Toward Controllable Growth of Carbon Nanotubes

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The 5th Rice University/Air Force Research Laboratory/NASA Workshop on Nucleation and Growth Mechanisms of SWCNTs
April 8-12, 2011, Guadalupe, Texas

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Prof. Jing Kong	

Outline of the talk

1. Introduction: Highlighted "Key Questions" from previous Workshop

2. Thermodynamic aspects of carbon nanotube growth

3. Summary: Hints for selective growth

4. Preferential growth of metallic tubes: The origin of selectivity

5. Conclusion: control parameters

Introduction

Ubiquitous applications of SWCNTs demand

reasonably homogeneous material

Controllable growth

Growth mechanism

"Key Questions" from previous Workshop

State of catalyst - solid (crystal/disorder) vs liquid

Diffusion path - surface vs bulk, sublayer diffusion

Role of carbides - promote vs terminate the growth

Why is so difficult to answer?

1. Definition of liquid

Solid/liquid - lower symmetry, lower coordination, no elastic strain
Same aspects for solid bulk /solid surface
XRD, TEM - distinguish liquid vs disorder, surface melted layer

2. Bulk/surface diffusion

Based on activation energy values (Arrhenius law)
Growth of MWCNTs
Detection of dissolved carbon - growth on diamonds

3. Carbides

Based on ex-situ or in-situ analyses of TEM, SEM, X-Ray

Established Synthesis methods

High temperature	Low temperature
Arc discharge and laser ablation	CCVD and derivatives

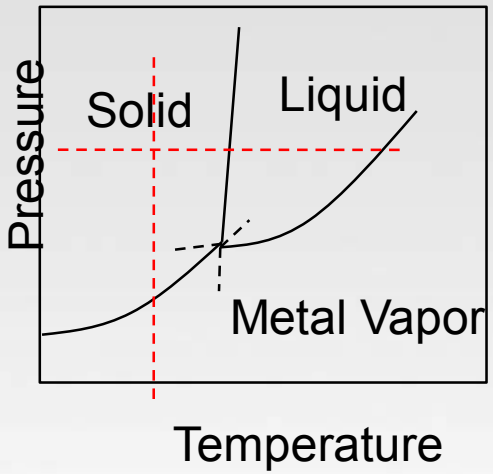
What is a distinguish feature ?

Temperature !

High or low, what is a criteria ?

Multiple roles of T related to "Key Questions"

Liquid/solid = □(T)



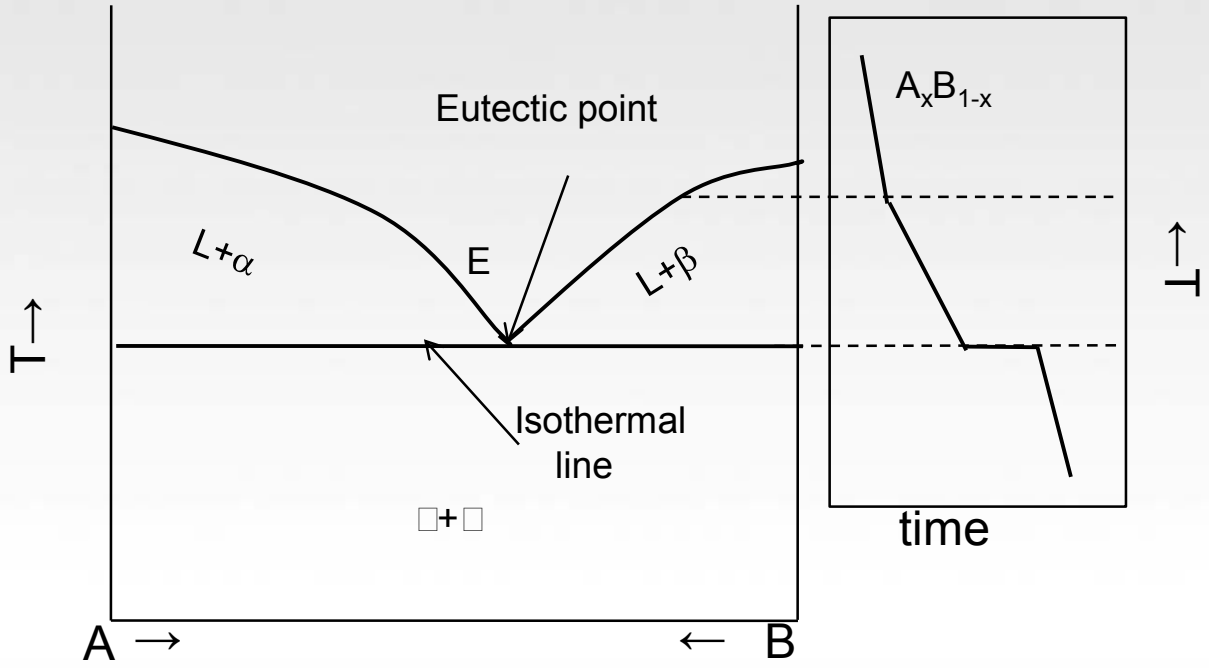
Bulk and surface diffusion = E_A (T)

Stable, metastable, no carbides = E(T)

Hidden common parameter - Carbon

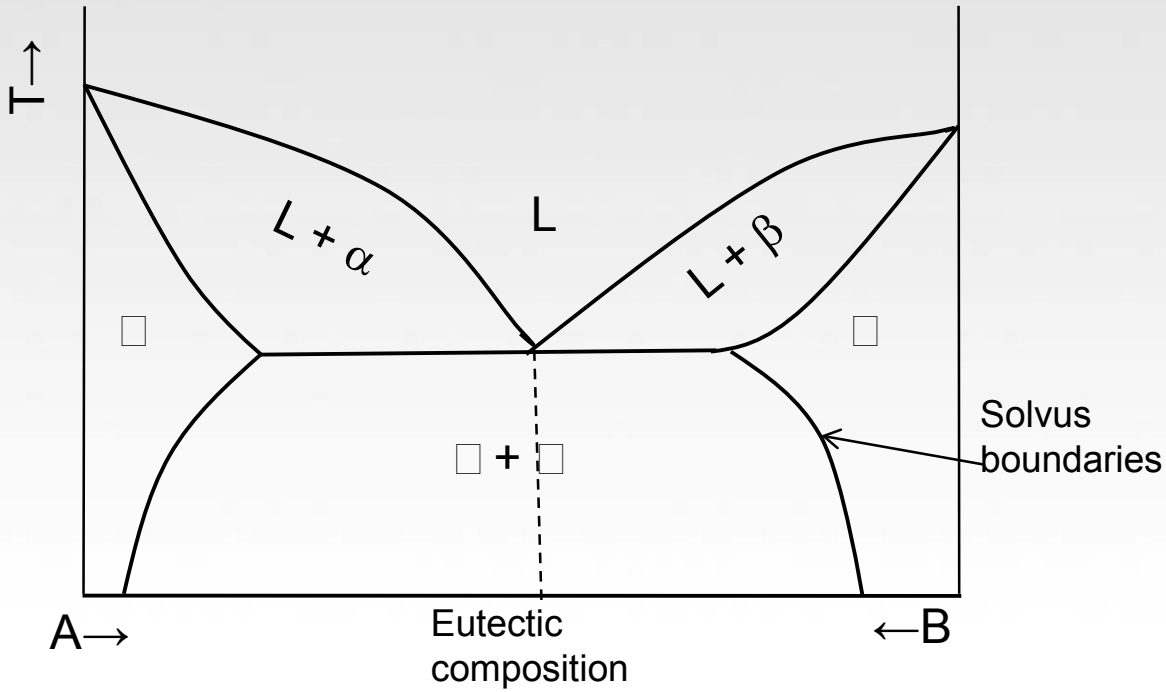
Hidden variable parameter - Catalyst composition - A

Role of carbides



Example of phase diagram infinite solubility in the liquid state and absence of solubility in the solid state.
Insets shows typical cooling curve.

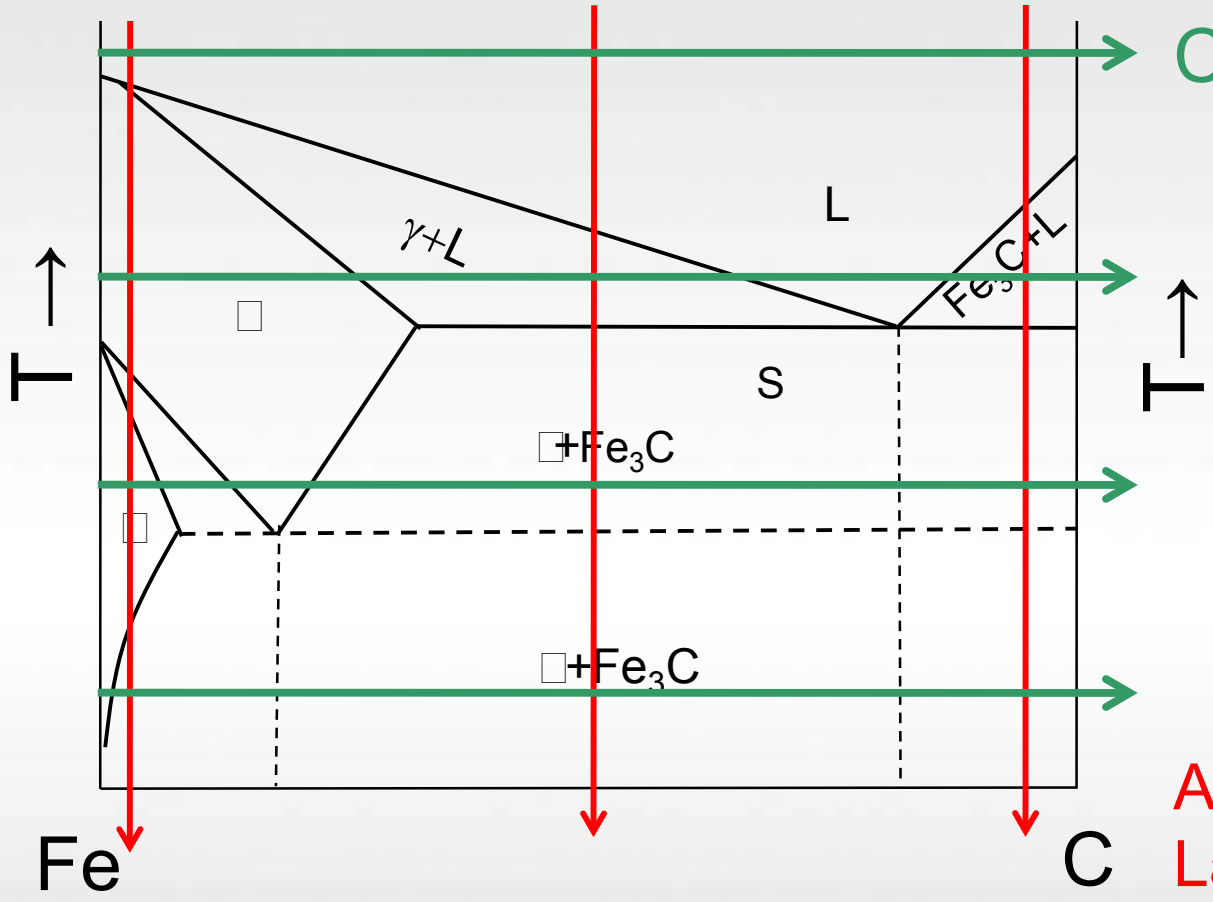
Role of carbides



Typical binary eutectic phase diagram that shows partial solid solubility.

Role of carbides

Binary phase diagram of iron-iron carbide system.

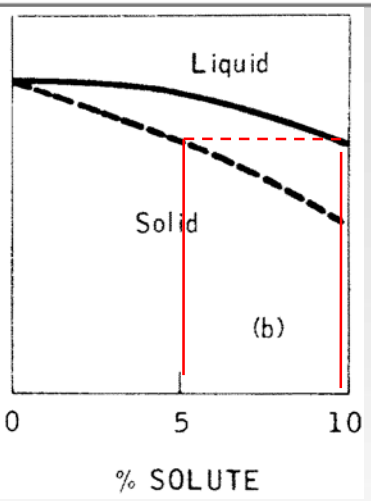


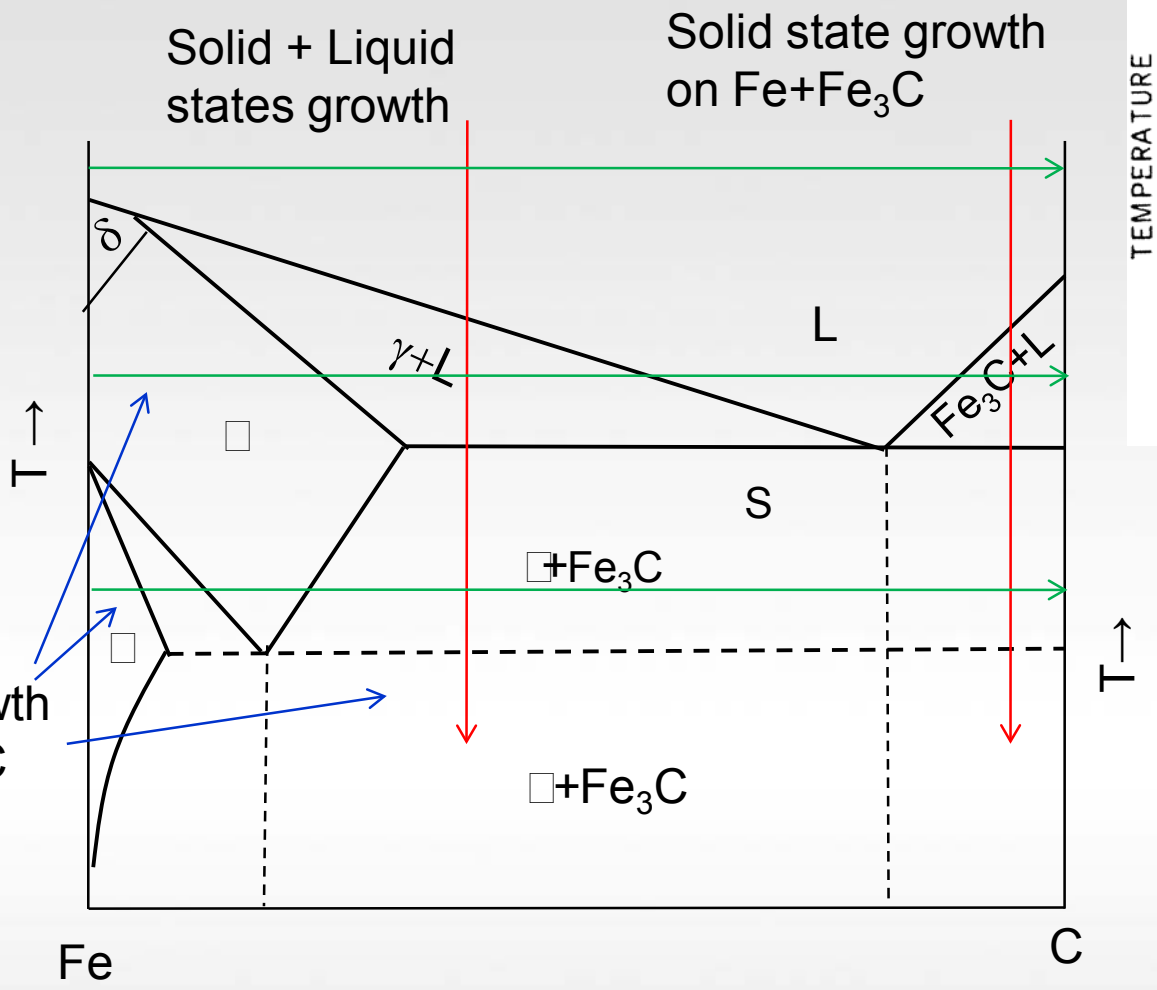
Depends on temperature and composition

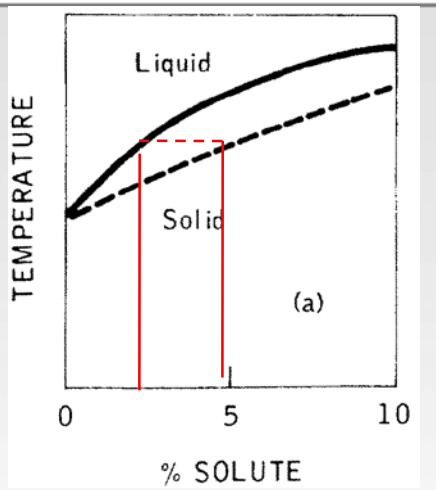
Key Questions

$$F_A = \square_A(T, C)$$

Iron-carbon binary phase diagram







$$\frac{X_S}{1-X_S} = \frac{X_B}{1-X_B} e^{Q/RT}$$

PRL 37, 1433 91976)

D_{Fe} ~10^{-8}cm^2/s

D_{Fe3C}~10^{-15} cm^2/s

$$F_A = \square_A(T,C)$$

Kinetics:

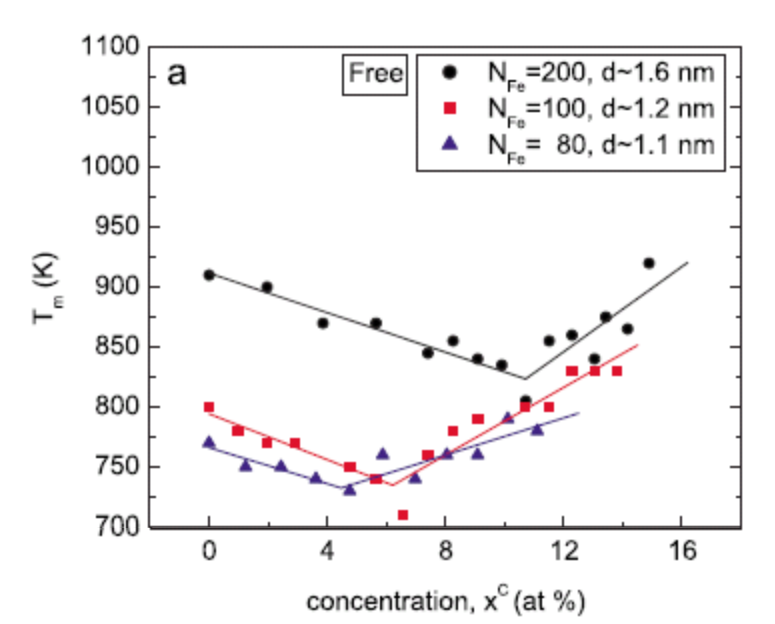
Heating/cooling rates

Carbon atoms dissolution/segregation rates

$$F_A = \square_A[T(t),C(T,t)]$$

Assumption :

The binary phase diagrams of nanoscale carbon-metal systems are same as for bulk ?!



Phys. Rev. Lett. 100, 195502 (2008)
Phys. Rev. B 75, 205426 (2007)

Towards chiral-selective synthesis

What potential control parameters do we have currently ?

1. Catalyst diameter-on some level controls the diameter of tubes

2. Catalyst structure - may correlate with the tube structure

How to exploit these features of catalyst ?

Ensure that catalyst is in <u>solid state</u>

Selective synthesis

S. M. Bachilo,…, D. Resasco *JACS* 125 (2003)
CVD Growth of SWCNTs with narrow chirality distribution

Li et al., *Nano Lett.* 4, 317 (2004)
Preferential growth by a plasma enhanced CVD method
~90 % semiconducting tubes

Qu, et al., *Nano Lett. 8, 2682* (2008)
Fast heating combined with plasma enhanced CVD
~ 96% semiconducting tubes

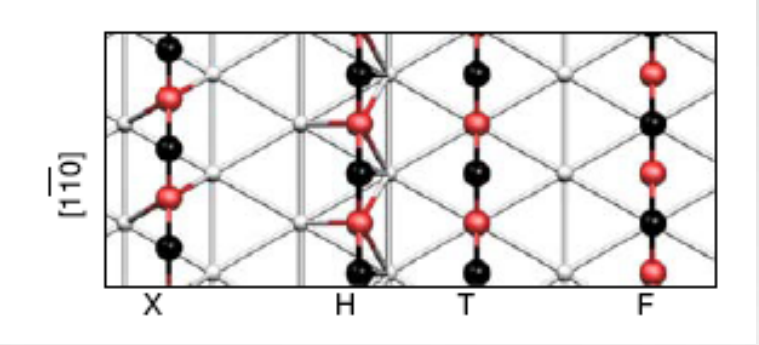
Origin of selectivity is not known

W. H. Chiang, R. M. Sankaran Nature Mat., 8, 882, 2009
Exploiting atmospheric-pressure microplasma technique
Conclusion:
Epitaxial relationship between SWCNTs chirality and the catalyst structure

Proposed models for selectivity

S. Reich, L. Li, J. Robertson
Chem. Phys. Lett., 421, 469, (2006)

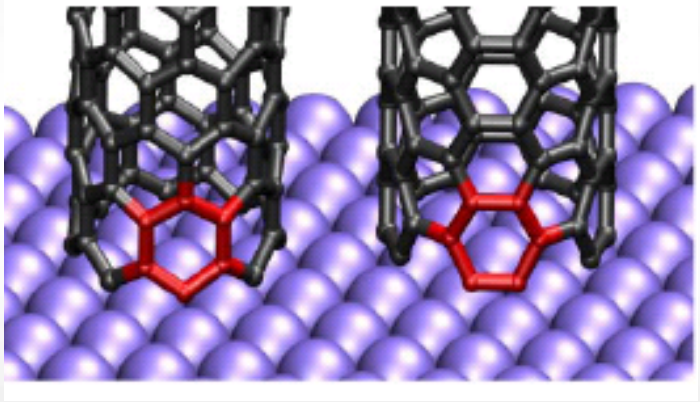
Control the chirality of carbon nanotubes by epitaxial growth



Lattice -matched caps and tubes are more stable

O. Yazyev , A. Pasquaerello
Phys. Rev. Lett, September 2008

Binding of the CNT through the "armchair" edges is favorable, but stability varies among the metals



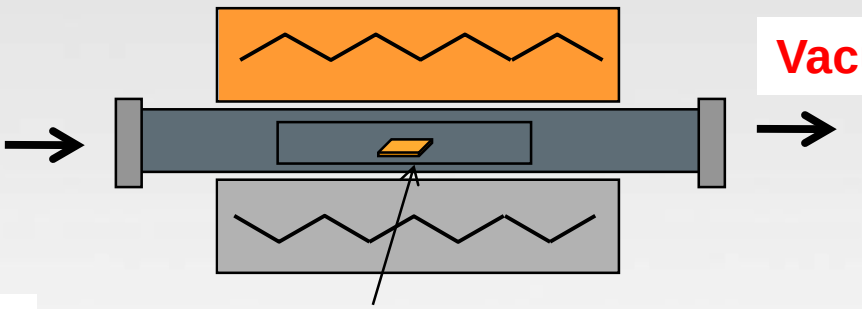
Our results

By varying the noble gas ambient He and Ar during Fe catalyst conditioning in the presence of H_2 and H_2O species, we altered fraction of tubes with metallic conductivity from 1/3 up to a max of 90%.

Science 326, 116 (2009)

CCVD Synthesis of SWCNT thin films

CH_4, Ar/He,
H_2, H_2O



Vacuum level: ~10^{-9} atm

Water bubbler

Dew point probe
(1ppb$_v$ level)

Si/SiO_2 (~300 nm) substrate

Typical conditions:

Catalyst precursor - $Fe(NO_3)_3$ $9H_2O$ in IPA with ratio 0.02-20mg

Catalyst conditioning ambient: Ar/H_2 or He/H_2 at T= 500□ 860°C

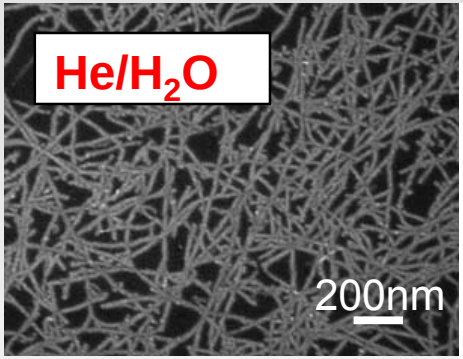
~3.5 mTorr of H_2O

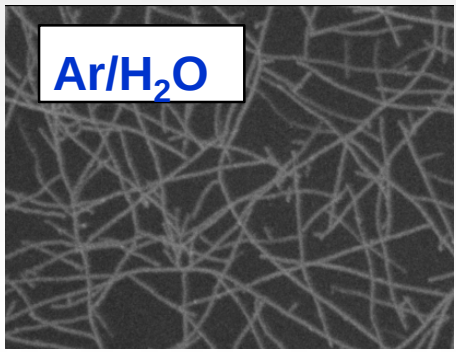
Carbon source: CH_4 , synthesis temperature T= 830-860°C

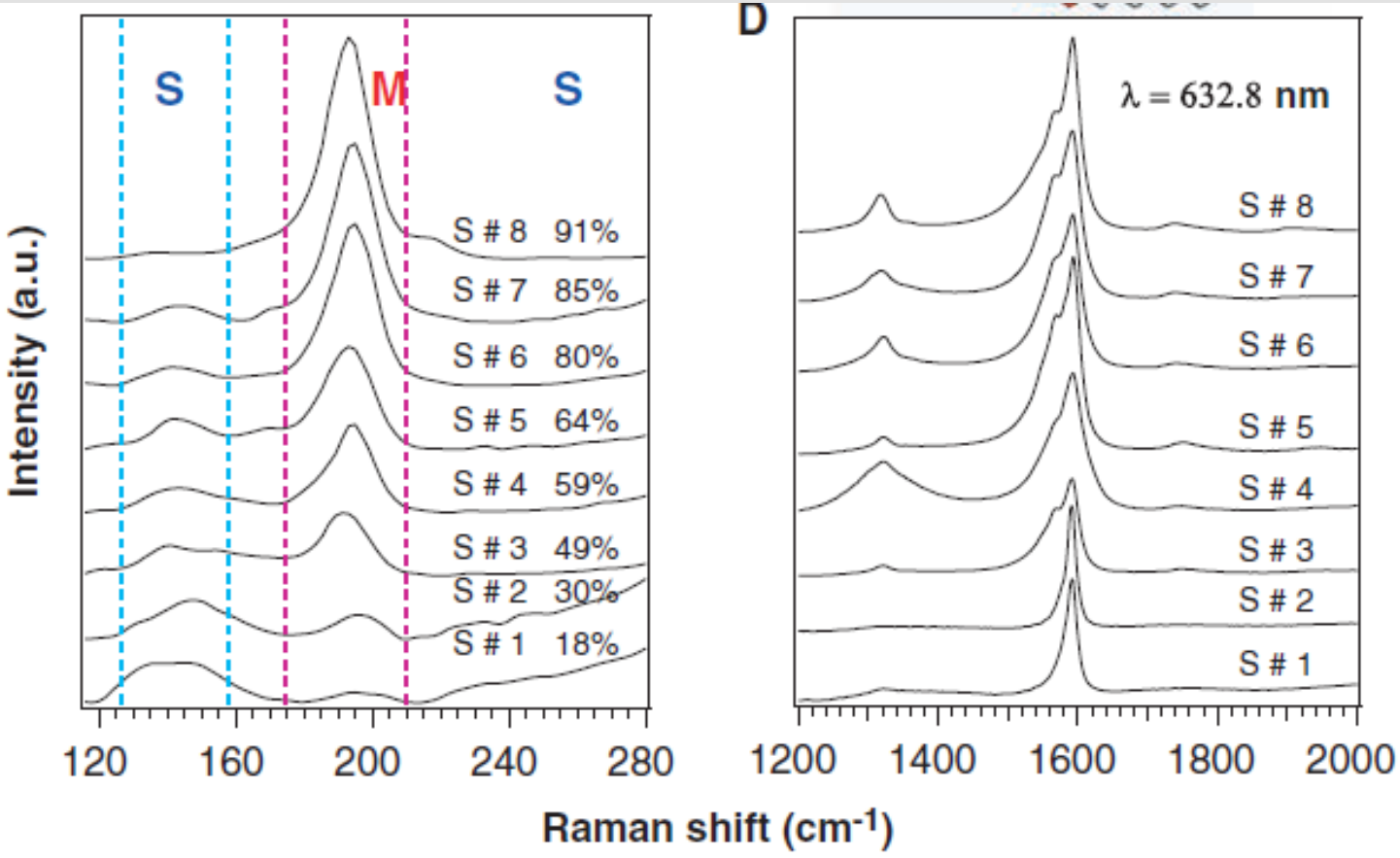
All gases 99.9999% or 99.999% of purity

Synthesis duration 1-5min.

Variation of catalyst ambient and annealing time





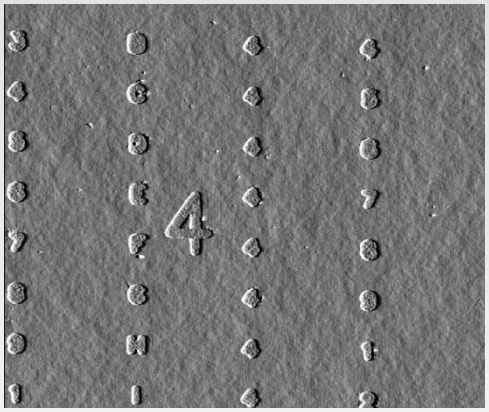


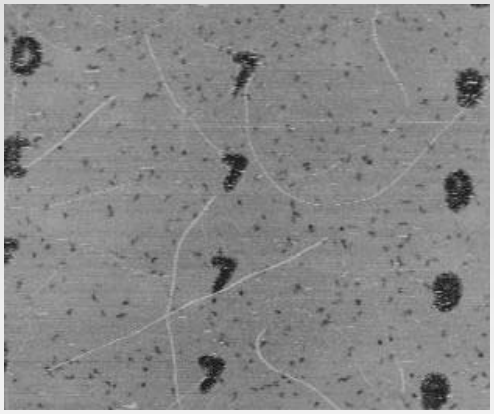
R= I(met.)/I(sem.)**= 0.34 □ 20.2**

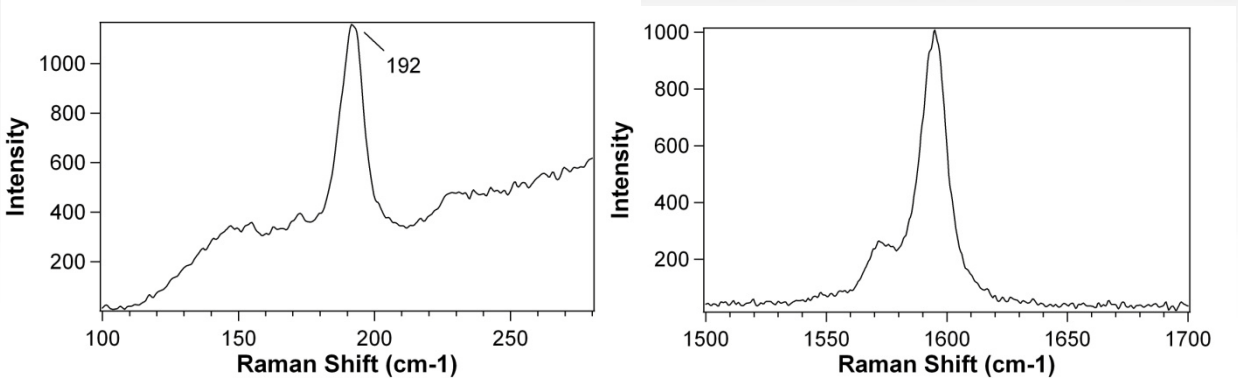
$$Metallic\% = \frac{100}{1 + \frac{\square_{ref}}{\square_{Sample}} \frac{N_s}{N_m}}$$

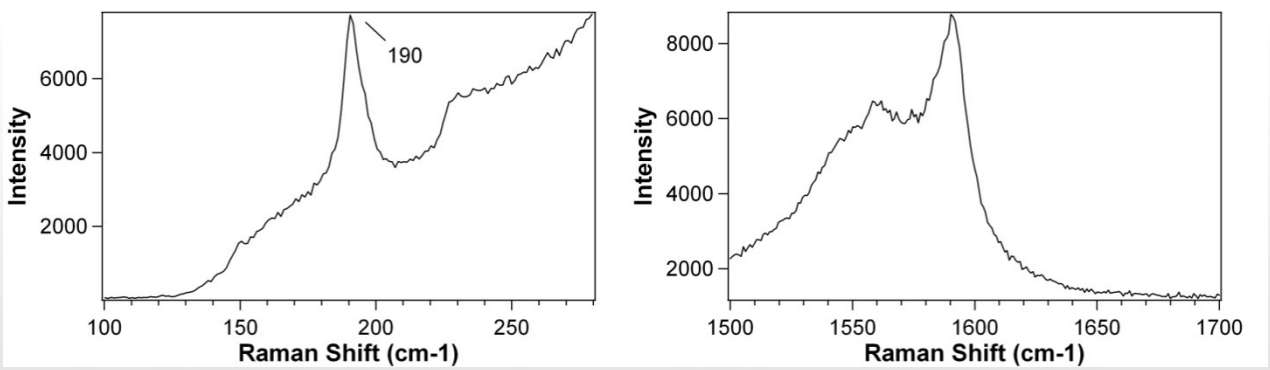
Krupke et al., Science 301, 344, (2003)

Preparation of samples for chirality assignment based on individual SWCNTs









Raman (632nm)

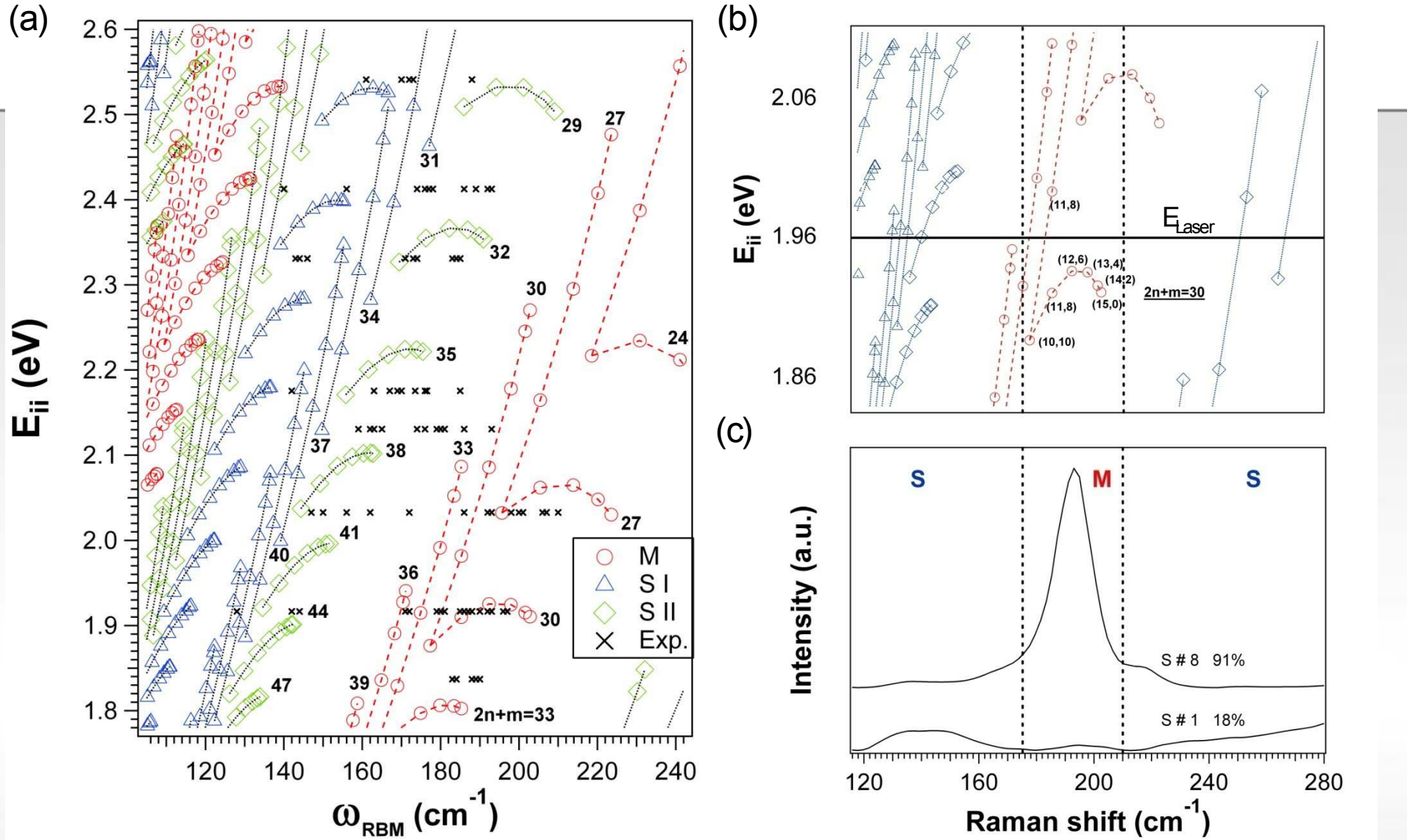
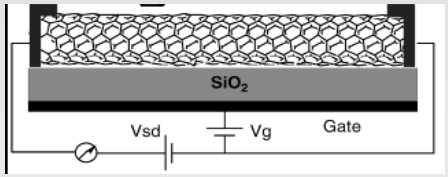


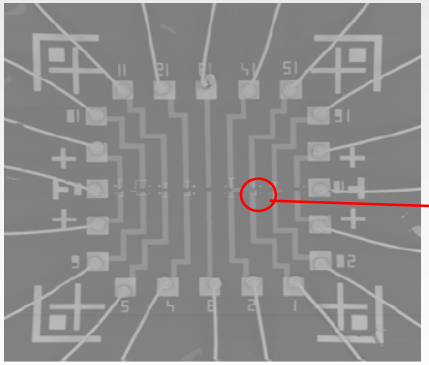
Fig. 1 (a) Optical transition energy E_{ii}(eV) vs. radial breathing mode frequency (ω_{RBM}) for metallic (M), type I (SI) and type II (SII) semiconducting SWNTs based on ref [PRB 2004]. Crosses (x) are experimental data. (b) Small version of the "Kataura" plot around the laser excitation (E_{Laser}=1.96eV) (c) Raman spectra of our typical (S#1, 18% metal) and highest metallic tube enriched (S#8, 91% metal) SWNTs in the low frequency range.

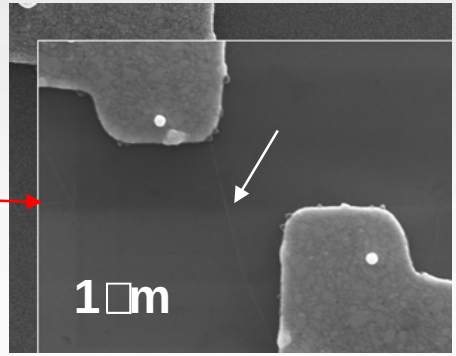
Combined electrical characterization (FET) & Raman analysis (□=632.8 nm)

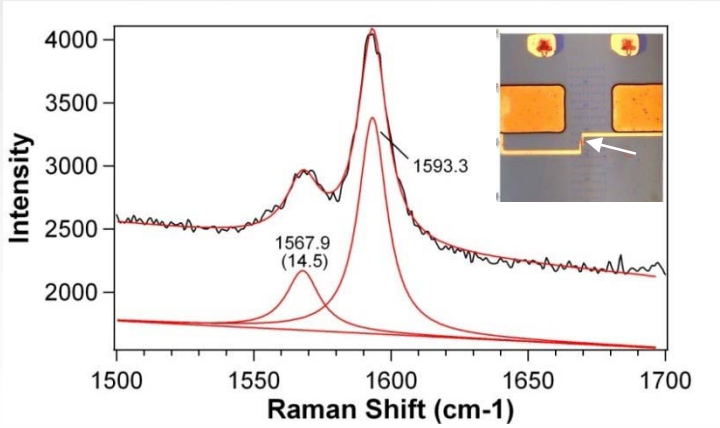


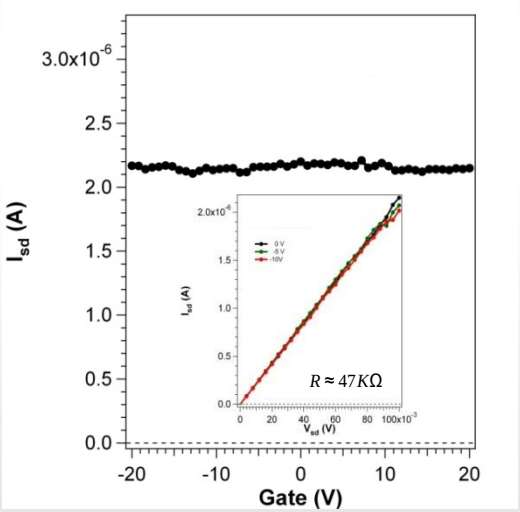
Ar ambient: 32 devices: **24% met.** **(18% based on Raman)**

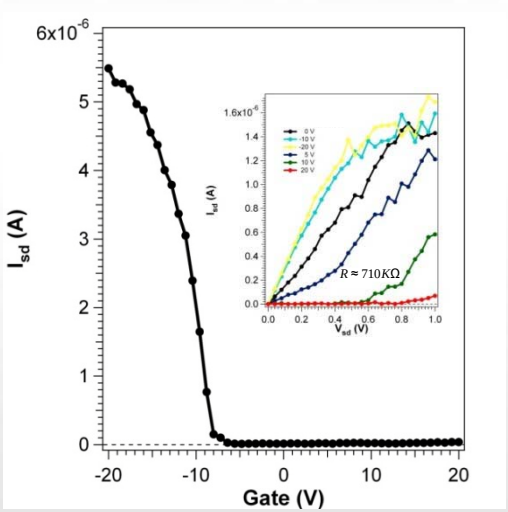
He ambient: 72 devices: **57% met.** **(50% based on Raman)**

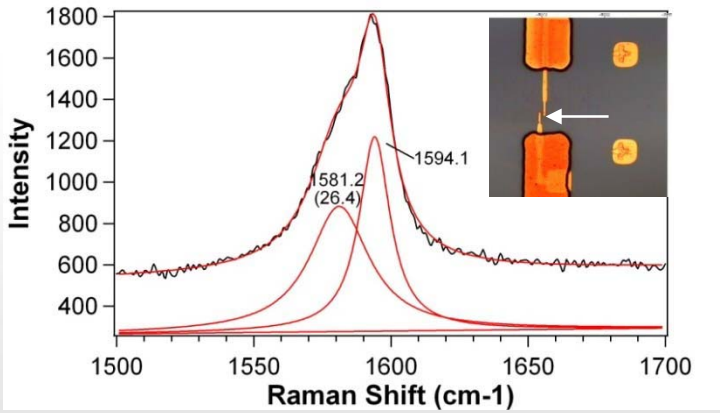




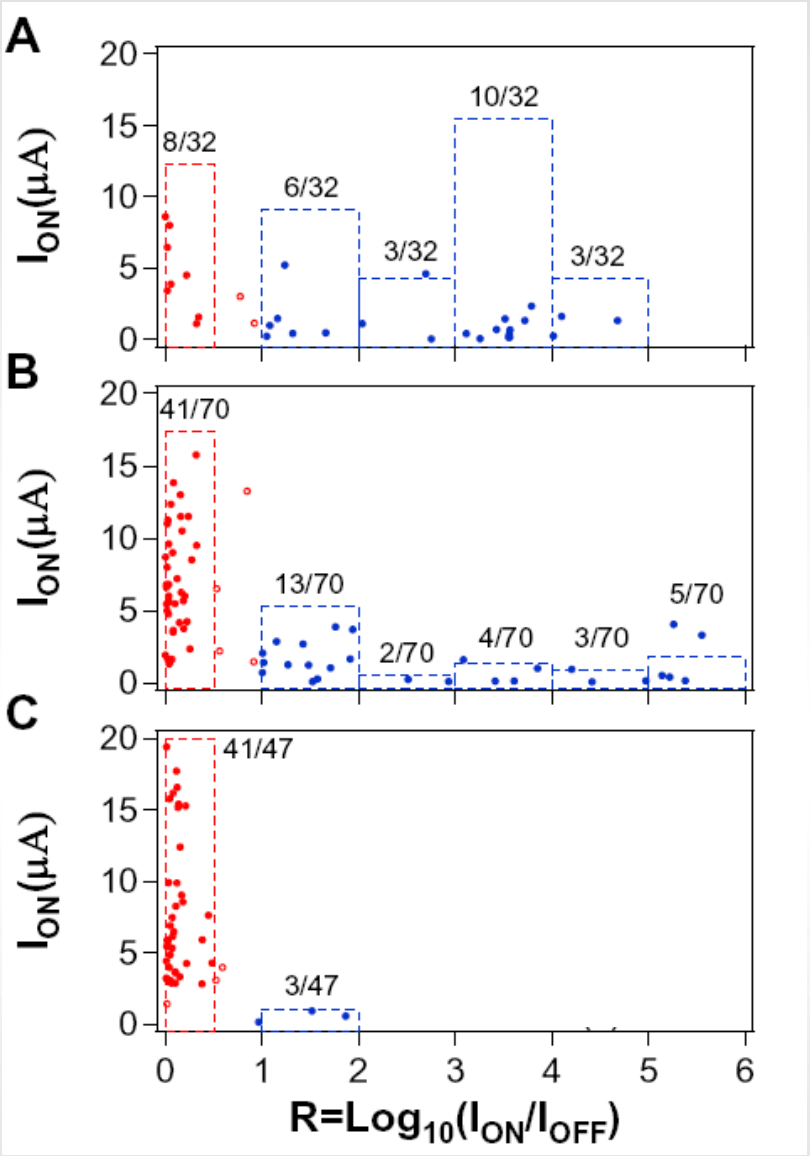








Results of Electrical Characterizations



Under Ar: (H_2O/ H_2)=9:1 ambient
~20% metallic & ~80% semiconducting
2-unsure

Under He: (H_2O/H_2)=9:1 ambient
~60% metallic & ~40% semiconducting
2-unsure

Under He: (H_2O/H_2)=8:2 ambient
~ 85% metallic & 15% semiconducting
3-unsure

Science, 326, p116 (2009)

Quantifying the Semiconducting Fraction in SWCNTs Samples through comapartive AF and photoluminescence

Nano Letters 9, 3203 (2009)

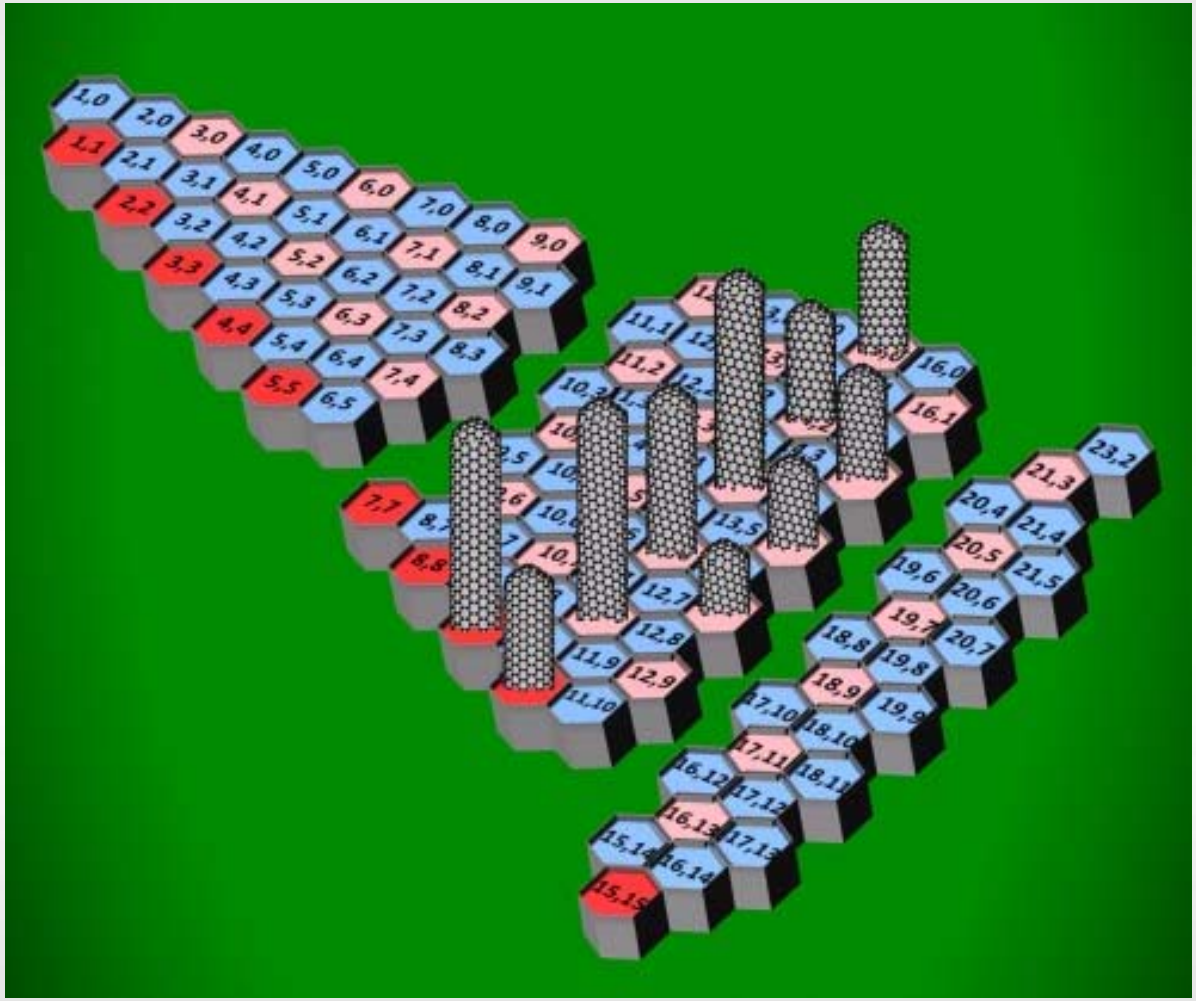
Anton V. Naumov,† Oleg A. Kuznetsov,§ Avetik R. Harutyunyan,§ Alexander A. Green,|| Mark C. Hersam,|| Daniel E. Resasco,⊥ Pavel N. Nikolaev,# and R. Bruce Weisman*,‡

Table 1. Compositions Determined for As-Produced or Processed SWCNT

sample	source	% semiconducting	% metallic
HiPco	Rice Univ.	62.9	37.1
CoMoCAT, standard grade	SWeNT Inc.	92.1	7.9
CoMoCAT, commercial grade	SWeNT Inc.	51.9	48.1
laser ablation, low temperature method	ERC Inc./NASA-JSC	54.7	45.3
CVD preferential growth	Honda Res. Inst. USA	15.4	84.6
HiPco, starting material	Northwestern Univ.	60.5	39.5
HiPco, semiconducting-enriched by DGU	Northwestern Univ.	96.0	4.0
HiPco, metallic-enriched by DGU	Northwestern Univ.	3.1	96.9

Determined chiralities

(15, 0); (14,2); (13,4); (12,6); (11,8); (10,10)
(9,9); (13,7); (14,5); (15,3)

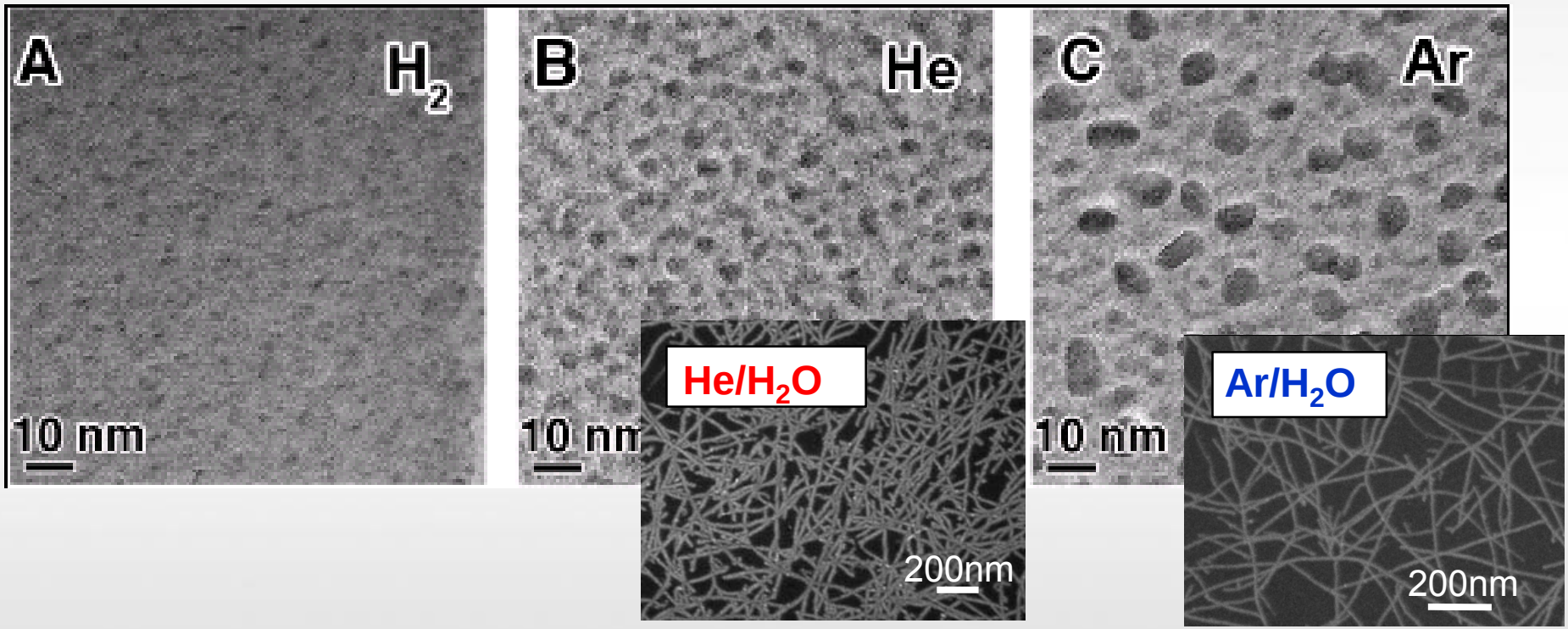


Origin of preferential growth ?

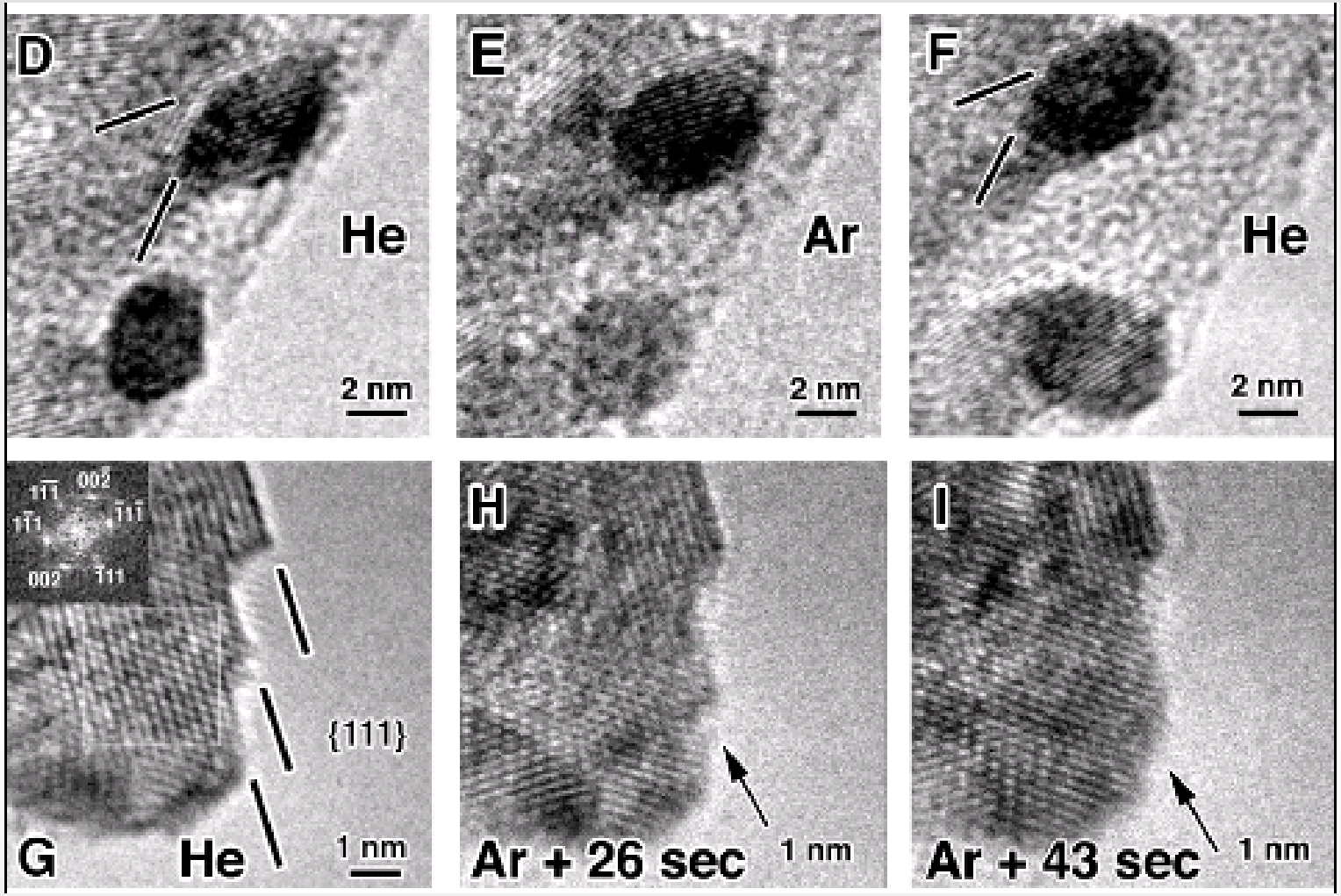
In situ TEM studies

Pressure of He, Ar - 550 mTorr, H_2O ~3.5mTorr at 500°C for 1h
All Fe particles preliminarily have been reduced under H_2 for 1 h at T= 500°C

Fe catalyst coarsening under different ambient

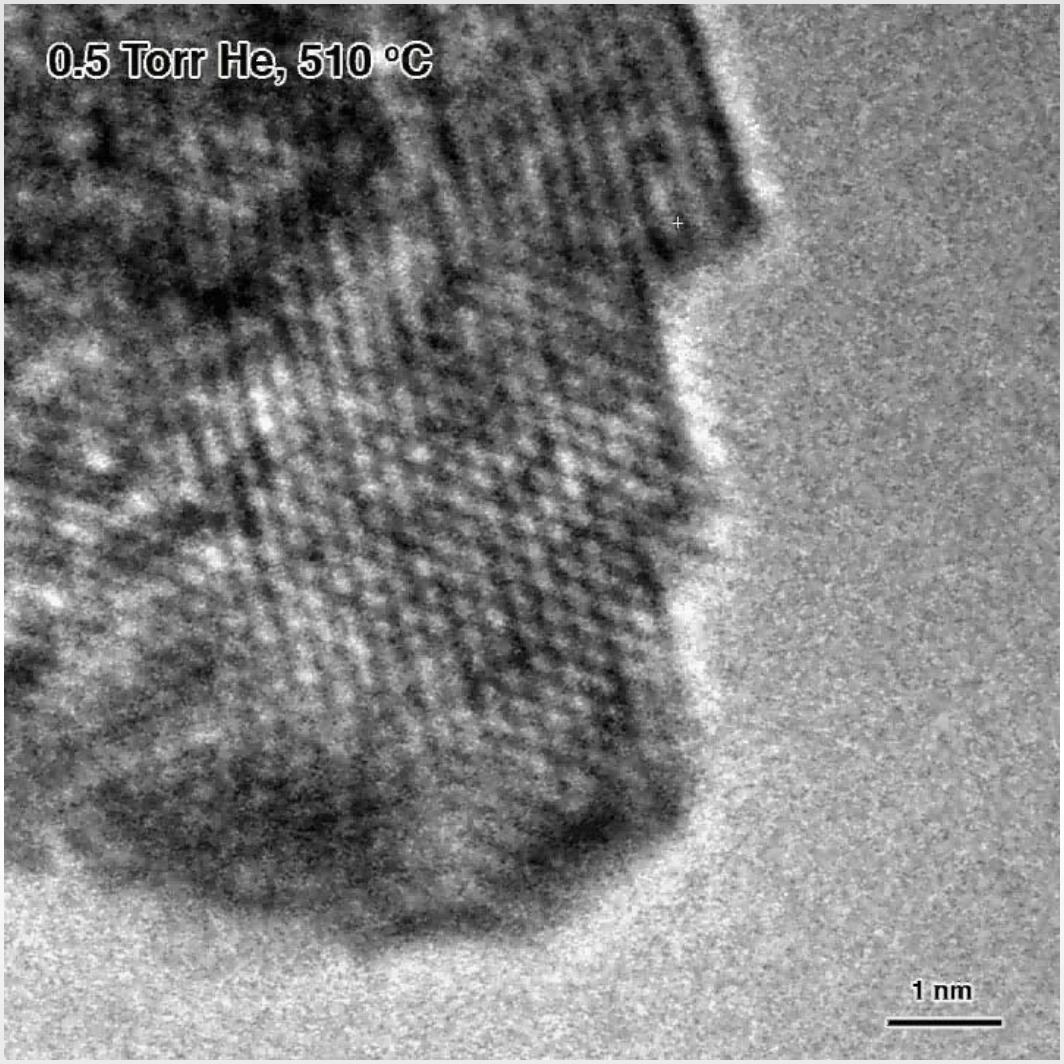


Catalyst morphology dynamic reconstruction under different ambient: In situ ETEM studies

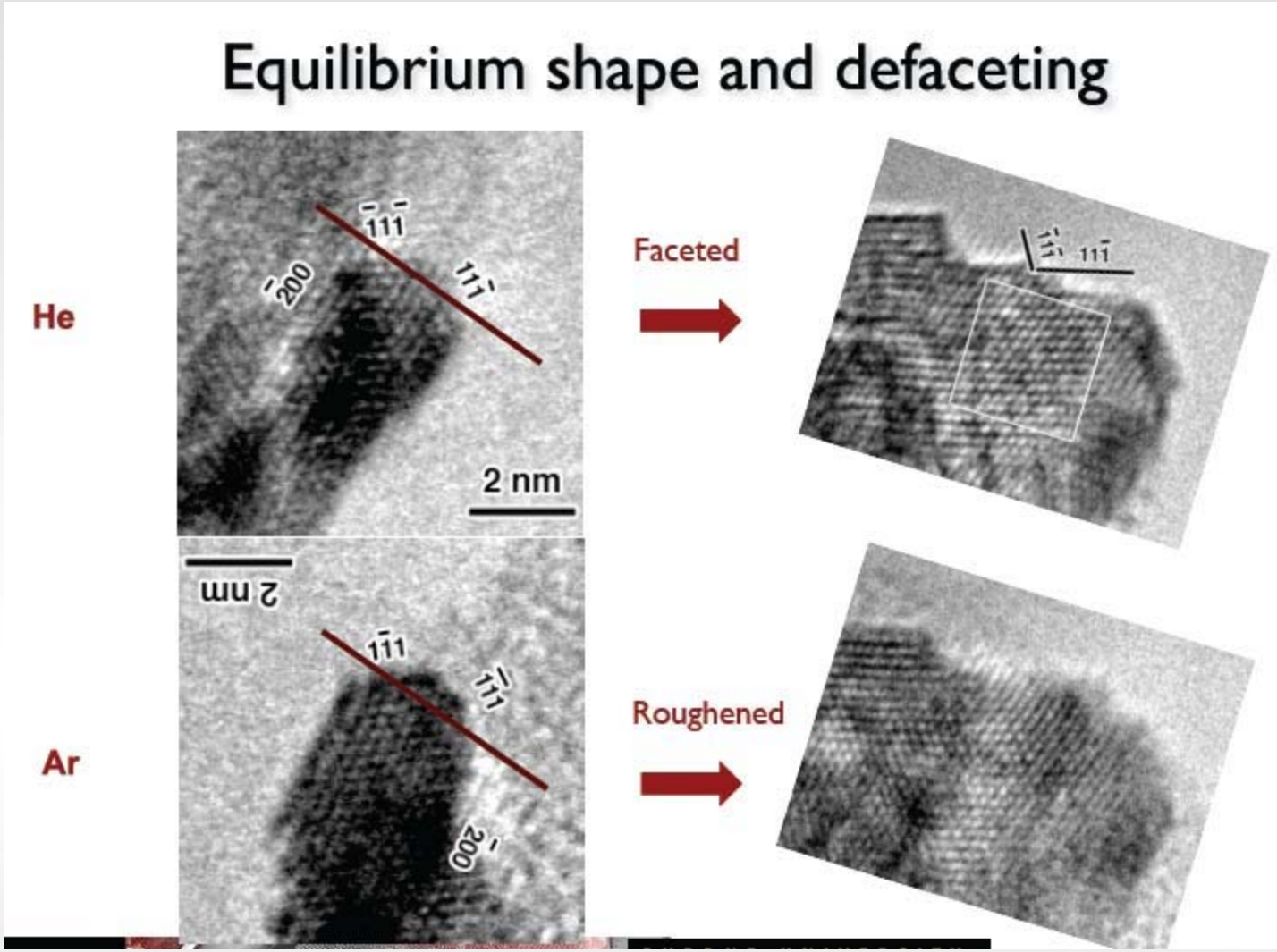


Reconstruction of Fe nanocatalyst under He/H_2O and Ar/H_2O ambient (0.5 Torr) at 550C

Morphology reconstruction of Fe nanocluster dependence on ambient gases (He/H_2O --□ Ar/H_2O)

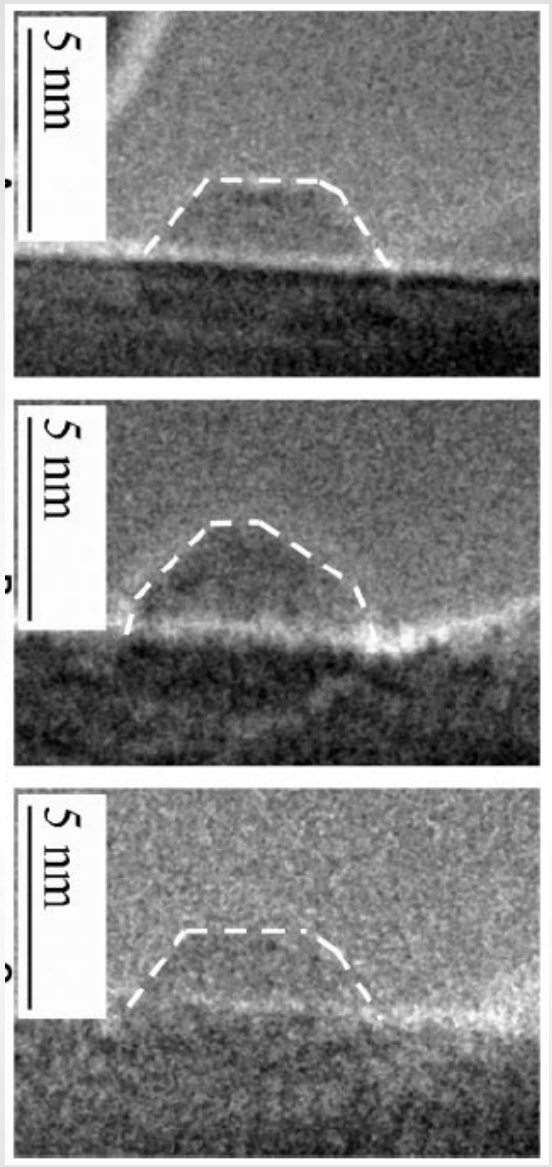


In -situ TEM under Ar/H_2O and He/H_2O



Under He/H_2O ambient Fe catalyst is more faceted and (111) facet is stable

Reversible shape changes of Cu nanocrystal on ZnO substrate



Under H_2 at 1.5 mbar

Under H_2/H_2O (3:1) at 1.5 mbar (total pressure)

Under H_2 at 1.5 mbar

Presence of H_2O molecules on cluster surfaces causes its reconstruction

P.L. Hansen et al., Science 295, 2053 (2002)

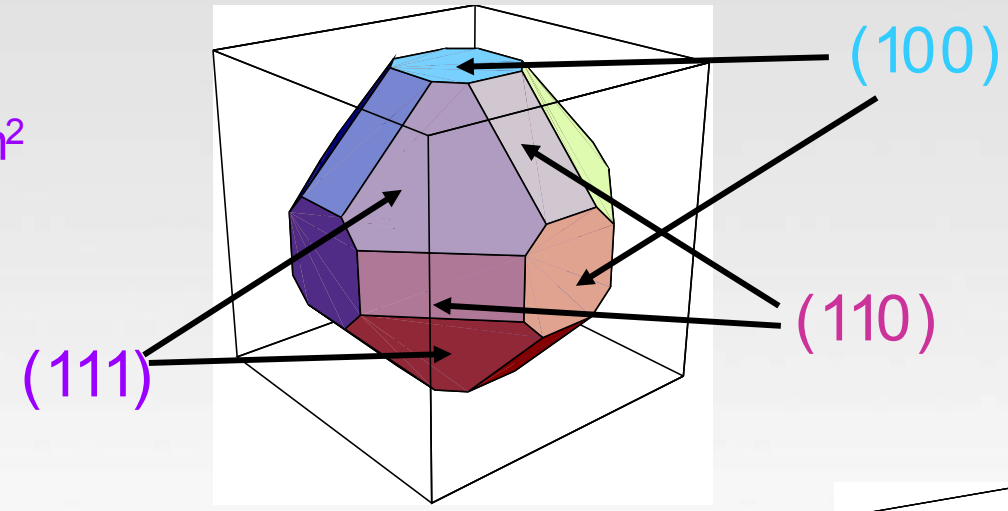
Morphology reconstruction of nanocatalyst under adgas (Wulff Construction)

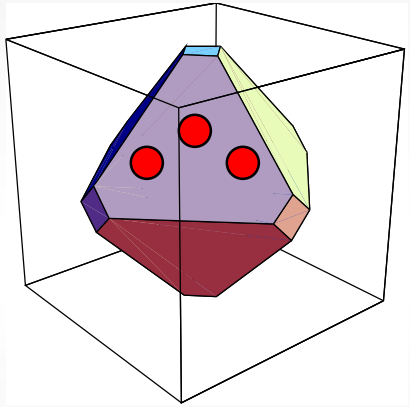
FCC particle

$\gamma_{111} = 1.97\ J/m^2$

$\gamma_{100} = 2.2\ J/m^2$

$\gamma_{110} = 2.1\ J/m^2$

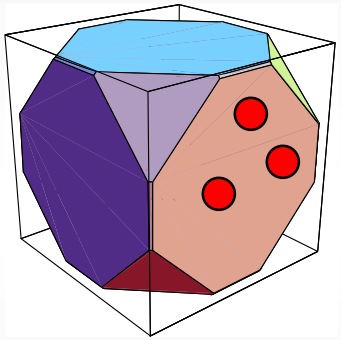




$\gamma_{111} = 1.5\ J/m^2$

$\gamma_{100} = 2.2\ J/m^2$

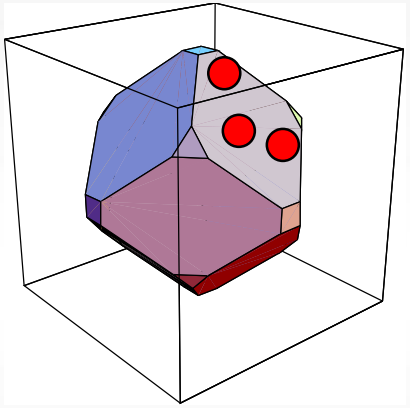
$\gamma_{110} = 2.1\ J/m^2$



$\gamma_{111} = 1.97\ J/m^2$

$\gamma_{100} = 1.5\ J/m^2$

$\gamma_{110} = 2.1\ J/m^2$



$\gamma_{111} = 1.97\ J/m^2$

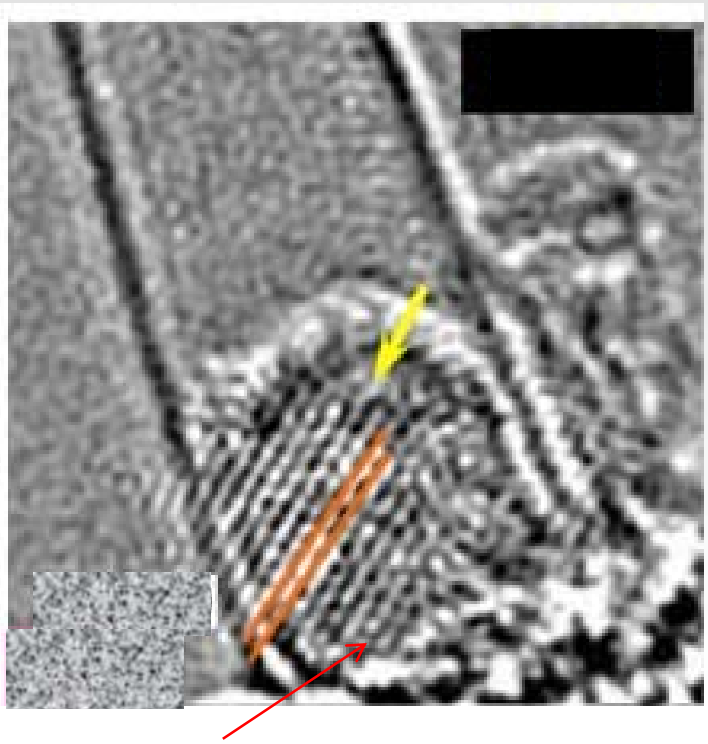
$\gamma_{100} = 2.2\ J/m^2$

$\gamma_{110} = 1.7\ J/m^2$

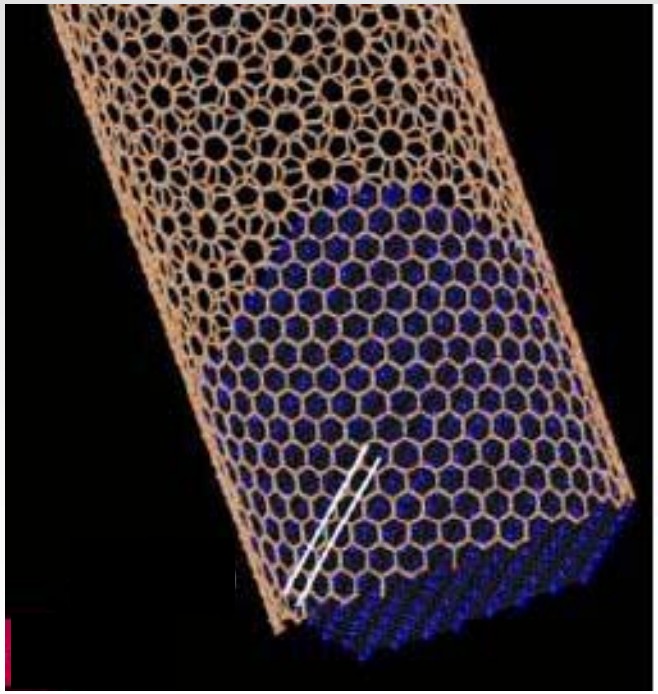
What is a mechanism of selectivity ?

Is there epitaxial relationship between metal catalyst structure and grown nanotube chirality?

Experimental Clues

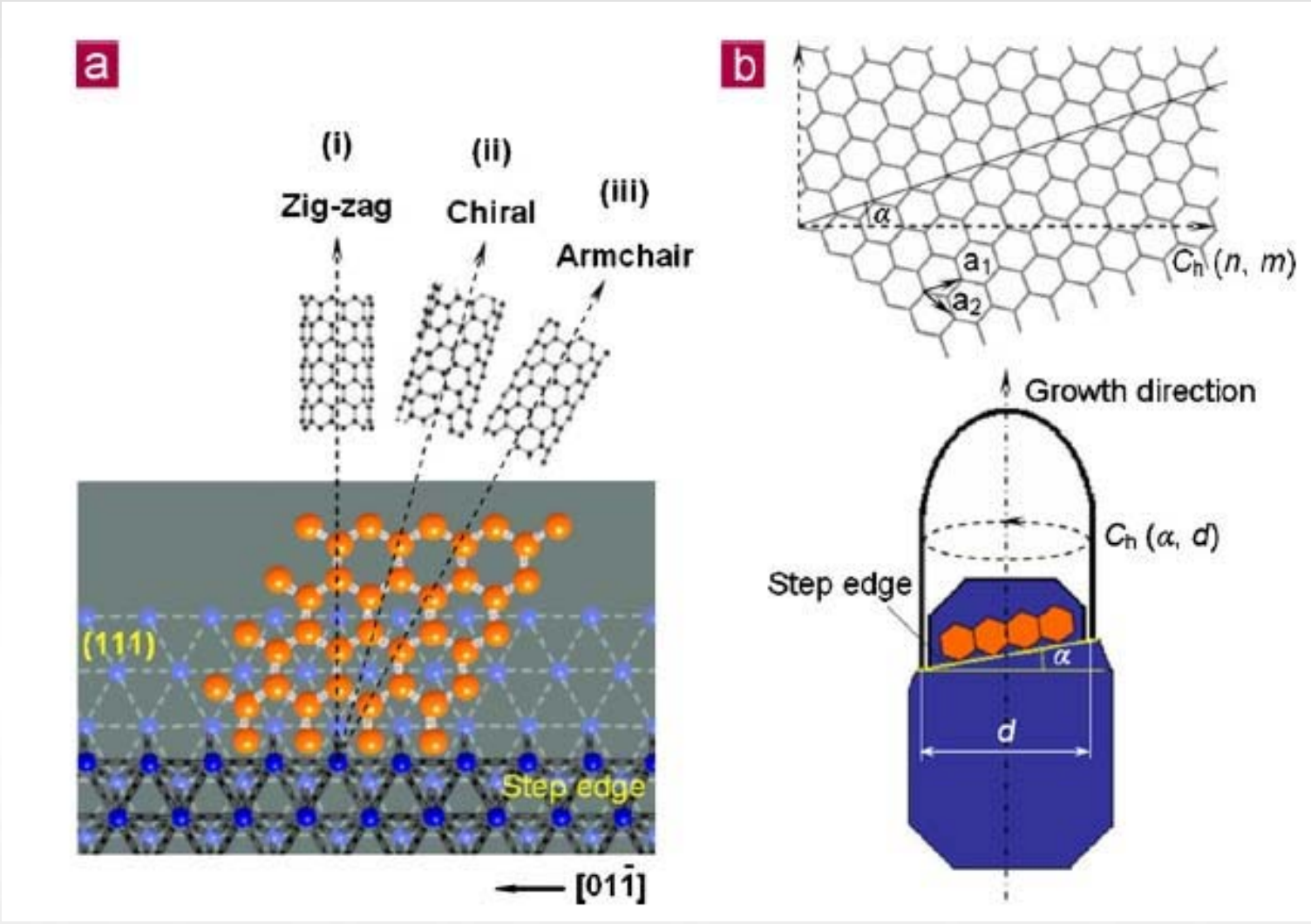


Co catalyst

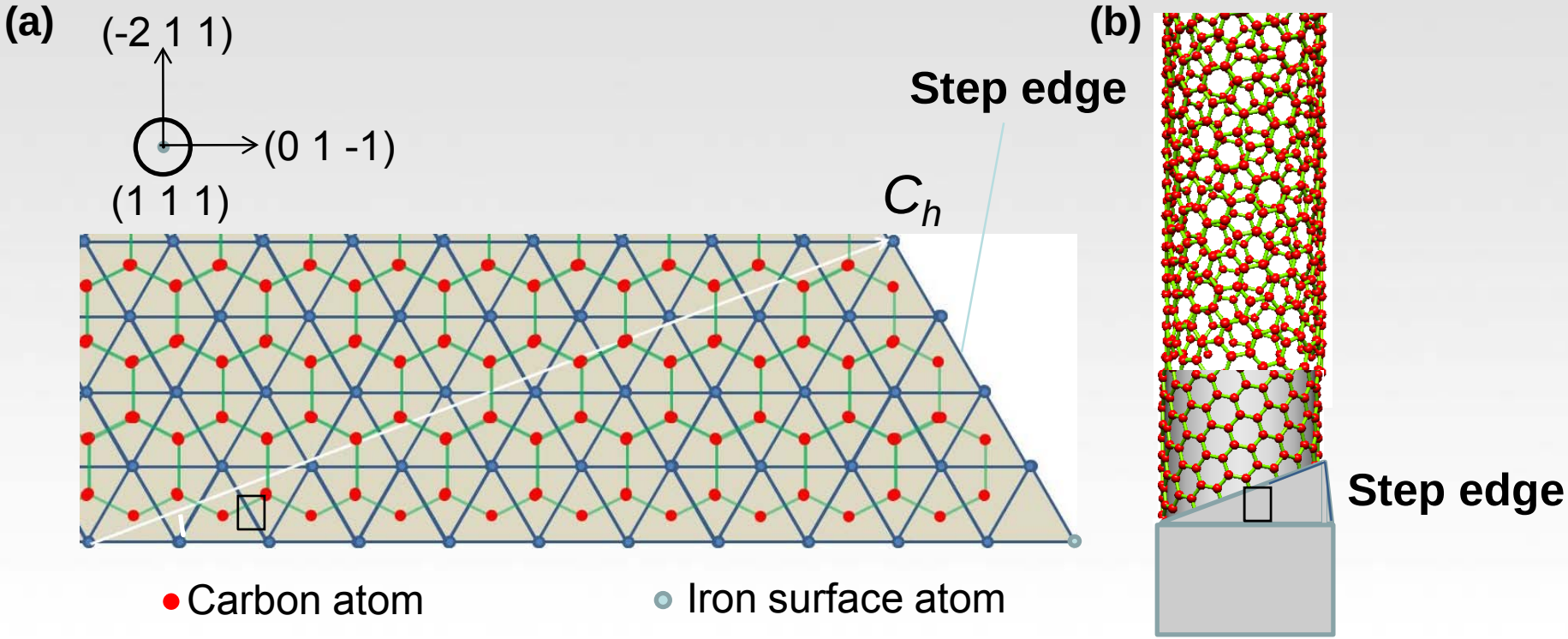


H. Zhu et al., J. Cryst. Growth. 310, 5473 (2008)

The nanotube chirality could be associated with the angle of the step edge on (111) plane of the catalyst with respect to the growth direction of CNT



H. Zhu et al. / Journal of Crystal Growth 310 (2008) 5473–5476



(a) Structural correlation between the unrolled honeycomb lattice of a nanotube and the underlying **FCC Fe (1 1 1)** surface, and
(b) schematic diagram illustrates how nanotube chirality forms at the step edge. C_h represents the nanotube chiral vector as determined by the step edge, which is directly related to the chiral angle □ and tube diameter *d* (*d*=C_h/2□).

The Best matches for each SWCNT structures with Low-indexes facets of Fe catalyst at 860□C

(n, m) (Diameter, Chiral angle)	Fe (1 1 1) (Diameter, Chiral angle) ΔD/D, Δ□/□	Fe (1 0 0) (Diameter, Chiral angle) ΔD/D, Δ□/□	Fe (1 1 0) (Diameter, Chiral angle) ΔD/D, Δ□/□
(15, 0) (1.182nm, 0□)	(1.173, 0□) **ΔD/D=-0.761%, Δ□/□=0%**	(1.198, 0□) **ΔD/D=1.354%, Δ□/□=0%**	(1.173, 0□) **ΔD/D=-0.761%, Δ□/□=0%**
(14, 2) (1.190nm, 6.587□)	(1.113, 5.818□) **ΔD/D=-6.471%, Δ□/□=-11.675%**	(1.394, 7.595□) **ΔD/D=17.143%, Δ□/□=15.303%**	(1.246, 6.371□) **ΔD/D=4.706%, Δ□/□=-3.279%**
(13, 4) (1.213nm, 13.004□)	(1.067, 12.218□) **ΔD/D=-12.036%, Δ□/□=-6.044%**	(1.229, 12.995□) **ΔD/D=1.319%, Δ□/□=-0.069%**	(1.205, 13.263□) **ΔD/D=-0.660%, Δ□/□=1.992%**
(12, 6) (1.251nm, 19.107□)	(1.257, 21.054□) **ΔD/D=0.480%, Δ□/□=10.190%**	(1.370, 19.654□) **ΔD/D=9.512%, Δ□/□=2.863%**	(1.306, 18.519□) **ΔD/D=4.396%, Δ□/□=-3.077%**
(11, 8) (1.302nm, 24.791□)	(1.361, 24.507□) **ΔD/D=4.531%, Δ□/□=-1.146%**	(1.319, 24.775□) **ΔD/D=1.306%, Δ□/□=-0.065%**	(1.297, 25.240□) **ΔD/D=-0.384%, Δ□/□=1.811%**
(10, 10) (1.365nm, 30□)	(1.354, 30.003□) **ΔD/D=-0.806%, Δ□/□=0.01%**	(1.407, 31.608□) **ΔD/D=3.077%, Δ□/□=5.360%**	(1.418, 29.173□) **ΔD/D=3.883%, Δ□/□=-2.757%**

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \mu)^2}.$$

Summary

There is definite correlation between catalyst facet structures and grown SWCNT chiralities

So, problem of selective growth of SWCNTs became a problem of our capability to make nanocatalysts with preferable facets

How to solve this problem at elevated temperatures ?

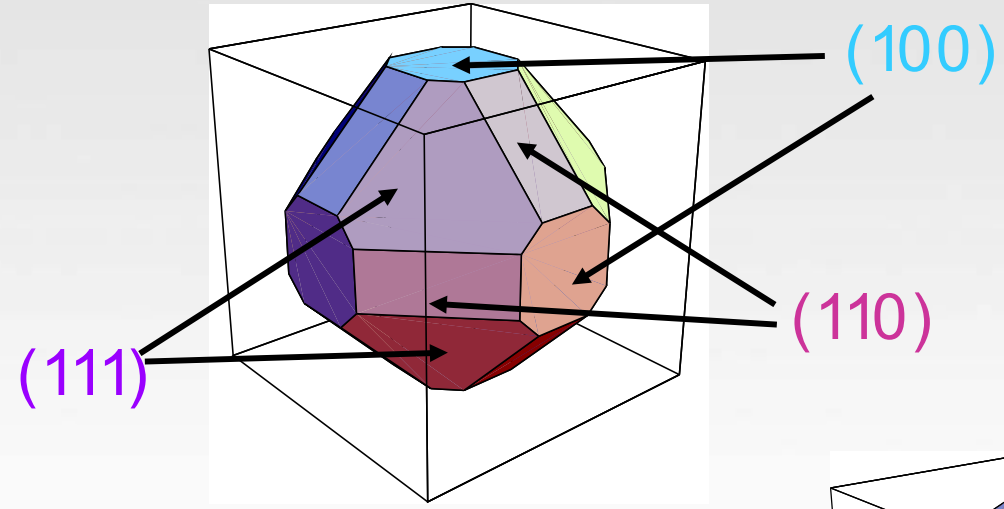
Preferential growth of specific facets by using **proper adgas** along with hydrocarbon source

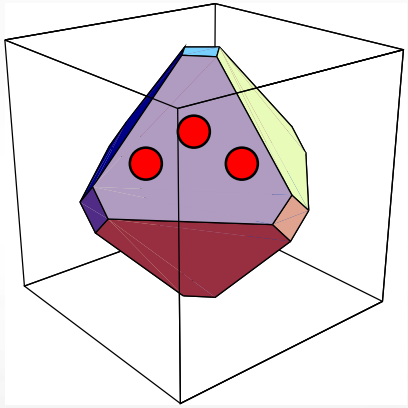
(e.g. CO/CH_4, CO_2/CH_4, H_2O/CH_4, CH_4/C_2H_4,…)

$\gamma_{111} = 1.97\ J/m^2$

$\gamma_{100} = 2.2\ J/m^2$

$\gamma_{110} = 2.1\ J/m^2$

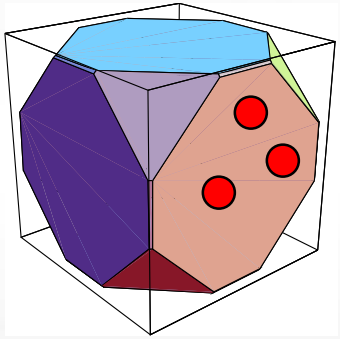




→ $\gamma_{111} = 1.5\ J/m^2$

$\gamma_{100} = 2.2\ J/m^2$

$\gamma_{110} = 2.1\ J/m^2$



→ $\gamma_{111} = 1.97\ J/m^2$

$\gamma_{100} = 1.5\ J/m^2$

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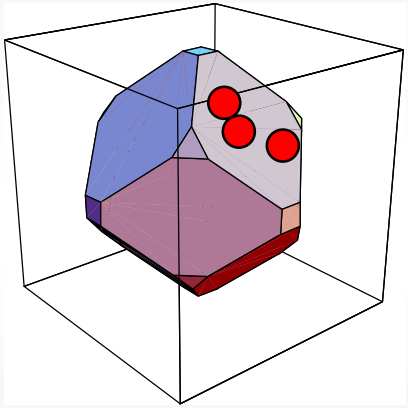


→ $\gamma_{111} = 1.97\ J/m^2$

$\gamma_{100} = 2.2\ J/m^2$

$\gamma_{110} = 1.7\ J/m^2$

Substrate effect

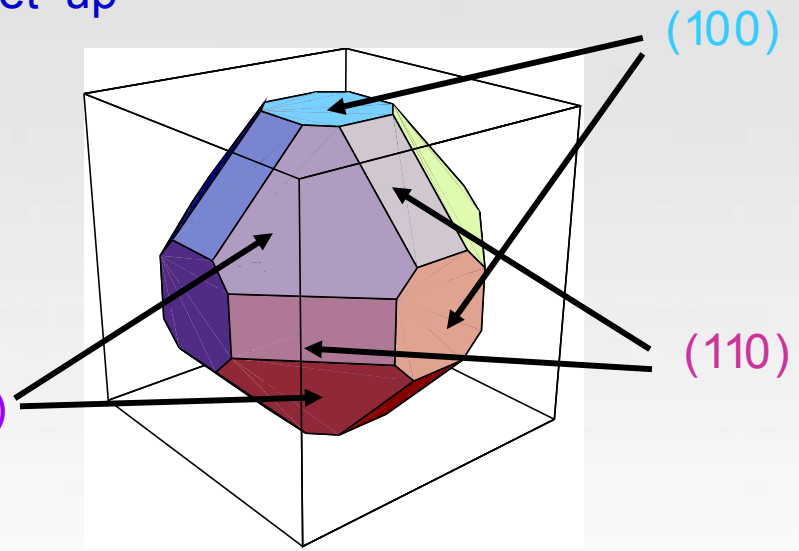
FCC particle with (100) facet up

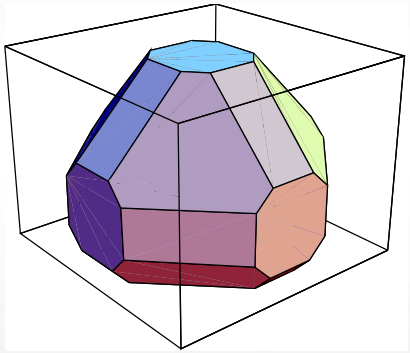
$\gamma_{111} = 1.97\ J/m^2$

$\gamma_{100} = 2.2\ J/m^2$

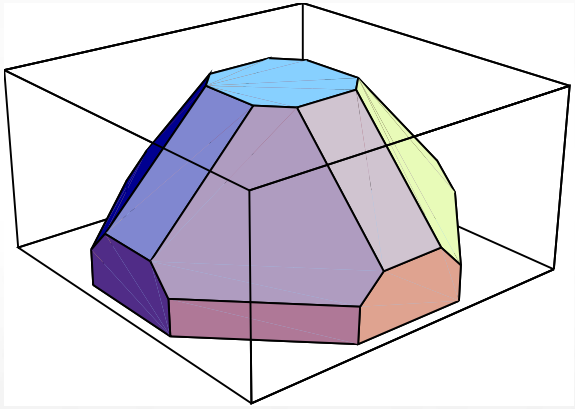
$\gamma_{110} = 2.1\ J/m^2$

(no interaction)

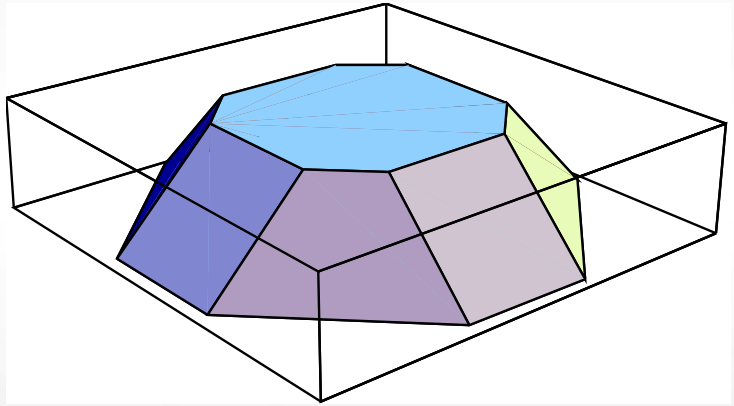




A weak interaction



Some interaction



Strong interaction

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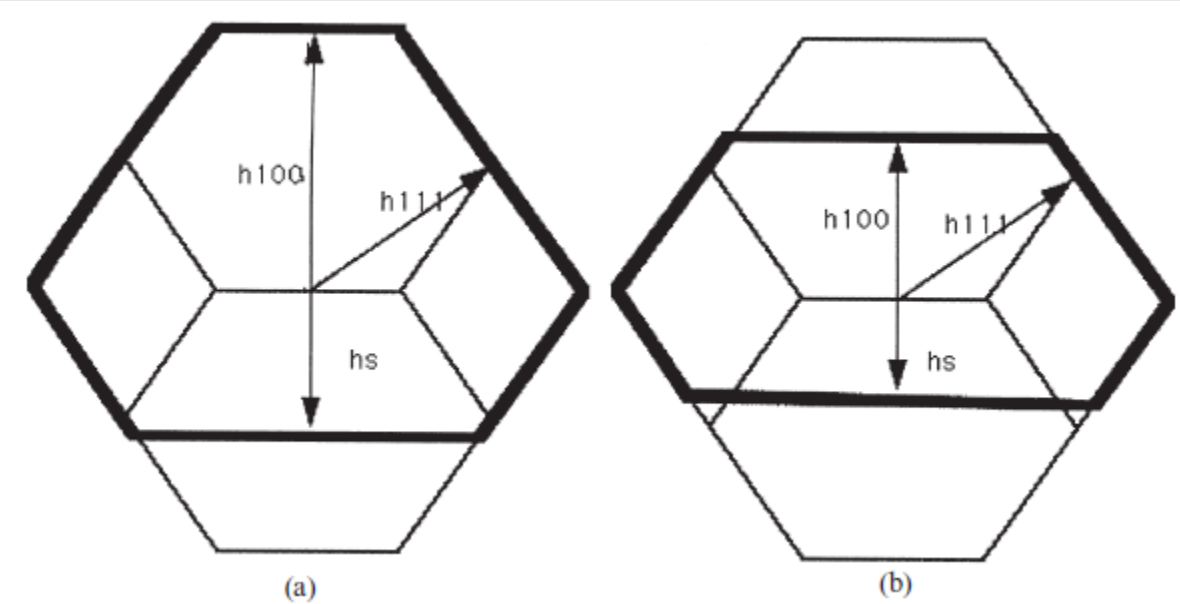

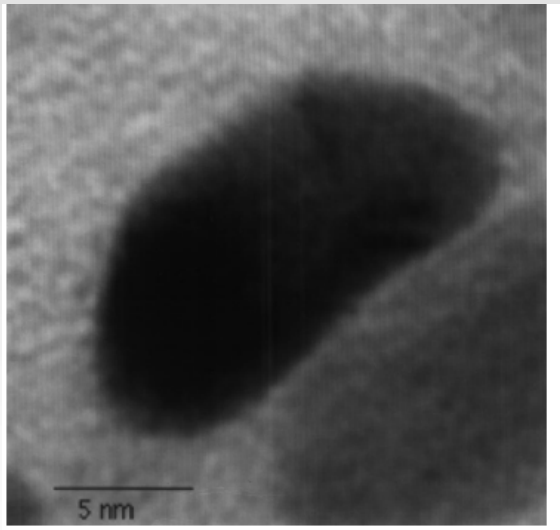

Pd particle on MgO annealed in UHV (T=550^{o}C)

Pd particle on MgO annealed in O_2 (10^{-3} Torr at 550^{o}C)

Light drawings correspond