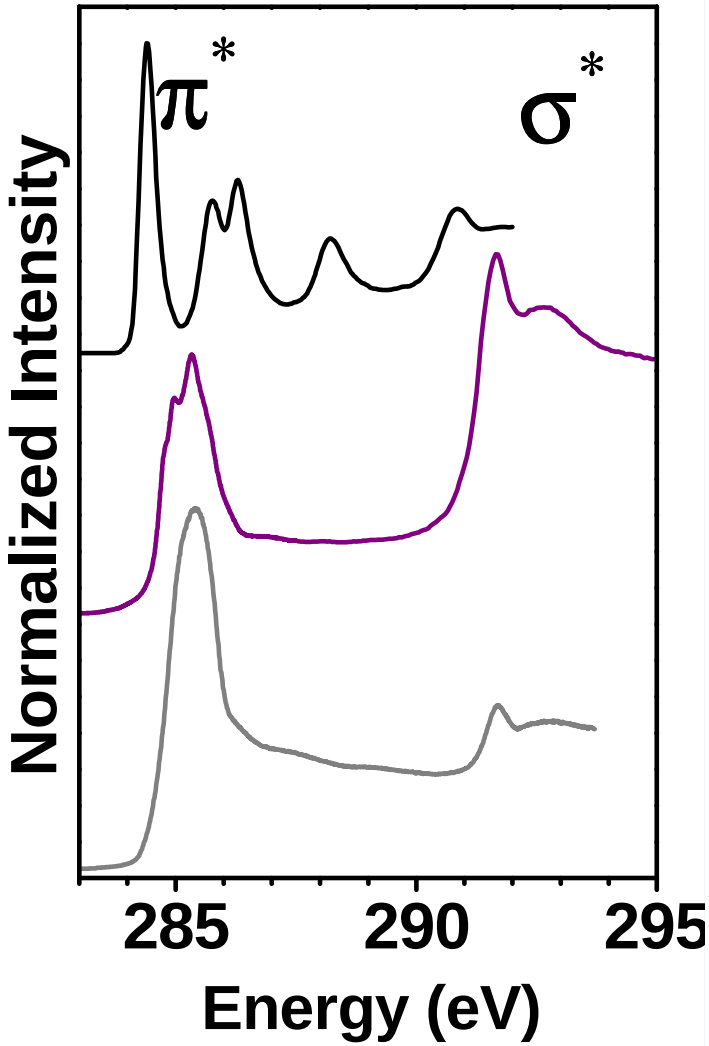
1 D



2 D

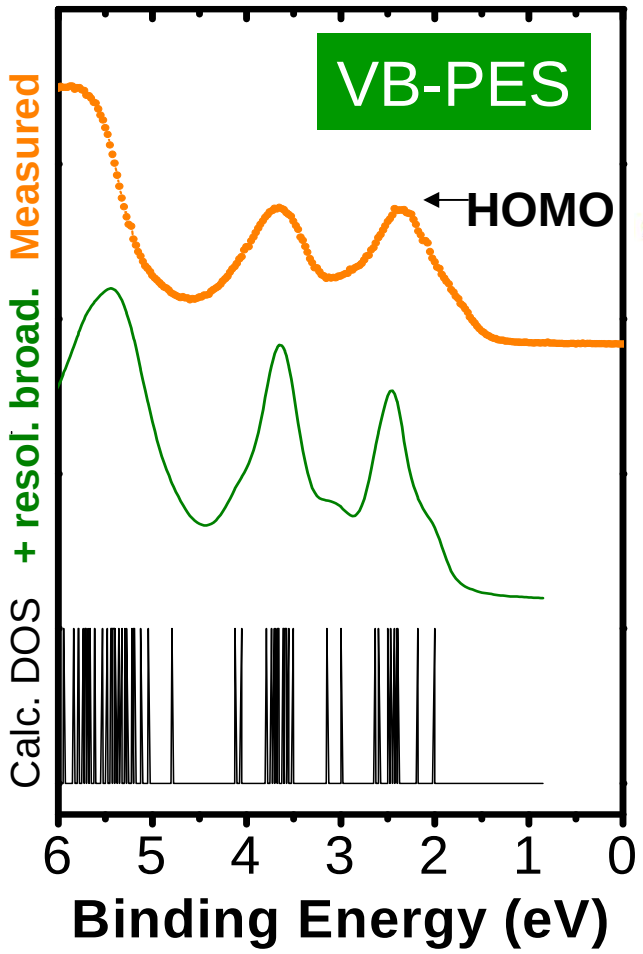
Matrix element weighted DOS of the valence band

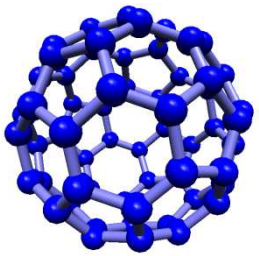
Conduction Band-XAS



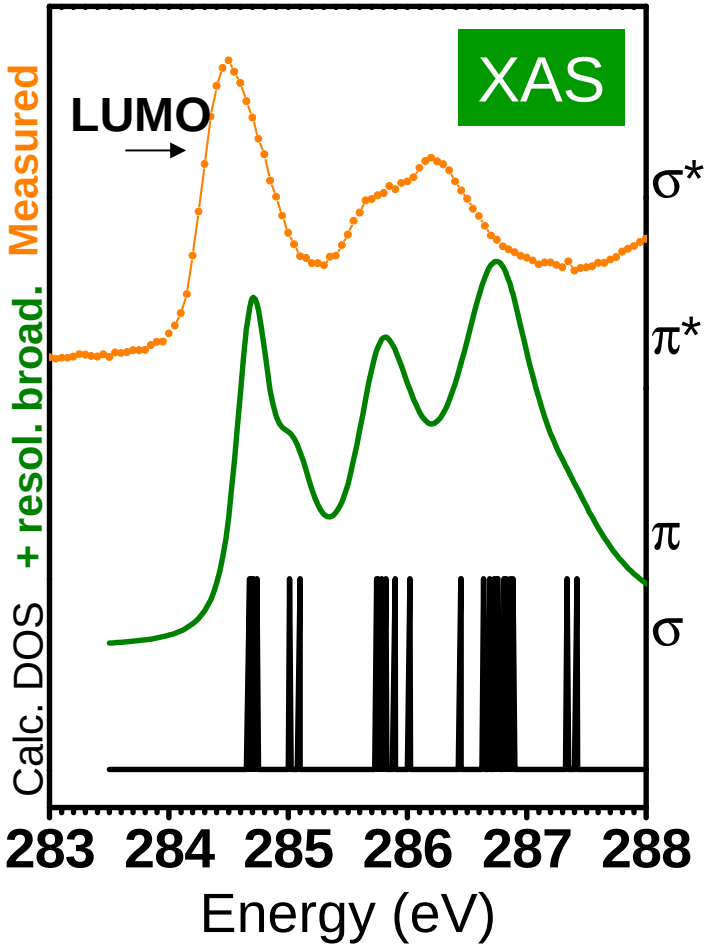
Site selective weighted projected DOS of the conduction band

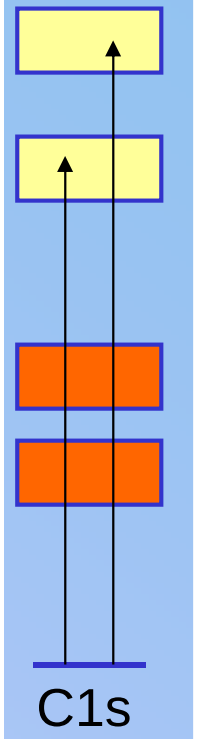
Quasi „0D“: Fullerenes





0D

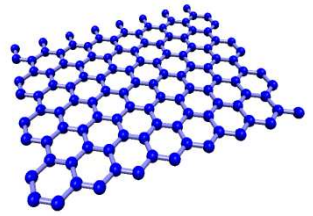




Quantum Chemical calculations of molecular orbitals match experimental DOS → small core hole effects in XAS

T.Pichler et al. PRL 78(1997) 4249

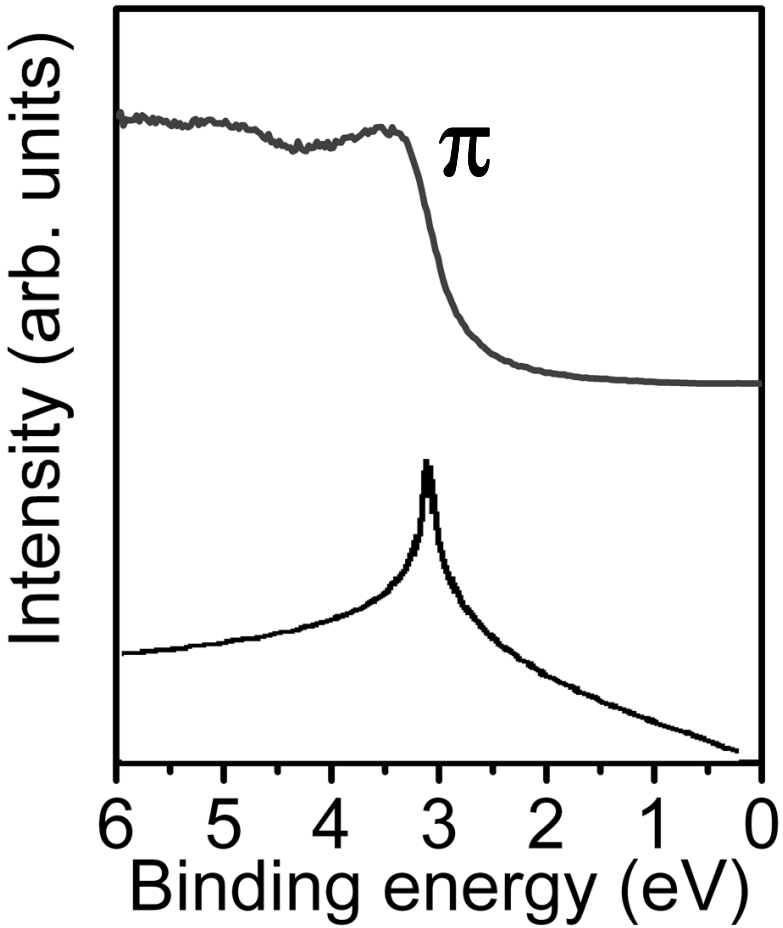
2D: Graphite-Graphene



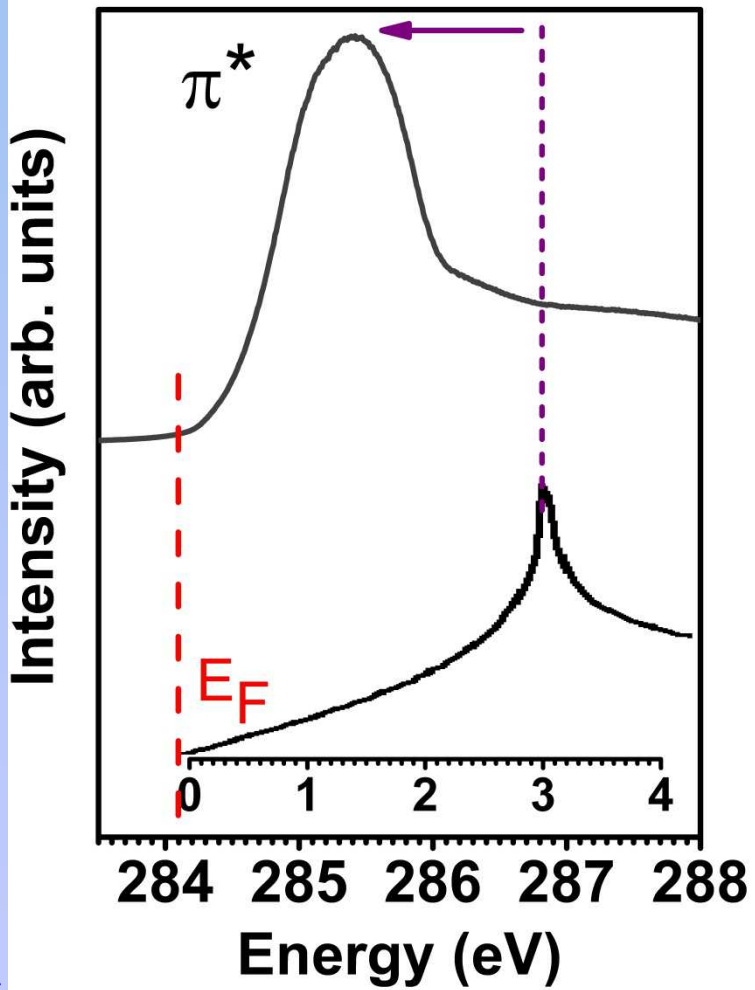
VB-PES

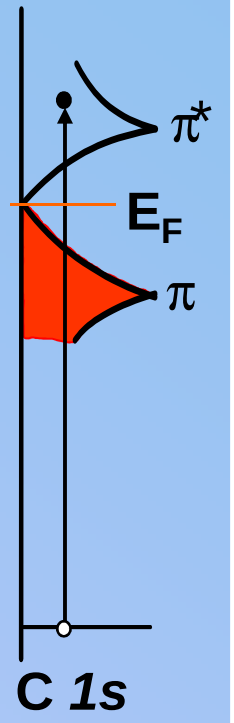
2D

XAS



TB-DOS of the valence band matches experimental DOS

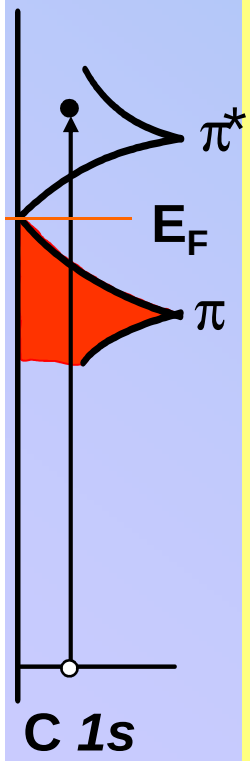


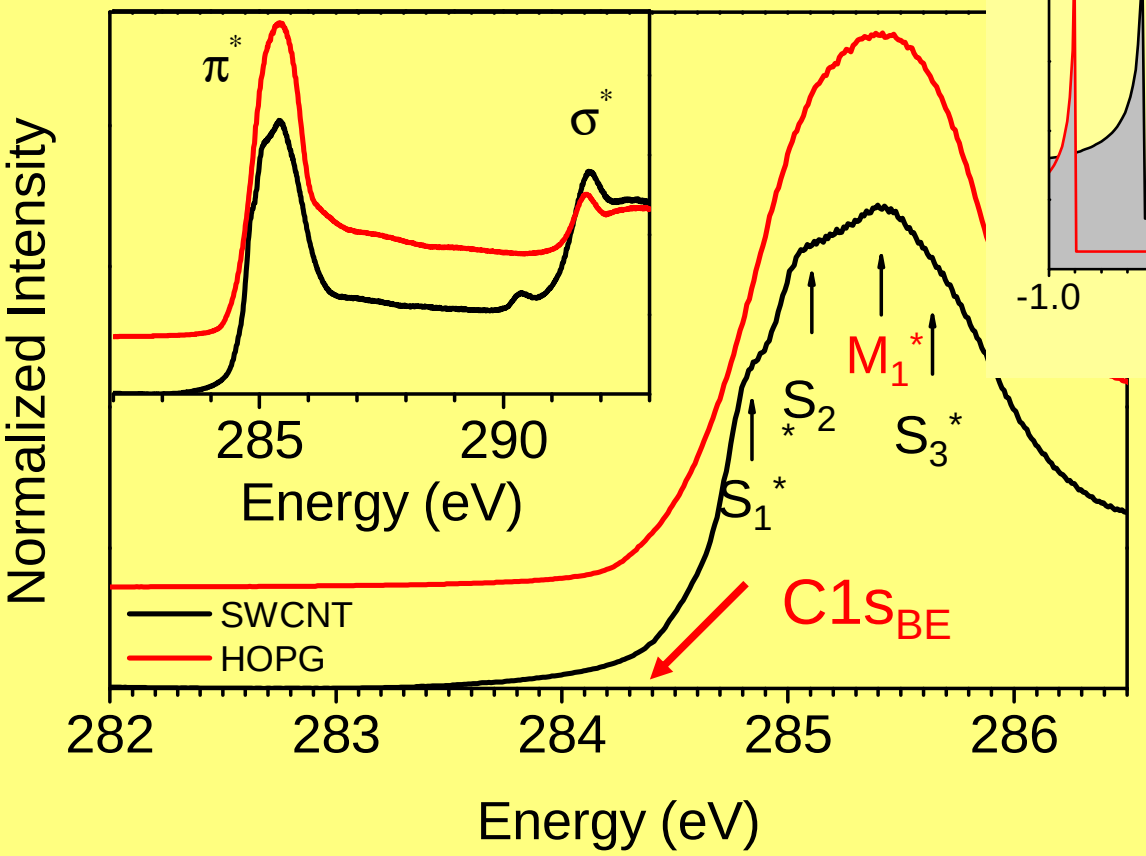


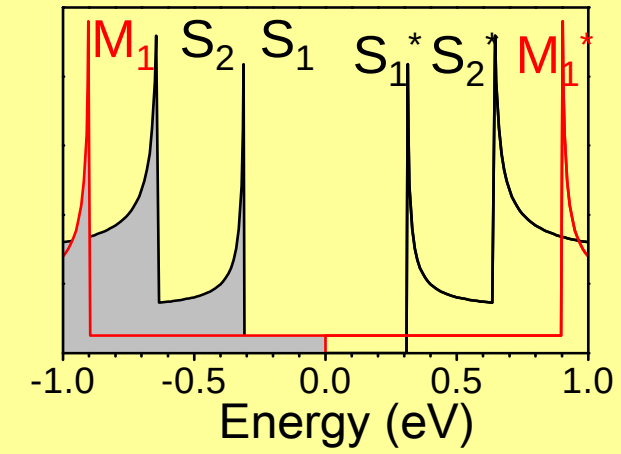
Bruhwiler et al.PRL 76 (1996)1761

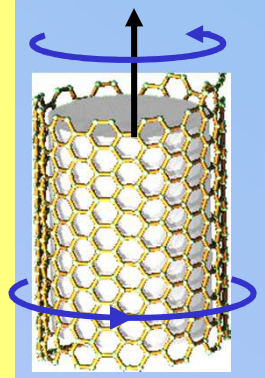
But: strong core hole effects in XAS of the conduction band

XAS: Conduction band of metallicity mixed SWCNT bundles









vHS

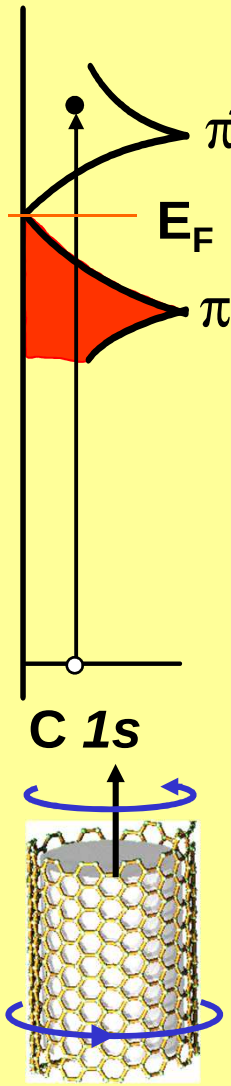
Site selective weighted projected DOS of the conduction band

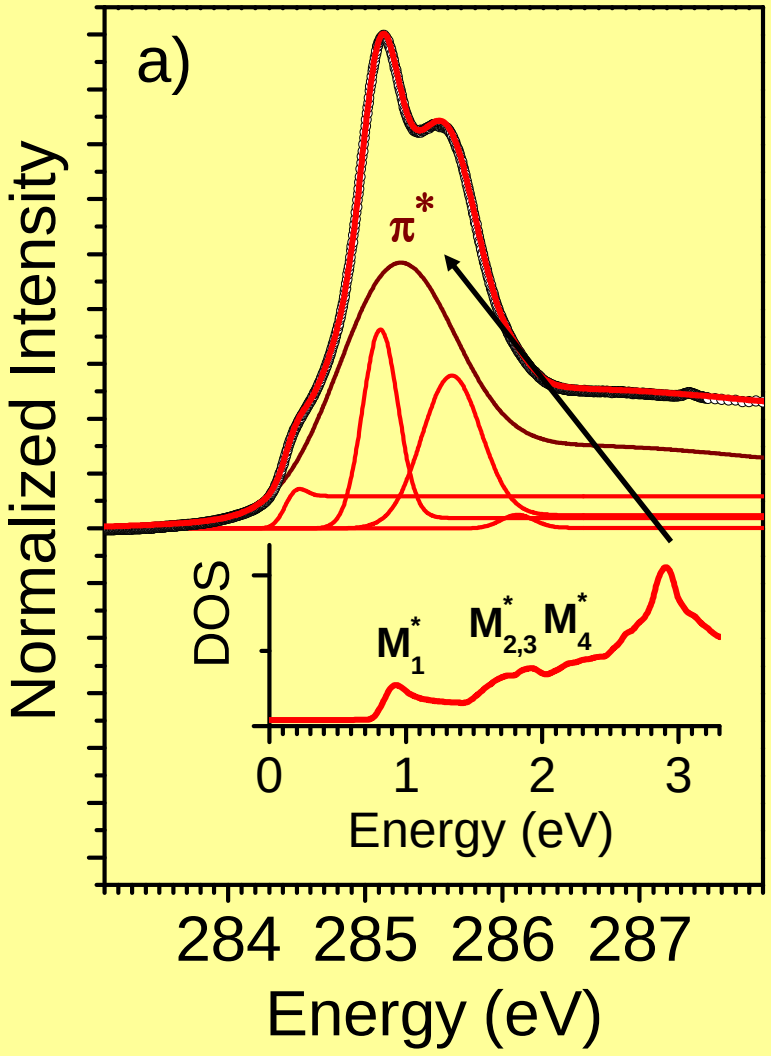
Fine structure in π* resonance: S_1*,S_2*, S_3*, and M_1*.

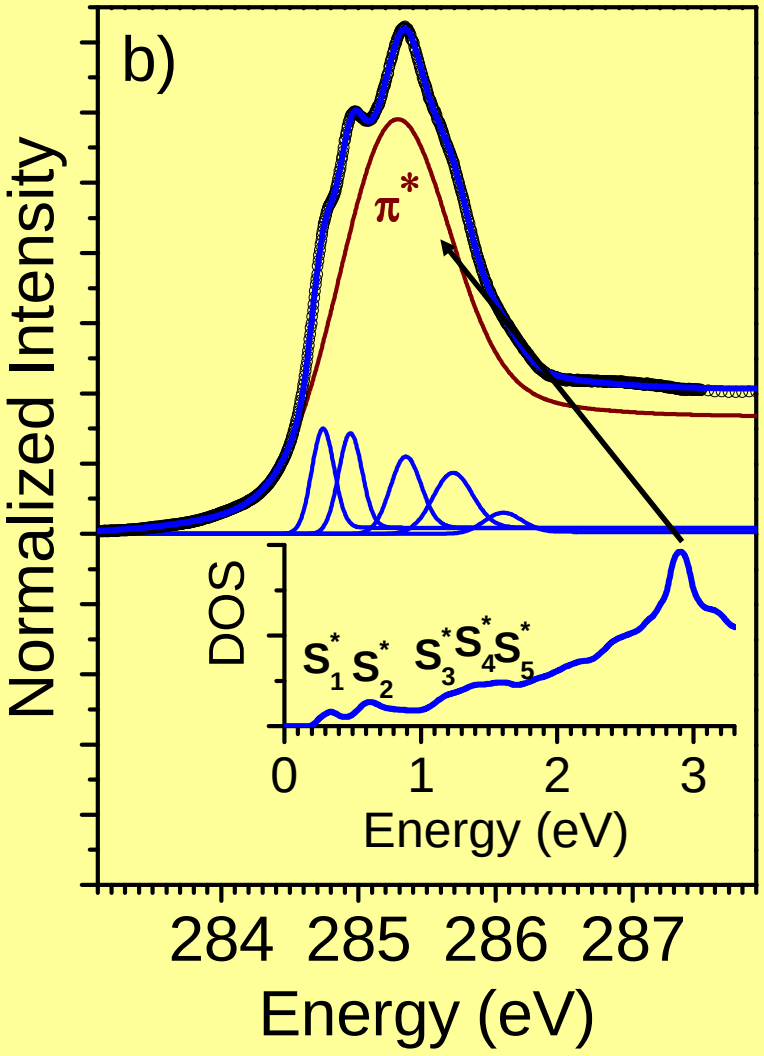
But: exitonic effects for the π* along tube axis like in graphite

C. Kramberger et al. PRB, 75, 235437 (2007)

vHS in DOS of conduction band: XAS fine structure





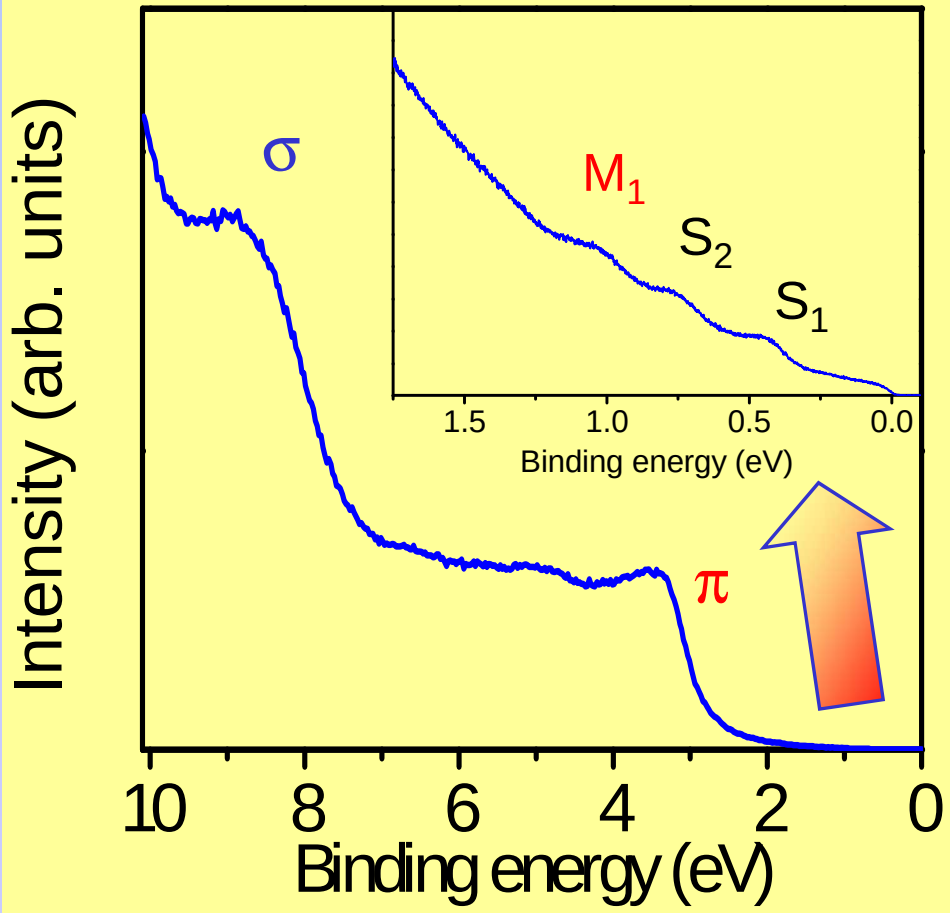


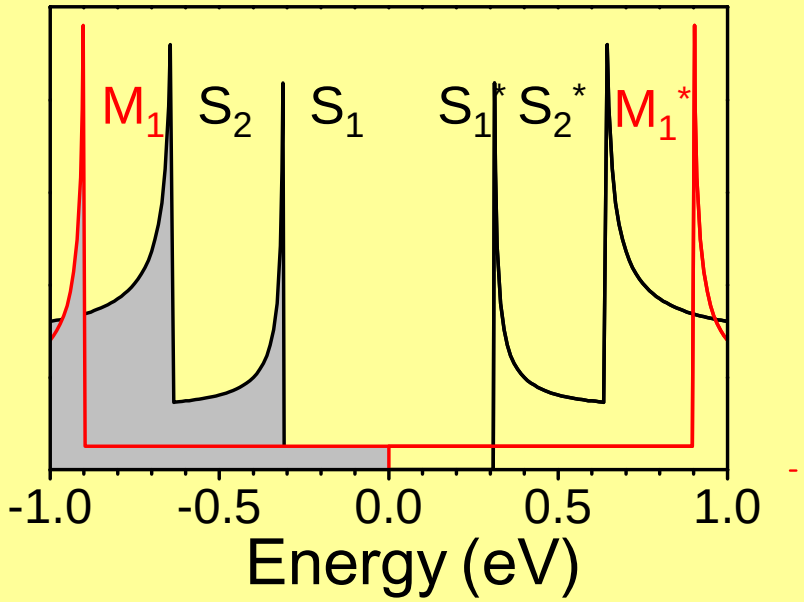
Strong excitonic effect on π* resonance (parallell),
vHS only weakly affected

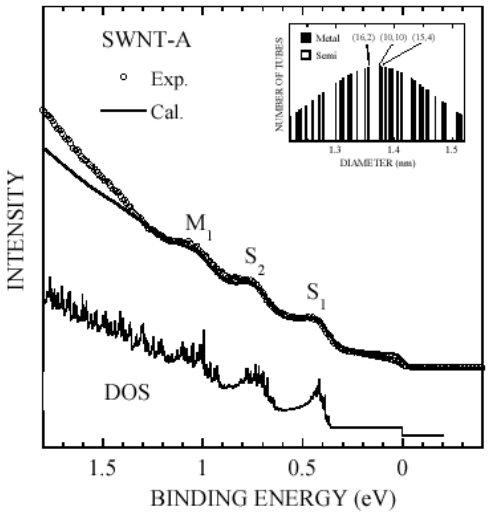
P. Ayala et al. PRB80, 205427 (2009)

Valence band of a metallicity mixed SWCNT bucky paper

High resolution angle integrated photoemission at T=35 K:





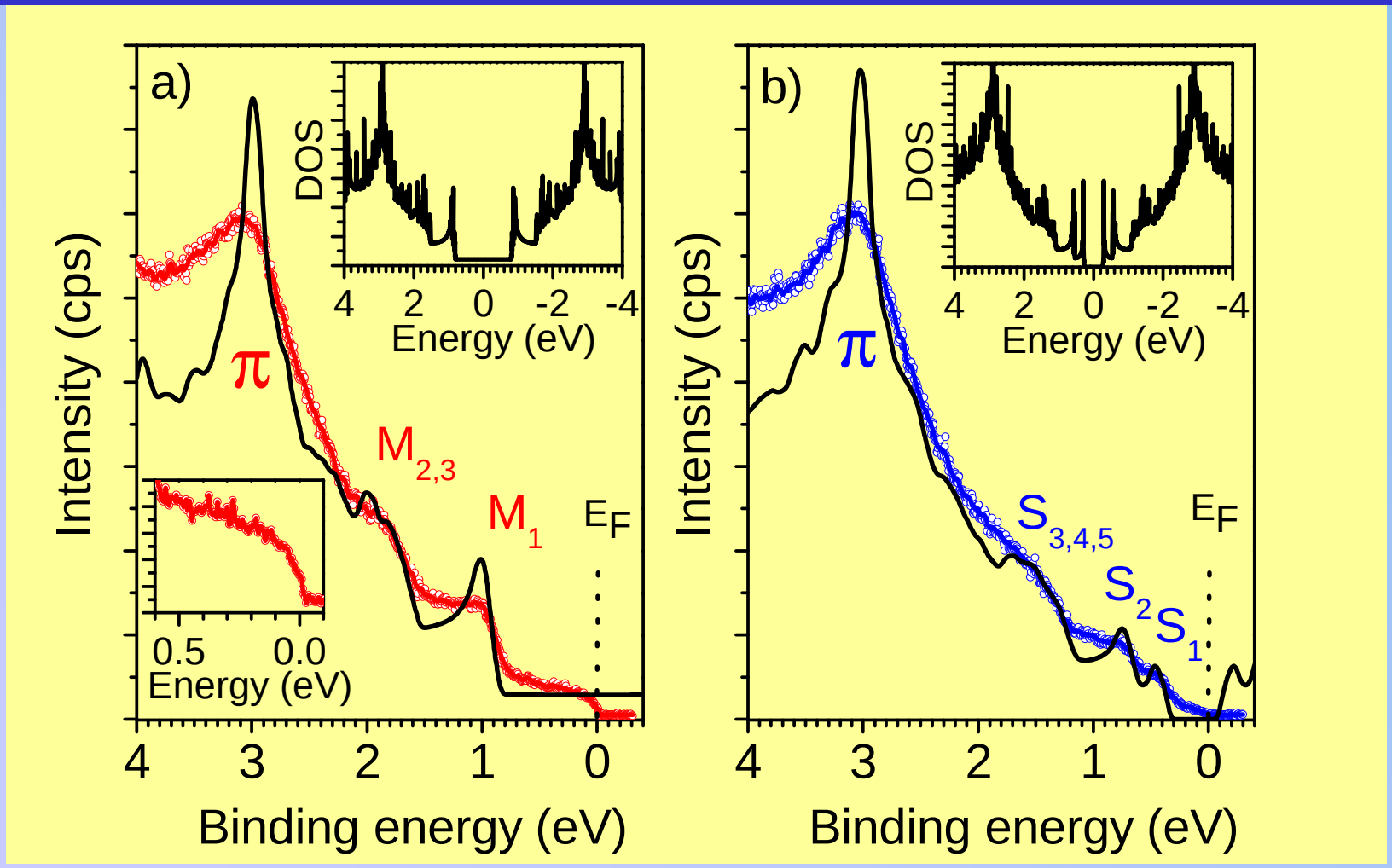


vHS of tubes: S_1, S_2, M_1

good agreement with TB calculations

e.g. H. Ishii et al, Nature, 426, 540 (2003), H. Rauf et al.

Diameter cumulative DOS in VB photoemission response



Very good agreement between PES peaks and diameter cumulative DOS!
Additional life time broadening in experiment!
Chemical potential for semiconducting tubes shifted by 0.1 eV!
No Fermi edge in metallic SWCNT

P. Ayala et al. PRB80, 205427 (2009)

Scaling in 1D and 3D metals: gain from photoemission

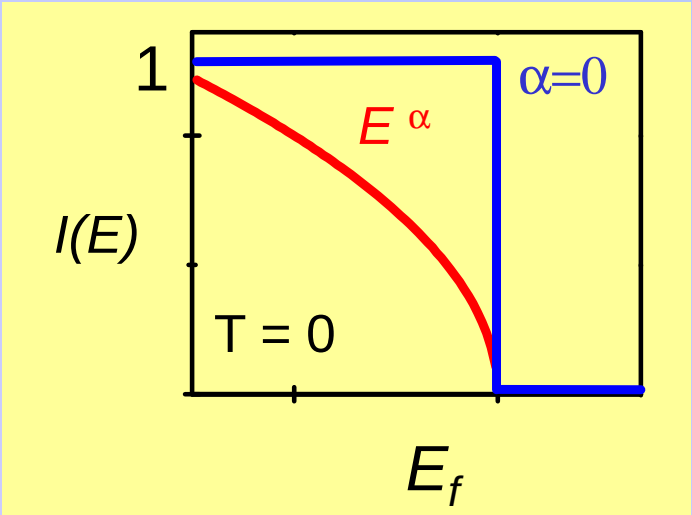
Photoemission intensity: I(E) ~ n(E) *f*(E)

3D metal: Fermi-liquid

•PES shows Fermi edge

$$f(E) = \frac{1}{exp[(E-E_f)/kT] + 1}$$

n(E) ~ const, $\alpha=0$, g=1



1D metal: Tomonaga-Luttinger liquid

- 1D paramagnetic metal
- correlated electron state interaction parameter g

g<< 1 repulsive Coulomb interaction

g>1 attractive interaction

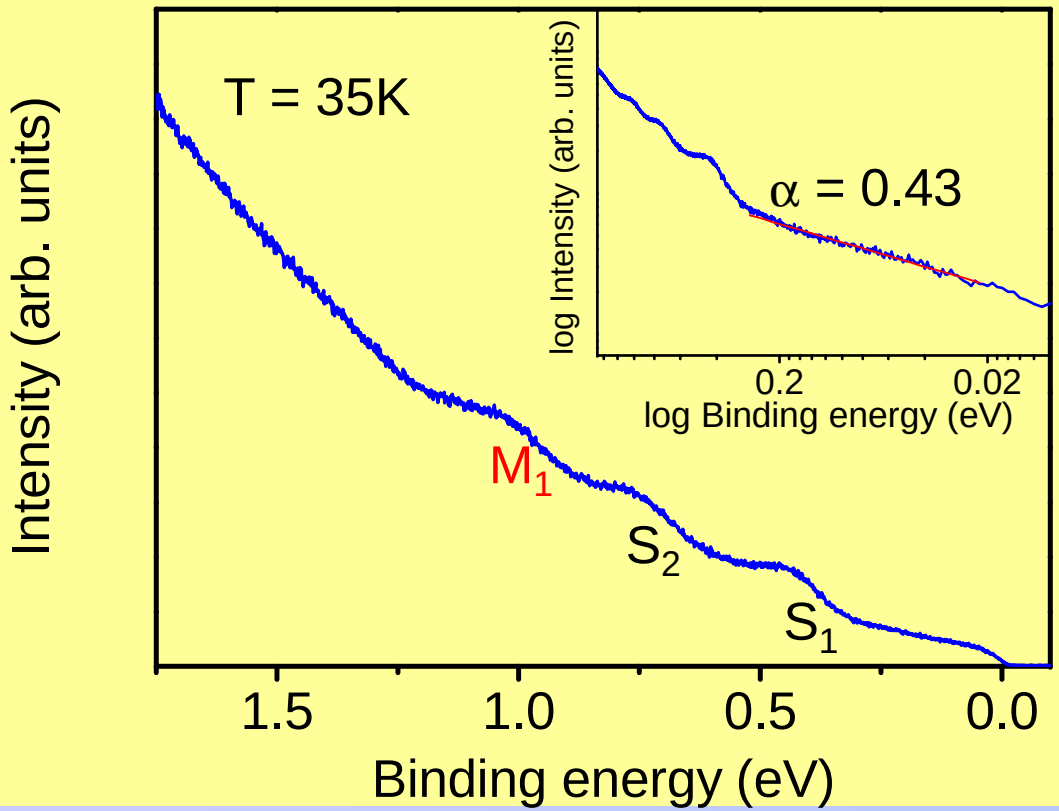
power law dependence of n(E):

$n(E) \sim E^{\alpha}$

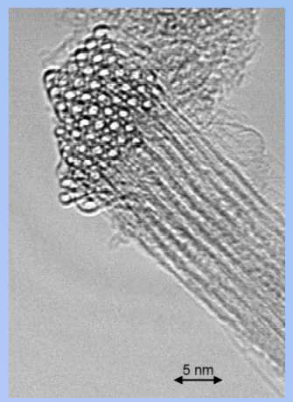
For SWCNT:

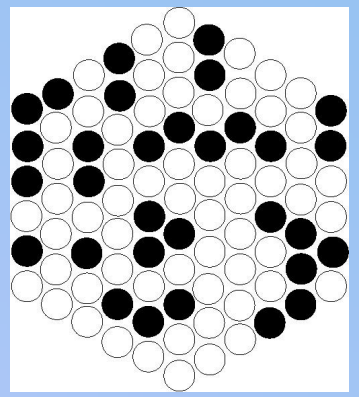
$\alpha=(g+1/g-2)/8 = 0.3–0.5$

Metallic tubes in metallicity mixed samples



Metallic SWCNT in a bundle of SWCNT have the renormalization of a Tomonaga-Luttinger liquid





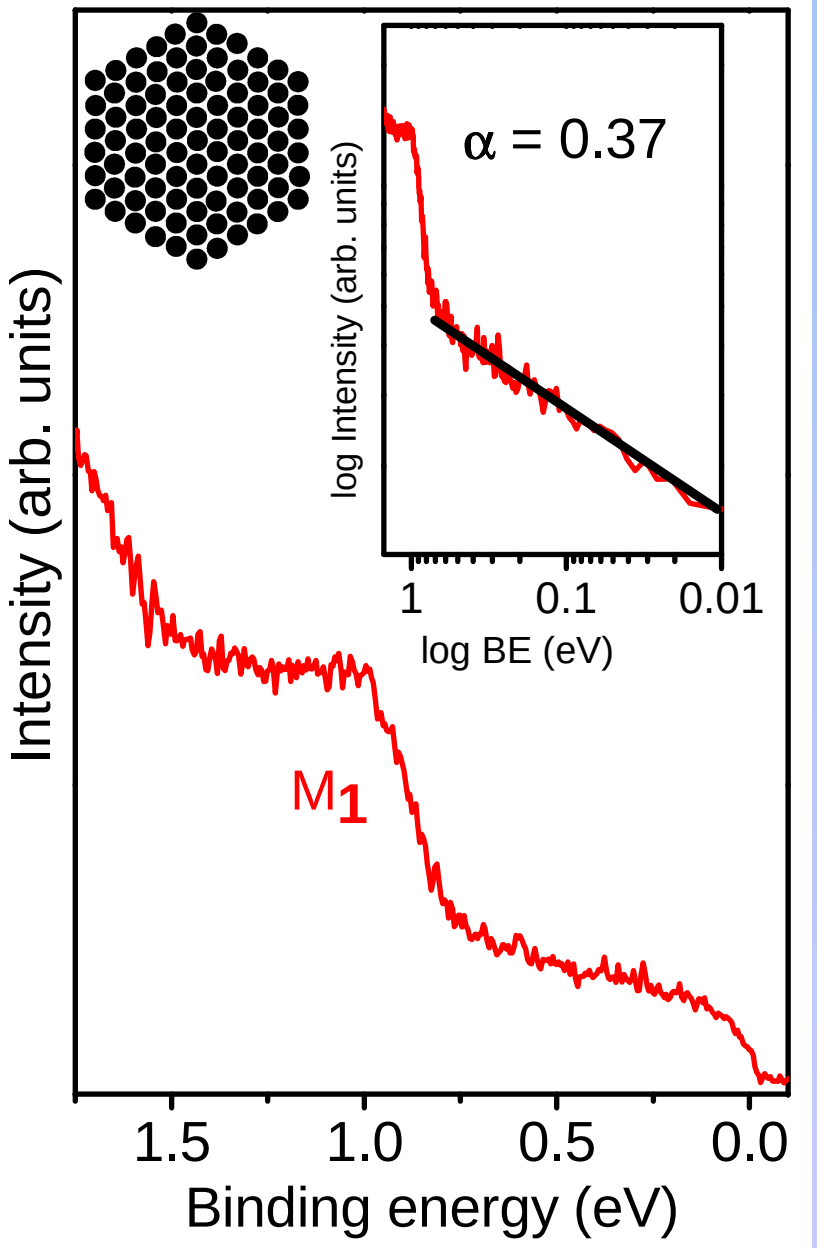
semiconducting
metallic

$\alpha = 0.43$, $g=0.18$

good agreement with theoretical predictions and results from transport measurements

H. Ishii et al, Nature, 426, 540 (2003); H. Rauf et al, PRL 93, 096805 (2004)

A bundle of undoped metallic SWCNT



No Fermi liquid!
No Fermi edge for metallic SWCNT!

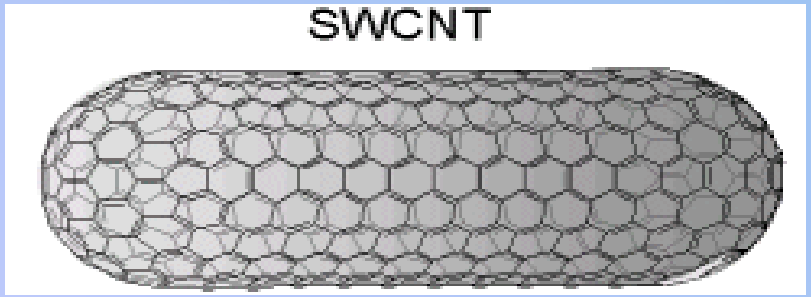
→ Undoped purely metallic SWCNT bundles are still 1D metals

→Still van der Waals interaction of the tubes in a bundle!

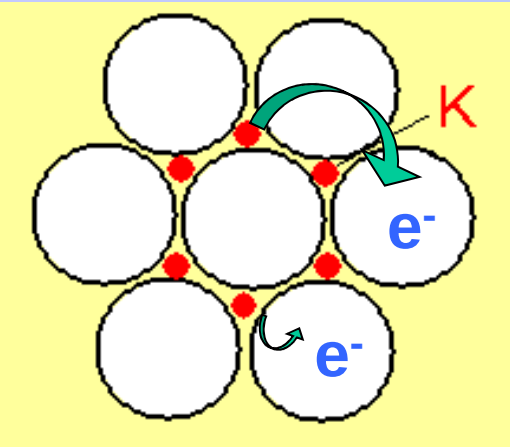
→ Implications on maximum conductivity in e.g. transparent electrodes

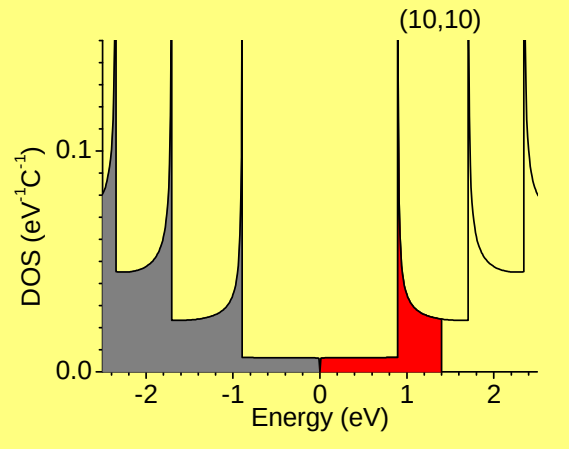
P. Ayala et al. PRB80, 205427 (2009)

Intercalation

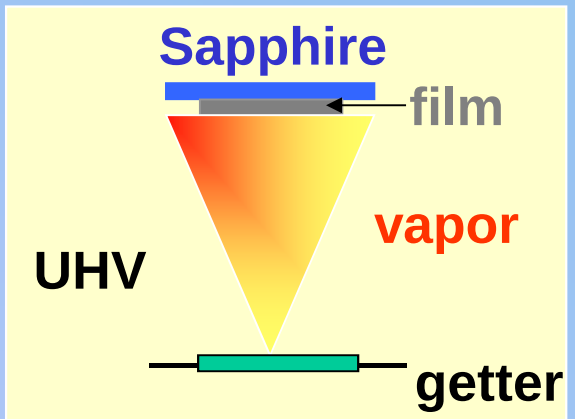


doping





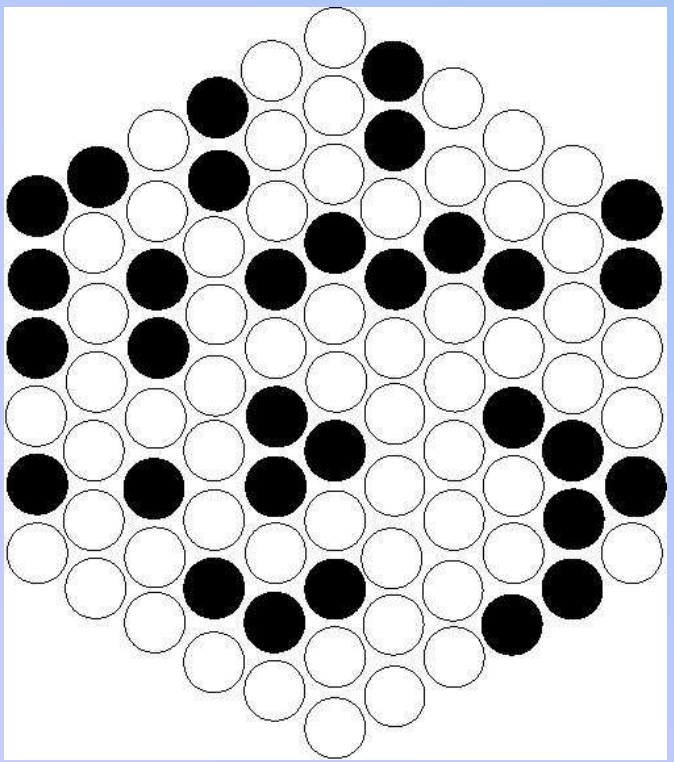
Alkali-metal intercalation



***in-situ* doping:**
UHV evaporation
(5×10^{-10} mbar)
Na, K, Rb, Cs and
Ba SAES getters

INTERCALATION:

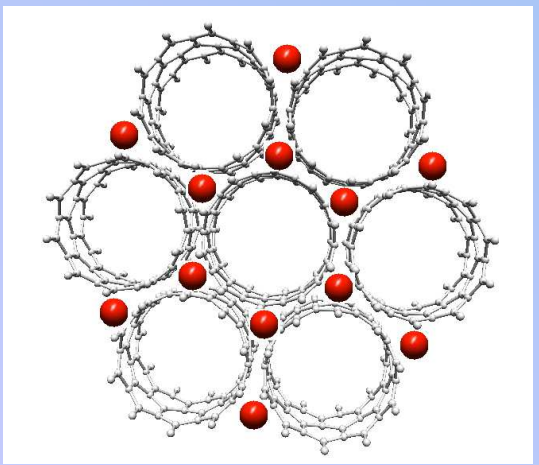
What happens with doping?



○ SC
● M

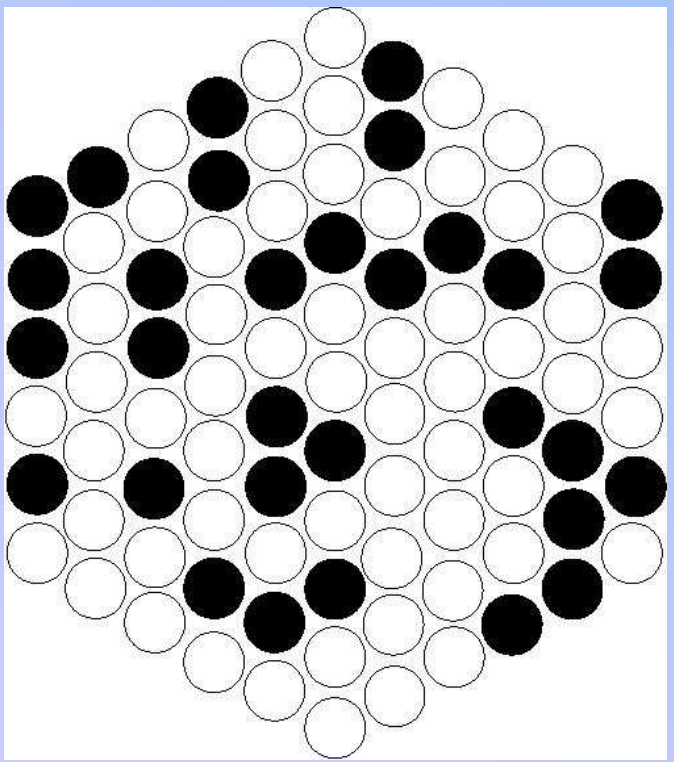
doping

?

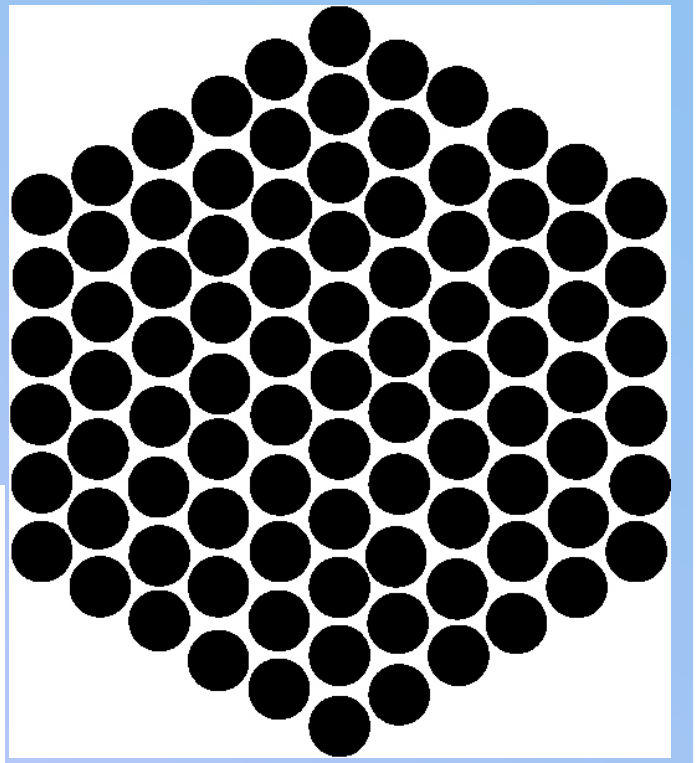


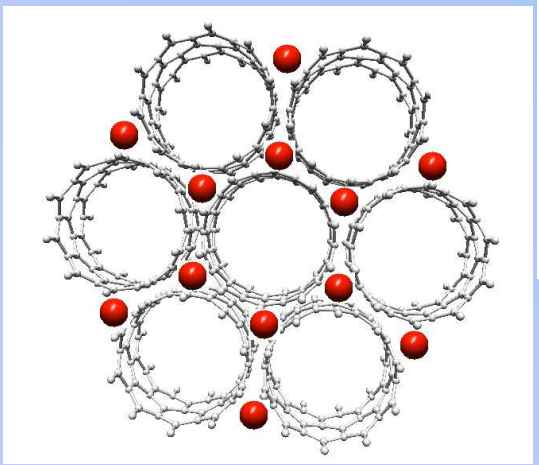
INTERCALATION:

What happens with doping?



doping



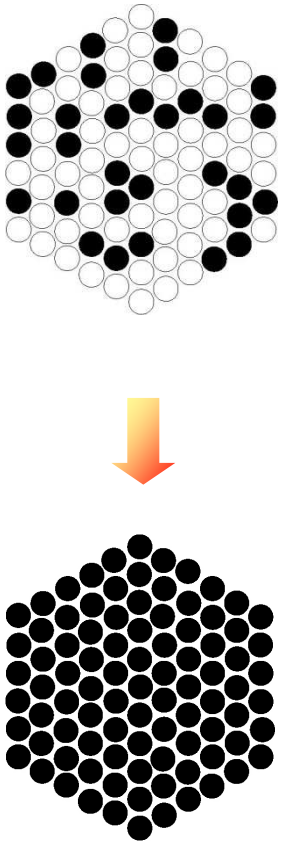


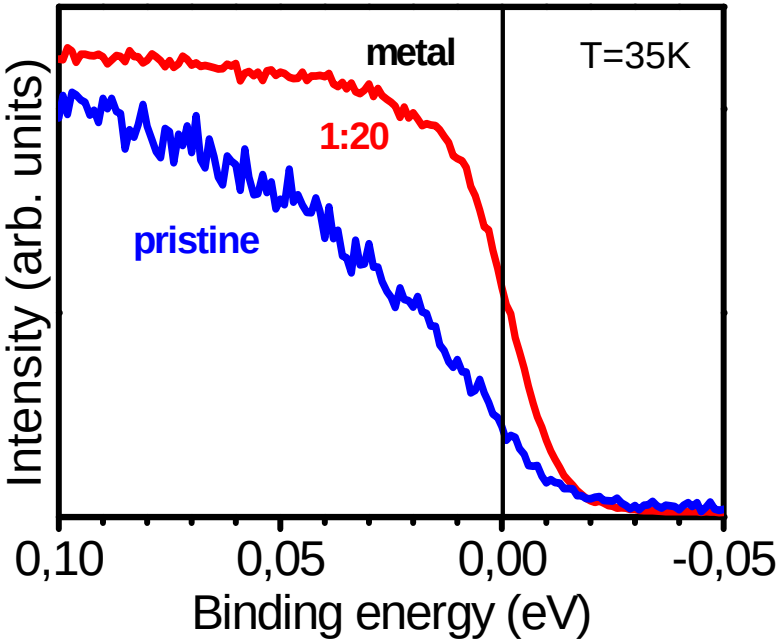
○ SC
● M

Is a bundle of **doped metallic** tubes a normal Fermi liquid or a Luttinger liquid?

Transition from a TLL to a FL

Crossover to a Fermi liquid





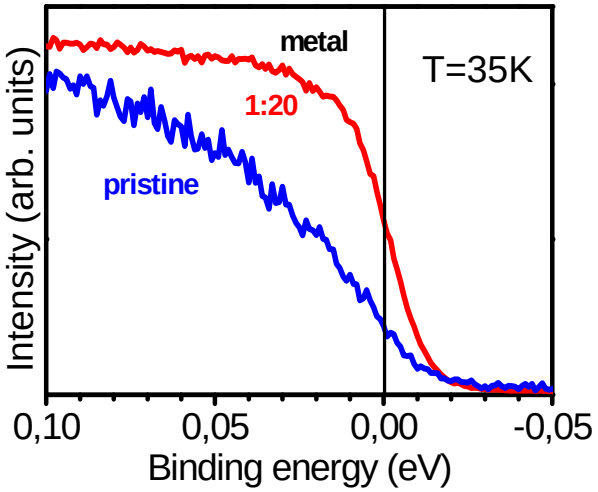
$\alpha = 0$

$\alpha = 0.43$

Dependence of the power law scaling factor alpha from the degree of doping.

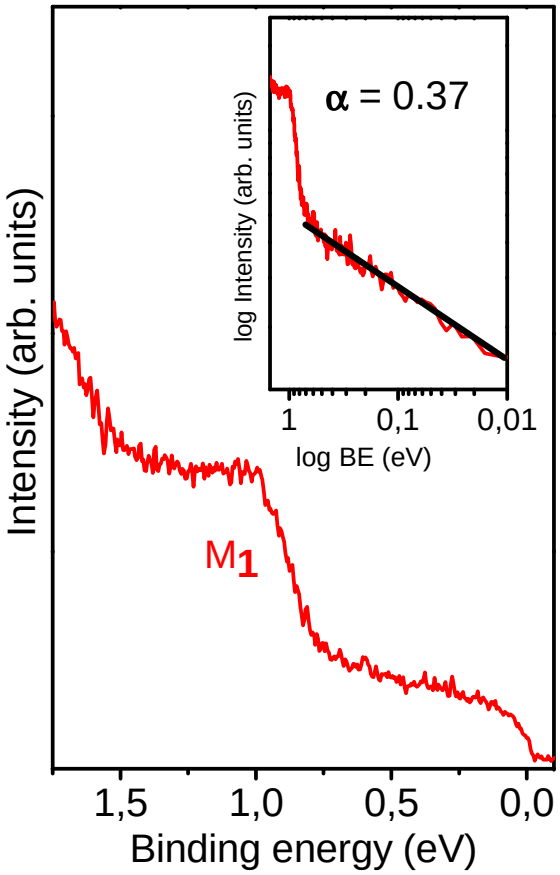
H. Rauf et al, PRL 93, 096805 (2004)

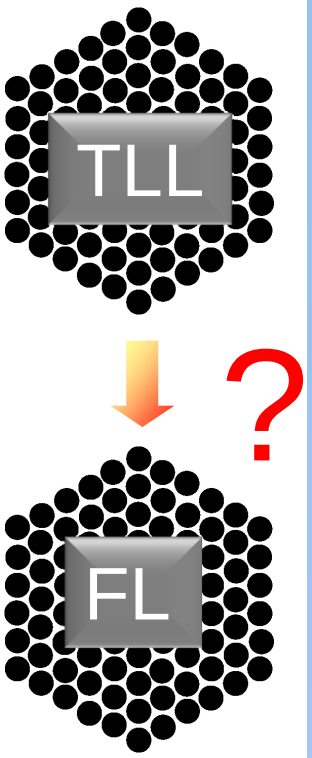
Where is the transition from a TLL to a FL?



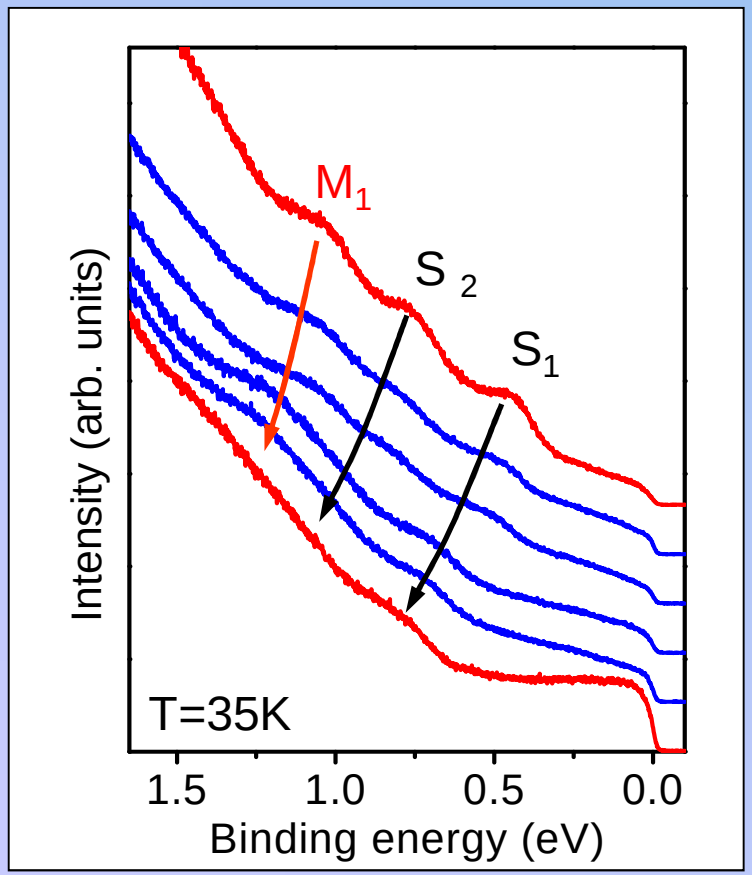
$\alpha = 0$

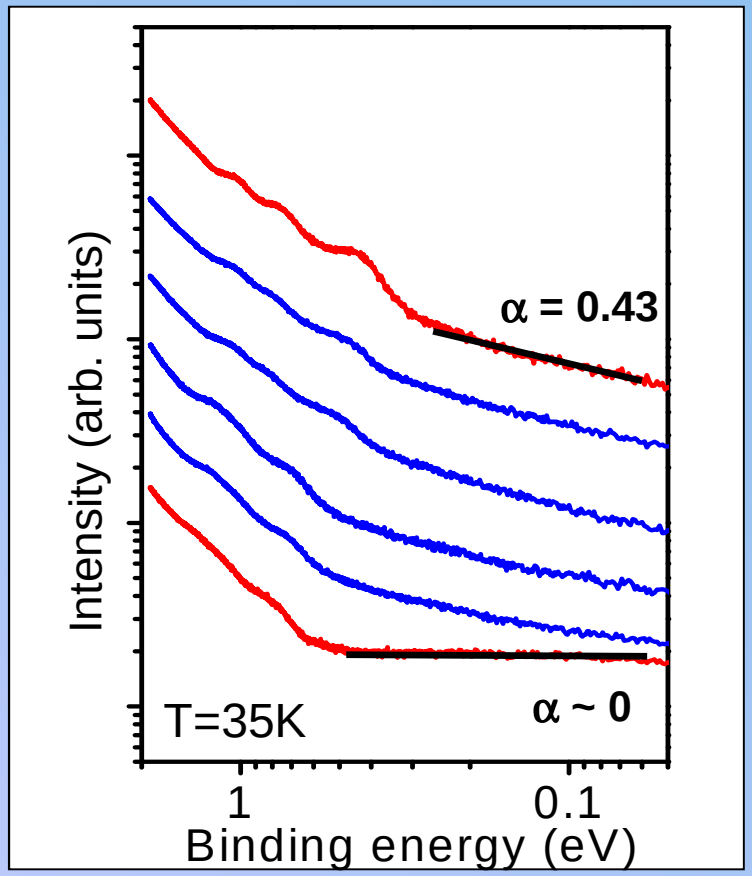
$\alpha = 0.43$

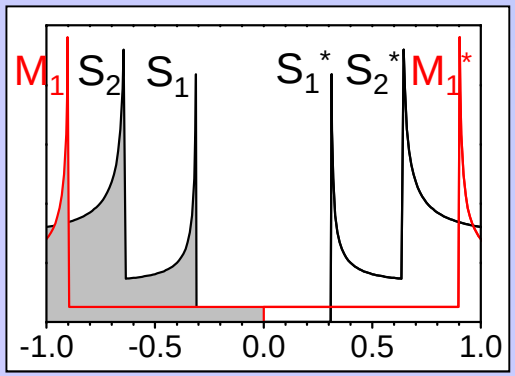




Rigid band shift in metallicity mixed samples

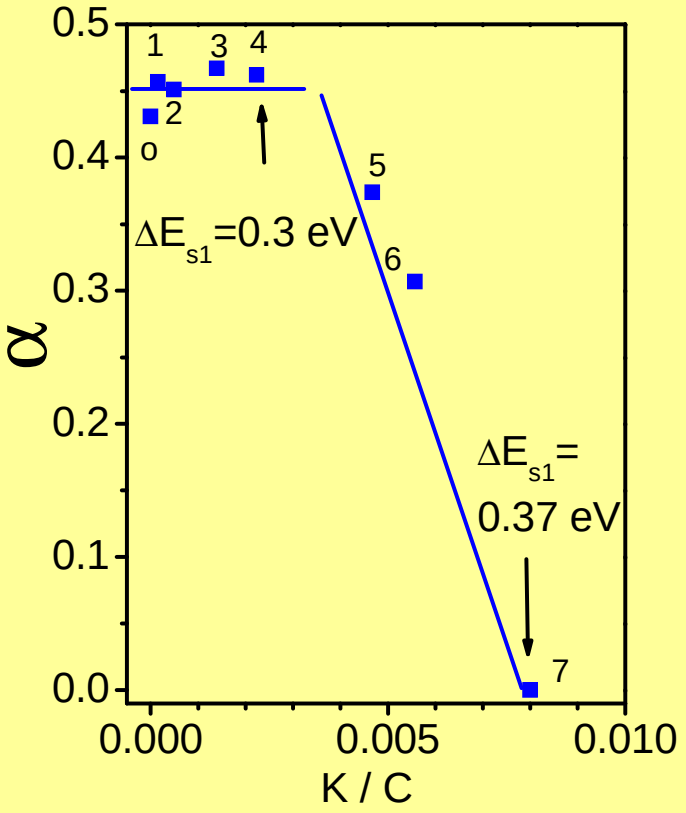


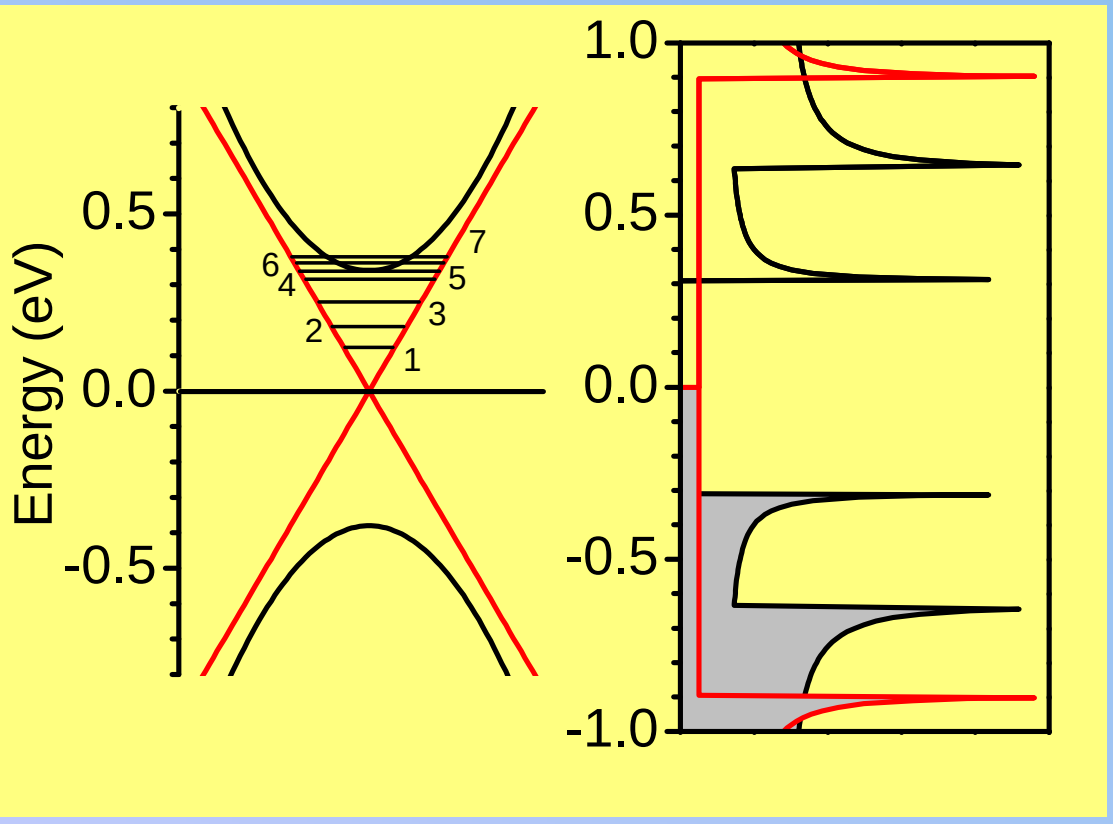




- S_1, S_2 and M_1 shift to higher binding energies
- power law behavior at first stable
- abrupt change at K:C = 1:125, $\Delta E(S_1)$ = 0.37eV

Doping dependence of the LL parameter α in mixed samples





Power law scaling vs. intercalation:

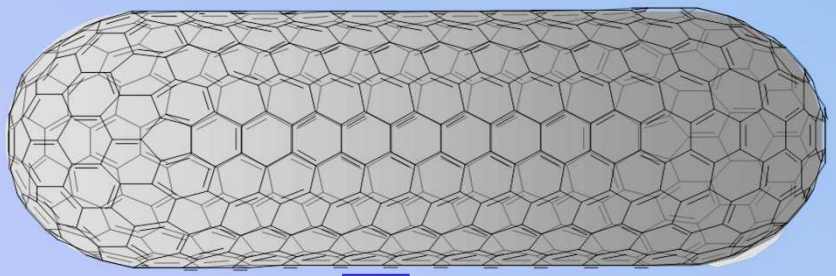
α= const. up to K/C=1/500, ΔE_{S1}=0.25 eV

α=0, g=1 above K/C=1/150, ΔE_{S1}>0.35 eV

⇨ a bundle of only metallic tubes is a normal Fermi liquid!

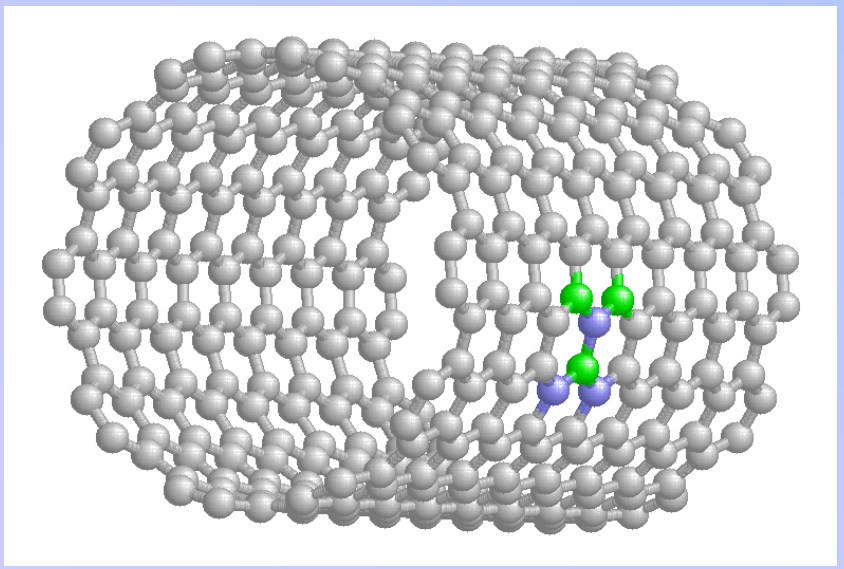
H. Rauf et al. PRL 93, 096805 (2004); C. Kramberger et al. PRB 79, 195442(2009)

Substitution: Heteronanotubes

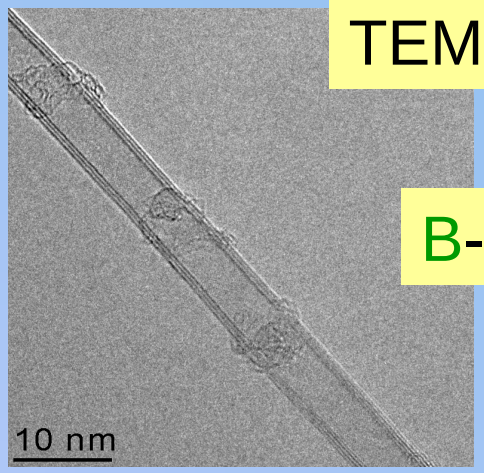


SWCNT

B,N Substitution

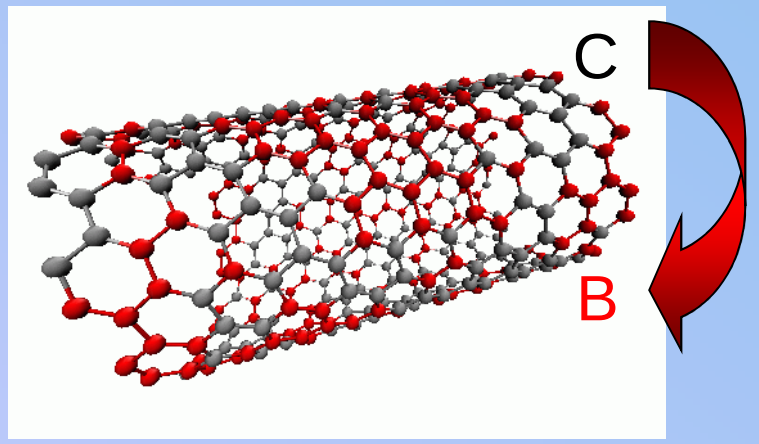


BCN-SWNT, MWBNT



TEM of DWBN-NT

B-SWNT, BC_3NT



E. Borowiak-Palen et al. Chem.Comm.1, 82 (2003), CPL, 387 , 516 (2003)
G. Fuentes et al. PRB 67, 35429 (2003), PRB 69, 245403 (2004), P.Ayala, et al., Reviews of Modern Physics (2010).

Filling of the inner space of SWCNTs with molecules

- Modified electronic properties?

What happens upon the formation of the peapods?

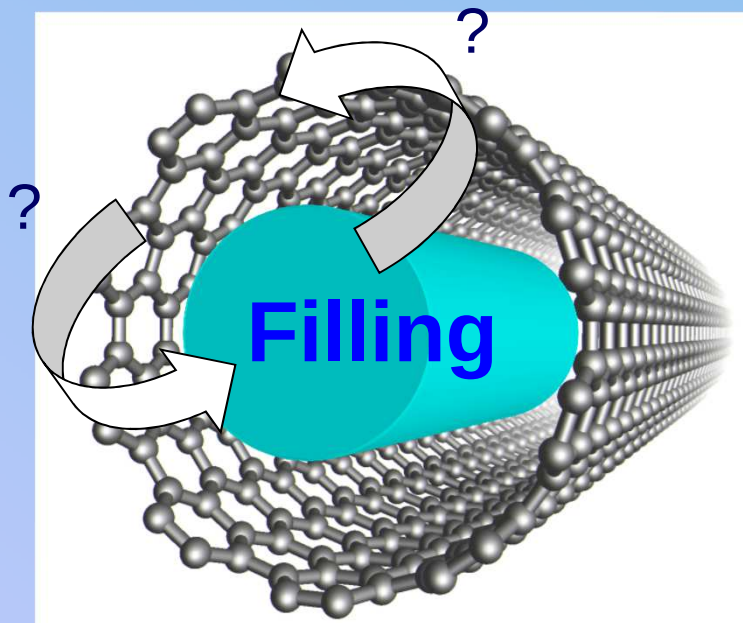
Charge transfer, chemical bonding

or orbital hybridisation?

Conversion to double-wall carbon nanotubes (DWCNT)?

Filling@SWCNT

so-called “peapod”



- Potential applications

Carrier tuning of SWCNT, protection for molecules and even drugs, stabilizing reactive compounds and nanocrystals, chemical reaction inside a 1D confined nano reaction tube, 1D spinchain for spin electronics, …

Examples

- Fullerenes@SWCNT

C_{60}@SWCNT :

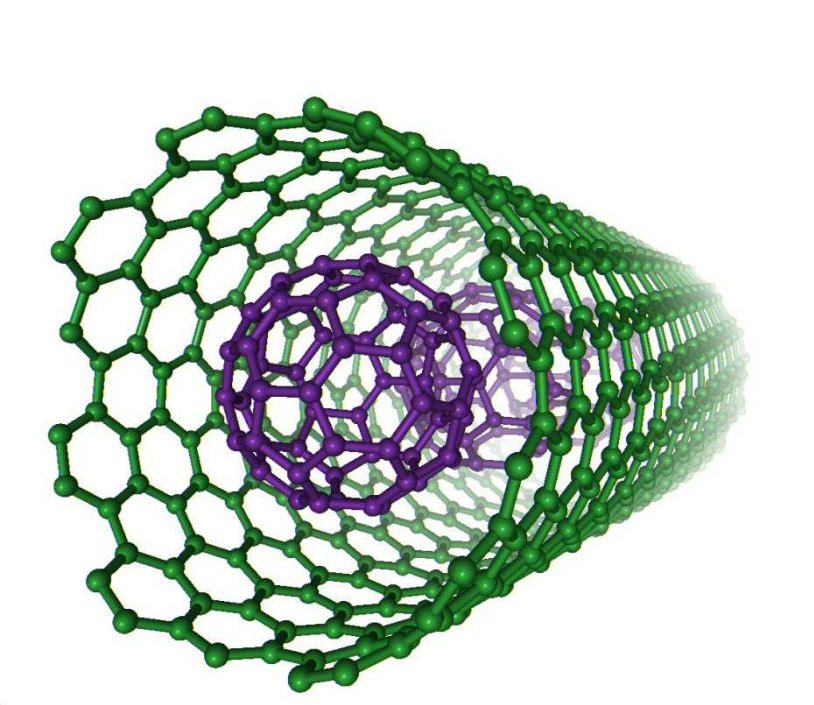
1D C_{60} chain inside SWCNT (TEM,Raman)

Gd@C_{82}@SWCNT :

Band gap modulation (STM,STS)

Dy_3N@C_{80}@SWCNT :

Charge transfer (PES)



C_{60}@SWCNT

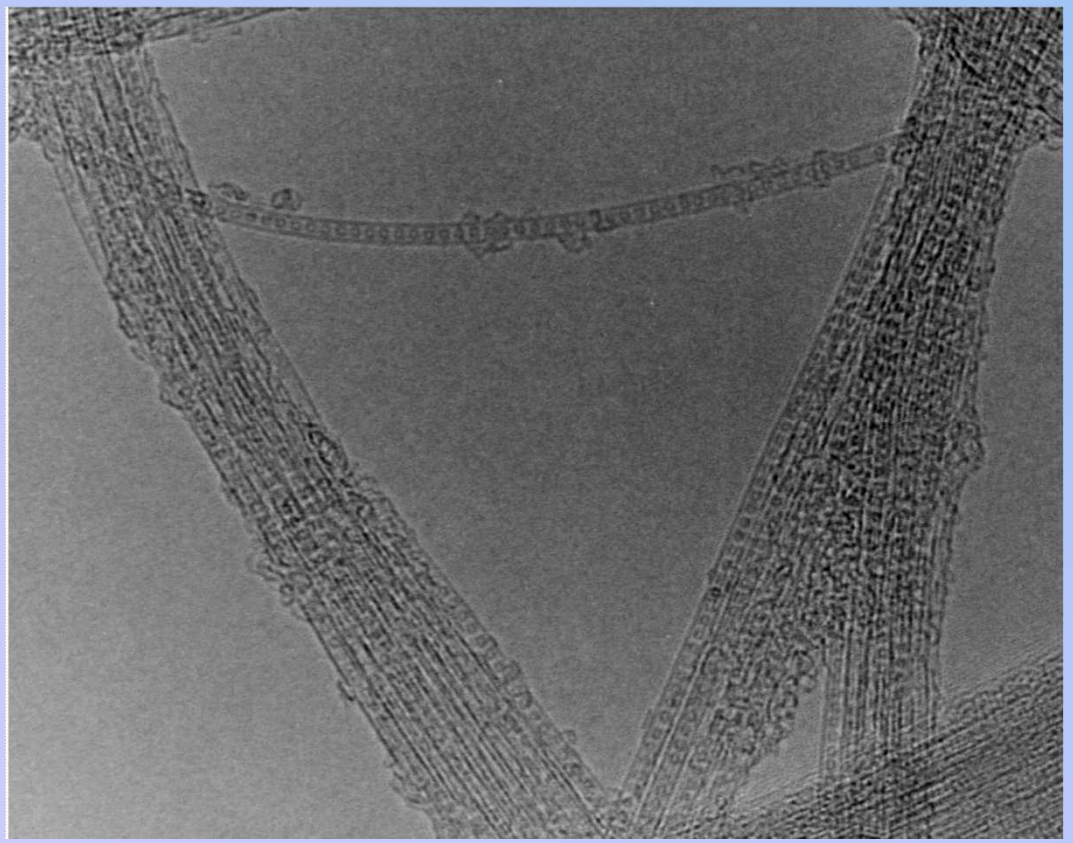
Conversion to DWCNT(TEM, Raman)!

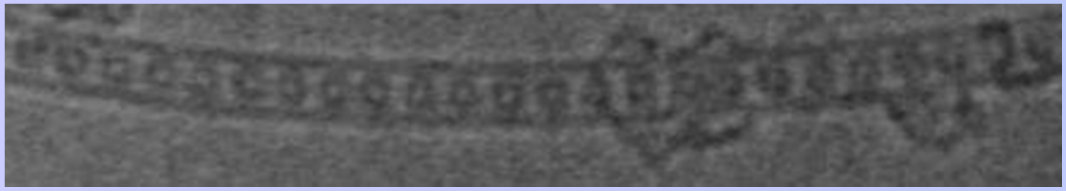
- Organic molecules @SWCNT

TCNQ, TDAE, Anthracene@SWCNT,
Metallocenes p- and n- type doping

Estimation of the local filling ratio by TEM

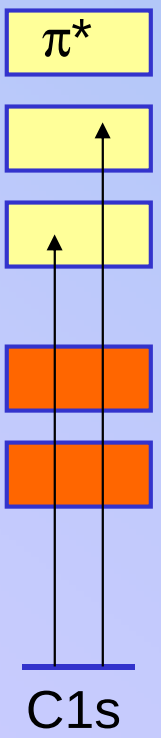
Peapods: e.g. C_{60} filled SWCNT

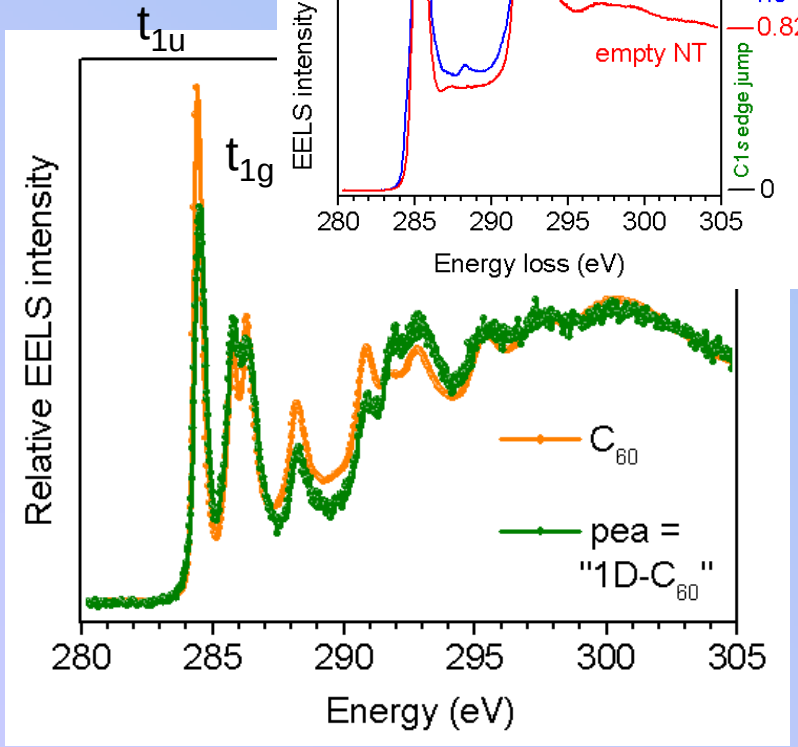


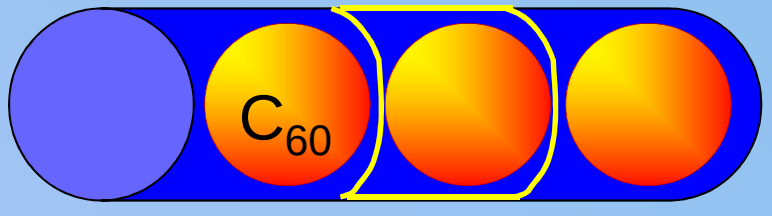


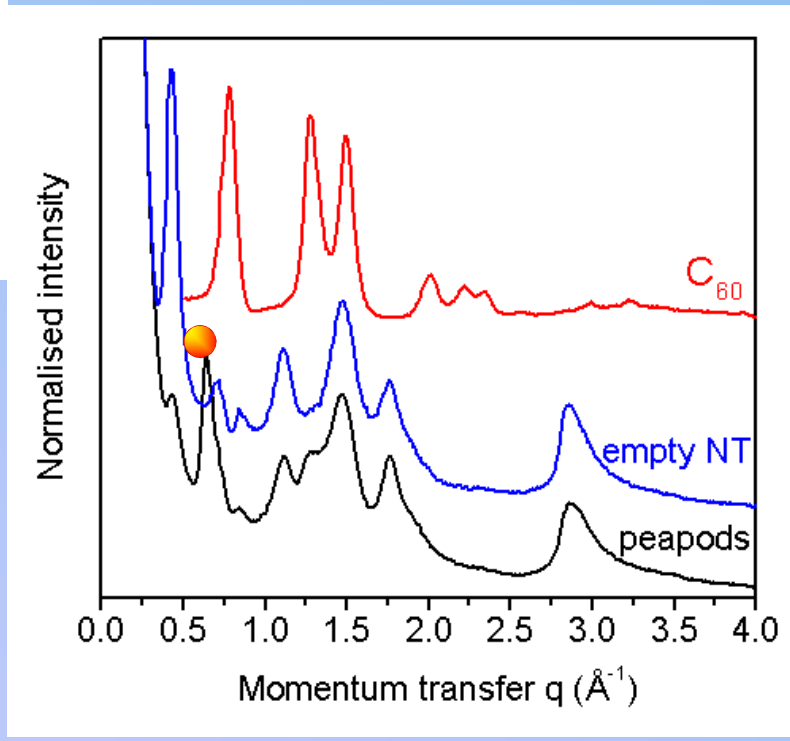
>90 % filling

Bulk filling ratio, structure in peapods







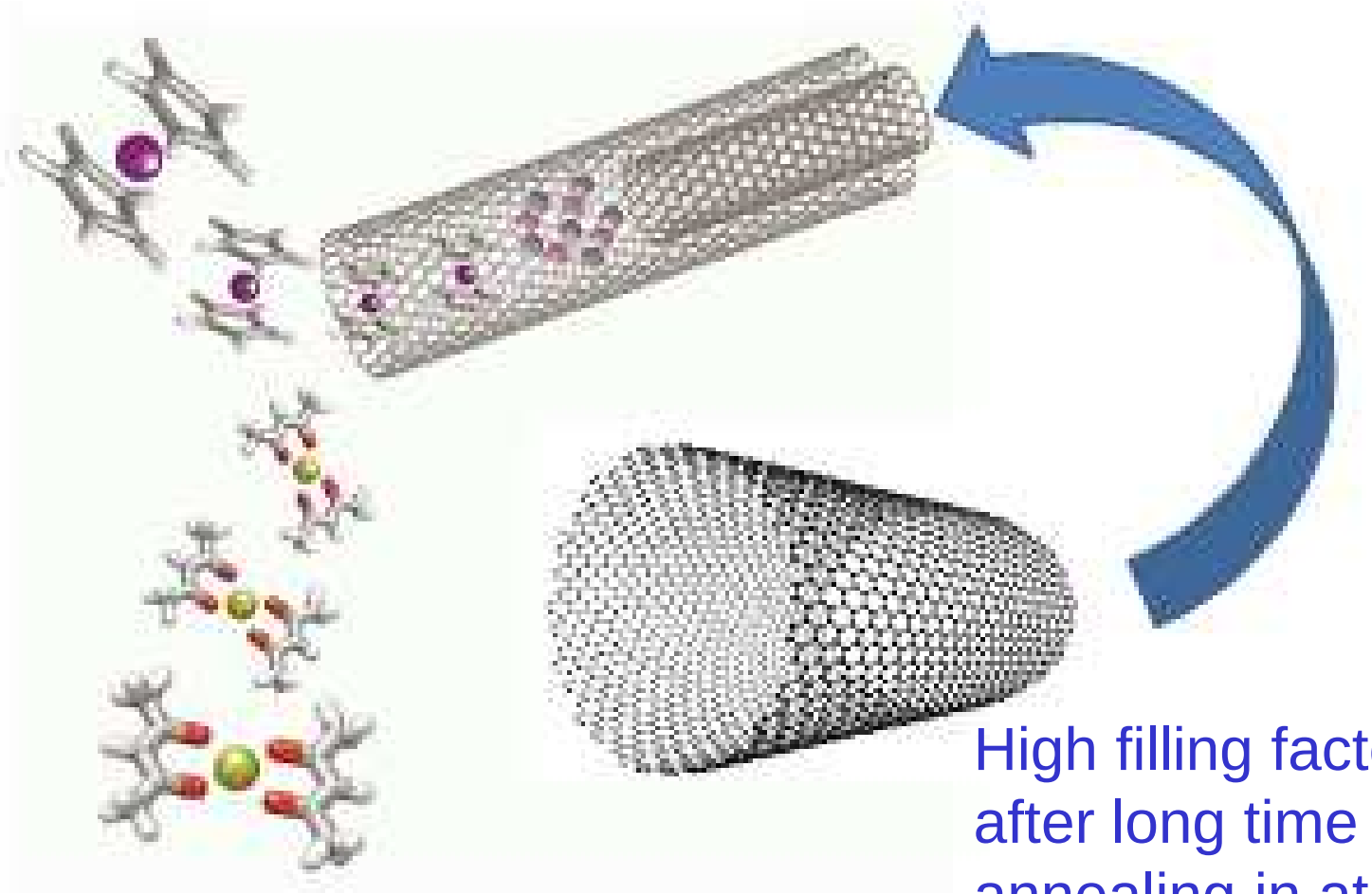


Maximum filling ratio with C_{60}: 100%
no charge transfer to C_{60}

C_{60} - C_{60} distance 9.7 Å
→ no C_{60} polymer in SWCNT

X. Liu et al., Phys. Rev. B 65, 45419 (2002), Synth. Met. 135-136, 715 (2003)

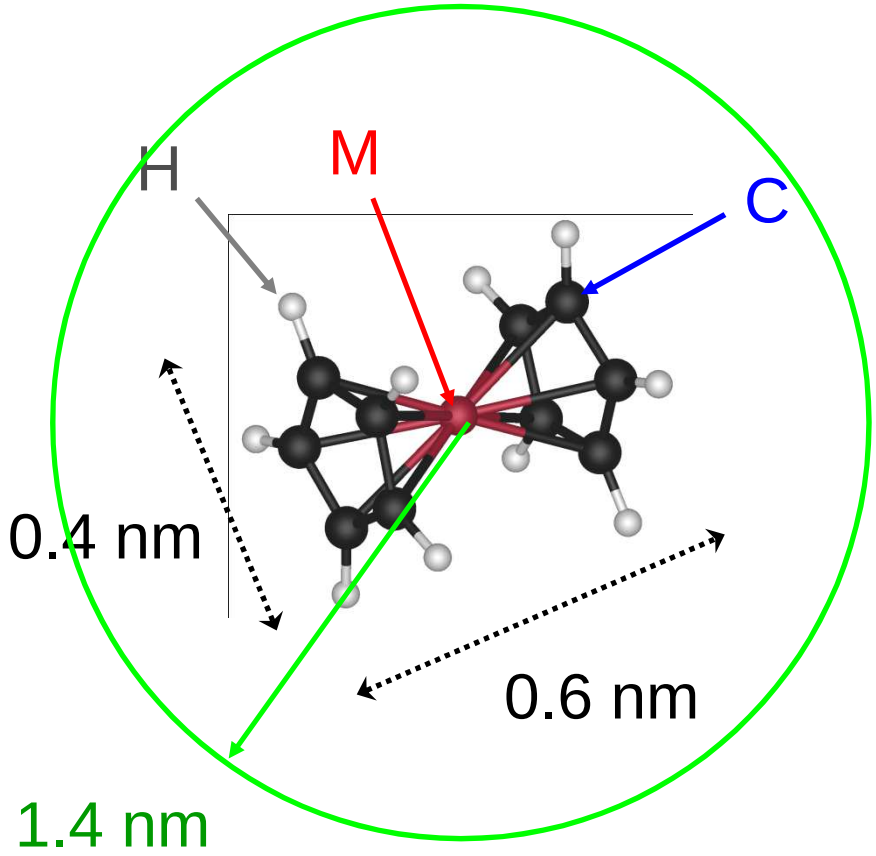
Ferrocene filling of SWCNT and transformation to DWCNT



High filling factor after long time annealing in at 150 C

Metallocene filling and chemistry inside SWCNT

Metallocenes : $TM(C_5H_5)_2$, $RE(C_5H_5)_3$



Metallocene consists of

- TM: Transition metal atoms
- RE: Rare-earth metal atoms
- Planar aromatic ligand: C_5H_5

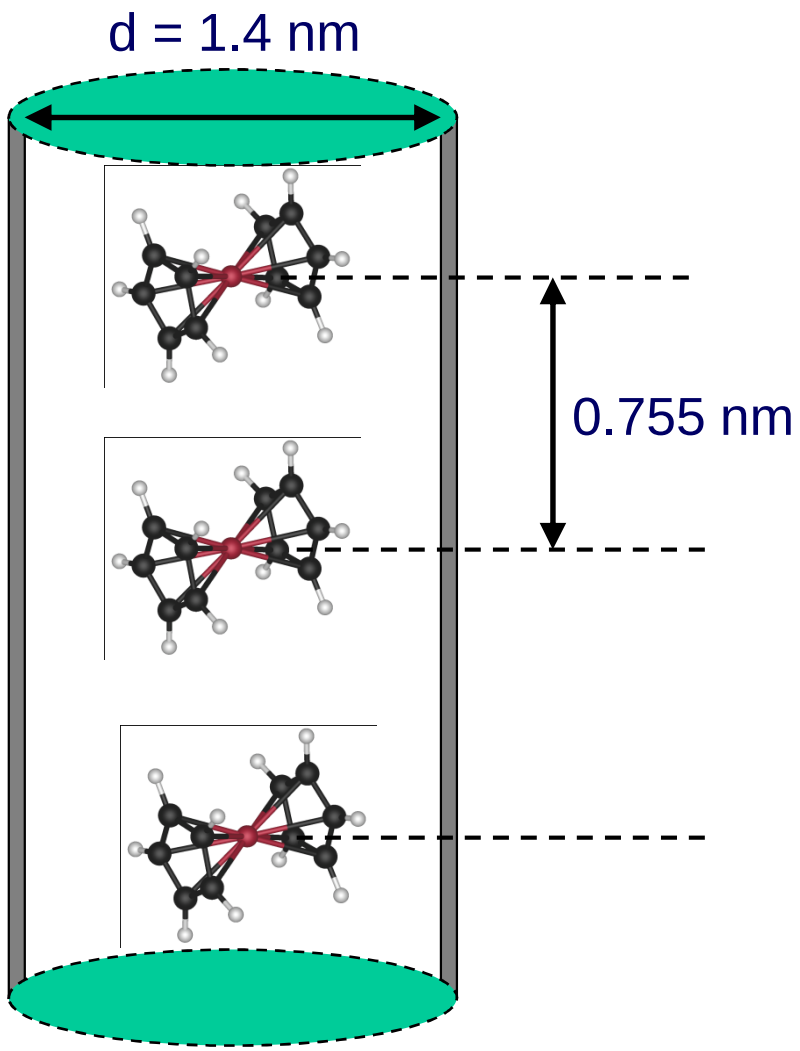
Electronic & magnetic & chemical properties varying with metal atoms.

M = Fe : Ferrocene

Most stable metallocene

Suitable size to be filled inside SWCNT !!!

Metallocene filling: Filling factor



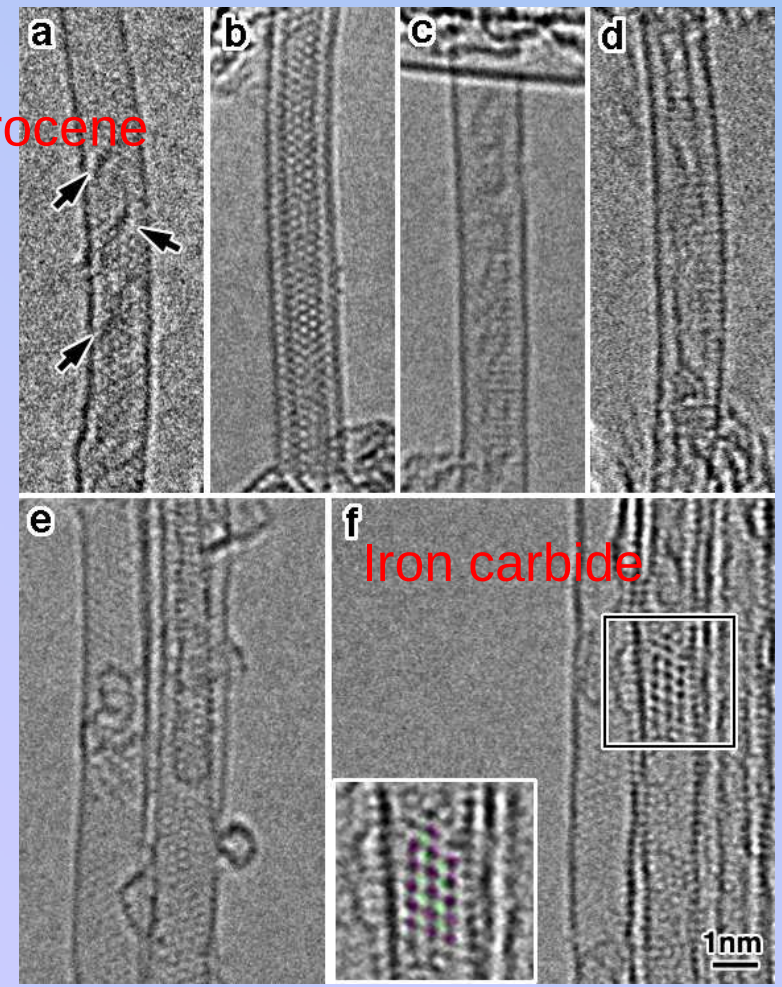
Assuming a 1D ferrocene chain inside SWCNT (d =1.4 nm) with adjacent ferrocene distance ~ 0.755 nm

Fe/C ratio ~ 0.003

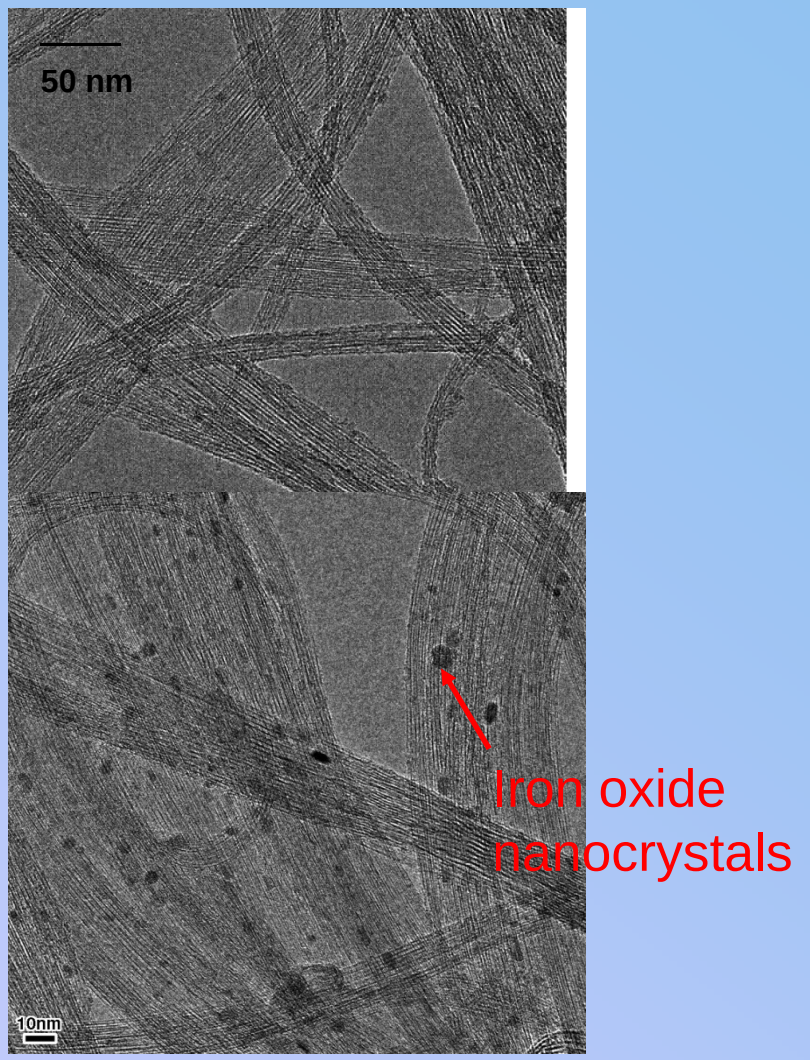
Filling factor ~ 35 %

Nanochemistry in 1D: Gain from TEM

High resolution

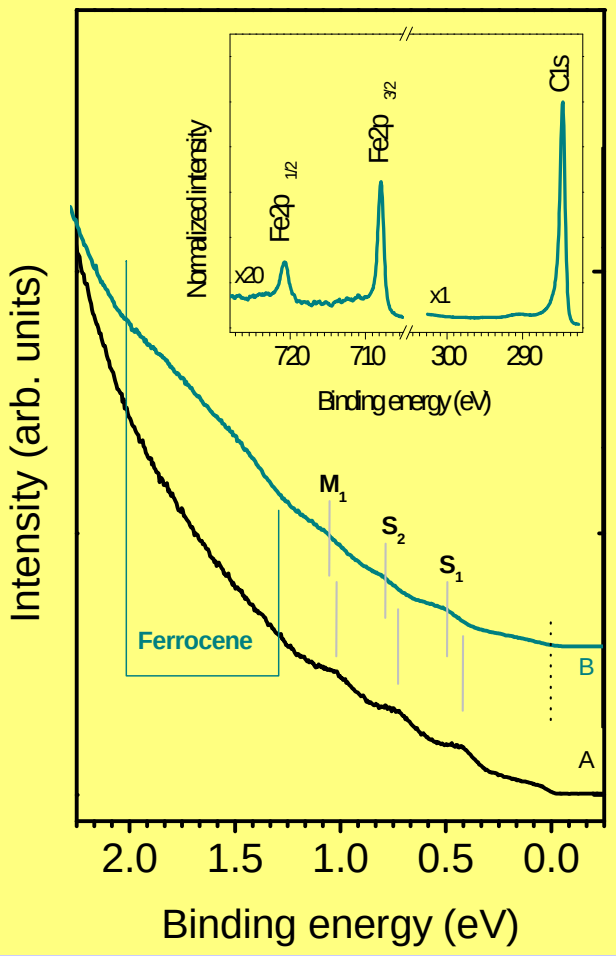


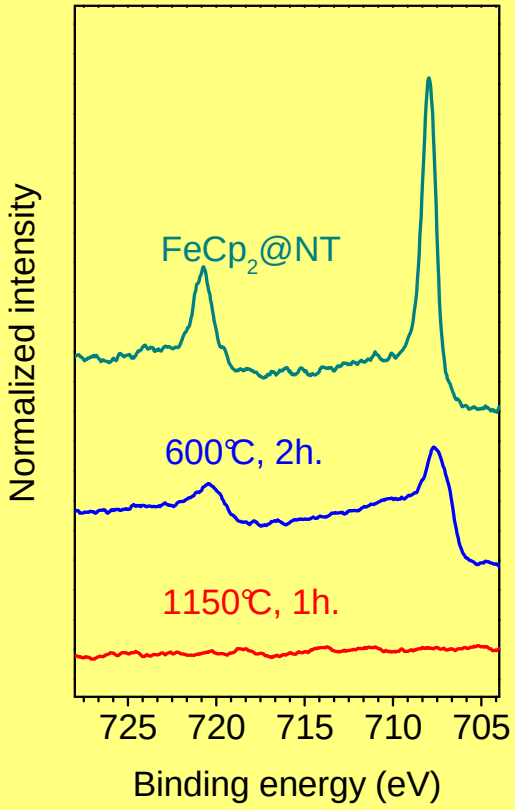
Overview

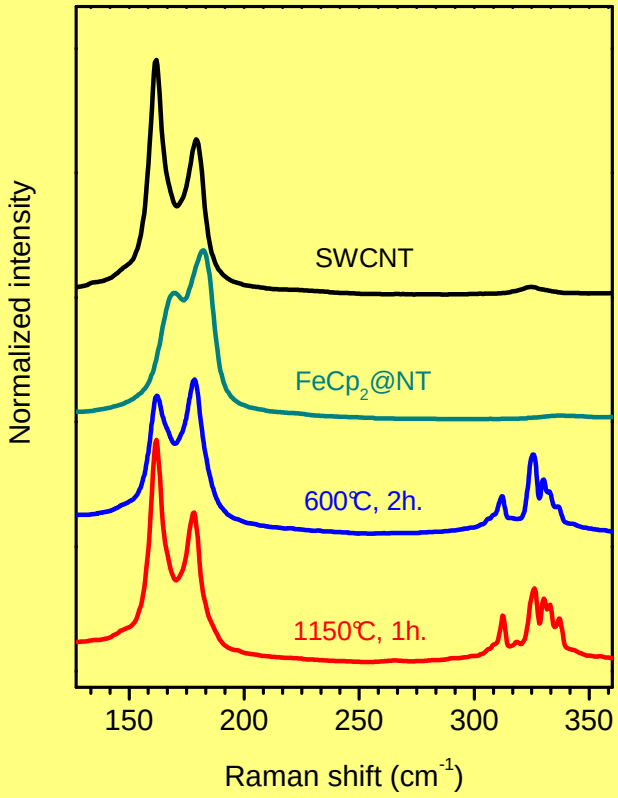


H. Shiozawa et al. Adv. Mat. (2008)

Ferrocene filled SWCNT and growth of DWCNT



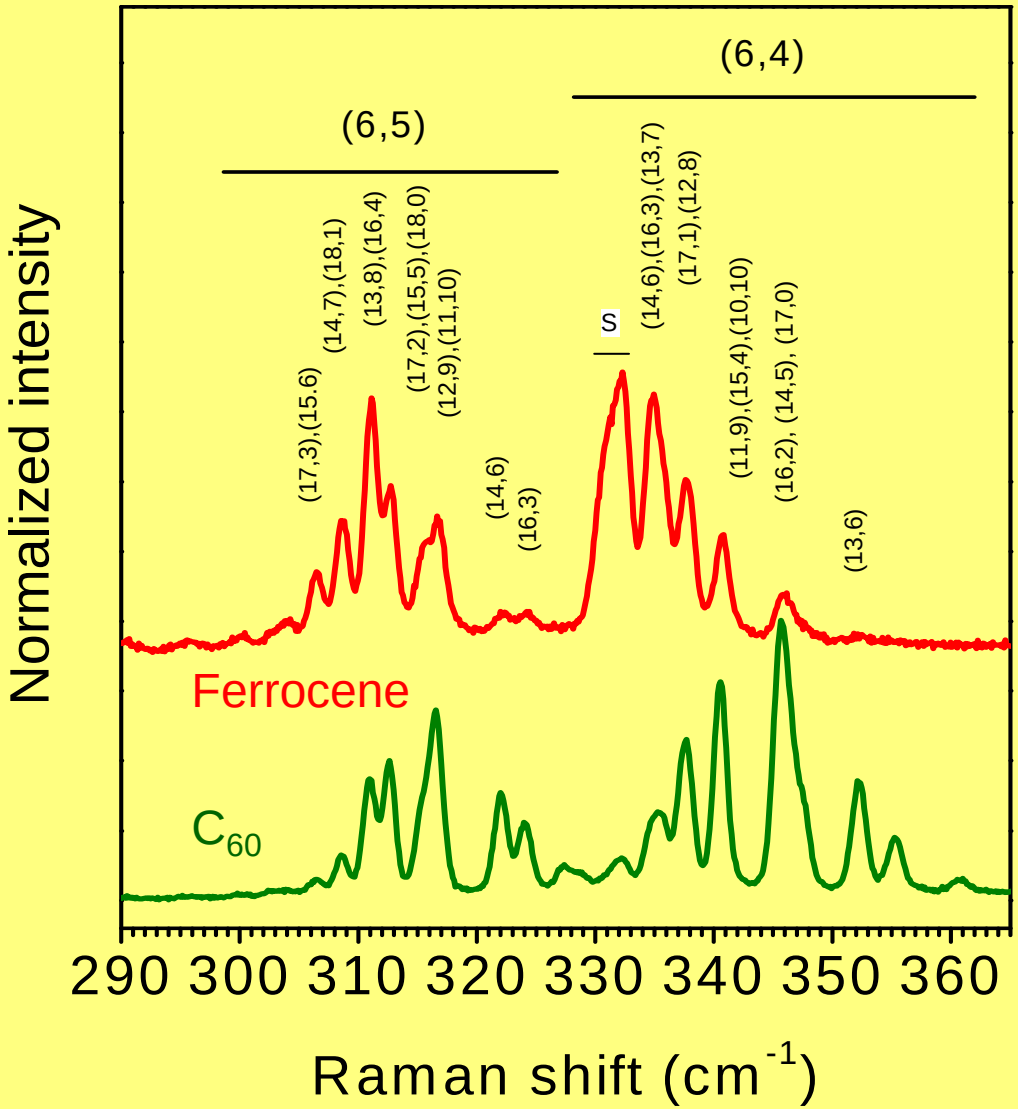


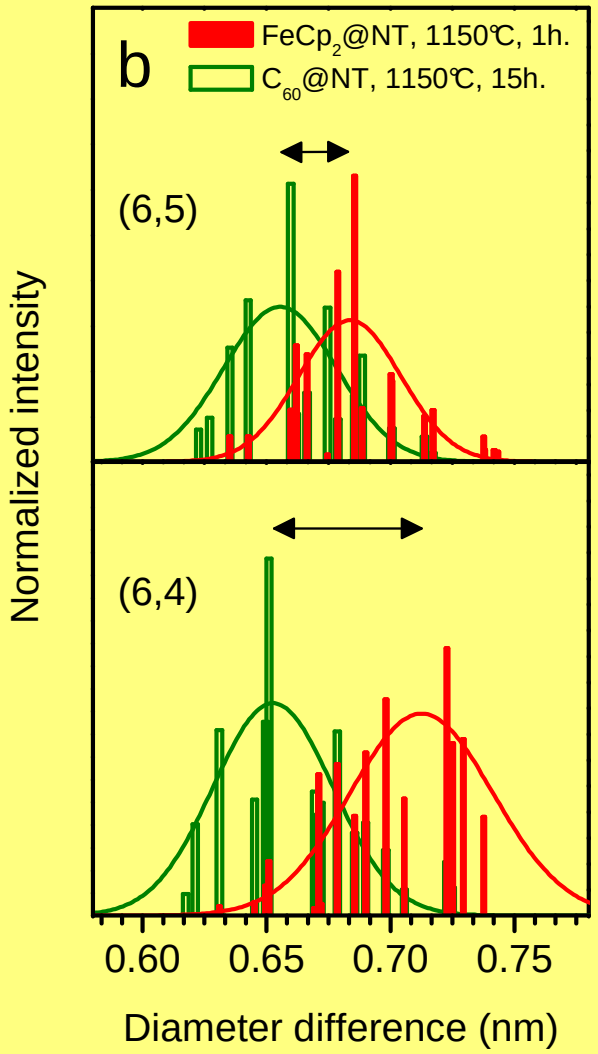


- Charge transfer ΔE_F=0.1 eV, ~0.2 e^- per ferrocene
- Power law behavior α =0.55
- growth of inner tubes at ~ 600 ℃

H. Shiozawa et al.
Adv. Mat. (2008);PRB (2008)

DWCNT/Inner tubes: Gain from high resolution Raman

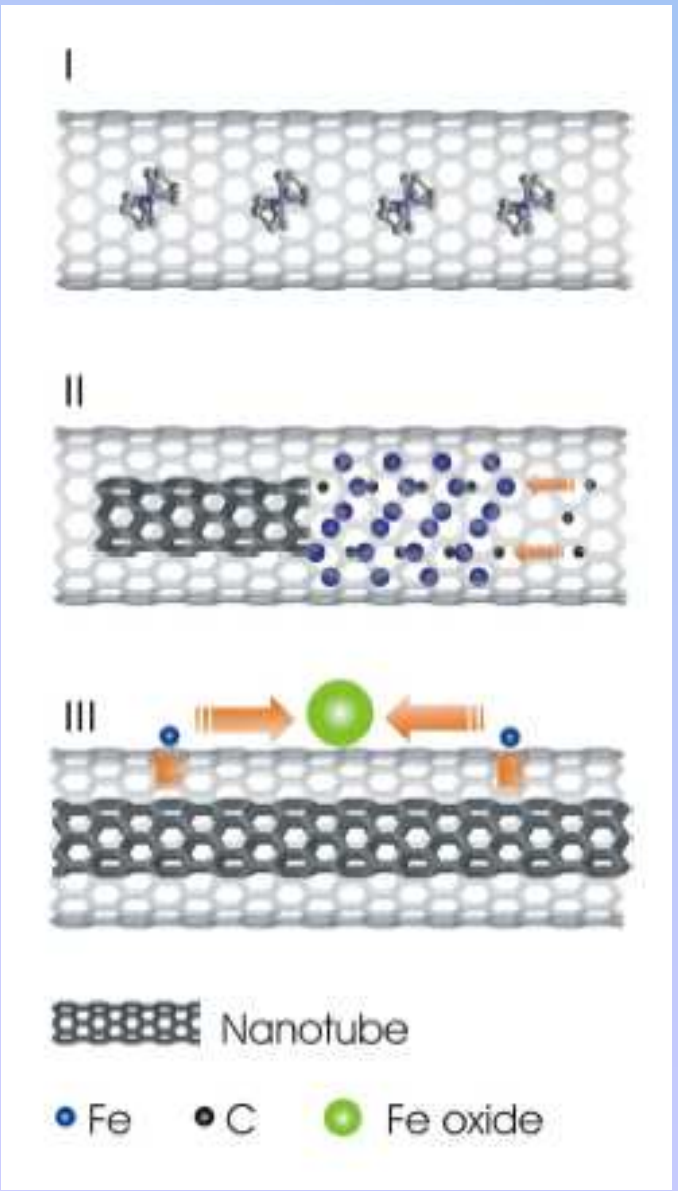




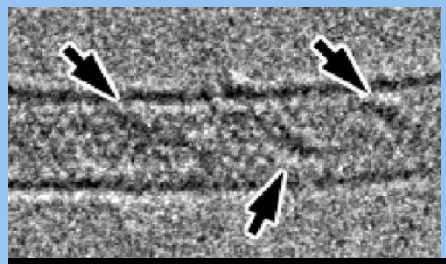
Catalytic growth of inner DWCNT differs from non-catalytic!

H. Shiozawa et al. Adv. Mat. (2008)

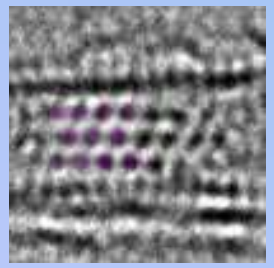
Temperature induced chemical reaction in a SWCNT nanoreactor

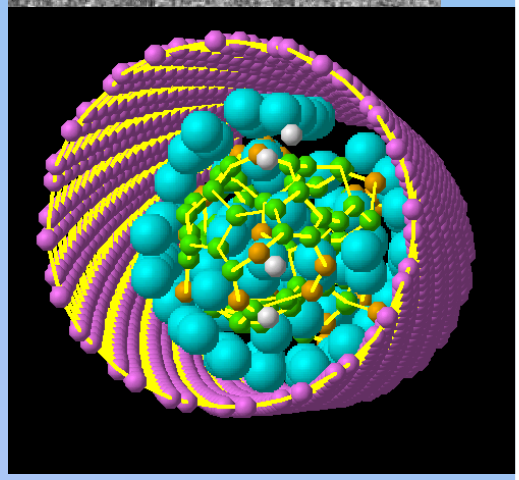


1. Ferrocene filling



2. Catalytic growth from Iron carbide particles



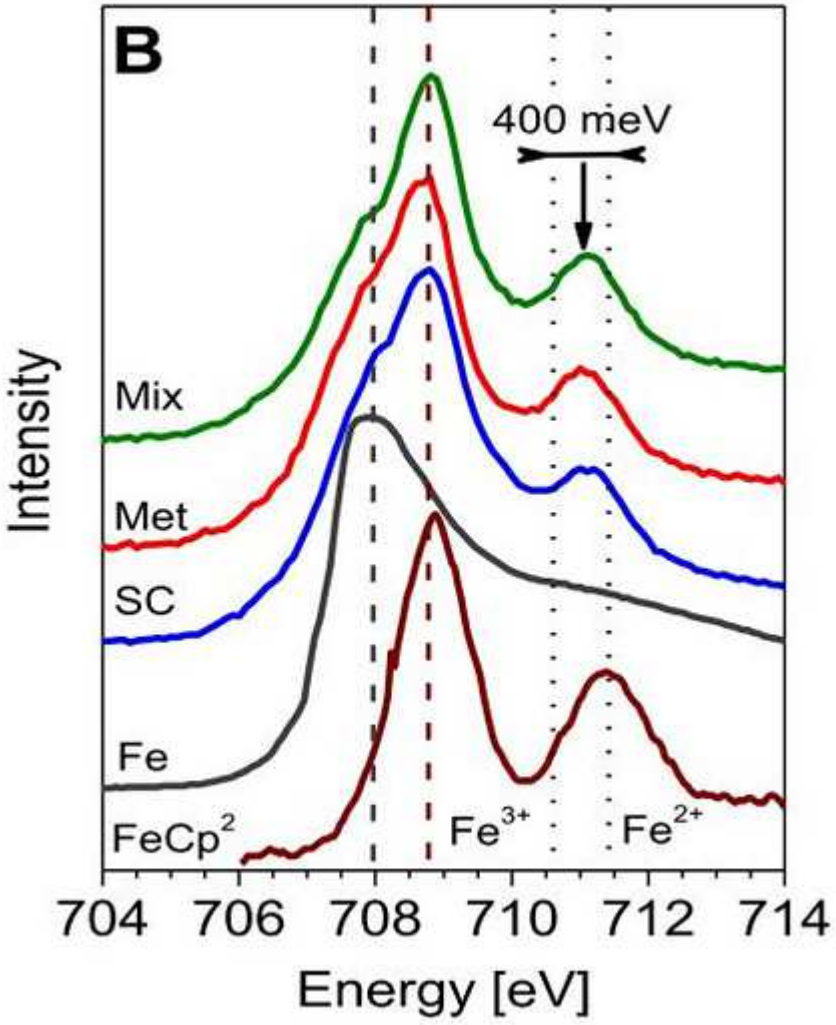


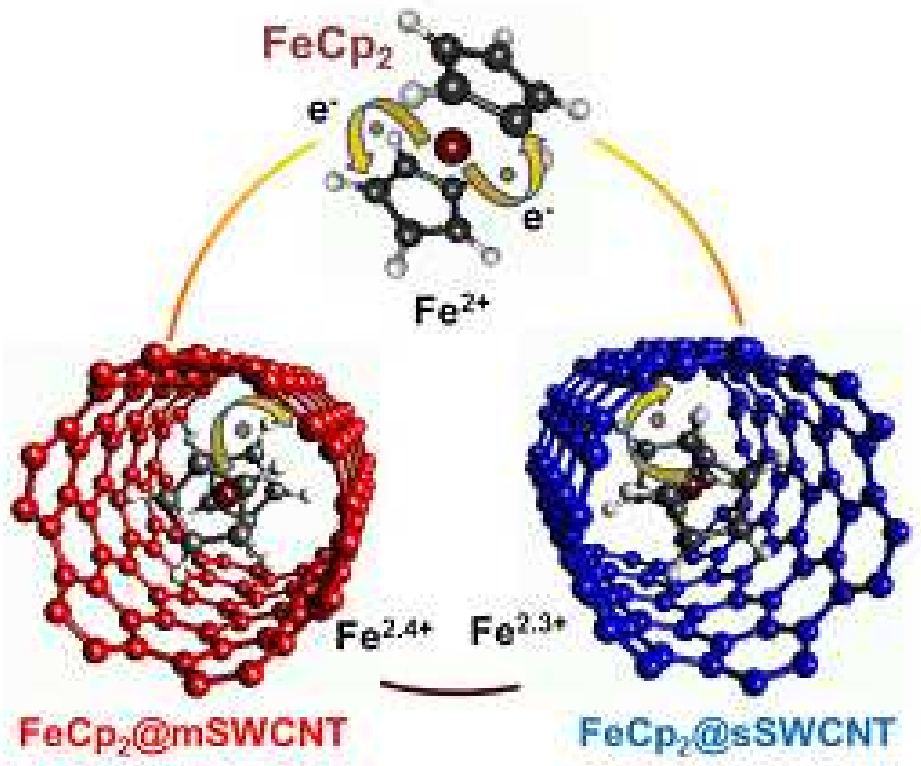
MD simulation
from S. Maruyama

3. Iron release via defects
Iron oxide nanocrystals

H. Shiozawa et al.
Adv. Mat. (2008); PRB (2008)

Ferrocene filling of metallicity sorted SWCNT

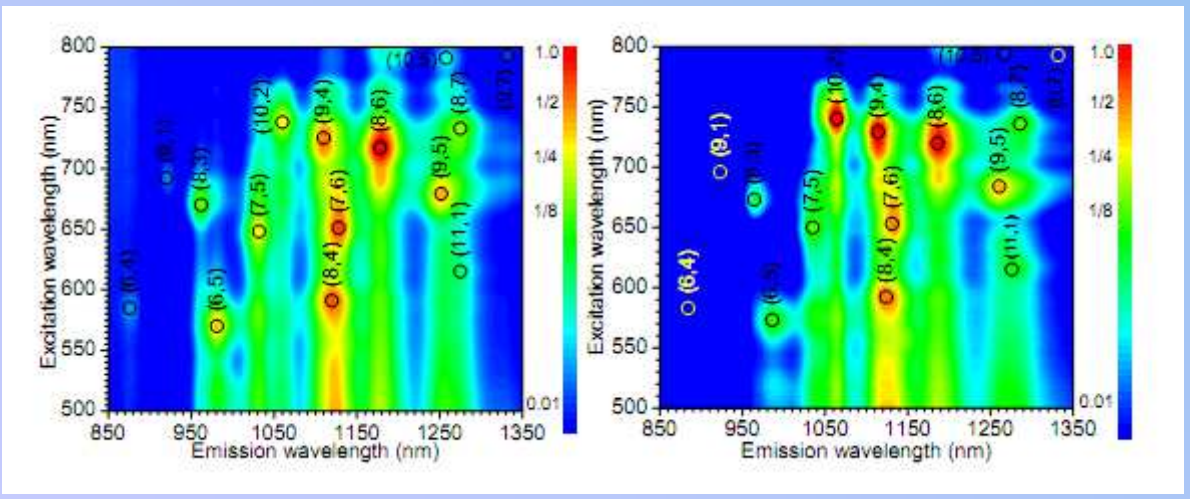


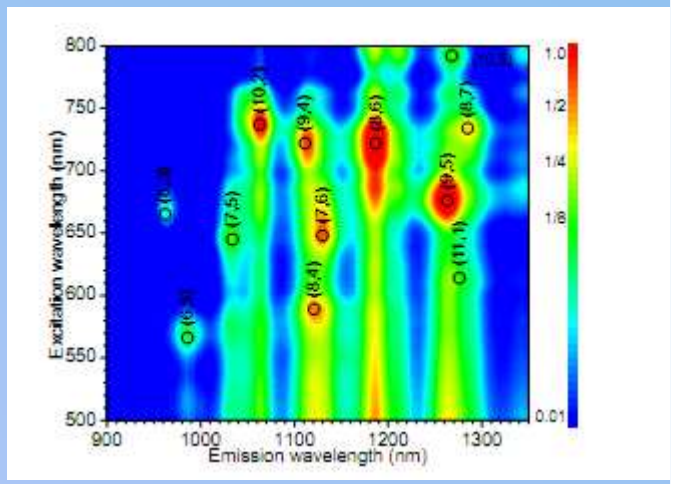


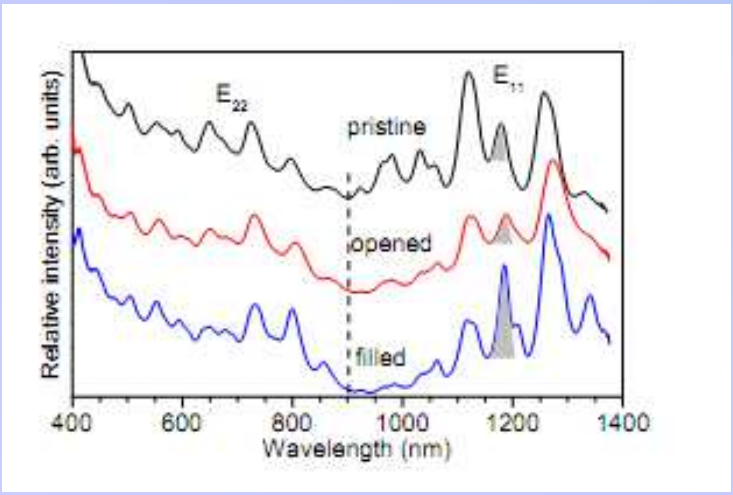
M. Sauer et al. submitted

PL of ferrocene filled Hipco SWCNT

Pristine **Opened** **Filled**

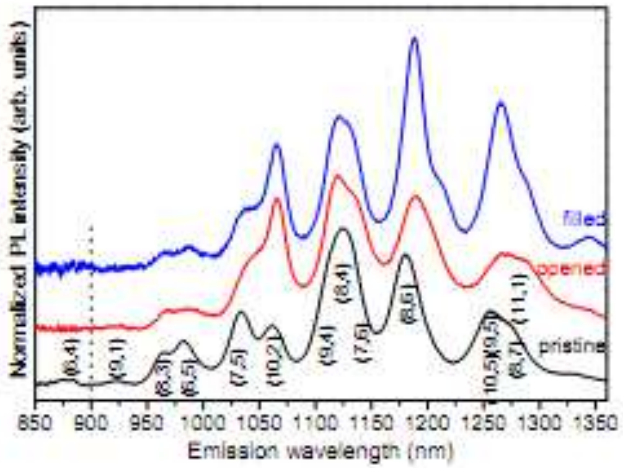


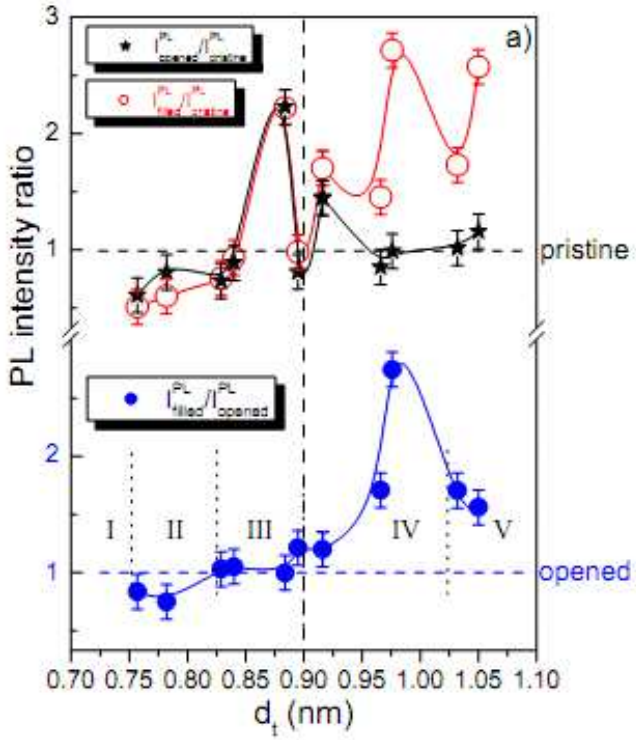


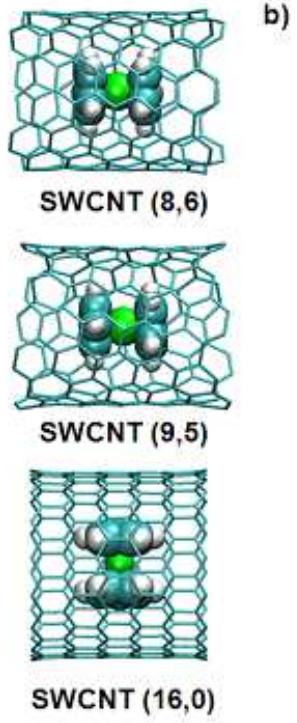


X. Liu et al. Advanced Functional Materials
DOI: 10.1002/adfm.201200224 (2012)

PL of ferrocene filled Hipco SWCNT







X. Liu et al. Advanced Functional Materials
DOI: 10.1002/adfm.201200224 (2012)

Summary for carbon nanostructures

Graphene and SWCNT are ideal 1D and 2D objects

Outstanding mechanical and electronic properties

Ideal systems to study basic correlation effects
even at room temperature!!!!!!

Tuneable electronic properties and interactions!!!

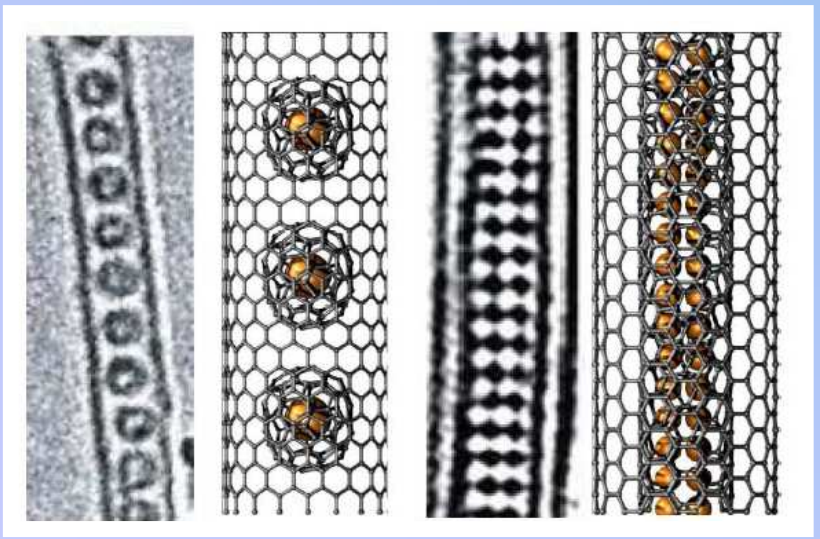
Interesting for both
basic research and applications

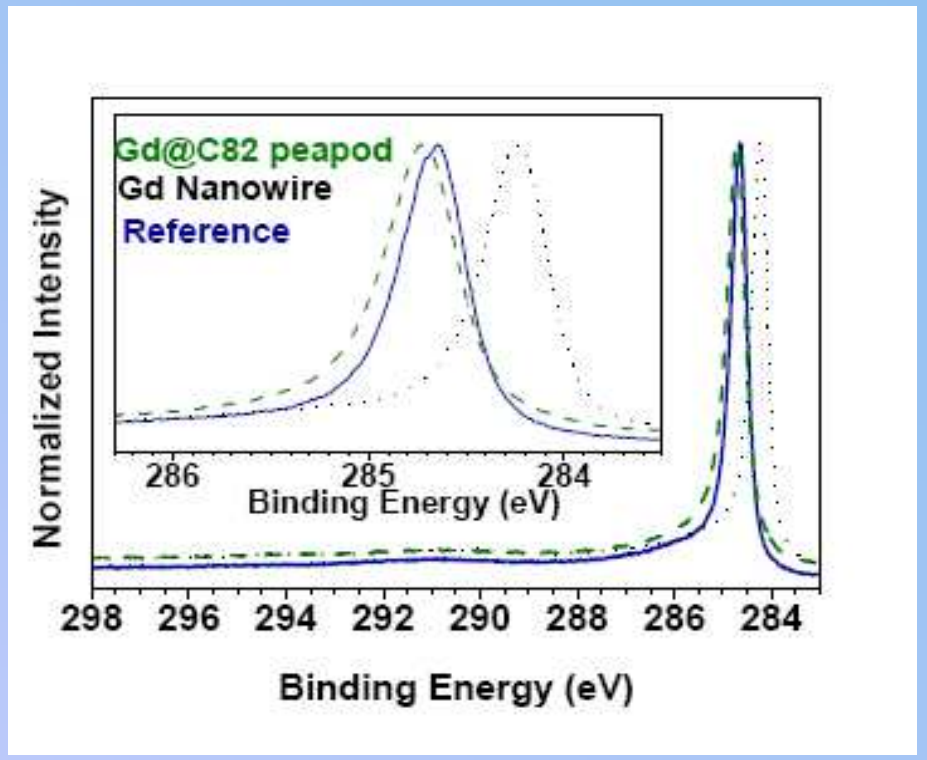
….. and now finally to something completely different….

….. It´s …..


My research group
in Vienna:
LOW DIMENSIONAL
QUANTUM SOLIDS
The beauty of instabilities…!!!
WANTED: PhD students, postdoc eager to
unravel the equilibrium ground state
dressed by correlations……!

$Gd@C_{82}@SWCNTs \rightarrow Gd@SWCNTs$

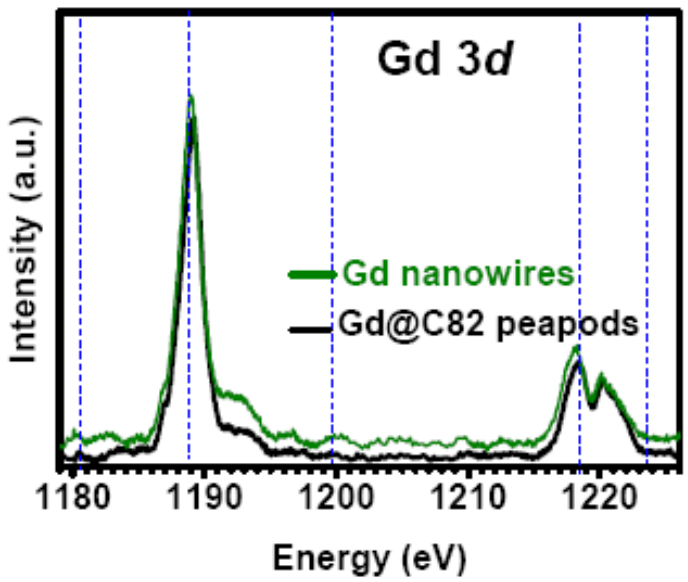


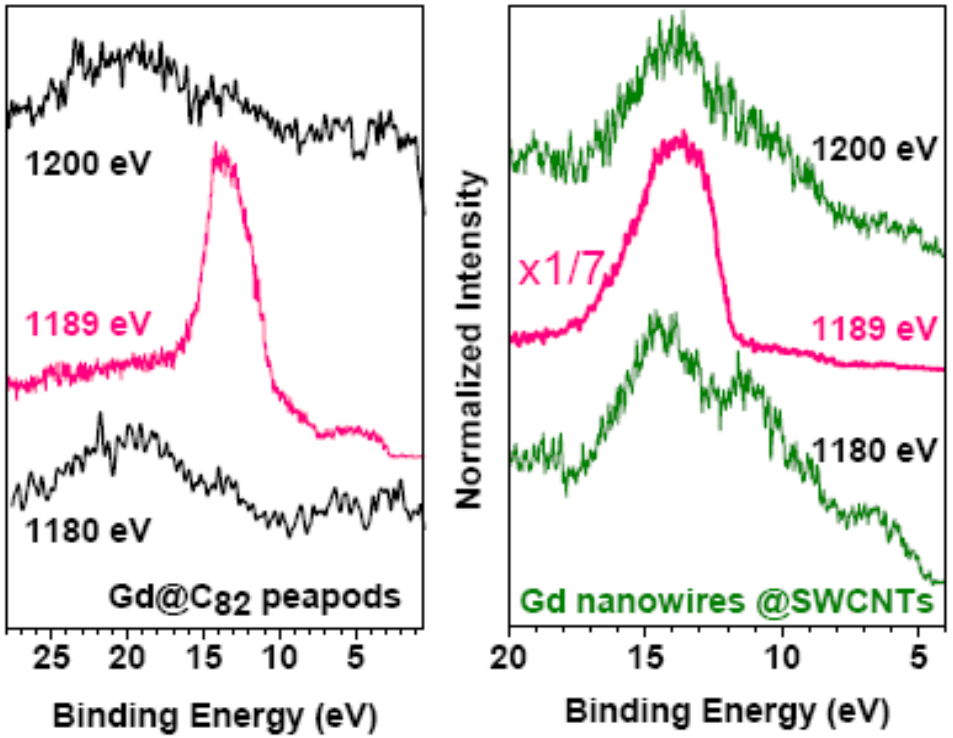


$Gd@C_{82}@SWCNTs$ undergo structural transformation upon heat treatment , yielding 1D Gd encapsulated nanowires.

P.Ayala et al., Materials Express 1,30 (2011).

$Gd@C_{82}@SWCNTs \rightarrow Gd@SWCNTs$



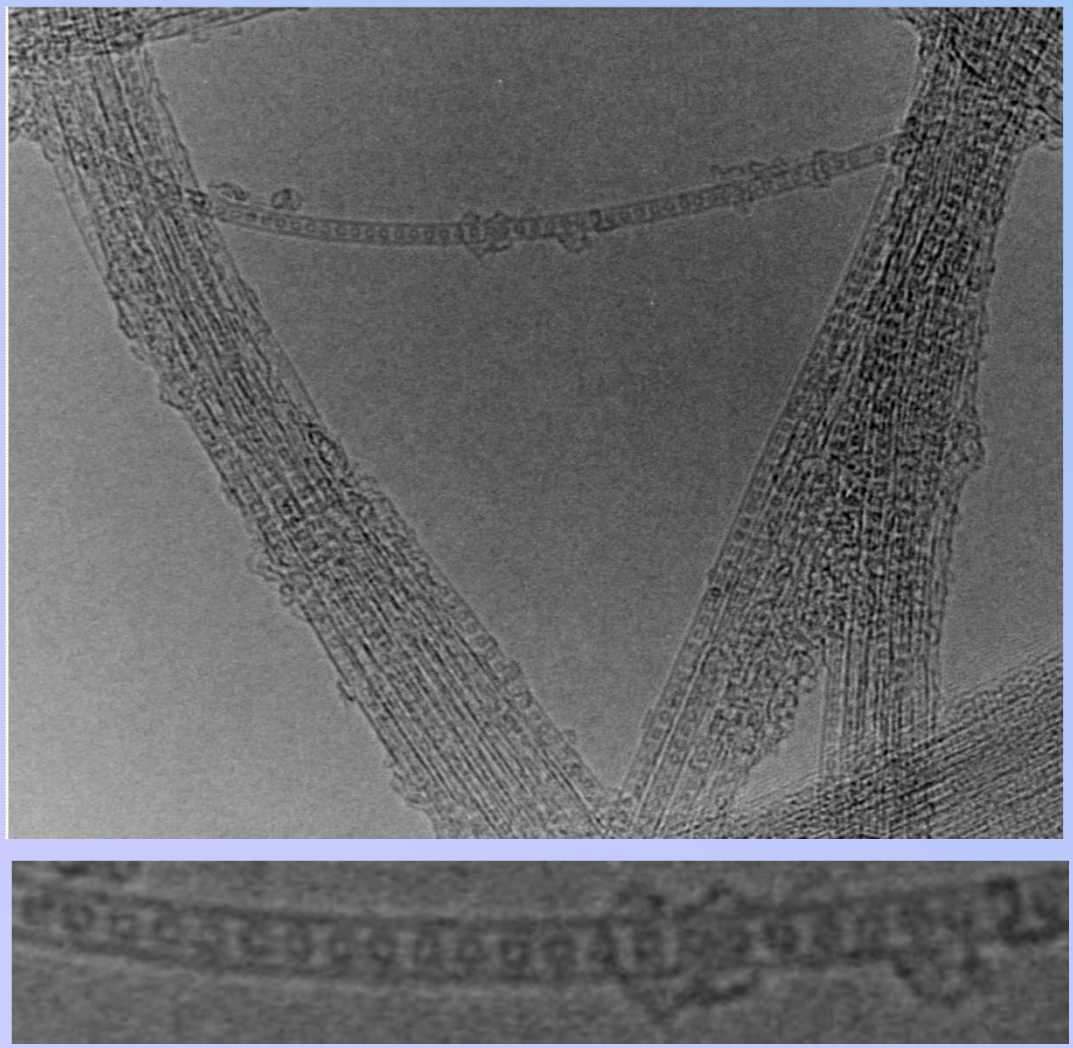


- XAS response in the 3*d* levels of Gd and RESPES.
- Stronger resonance for Gd nanowires → smaller hybridisation

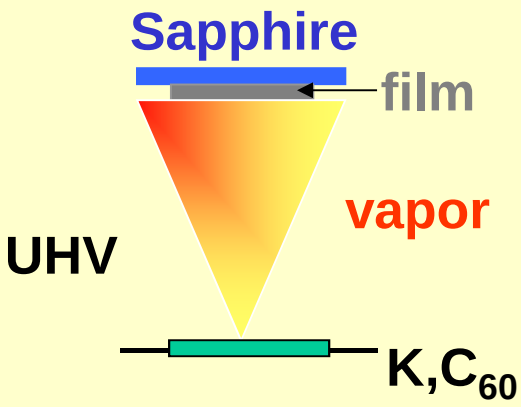
P.Ayala et al., , Materials Express 1,30 (2011).

Combinational doping: Intercalation of peapods

Peapods: e.g. C_{60} filled SWCNT

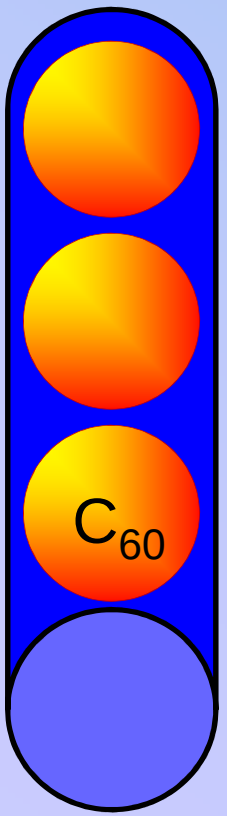


Filling/Intercalation

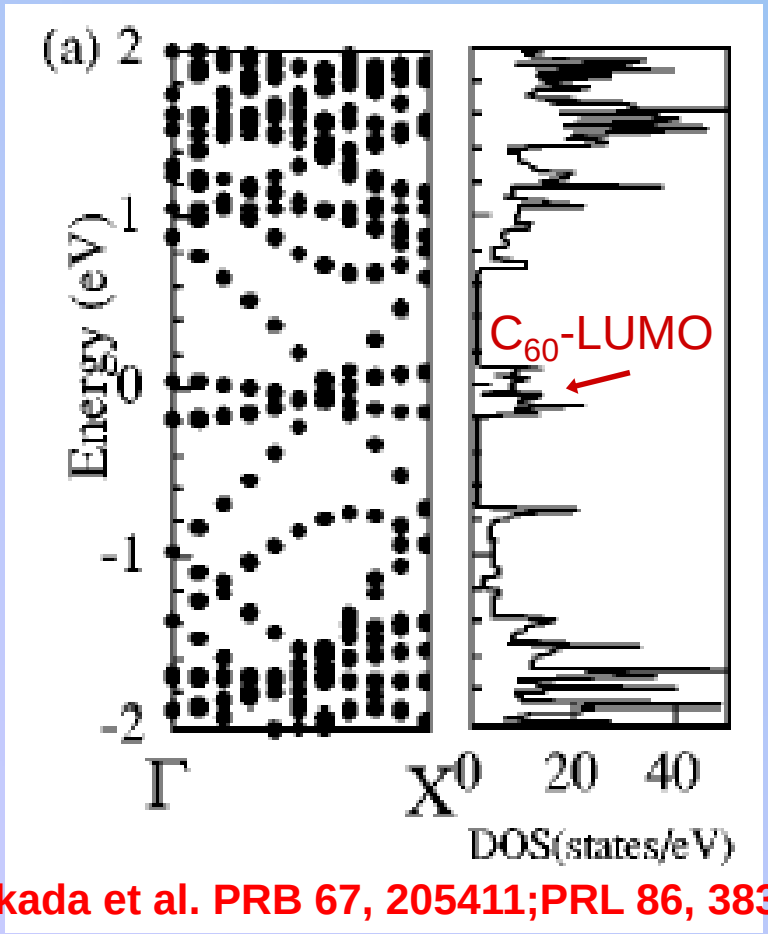


***in-situ* filling:**
UHV evaporation ($5x10^{-10}$ mbar)
K, C_{60} at 120/400 C
Equilibration 12 h at RT/350 C
Annealing at T=650 C

Electronic structure of C_{60} peapods: Predictions



Calculated DOS



Okada et al. PRB 67, 205411;PRL 86, 3835

Influence of more conduction channels

Que PRB 66, 193405

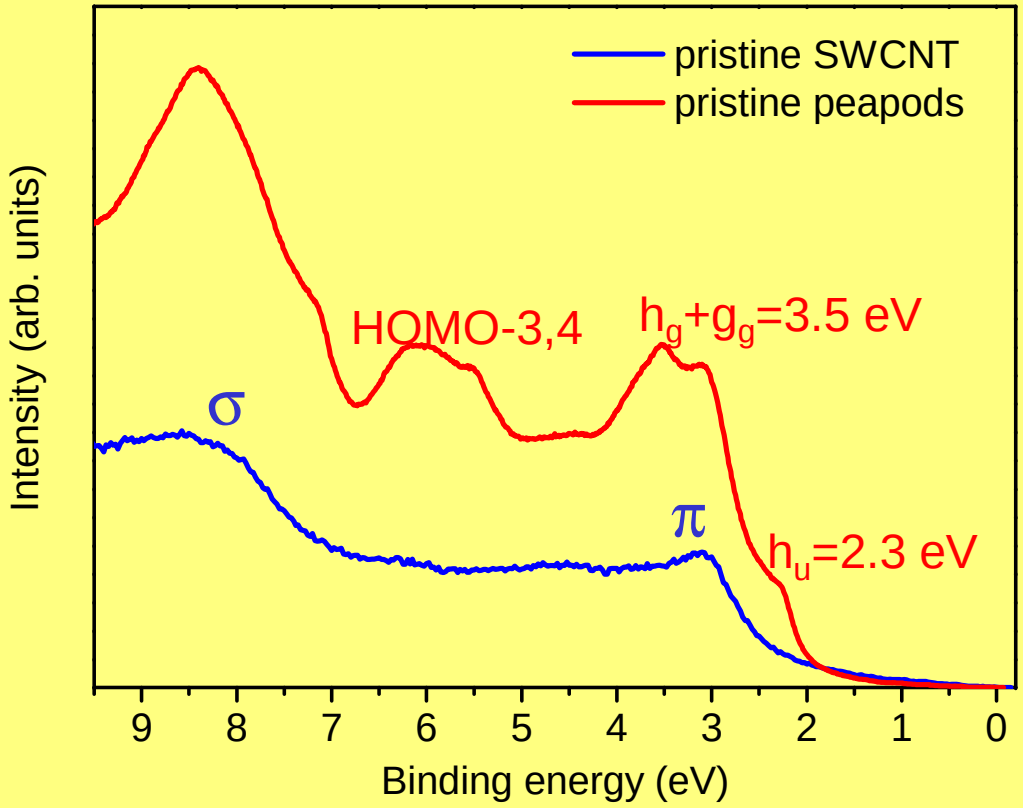
$1/g_p^2 = 2/g_t^2 - 1$

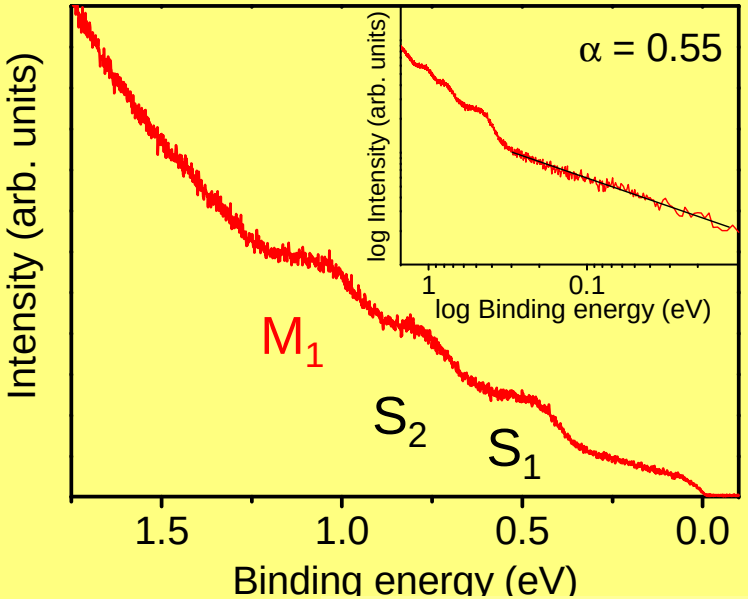
$\alpha_t = 0.46$
$g_t = 0.18$

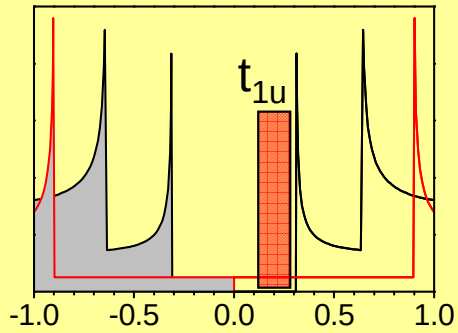
$g_p = 0.13$, $\alpha_p = 0.73$

- C_{60}-LUMO states near the Fermi level, 4 bands
- noticeable increase of α expected

Electronic structure of C_{60} peapods







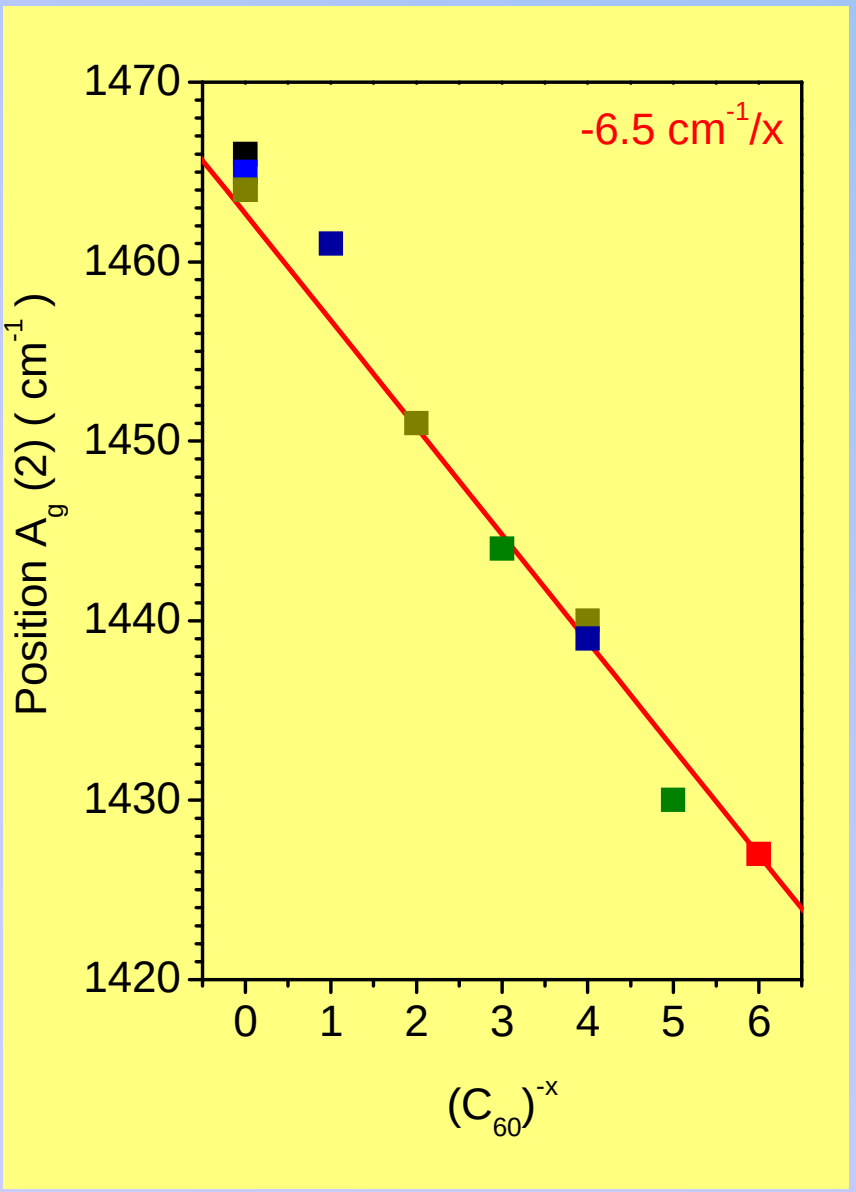
C_{60} derived molecular orbitals (Mos) observed

Binding energies as in bulk C_{60}, 100% filling

➡ Power law α=0-48-0.55 → basically no increase !!!

H. Rauf et al., PRB 72, 245411 (2005)

Combinational doping: Intercalation of C_{60} peapods

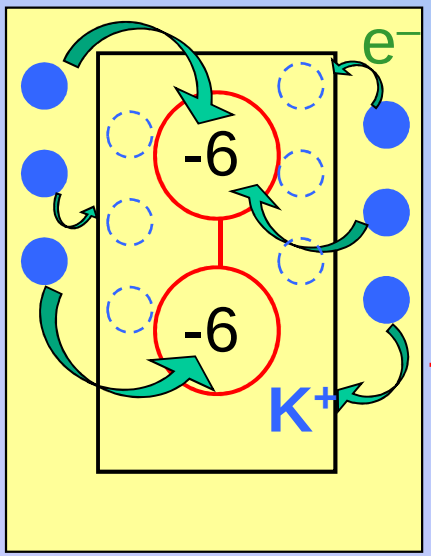


Competitive charge transfer to SWCNT and C_{60} peas !

Raman: $A_g(2)$ of C_{60}^{-x}:

- charge transfer up to C_{60}^{-6}
- no line phases:

  0.8 <x< 5.3 average charge transfer
- charge transfer induced polymerization



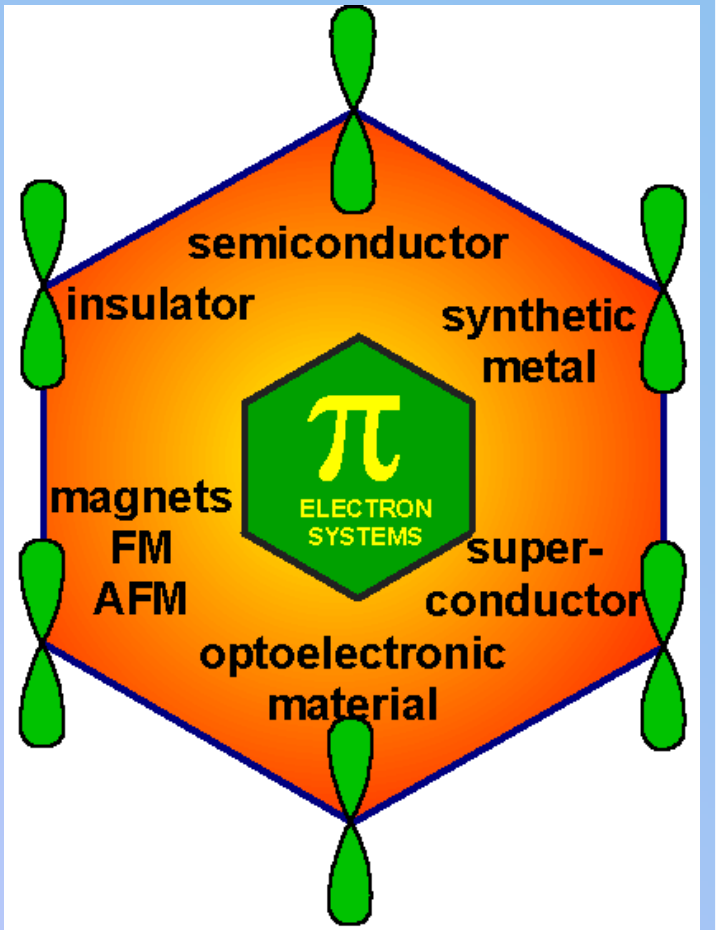
T. Pichler et al.,
PRL 87, 267401 (2001),
PRB 67, 125416 (2003).

Why carbon nanotubes?

- **Archetypical 1D system:**

  New electronic, optical and structural properties:

  - Ideal 1D quantumwires
  - Hard, ductile Nanowires
  - Molecular Magnets, Spintronics
  - Protection for reactive elements and molecules
  - Gas storage, gas sensing
  - FET, VIAS, optoelectronic
  - Sources for field emission
  - Organic superconductors
  - Li-Ion batteries
  - Sensors, actuators, NT-yarns, composits, drug delivery…..



⇨ Ideal tools for nanoelectronics/optics/mechanics/(bio)chemistry