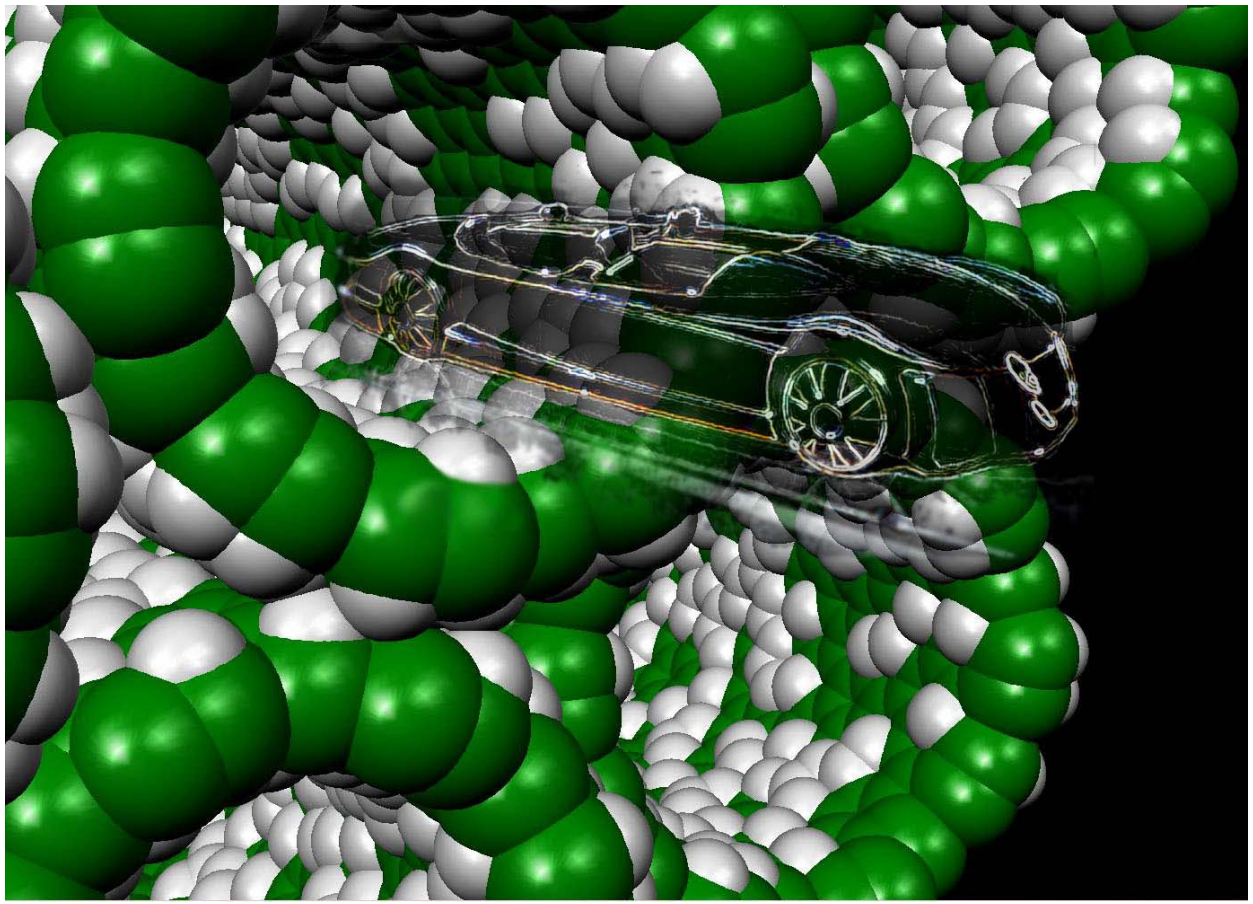
Hydrogenation of Single Walled Carbon Nanotubes

Anders Nilsson

Stanford Synchrotron Radiation Laboratory (SSRL) and Stockholm University



Coworkers and Ackowledgement

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Highlights:
http://www-ssrl.slac.stanford.edu/research/highlights_archive/swcn.html
http://www-als.lbl.gov/als/science/sci_archive/129nanotube.html

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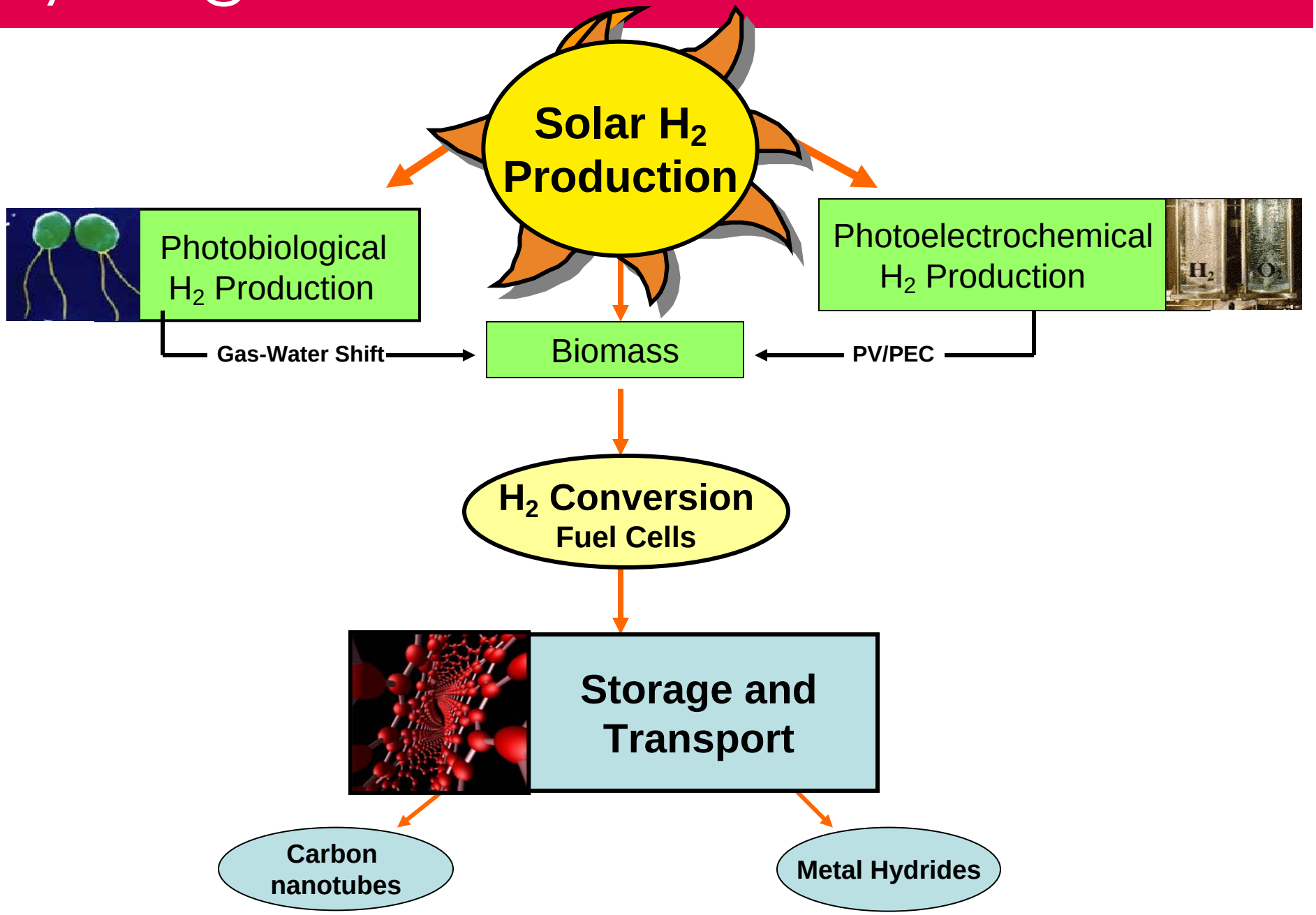
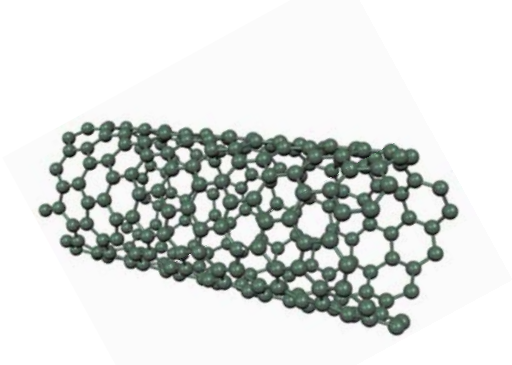
GCEP
Global Climate & Energy Project
STANFORD UNIVERSITY

Hydrogen Dream

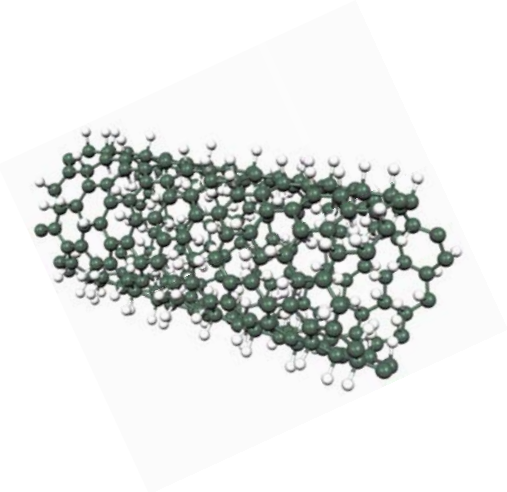


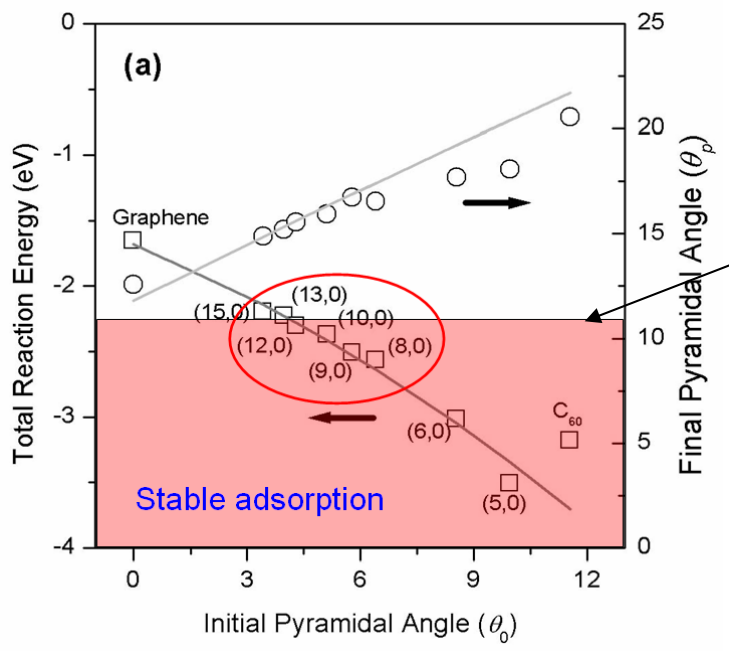
Chemisorption of H atoms on Carbon Nanotubes

***Idea:* to store hydrogen in the chemisorbed form on the nanotube surface**



hydrogenation





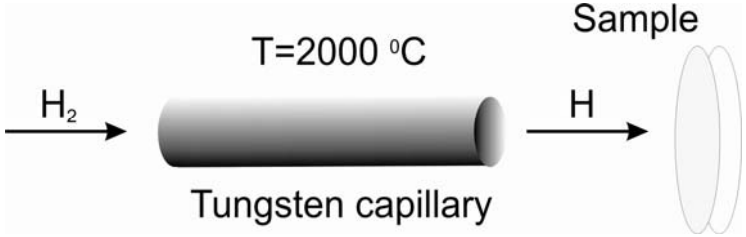
H-H bond energy 4.5 eV

Adsorption Energy Decreases with diameter

KJ Cho et.al.

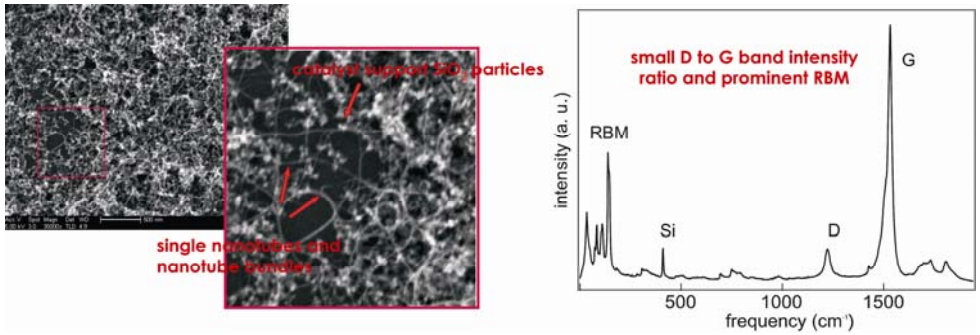
Investigation strategy

Hydrogenation: *in situ* atomic hydrogen treatment



- elimination of H_2 dissociation step from hydrogenation process
- well controlled environment (base pressure < 1 10^{-9} Torr)

Samples: "as grown" CVD SWCN films



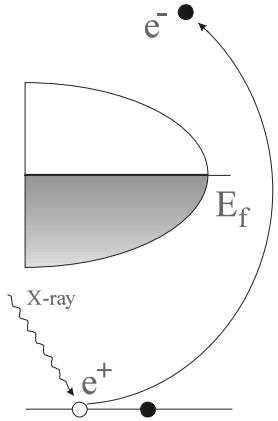
- low defect / amorphous carbon concentration (small D to G band intensity ration)
- low concentration of contamination (*in situ* annealing up to 900 C)

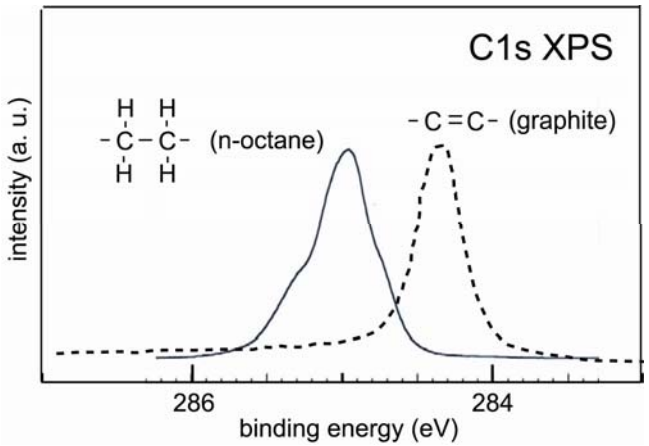
Probing tools: X-ray photoelectron spectroscopy (XPS) and X-ray adsorption spectroscopy (XAS)

- XPS and XAS allow to observe the formation of C-H bonds through the modification of the carbon nanotube electronic structure around specific carbon atoms

Probing tools

X-ray photoelectron spectroscopy (XPS)

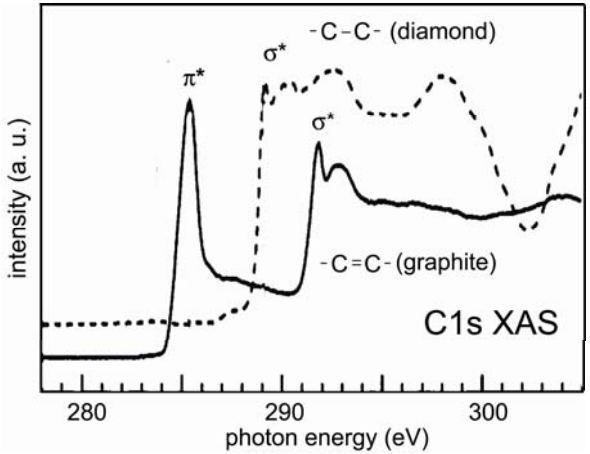


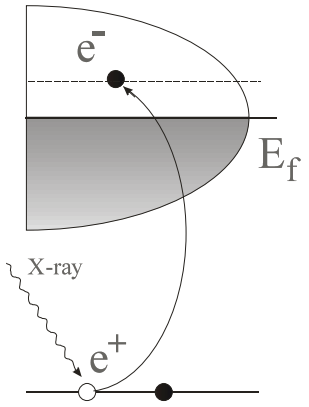


C1s XPS spectra of n-octane and graphite (Weiss et al., 2003, Bennich et al., 1999)

X-ray absorption spectroscopy (XAS)

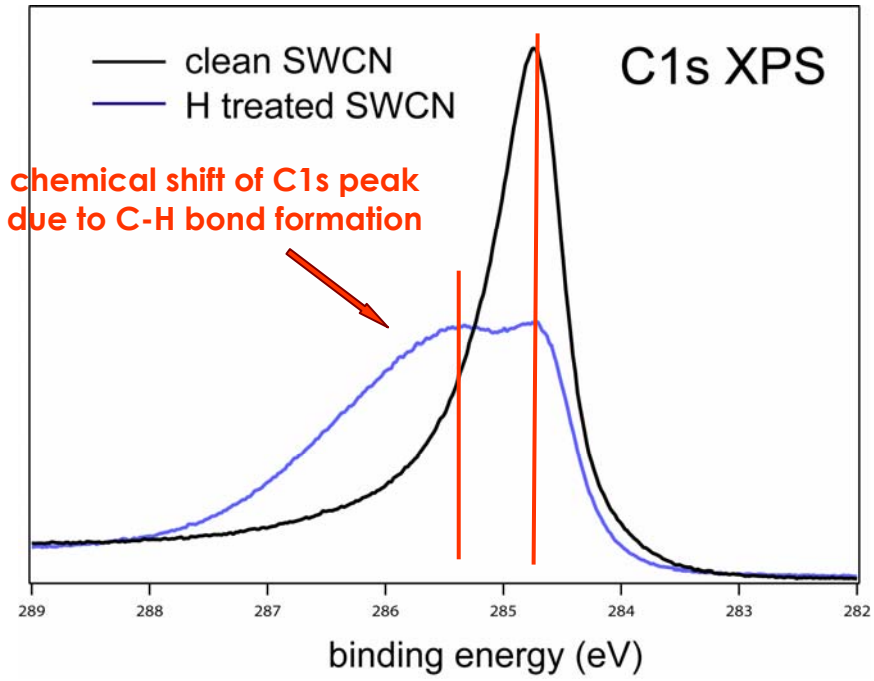
Carbon K-edge XAS spectra of graphite and diamond (Garo et al., 2001)



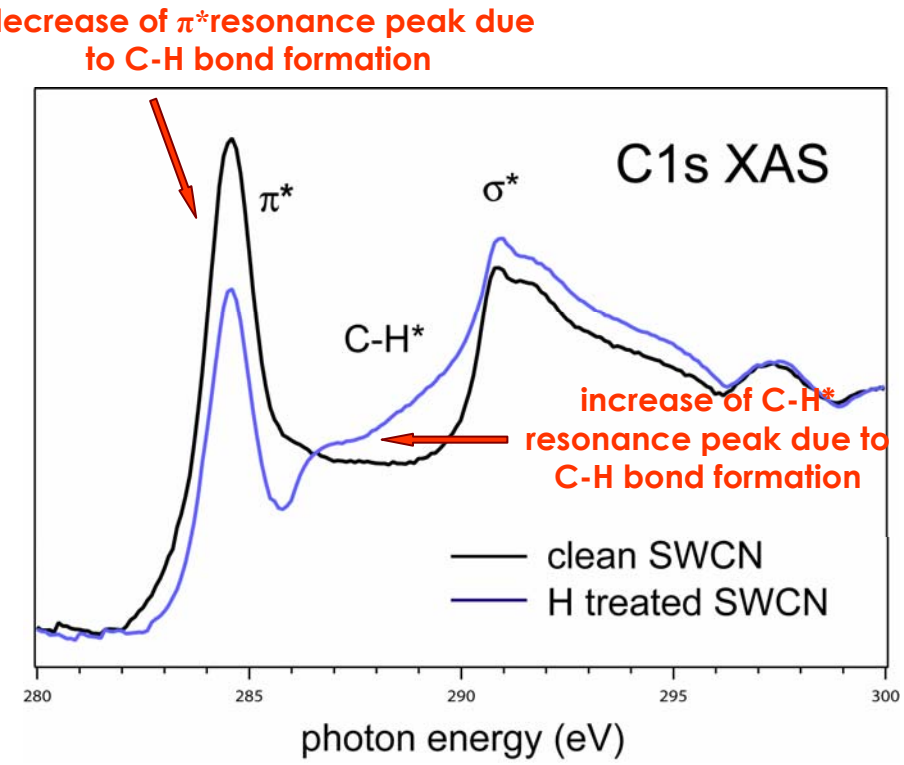


Hydrogenation induced changes in XAS and XPS spectra

C1s XPS spectra of the clean and hydrogenated SWCN films



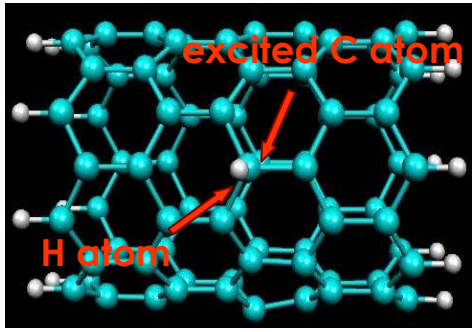
Carbon K-edge XAS spectra of clean and hydrogenated SWCN films



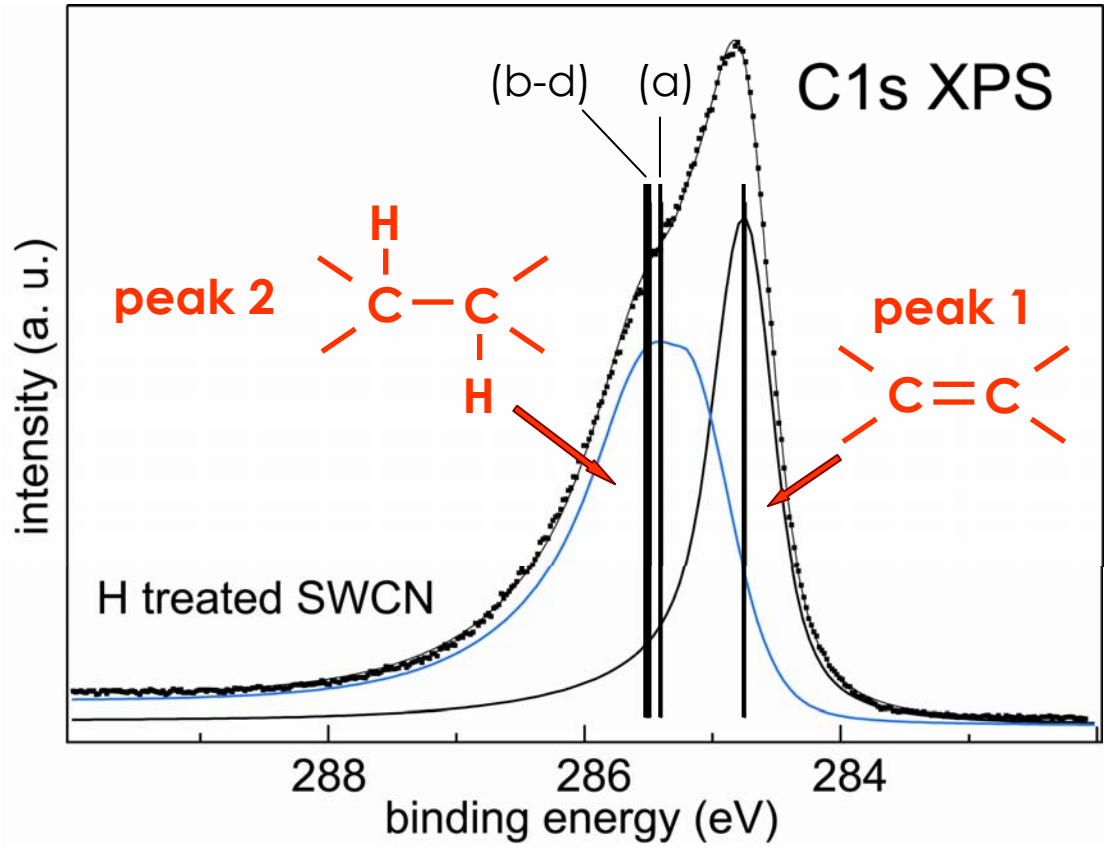
The hydrogenation degree determination from XPS spectra

Calculated C1s chemical shift values (MD and DFT)

	(n,m)	D, nm	Shift, eV
(a)	(10,0)	0.78	0.65
(b)	(12,0)	0.94	0.77
(c)	(15,0)	1.16	0.74
(d)	(22,0)	1.72	0.76



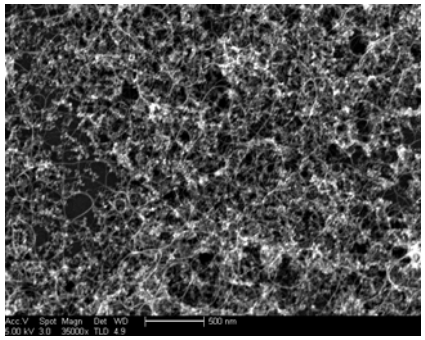
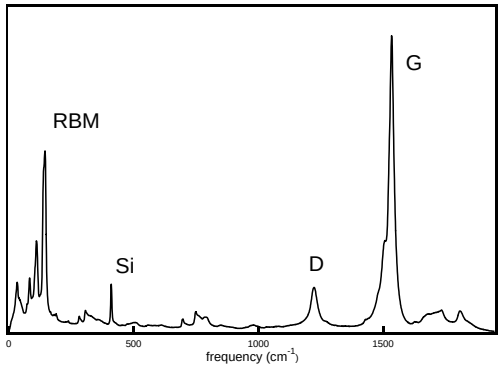
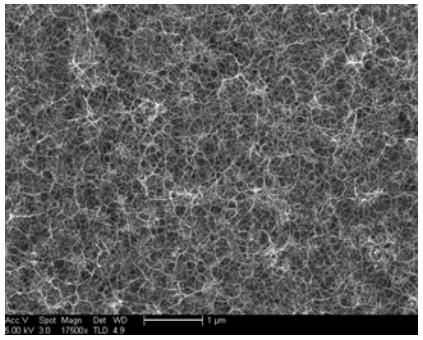
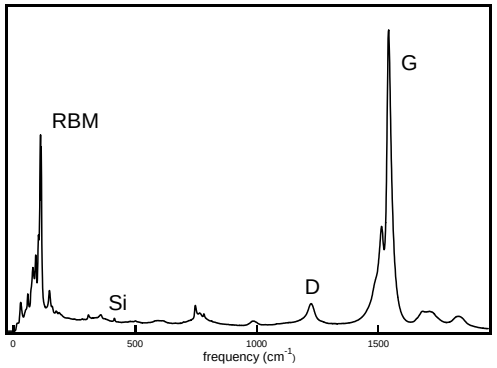
Decomposition of C1s XPS for hydrogenated SWCN film



Hydrogenation = $I_{peak\ 2}/(I_{peak\ 1}+I_{peak\ 2})*100$ at %

Samples

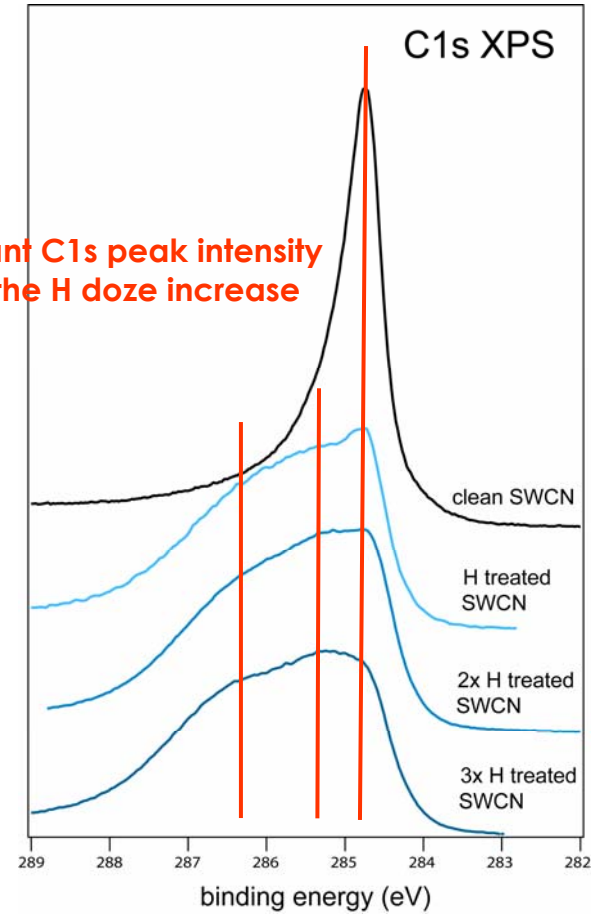
"as grown" chemical vapor deposition (CVD) SWCN films

	Growth condition	SEM picture	Raman spectra
Type 1	Catalyst: FeCo on SiO_2 Gas: 400 sccm CH_4, 70 sccm H_2 Temperature: 850 C		
Type 2	Catalyst: FeCoMo on SiO_2 Gas: 300 sccm EtOH, 300 sccm Ar Temperature: 850 C		

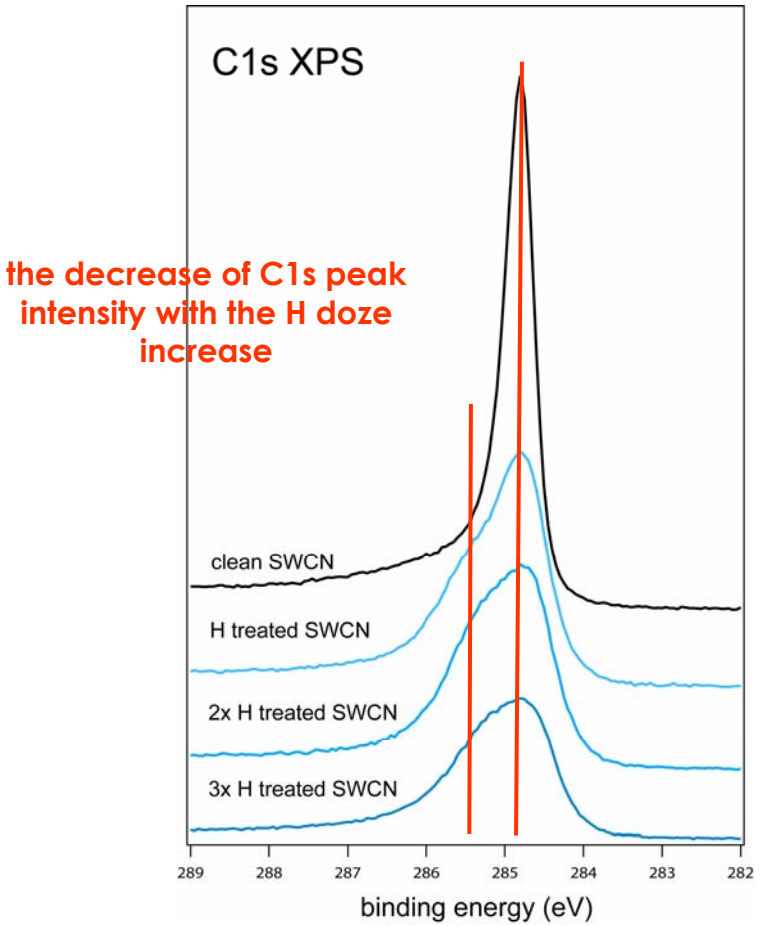
- prominent RBM band - relatively narrow SWCN diameter distribution
- small D to G band intensity ration - low defect/ amorphous carbon concentration
- most of SWCN are in the bundles

The influence of SWCN diameter on hydrogenation process

Hydrogenation sequence of SWCN, type 1

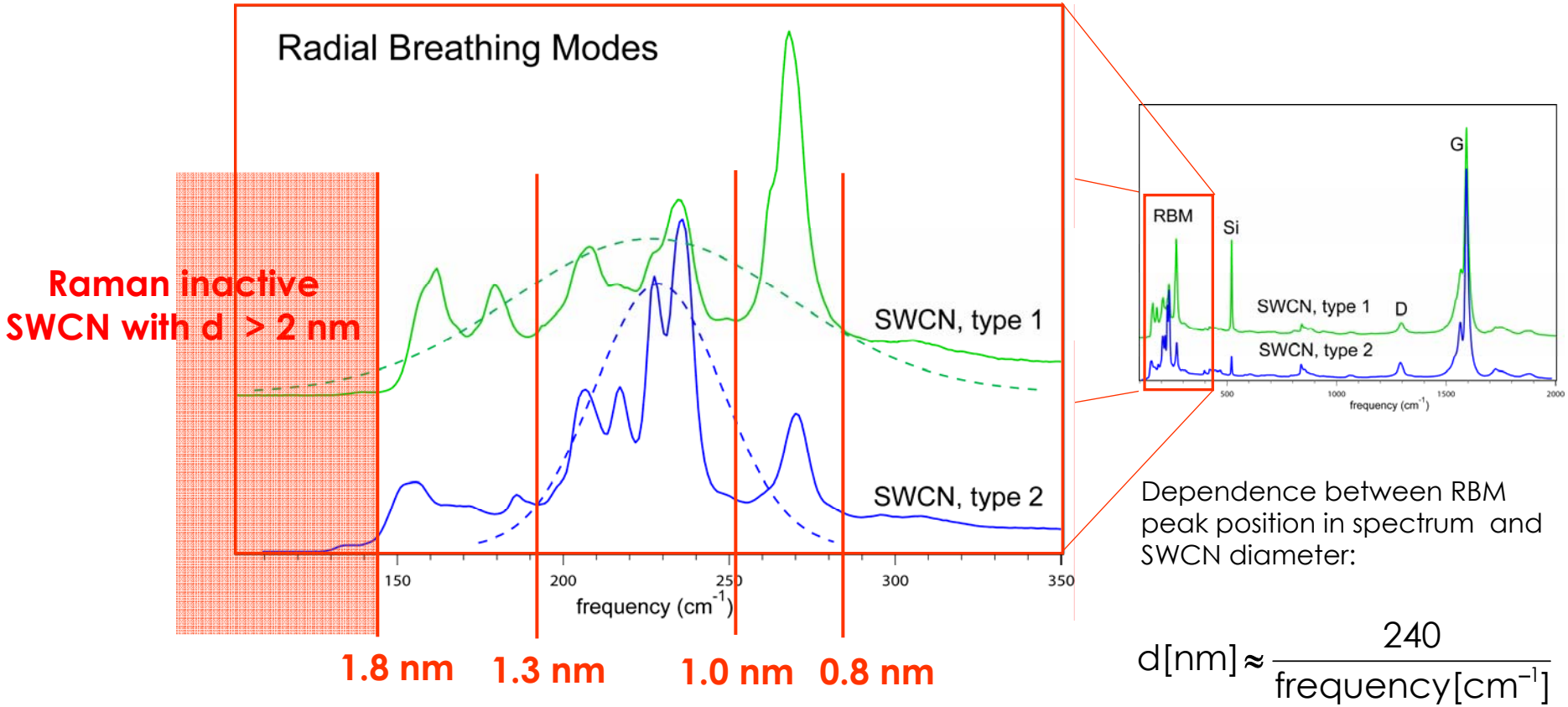


Hydrogenation sequence of SWCN, type 2



For the SWCN, type 2 under H treatment **etching of the material** starts before reaching high degree of hydrogenation in comparison with SWCN, type 1

The influence of SWCN diameter on hydrogenation process



Dependence between RBM peak position in spectrum and SWCN diameter:

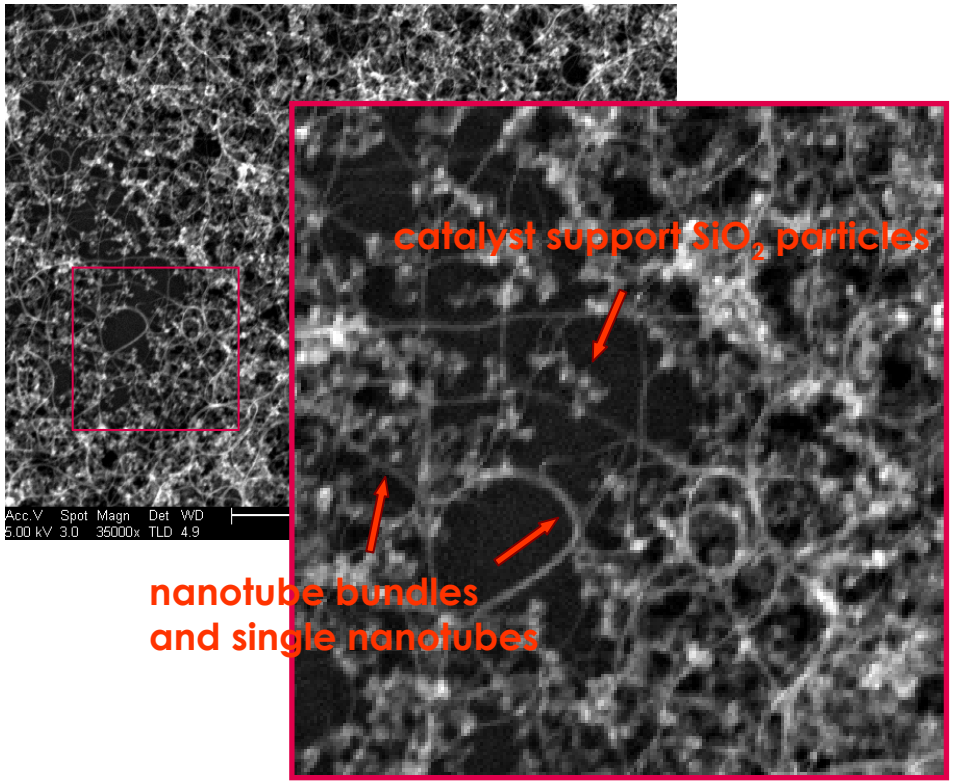
$$d[\mathrm{nm}] \approx \frac{240}{\mathrm{frequency}[\mathrm{cm}^{-1}]}$$

- theoretical prediction of H induced "unzipping" for the small (d < 1.2 nm) SWCN (Lu et al PRB 68, 205416)
- experimentally observed selective H^+ plasma etching for different types of SWCN (Zhang et al JACS 2006, 128, 6026)

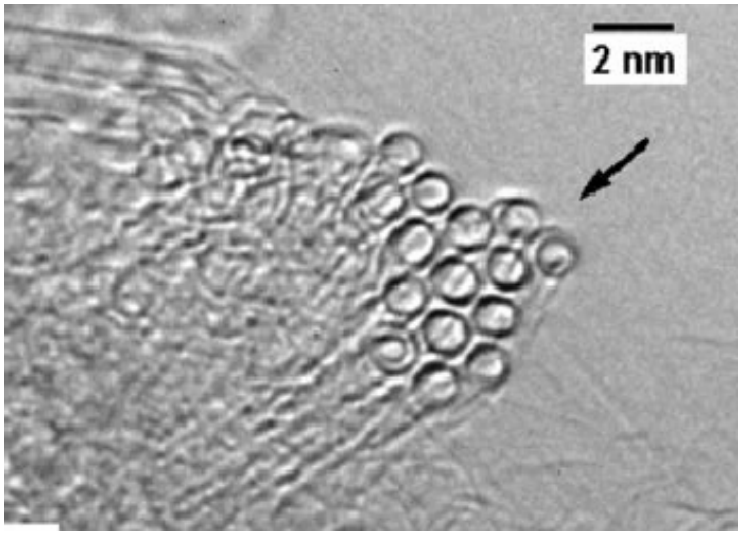
For SWCN with **different diameters** H induced etching of the material starts at **different degree of hydrogenation**

The morphology of SWCN film

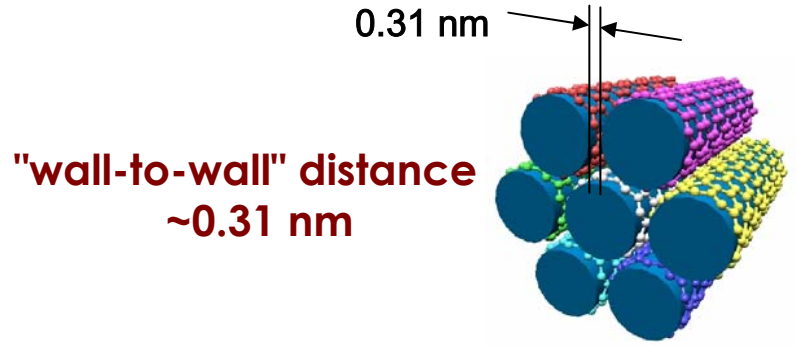
SEM picture of studied film



TEM picture of SWCN bundle



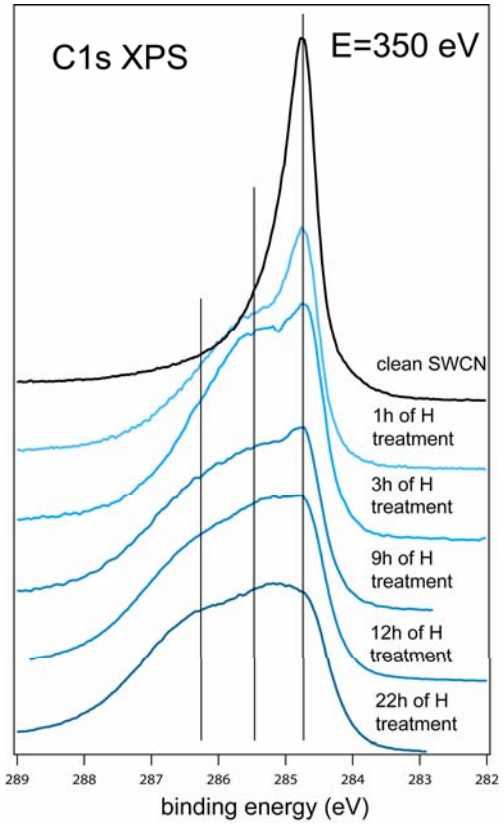
(Terrones et al Science 228, 1226)

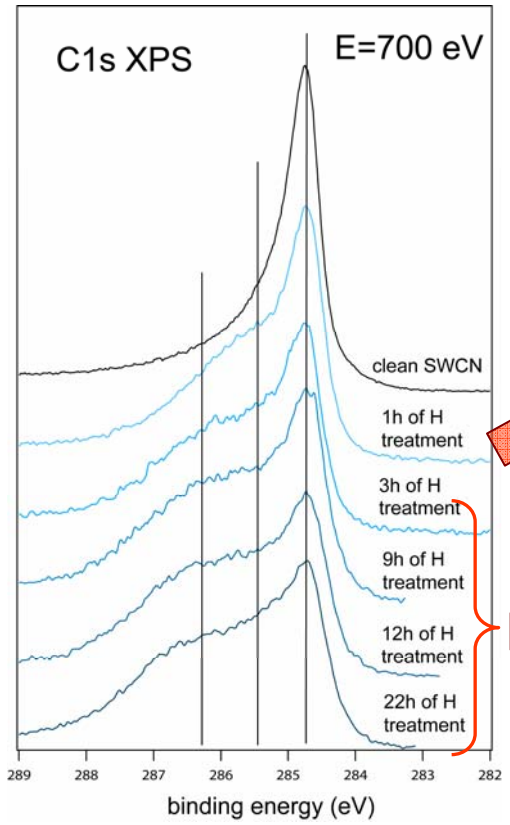


How does bundling morphology influence on hydrogenation ?

The hydrogenation depth of SWCN film

Hydrogenation sequence for SWCN, type 1 measured at different excitation energies

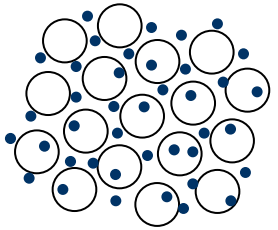




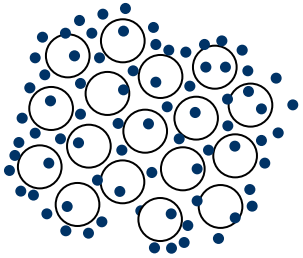
$E_{hυ}$= 350 eV (E_{kinC1s}= 65 eV)
λ ≈ 0.3 nm (more surface sensitive)

$E_{hυ}$=700 eV (E_{kinC1s}= 415 eV)
λ ≈ 1 nm (more bulk sensitive)

uniform hydrogenation of SWCN bundle up to ~50 -60 %



Increase of hydrogenation degree only on the SWCN bundle surface at additional H treatment



Hydrogenation is **not uniform** across the SWCN bundle

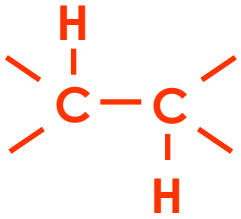
Structure of XPS C1s spectrum for highly hydrogenated SWCN

Peak 1

Clean C atoms in SWCN walls

Peak 2
$\Delta E_{1-2} \approx 0.7$ eV

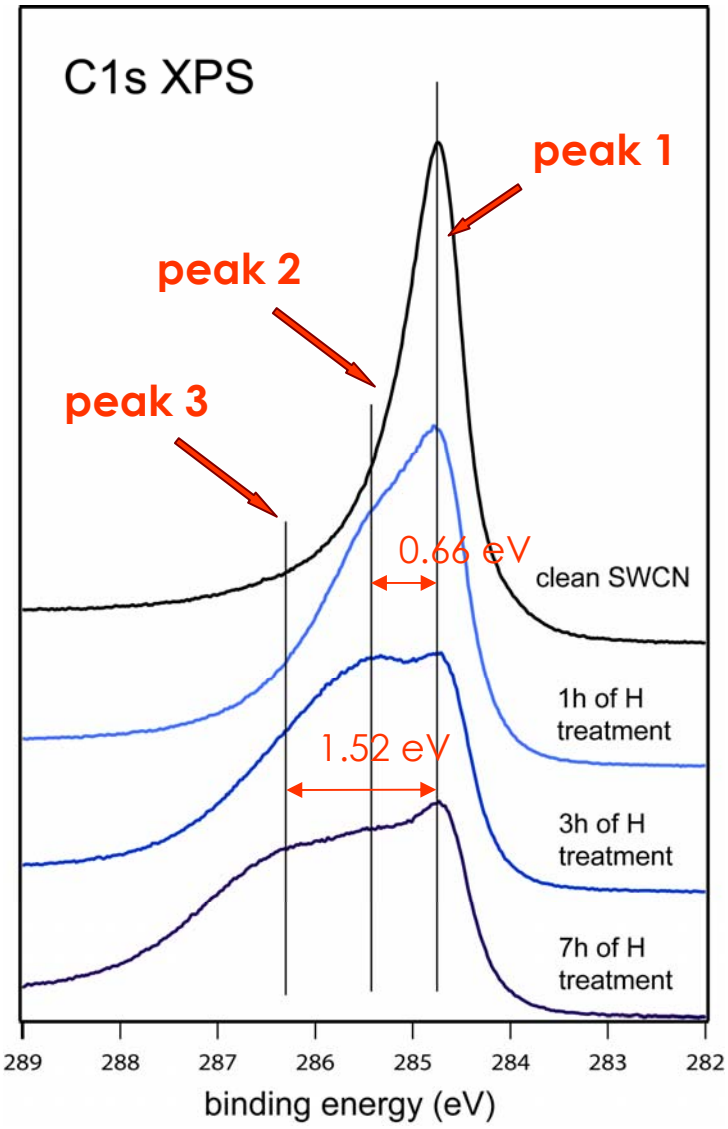
C-H bonded C atoms in SWCN walls



Peak 3
$\Delta E_{1-3} \approx 1.5$ eV

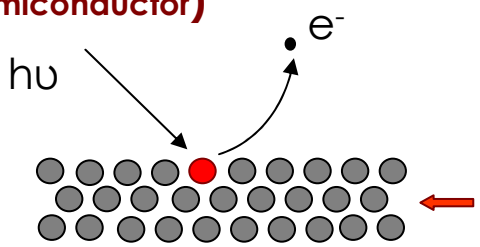
C-H bonded C atoms in SWCN walls **with different electron screening mechanism in photoionization process**

Hydrogenation sequence of SWCN, type 1



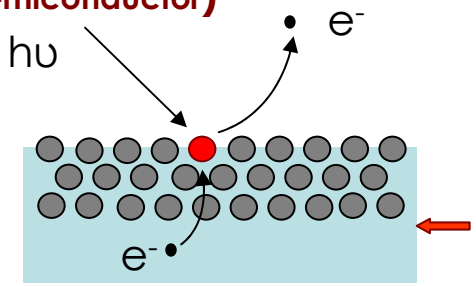
The electron screening in photoionization process

Atom photoionization in the system without delocalized electrons (insulator or wide bandgap semiconductor)



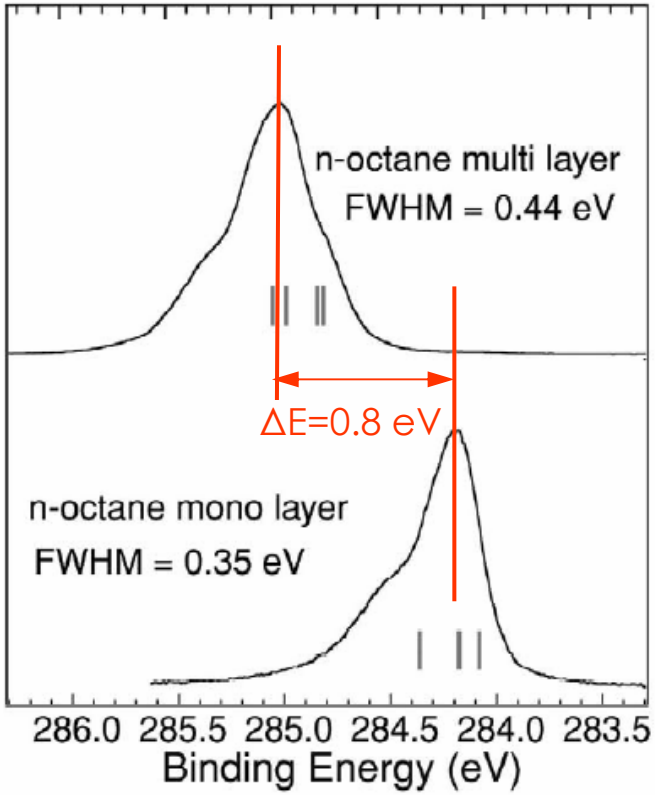
No delocalized electrons in the system

Atom photoionization in the system with delocalized electrons (metal or narrow bandgap semiconductor)



Delocalized electrons in conduction bend

The transfer of delocalized electron to the ionized atom changes the final state

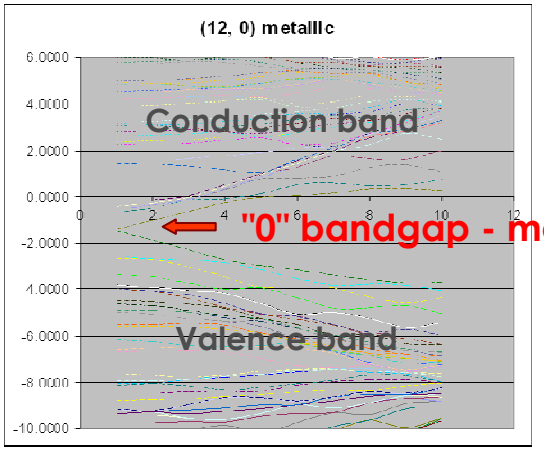


C1s XPS spectra of monolayer of n-octane on Cu substrate and n-octane multilayer (Weiss et al., 2003, J. of Elect. Spectr. 2003, 128, 129)

The presence of delocalized electrons in the system leads to the **different final state** in the photoionization process and **peak shift** in the XPS spectrum

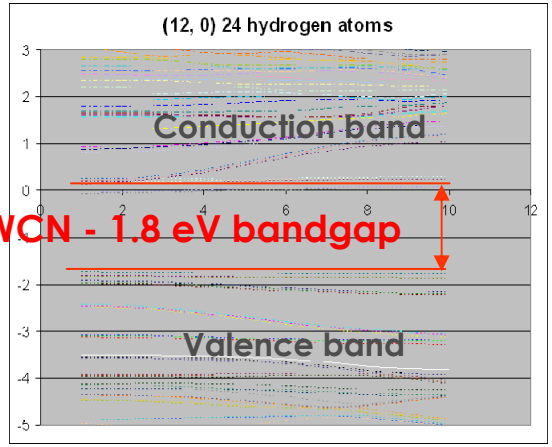
The electron screening in hydrogenated SWCN

Hydrogenation induced band gap increase in SWCN



"0" bandgap - metallic SWCN

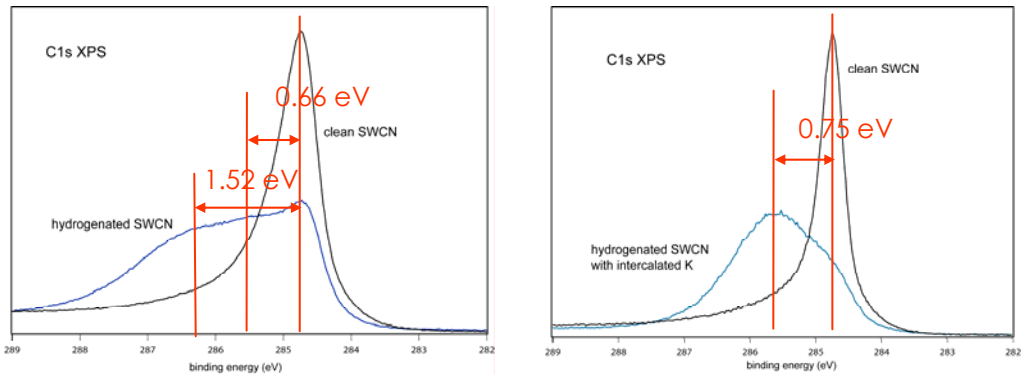
Insulating SWCN - 1.8 eV bandgap



Calculated DOS of clean (12,0) SWCN

Calculated DOS of hydrogenated (12,0) SWCN

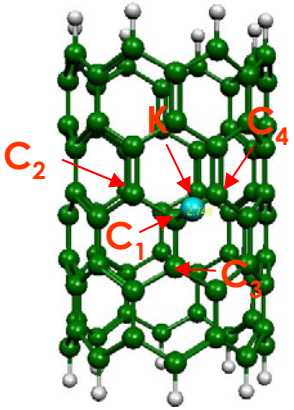
Hydrogenated SWCN with intercalated K



C1s XPS spectra of hydrogenated SWCN with (right) and without (left) intercalated K

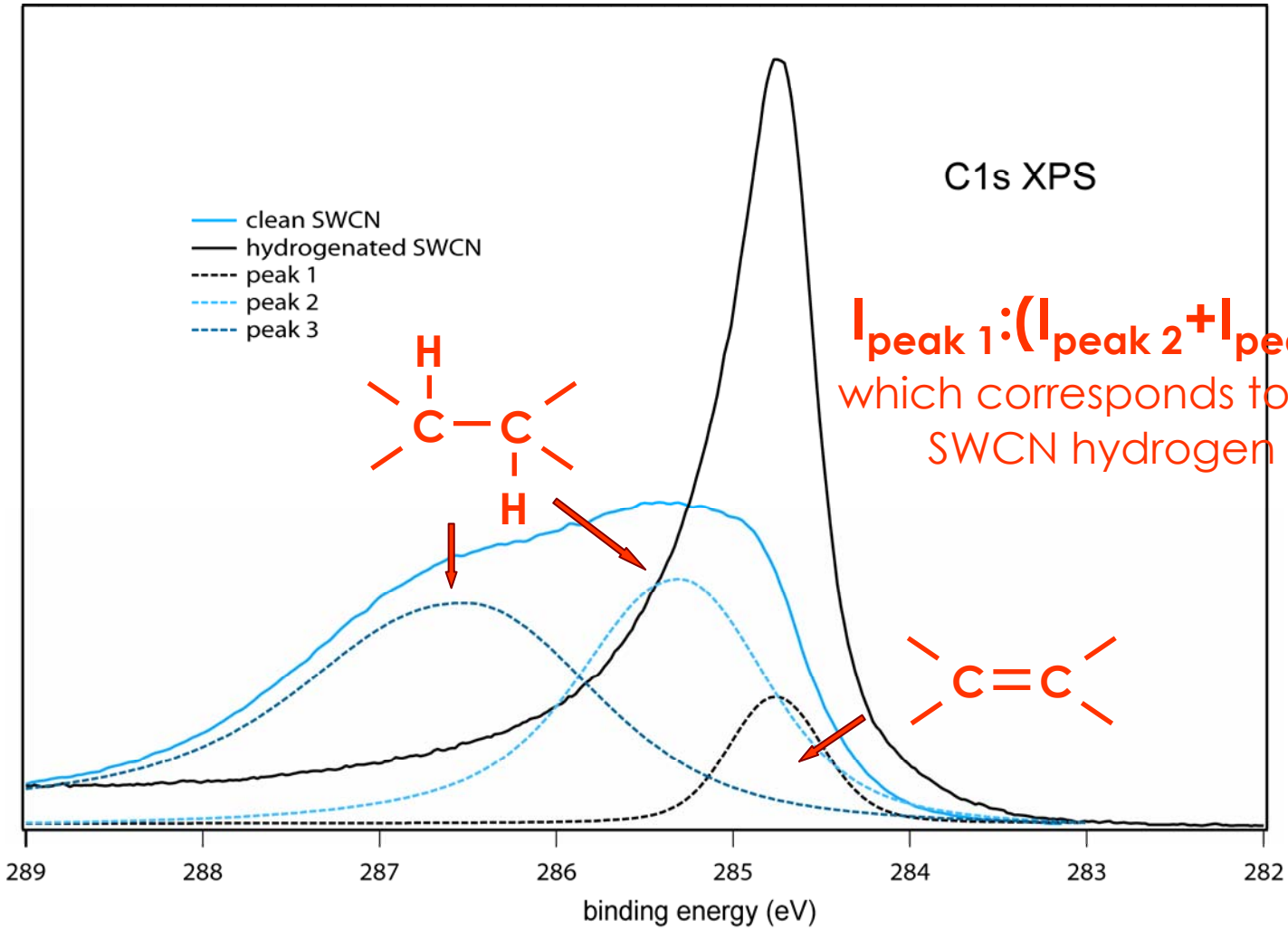
Calculated Values of the C1s shift due to the influence of the delocalized electron donated by adsorbed K atom

atom	shift, eV
C_1	-0.483
C_2	-0.403
C_3	-0.372
C_4	-0.739



The hydrogenation degree of SWCN

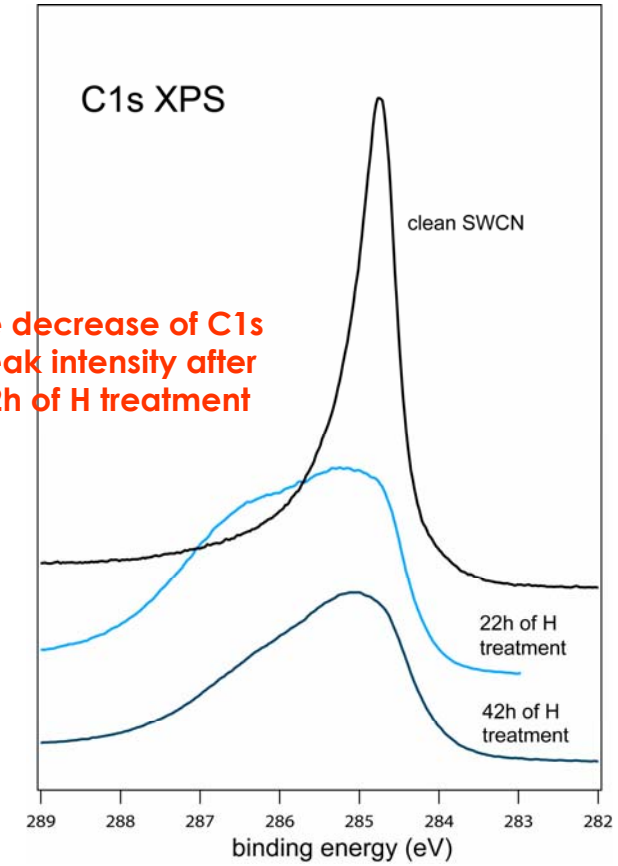
Decomposition of C1s XPS for hydrogenated SWCN film



$I_{peak\ 1}:(I_{peak\ 2}+I_{peak3}) = 1:10$
which corresponds to **~7 wt %** of SWCN hydrogen capacity

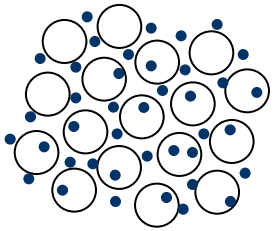
The interaction of atomic H with SWCN

Hydrogenation sequence of SWCN, type 1



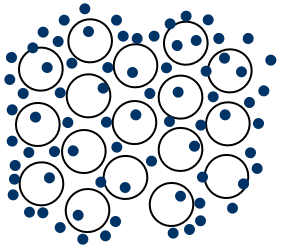
the decrease of C1s peak intensity after 42h of H treatment

1. uniform hydrogenation of SWCN bundle up to 50 - 60 at %



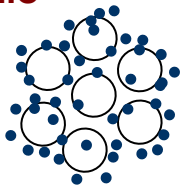
more atomic H

2. almost 100 at % hydrogenation of outer SWCN in the bundle



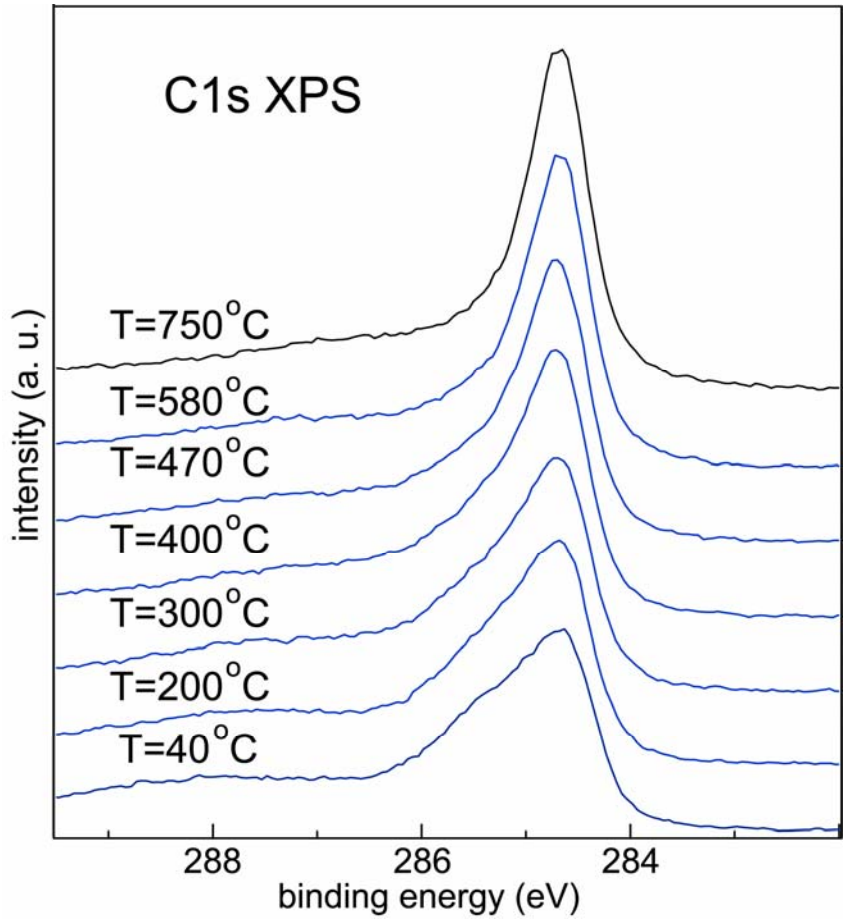
more atomic H

3. etching of outer 100% hydrogenated SWCN in the bundle



Hydrogen desorption temperature

C1s XPS spectra measured during annealing of H treated SWCN, type 1

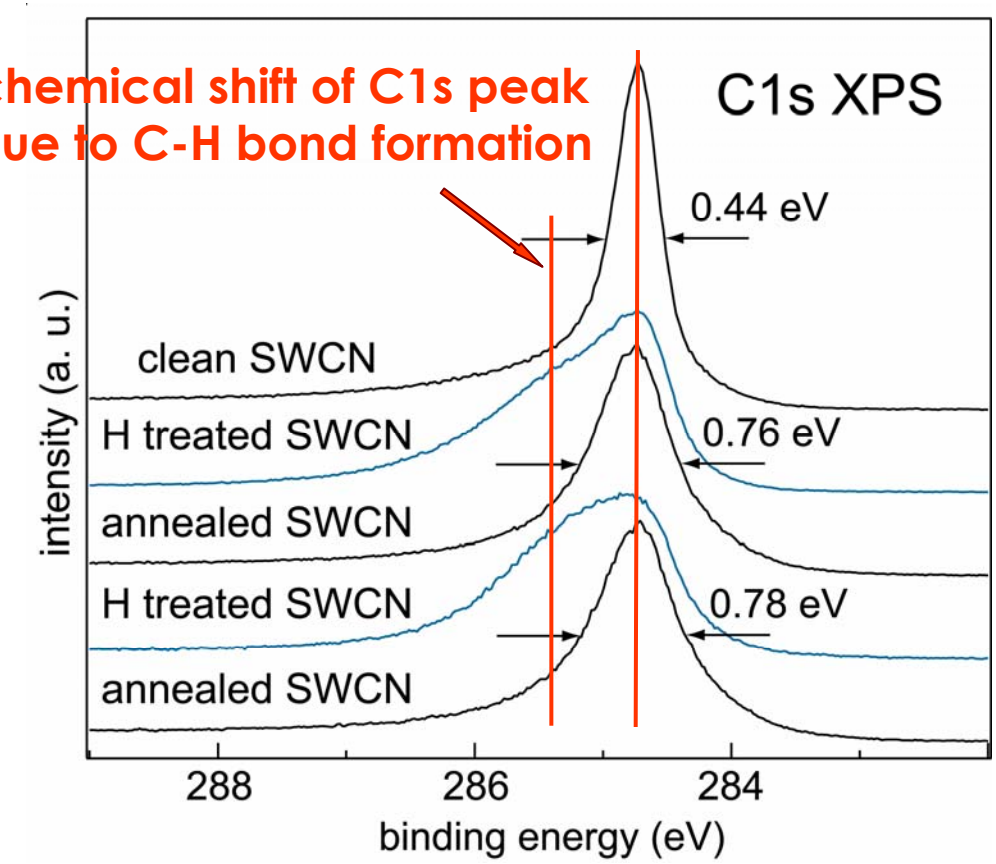


C1s peak shape change due to C-H bond cleavage was observed

Hydrogen desorption is observed in the range from **300 °C** to **600 °C**

Hydrogenation cycling

C1s XPS spectra of SWCN, type 1 exposed to two cycles of hydrogenation / dehydrogenation

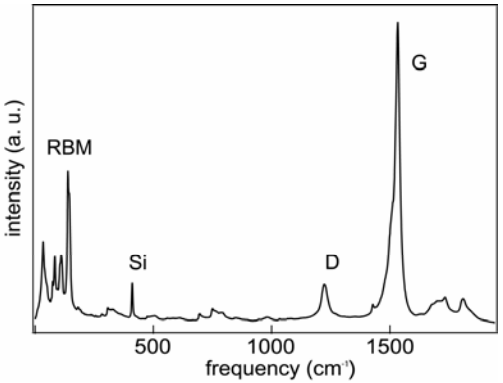


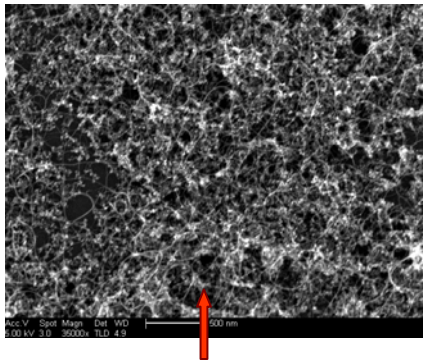
Hydrogenation of SWCN film can be **cycled**

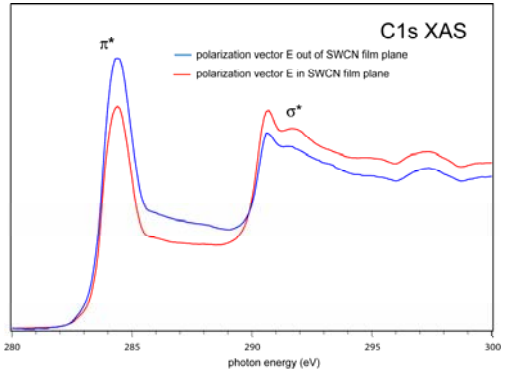
Hydrogenation cycling

Raman spectra | SEM picture | XAS spectra

Clean SWCN film

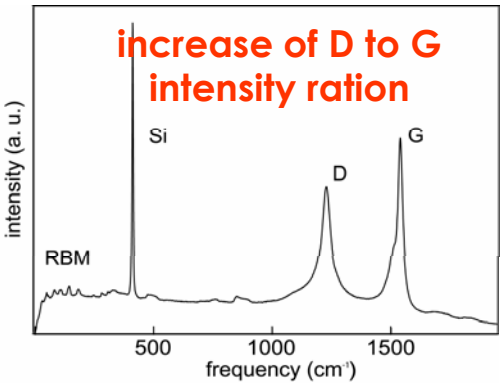


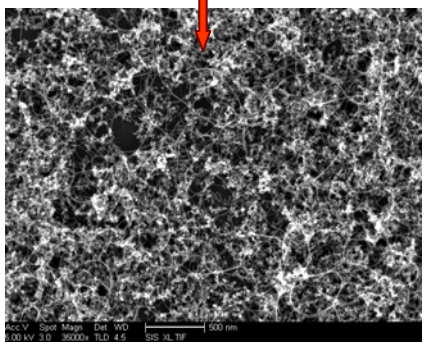


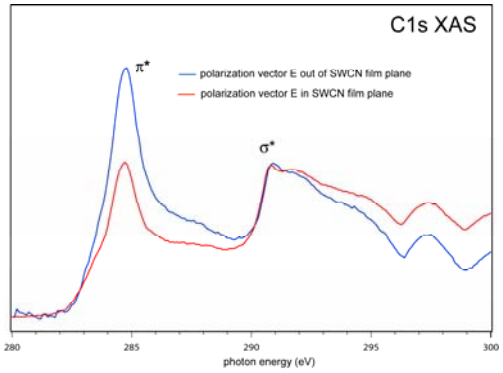


same morphology

SWCN film exposed hydrogenation / dehydrogenation cycle



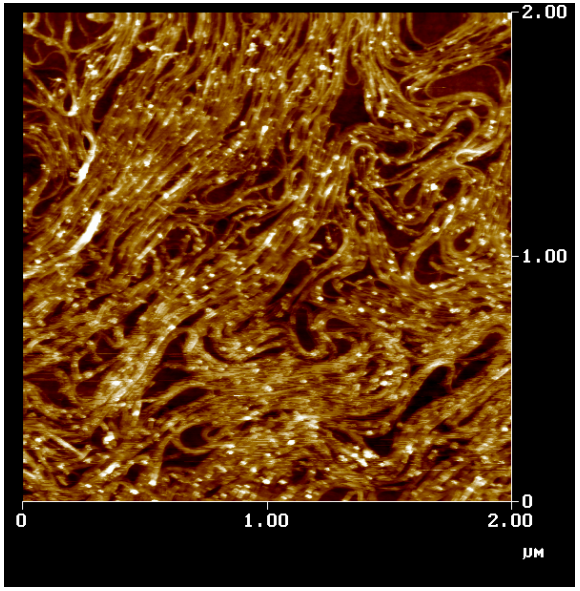




Hydrogenation leads to the increase of the defect number in SWCN

Refining H-SWCN interaction

• to exclude the SWCN bundle influence on the observed results and to figure out the diameter range of SWCN which are stable at high degree of hydrogenation

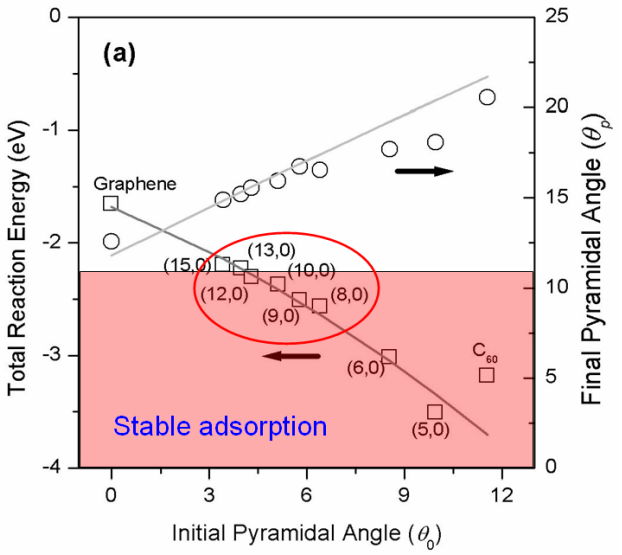


Step 1: to perform XAS and XPS spectroscopic study of H interaction with SWCN material using SWCN monolayers with known diameter distribution using AFM

The AFM image of SWCN monolayer prepared by Langmuir - Blodgett technique

Control of thermodynamics

- **technologically acceptable temperature range of H release is from 70 °C to 120 °C.**



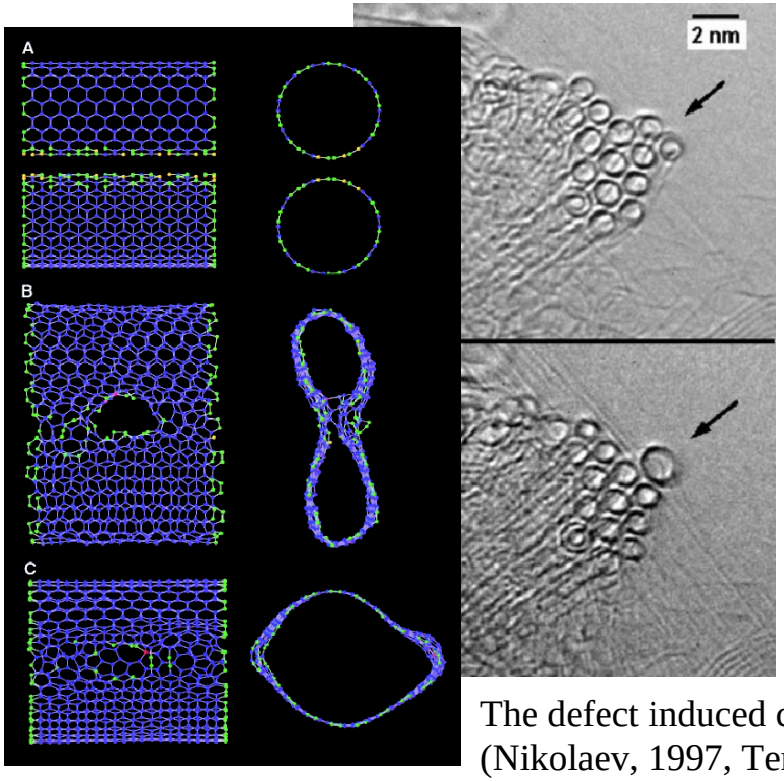
Dependence of the C-H bond energy on the size of the SWCN according to the numerical modeling (KJ Cho, 2003).

Step 2: to perform TP XPS measurements of fully hydrogenate SWCN films with two different diameter distribution.

Activation barrier?

Structural changes

- **the role of defects in the SWCN hydrogenation process**
- **nanotube coalescence due to induced defects**
- **presence of CH_2 groups in hydrogenated SWCN**

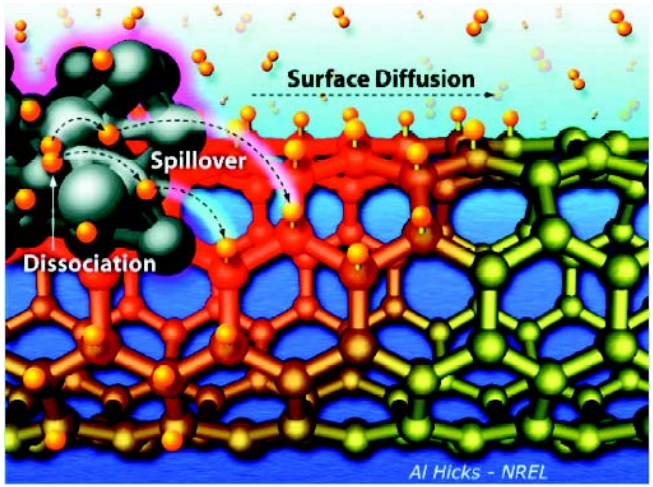


The defect induced coalescence of SWCN
(Nikolaev, 1997, Terrones, 2000)

Step 3: to study SWCN material during several cycles of hydrogenation/ dehydrogenation using IR and Raman spectroscopies and STM

Dissociation of molecular hydrogen

- **hydrogenation of SWCN with molecular hydrogen**



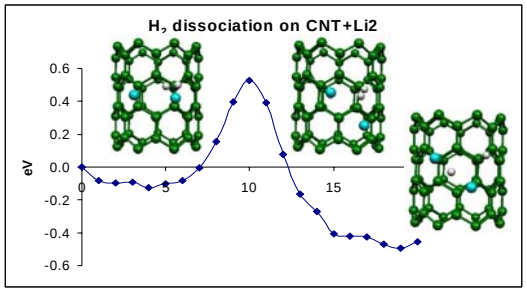
Hydrogenation via spillover mechanism (A.Lueking , 2002, A.Lueking , 2004)

Step 4: to study *in-situ* the interaction of SWCN with metals (Pt, Pd, Ni etc) capable to catalytically split H_2

Step 5: to study interaction of H_2 with SWCN - metal complexes.

Increased capacity

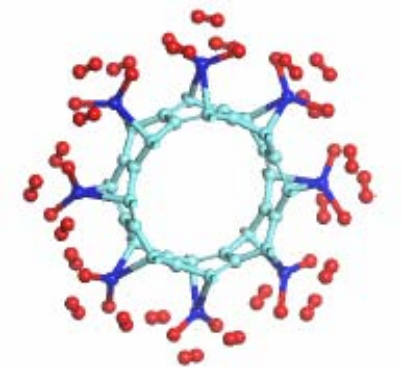
- **chemisorption of hydrogen in Li-SWCN network**



Step 6: to perform spectroscopic study of H interaction with SWCN with intercalated Li

- binding energy of H 0.457 eV
- dissociation barrier for H_2 around 0.529 eV

- **molecular hydrogen adsorption on Ti-SWCN complex**



Step 7: to perform spectroscopic study of H_2 interaction with Ti-SWCN complexes

Theoretical model of C_4TiH_8 with 7.7 wt% of H storage capacity (T. Yildirim, 2005)

Conclusions

- SWCN with different diameters can reach different hydrogenation degree before "unzipping" and etching

- for specific SWCN it is possible to hydrogenate **almost 100 at %** of the carbon atoms in the walls to form C-H bonds which corresponds to **7.7 weight %** of hydrogen capacity

- the hydrogenated SWNT are stable from ambient temperature to **300 °C**

- hydrogenation/dehydrogenation process can be **cycled**.