Dendrimer-Templated Catalyst for Controlled Growth of Single-Wall Carbon Nanotubes by PECVD

Placidus Amama

Research Projects

Catalyst Fabrication and Controlled CNT Growth by PECVD

T.D. Sands, T.S. Fisher

Electrical Characterization of CNTs

C. Lan, T.S. Fisher, R. Reifenberger

Low-Temperature Growth of CNTs

B. Cola, T.D. Sands, T.S. Fisher

CNT Based Electrochemical Biosensor

S. Kim, T.S. Fisher

CNT Growth Mechanism

T.D. Sands, T.S. Fisher

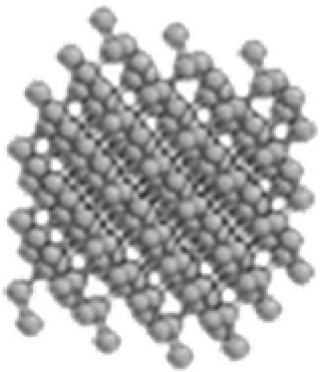
CNT Thermal Interfaces

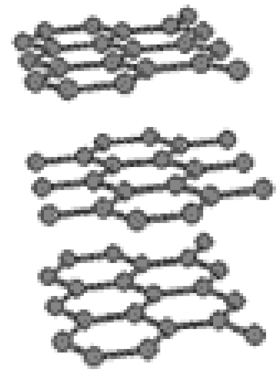
B. Cola, X. Xu, T.S. Fisher

Outline

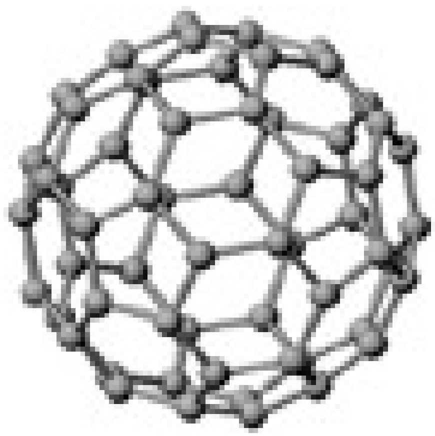
- Background
- Dendrimer template
  - *Annealing ambient*
  - *Metal-substrate interaction*
  - *H_2-prereduction*
  - *Positive and negative dc bias voltage*
- Control of SWNT chirality
- Low-temperature growth
- Growth mechanism
- Summary
- Acknowledgements

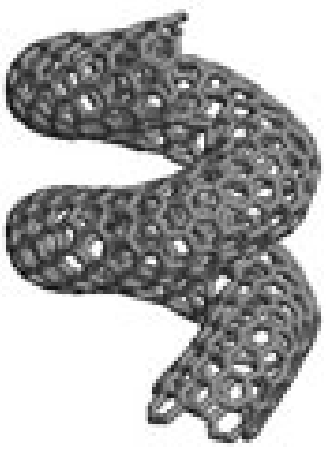
Gallery of Carbon


Diamond


Graphite


Carbon chain


C_{60}

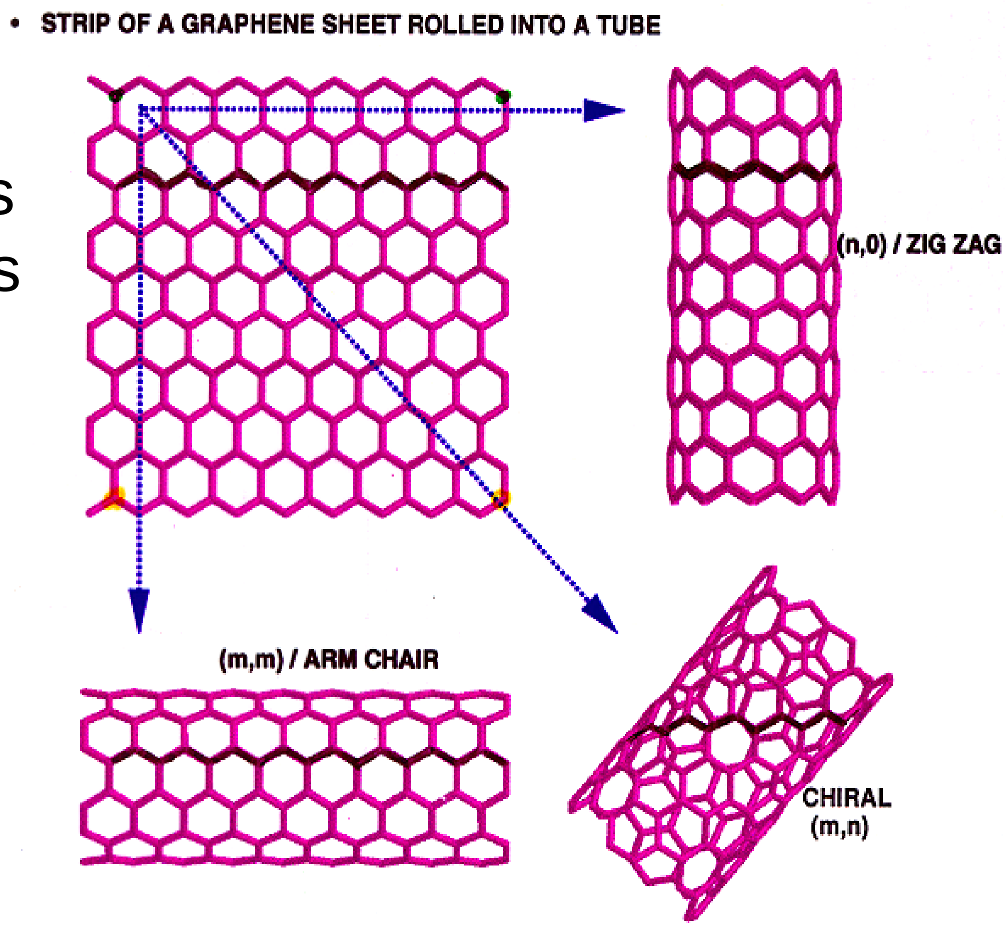

CNT

Discovered 1991 by **Ijima** while studying C_{60} production ["Helical microtubules of graphitic carbon", S. Iijima, Nature **354**, 56 (1991)]

http://www.seed.slb.com/en/scictr/watch/fullerenes/index.htm

SWNT Types

- The graphene sheet can be 'rolled' in different ways to form different tube types
- Each type has different electrical properties



http://www.ipt.arc.nasa.gov/Graphics/cnt_based_nanotech.pdf

Some Interesting Properties and Characteristics of CNTs

- Mechanical
  - Young's modulus ~1 TPa (5X steel) (Treacy et al. 1996)
- Electrical
  - Metallic or semiconductor behavior, depending on wall structure of SWNTs
  - Ballistic conductor, *R* =6500 Ω, ~independent of length (Frank et al., 1998)
  - Field emission threshold field ~1 V/micron (Bonard et al., 2001)
- Thermal
  - Room-temperature thermal conductivity ≈3000 W/mK (8X copper)
  - Similar to diamond and graphite
- Others
  - High chemical (such as lithium) storage capacity
  - High aspect ratio (length = ~1000X diameter)
  - Excellent catalyst support

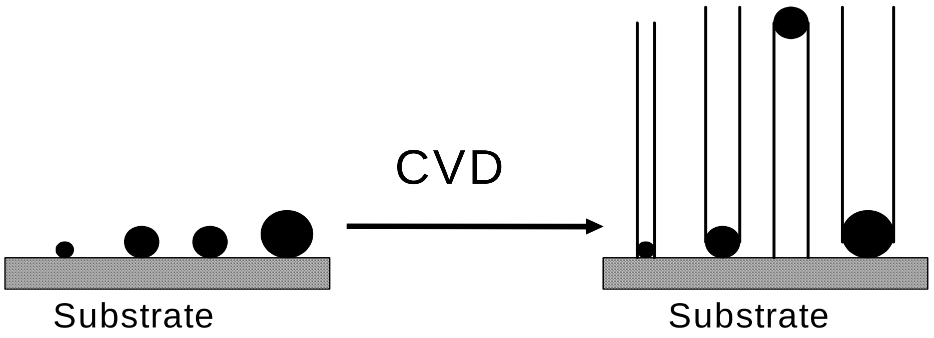
Barriers to Device Design and Commercialization of CNTs

- Homogeneous electronic properties through control of nanotube diameter and chirality
- Fundamental understanding of the growth mechanism
- High growth temperatures
- Presence of defects and impurities

Growing Carbon Nanotubes

Processing methods that can produce scalable quantities:

- Electric arc discharge – *S. Iijima, NEC R&D Group, Japan*
- Laser ablation – *R. Smalley, Rice University*
- Chemical Vapor Deposition (CVD)- *H. Dai, Stanford University*
  - *Plasma-enhanced CVD*
  - *Thermal CVD*



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Dendrimer Template: Objectives

- Synthesize monodispersed Fe nanoparticles (< 3 nm) for SWNT growth
  - *Using PAMAM dendrimer as a "nanotemplate"*

- Control CNT properties: wall selectivity, purity, alignment, chirality, and diameter
  - *Annealing ambient (H_2, N_2, Ar and vacuum)*
  - *H_2 prereduction*
  - *Metal-substrate interaction*
  - *Positive and negative dc bias voltage*

- Reduce the growth temperature of CNTs

- Investigate the active specie involved in CNT nucleation

What is a Dendrimer?

Discovered in the early 1980's by Dr. Don Tomalia

- Discrete, well-defined polymers
- Synthetic 3D macromolecule
- Synthesized in a series of repetitive reactions from simple monomer units

http://www.almaden.ibm.com/st/chemistry/ps/dendrimers/

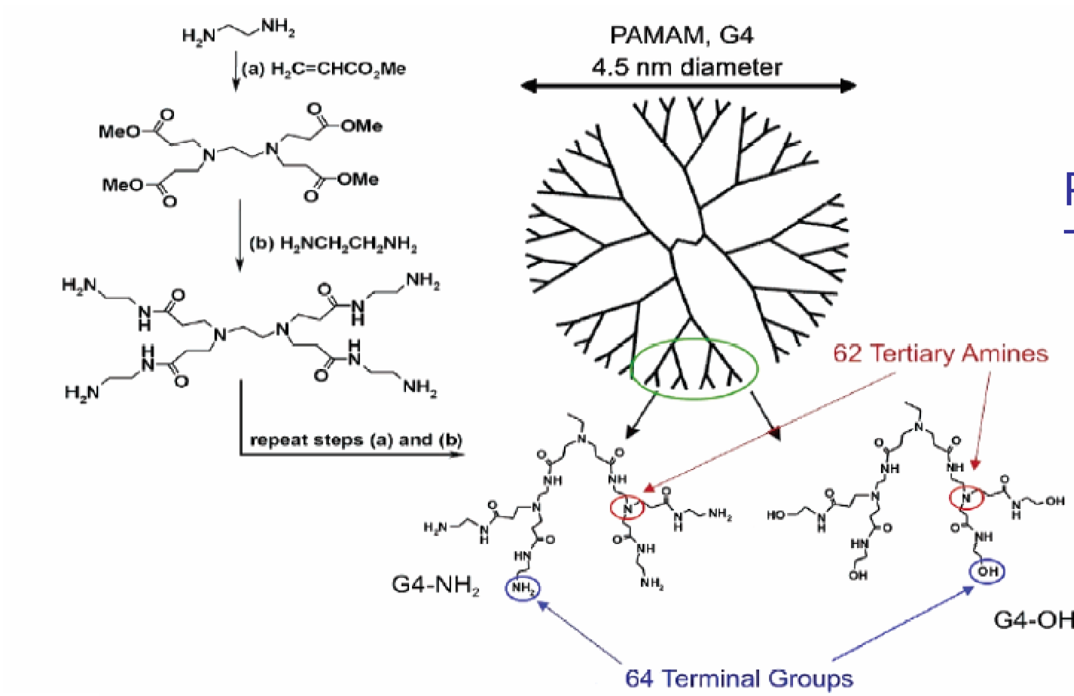
Novel attributes of dendrimers

- Uniform composition and structure
- Nanoparticles are stabilized by encapsulation
- The core or peripheral functional groups can be tailored
- Encapsulation of metal nanoparticles occurs mainly by steric effects

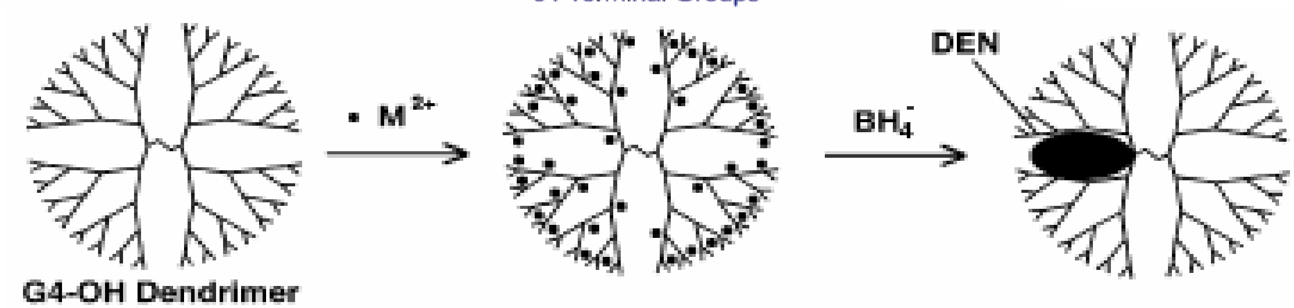
R.W.J. Scott, O.M. Wilson, R.M. Crooks, *J. Phys. Chem.* B **2005**, *109*, 692

Mechanism of Formation

G-4 Poly(amidoamine) (PAMAM) dendrimer-stabilized transition metal nanocomposite



Peripheral NH_2 (pK_a = 9.23)
Tertiary NH_2 (pK_a = 6.30)



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Characterization Tools

- Raman spectroscopy

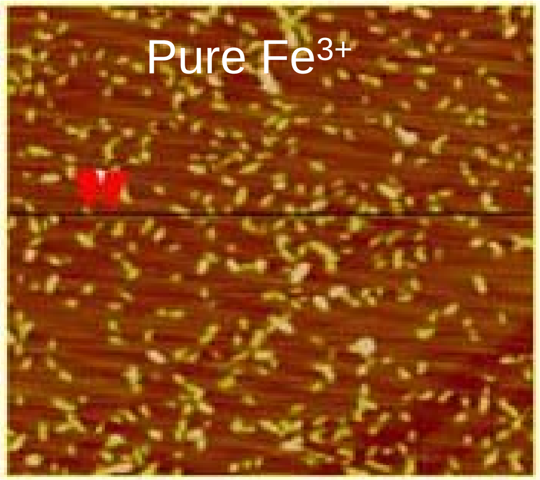
  Excitation wavelengths: 514, 574, 633, **785** nm

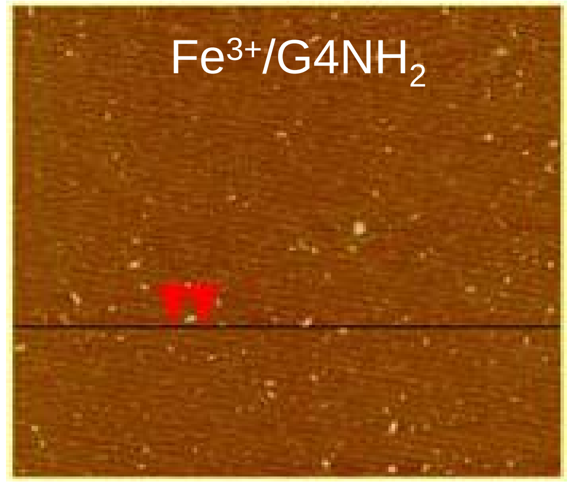
  - G-band (1500-1600cm^{-1})
  - D band (1200-1400cm^{-1})
    Purity index (G/D ratio)
  - Radial breathing mode (RBM) (100-400cm^{-1})

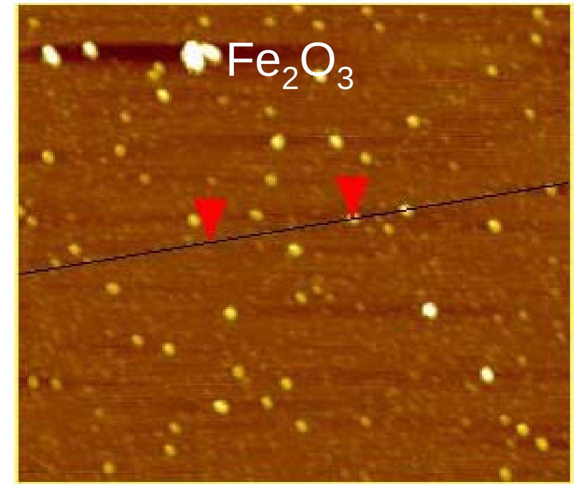
$$W_{RBM}(cm^{-1}) = 12.5 + 223.5/d(nm)$$

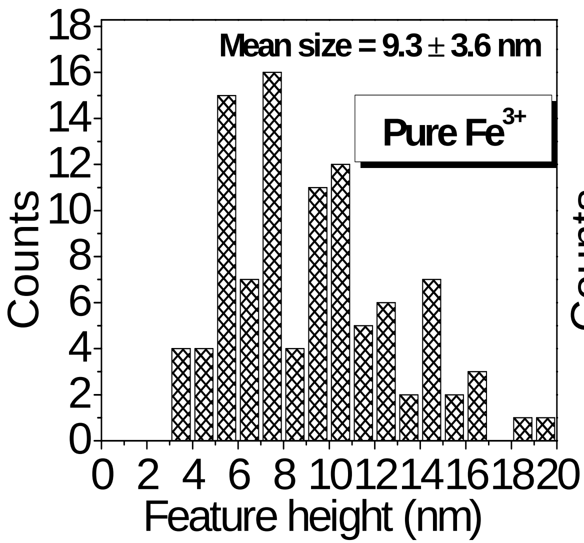
- FESEM
- AFM
- TEM
- XPS

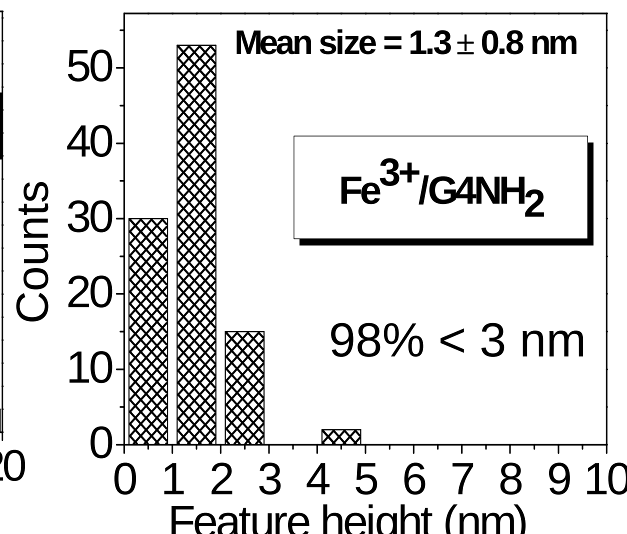
AFM Images, Topographic Height Profiles, and PSDs of Fe Nanoparticles

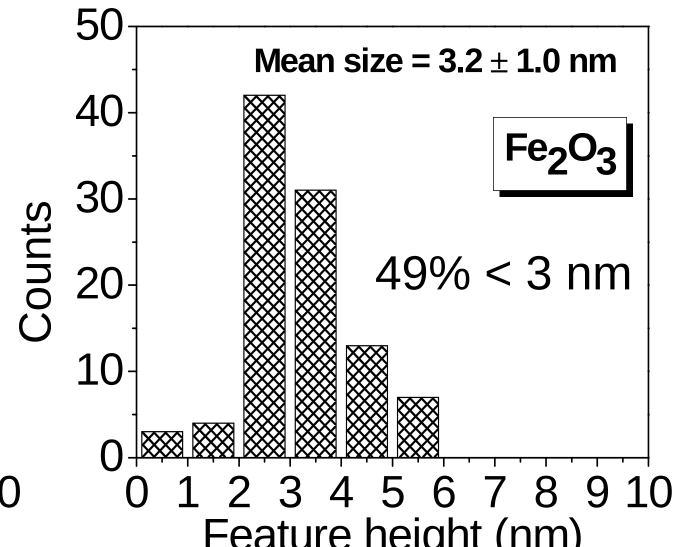






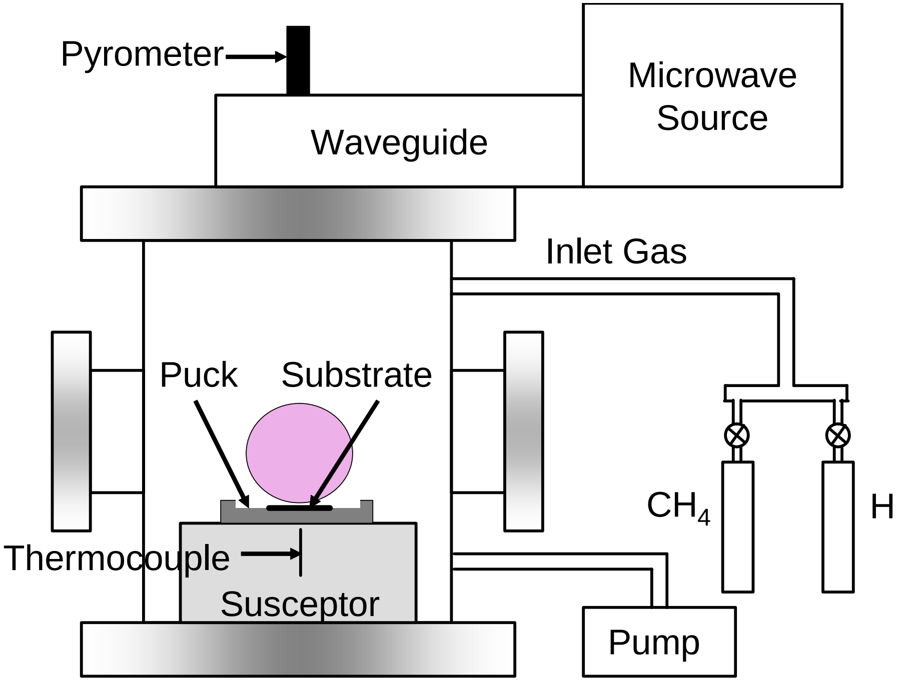






Supported on mica

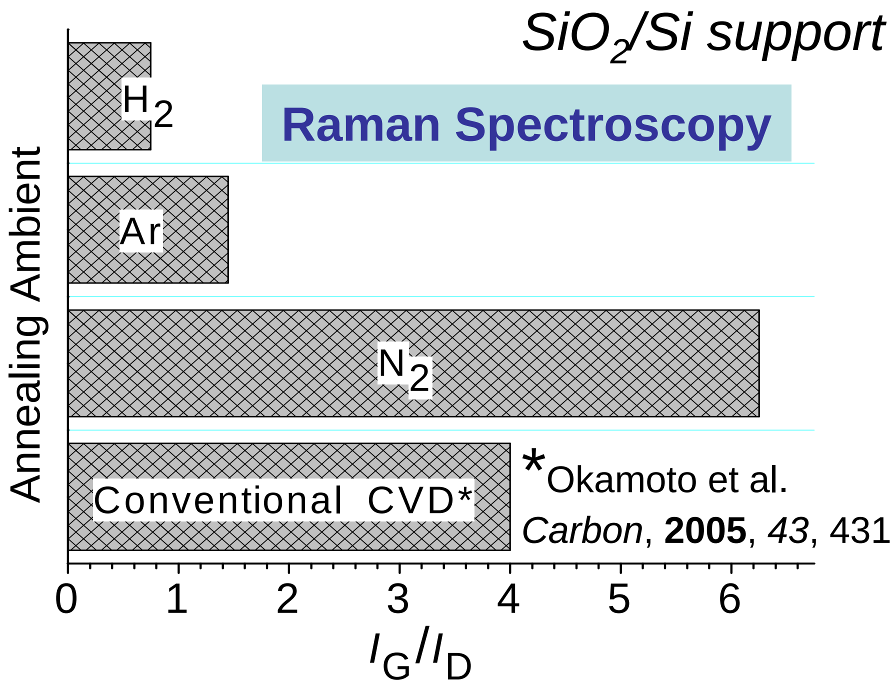
PECVD Growth of CNTs

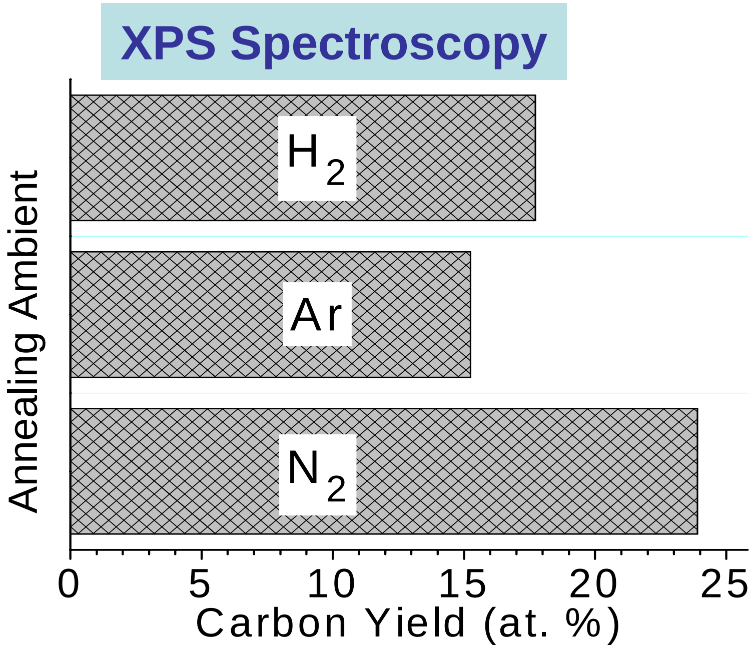


- **Advantages**
  - High-quality CNT synthesis
  - Vertical alignment
  - Low-temperature growth
  - Controllability of PECVD
    - Typical substrate temperature 600-1000°C
    - Max. 1.5 kW microwave source (2.5 GHz)
    - Max. 600V dc substrate bias
    - 3 to 200 torr chamber pressure
    - Feed gases: H_2, CH_4, and N_2

M.R. Maschmann, P.B. Amama, A. Goyal, Z. Iqbal, R. Gat, T.S. Fisher, *Carbon* **2006**, *44*, 10

CNT Quality, Yield, and Selectivity





Substrate	Annealing Ambient (I_G/I_D Ratio)		Selectivity (N_2-Annealed)
	N_2	Ar	
SiO_2/Si	6.25	1.45	SWNTs, MWNTs
Ti/Si	0.90	0.28	SWNTs, MWNTs
Al_2O_3 (sapphire)	9.30	4.80	Mostly SWNTs
Al_2O_3 (PAA)	11.4	10.8	Mostly SWNTs

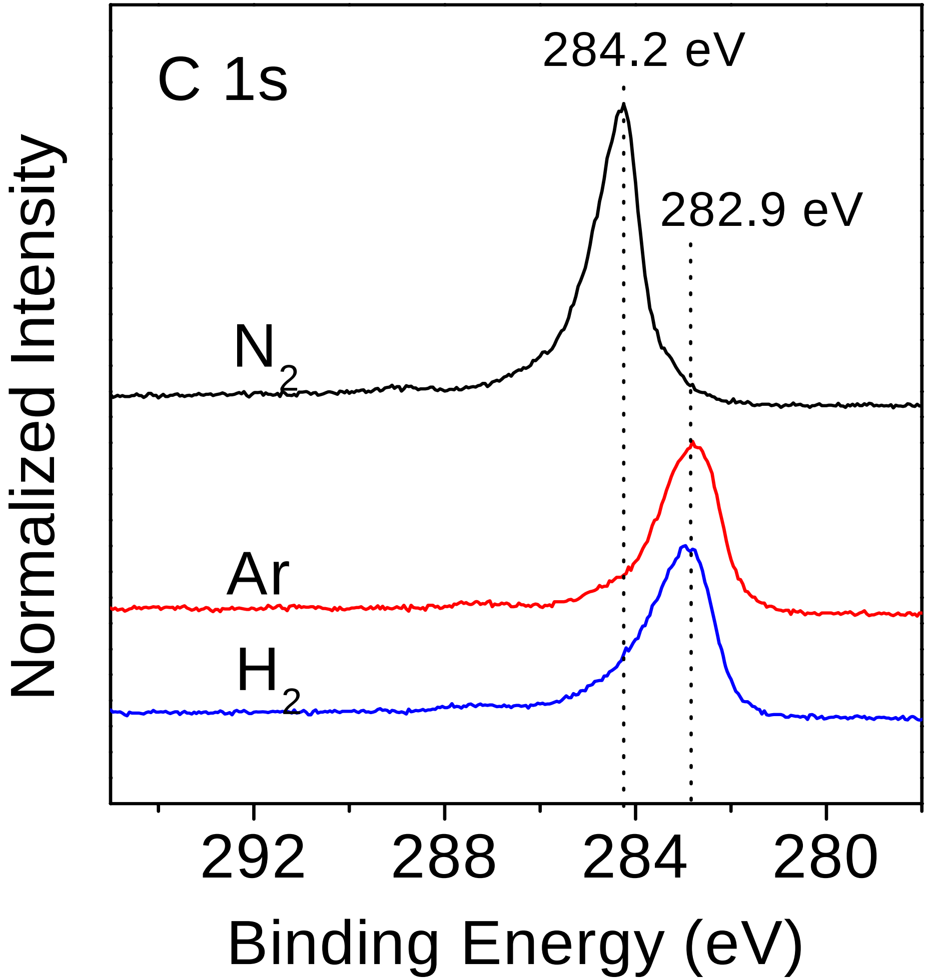
Ex-situ XPS Analysis: Raw Data

Al_2O_3 supports

The standard binding energy (BE) for CNTs is 284.3 eV

Observed shift in BE = 1.3 eV

FWHM of C 1s peak
N_2 = 1.03 eV
Ar = 1.36 eV
H_2 = 1.14 eV

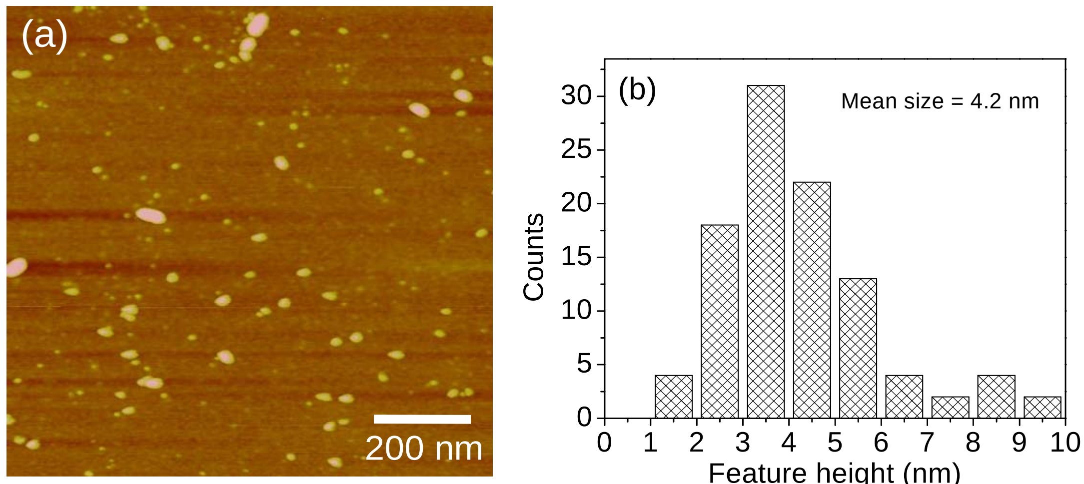


P.B. Amama, D. Zemlyanov, D.N. Zakharov, R.S. Katiyar, T.D. Sands, T.S. Fisher, *manuscript in preparation*

Effect of Annealing Ambient on the PSD of Fe_2O_3 Nanoparticles

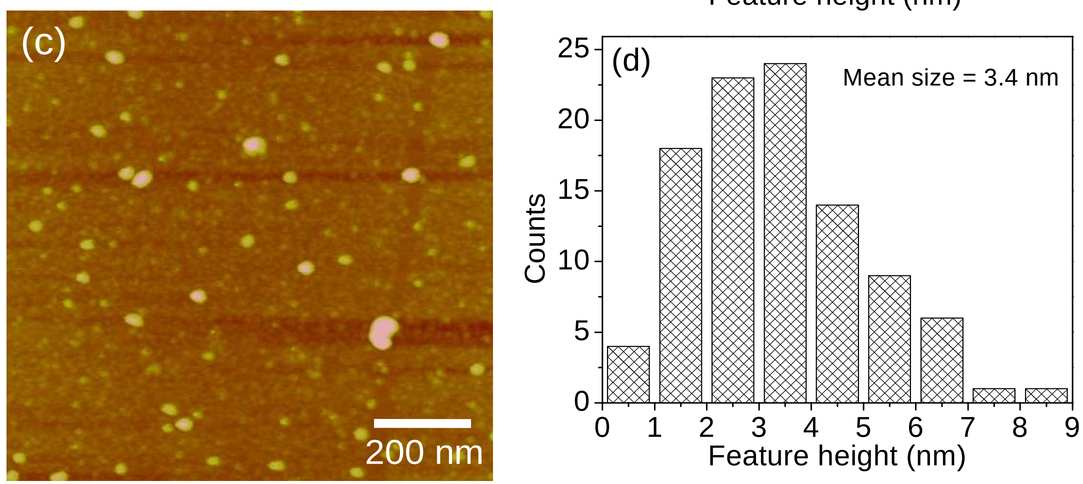
Ar-Annealed Fe_2O_3

22% < 3 nm



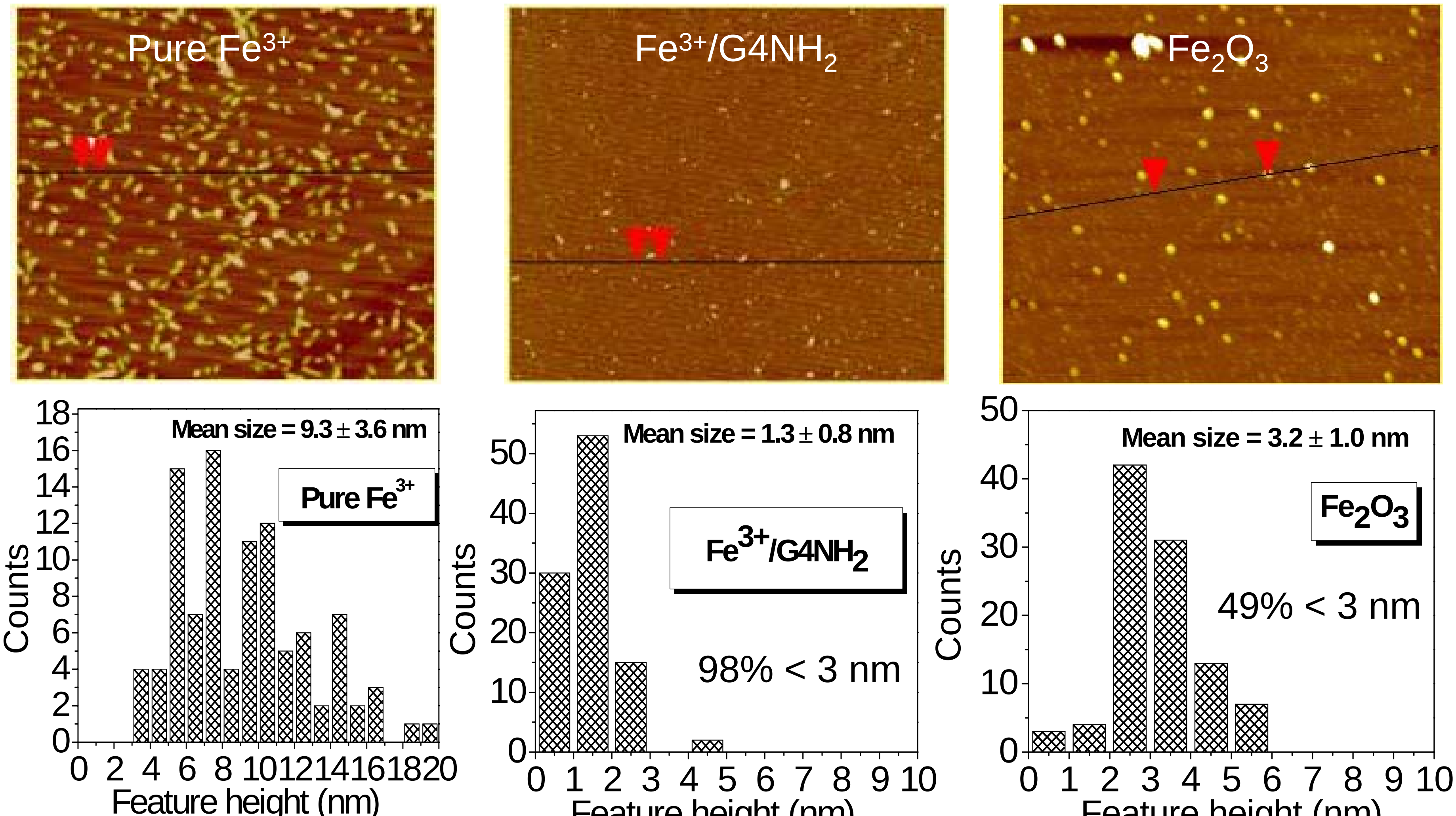
N_2-Annealed Fe_2O_3

45% < 3 nm



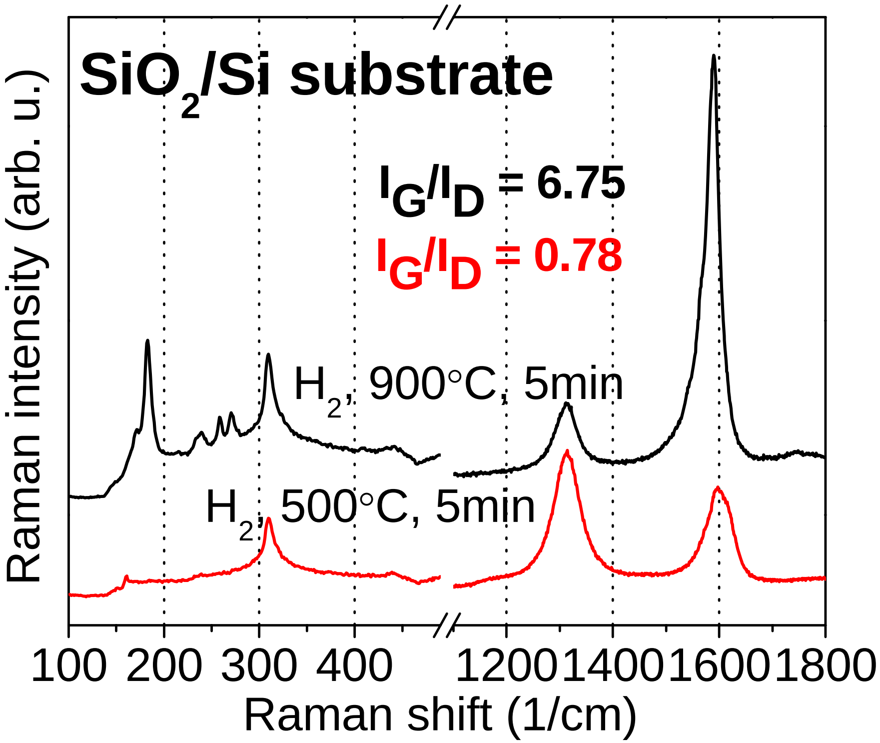
P.B. Amama, M.R. Maschmann, T.S. Fisher, T.D. Sands, *J. Phys. Chem. B* **2006**, *110*, 10636

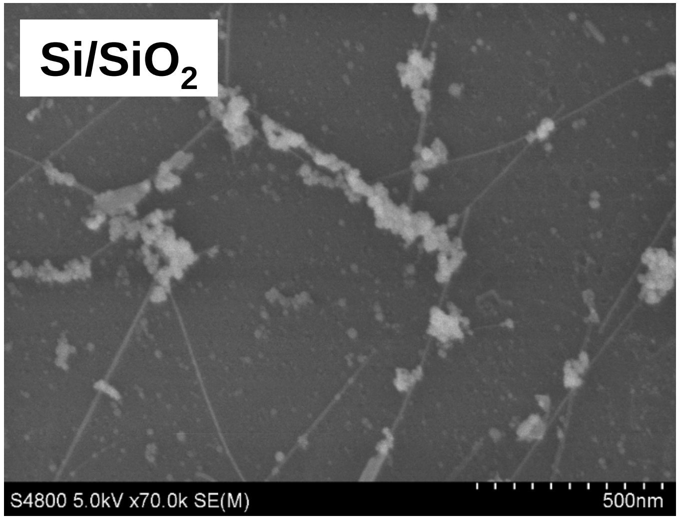
AFM Images, Topographic Height Profiles, and PSDs of Fe Nanoparticles



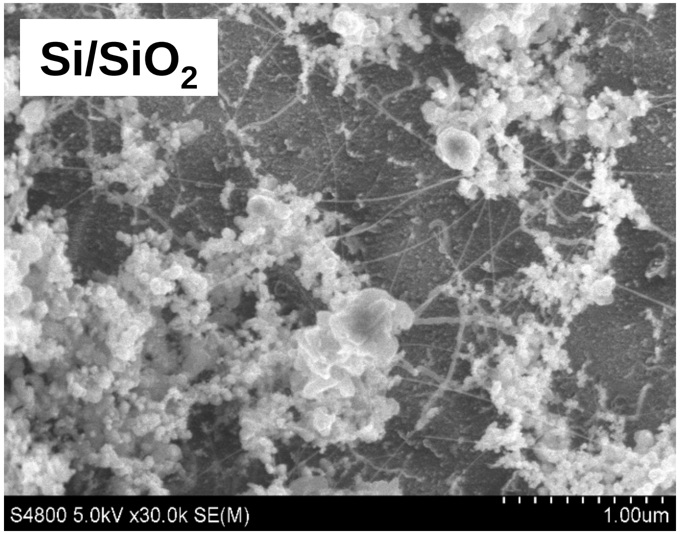
Supported on mica

Pretreatment: H_2 Prereduction





900 °C
5 min



500 °C
5 min

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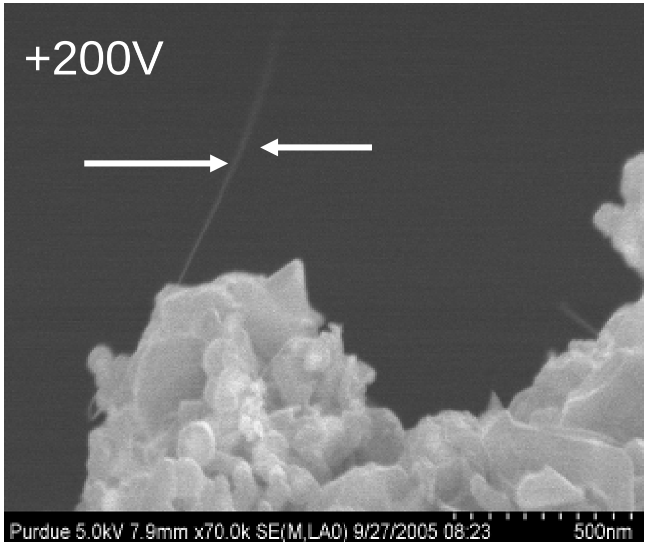
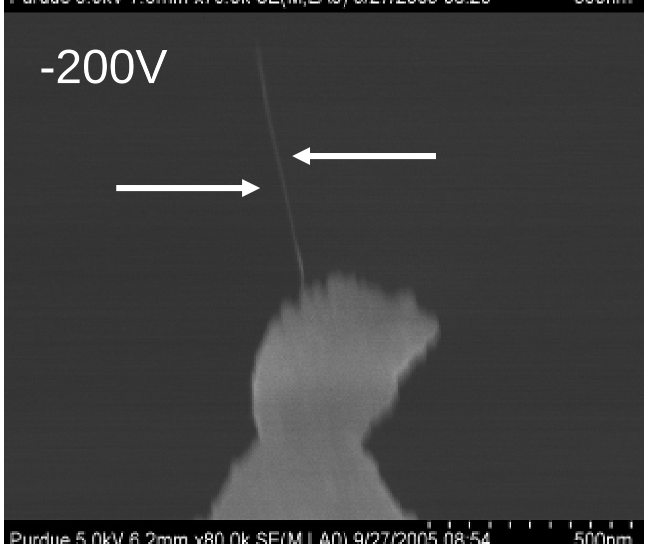
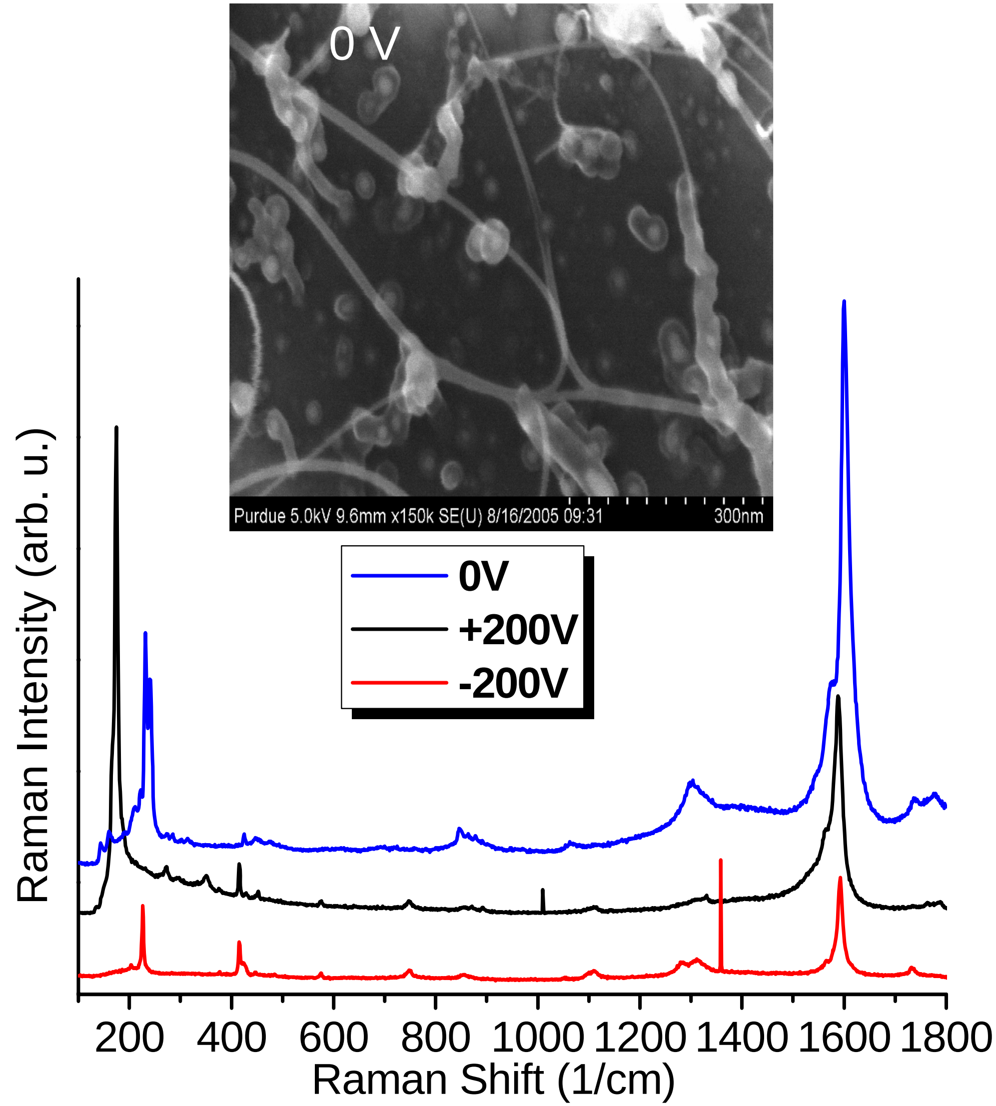
Growth Under dc Bias Voltage





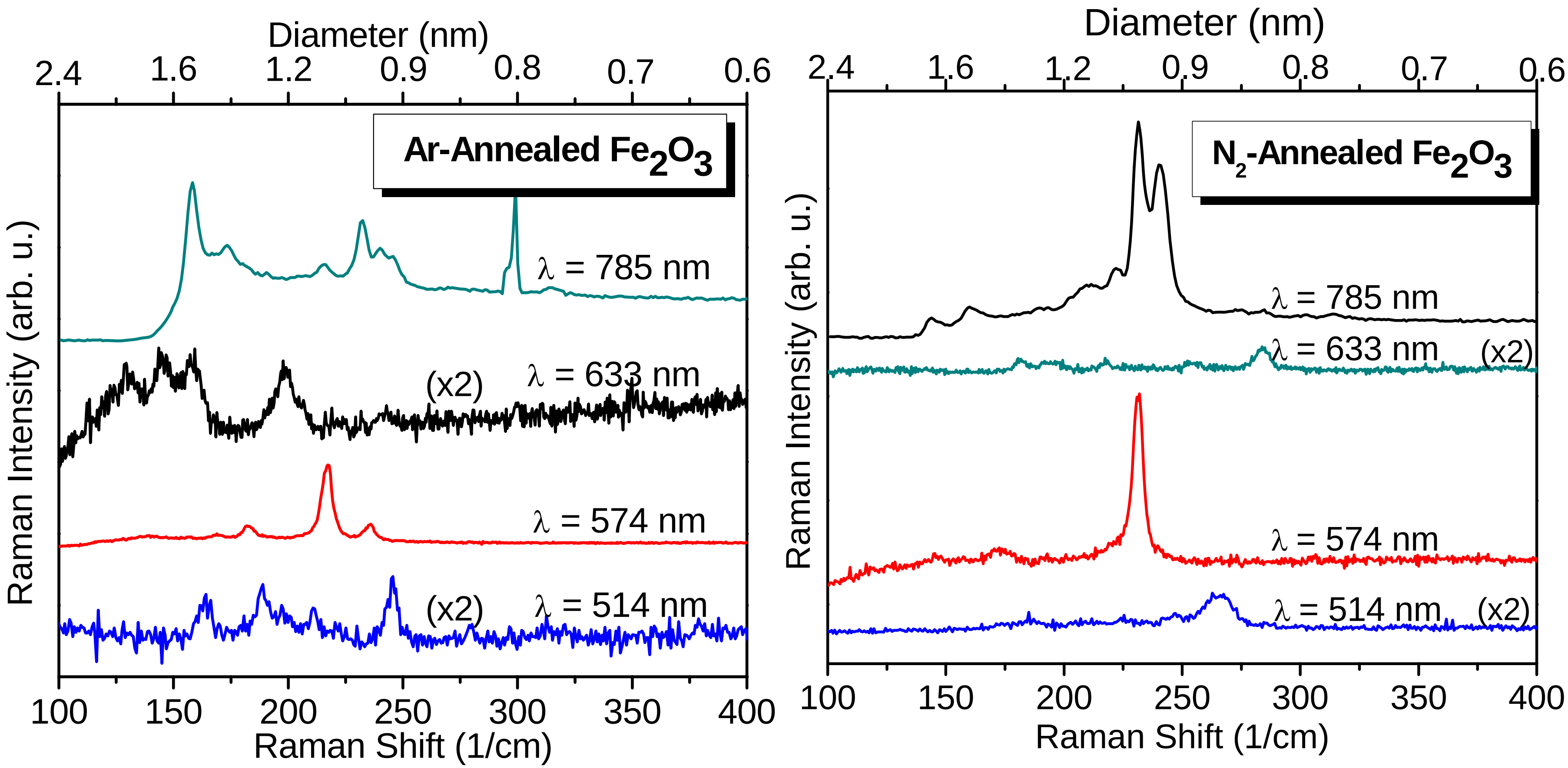


P.B. Amama, M.R. Maschmann, T.S. Fisher, T.D. Sands, *J. Phys. Chem. B* **2006**, *110*, 10636

Diameter Distribution of SWNTs

Multi-excitation wavelength Raman spectroscopy

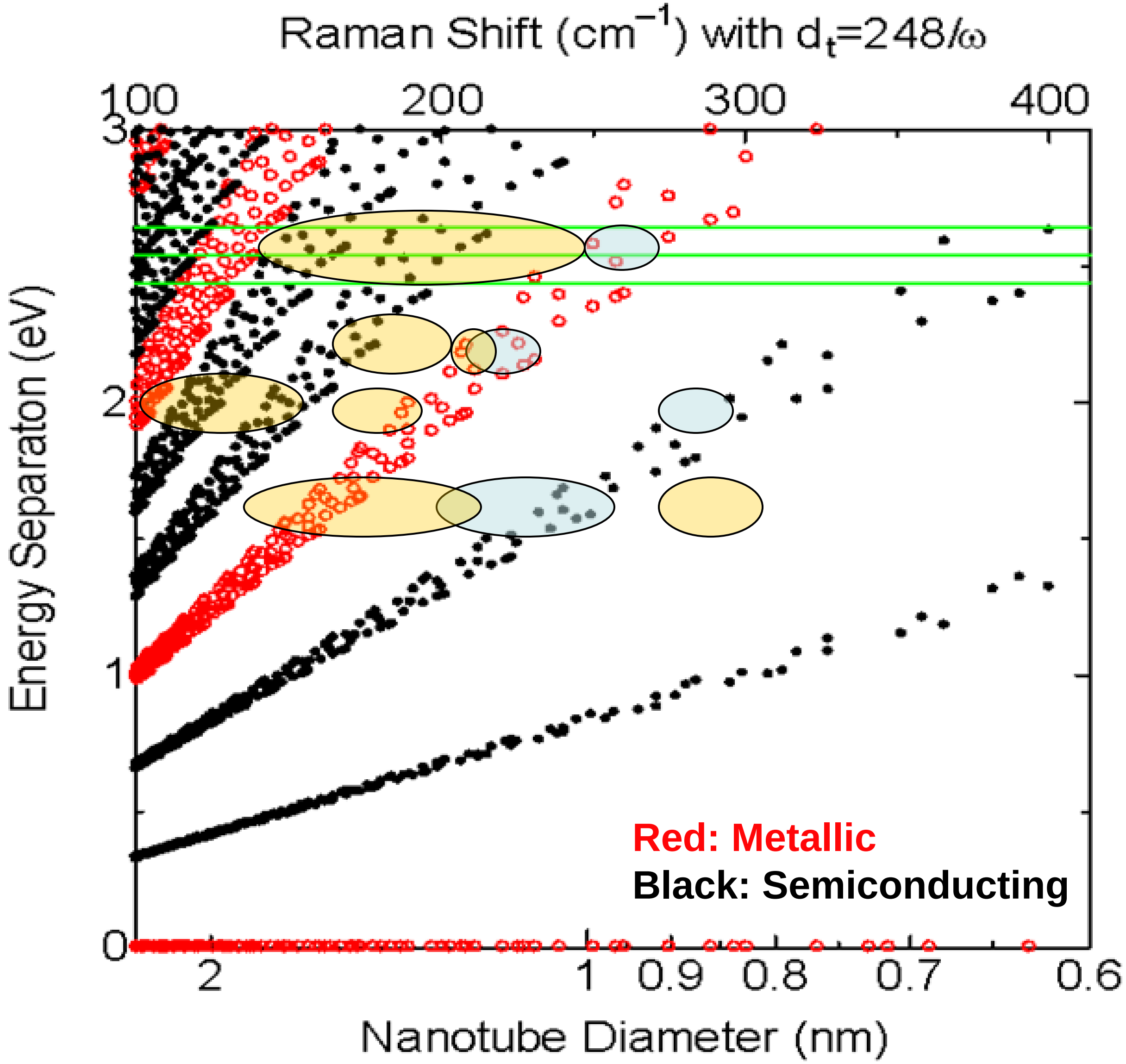
$$W_{RBM}(cm^{-1}) = 12.5 + 223.5/d(nm)$$



P.B. Amama, D. Zemlyanov, D.N. Zakharov, R.S. Katiyar, T.D. Sands, T.S. Fisher, *manuscript in preparation*

Comparison of RBMs with the Kataura Plot

H. Kataura *et al.*, *Synthetic Metals* **1999**, *103*, 2555



SWNTs grown from N_2-annealed Fe_2O_3

SWNTs grown from Ar-annealed Fe_2O_3

Outline

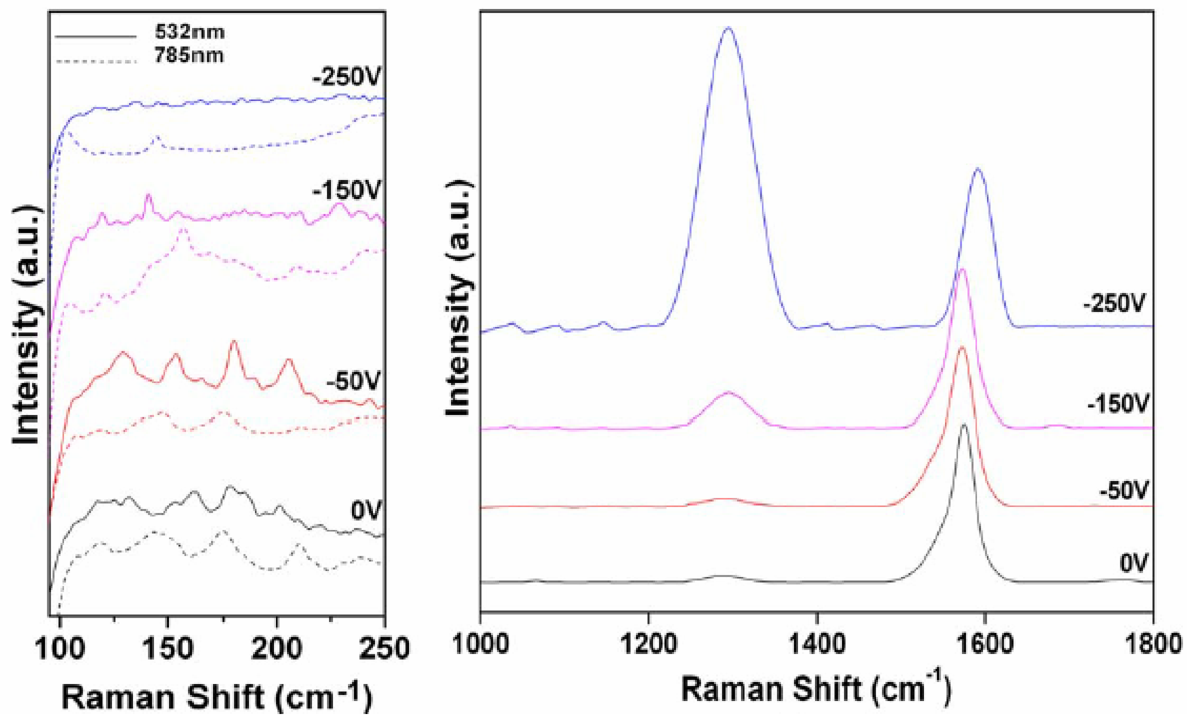
- ➢ Background
- ➢ Dendrimer template
  - – *Annealing ambient*
  - – *H_2 prereduction*
  - – *Metal-substrate interaction*
  - – *H_2-prereduction*
  - – *Positive and negative dc bias voltage*
- ➢ Control of SWNT chirality
- ➢ Low-temperature growth
- ➢ Growth mechanism
- ➢ Summary
- ➢ Acknowledgements

Application of Negative dc Voltage Bias

Using Co/MgO catalyst

- ➢Larger diameter and semiconducting SWNTs are favored under negative dc voltage bias

- ➢I_G/I_D decreases with positive dc voltage bias



M.R. Maschmann, P.B. Amama, A. Goyal, Z. Iqbal, T.S. Fisher, *Carbon* **2006**, *44,* 2758.

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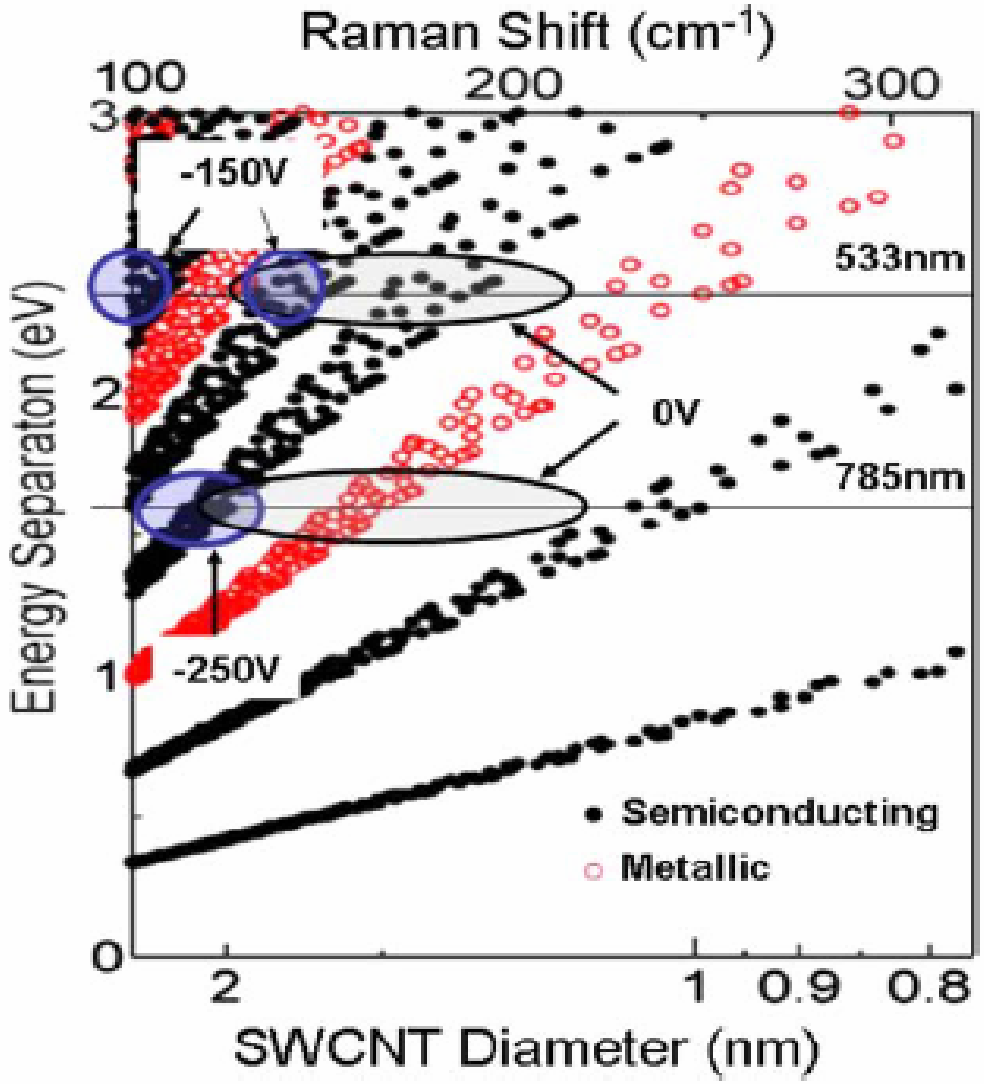
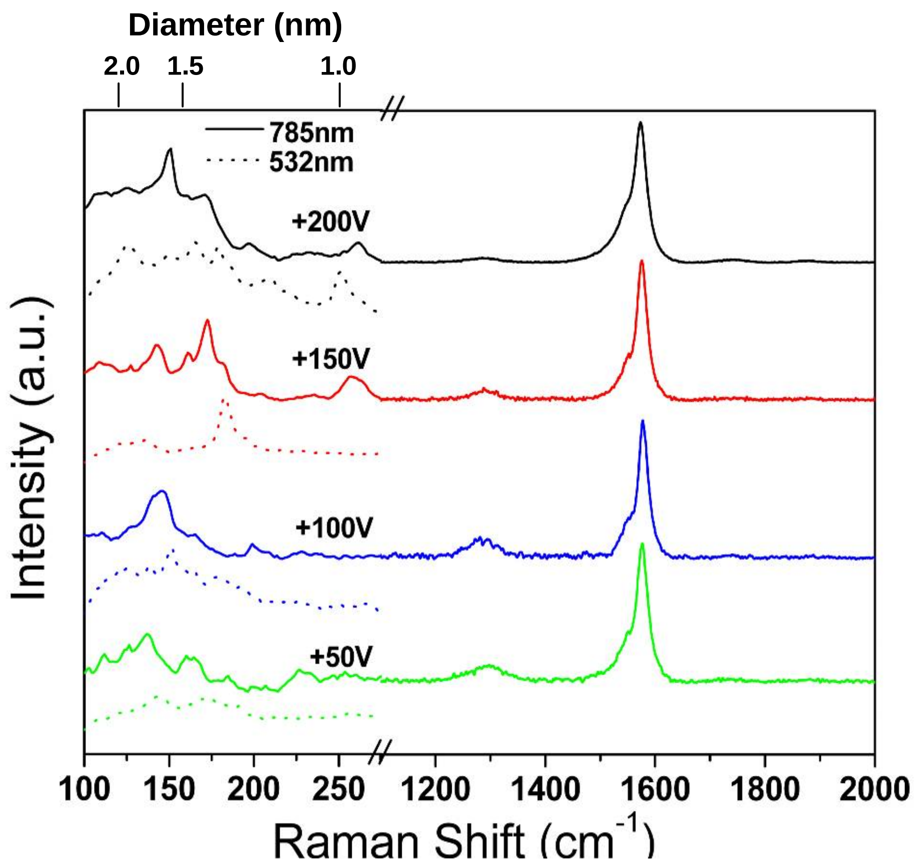


M.R. Maschmann, P.B. Amama, A. Goyal, Z. Iqbal, T.S. Fisher, *Carbon* **2006**, *44,* 2758.

Positive dc Substrate Bias

Using Co/MgO catalyst

- Dual-wavelength Raman spectra show emergence of RBM above 250 cm^{-1}
- No chirality preference observed
- I_G/I_D increases with positive bias
  - Increase in SWNT density
  - Mitigation of H^+ damage



M. R. Maschmann et al. *manuscript in preparation*

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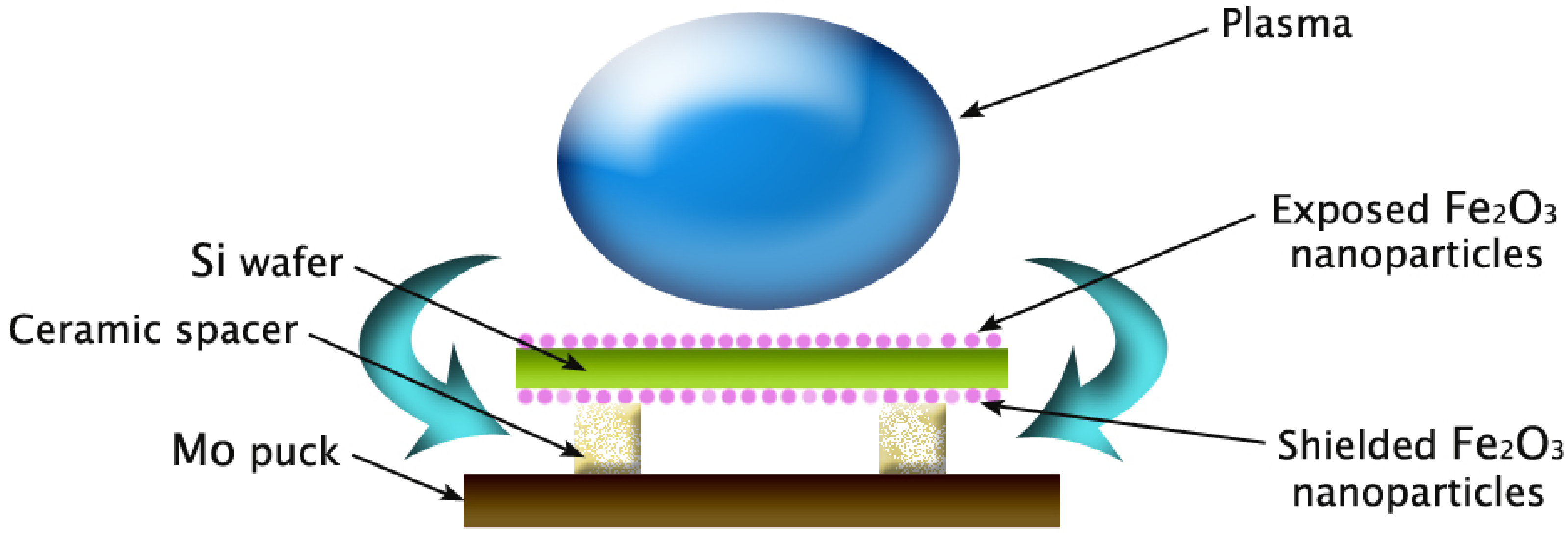
Shielded Growth Approach

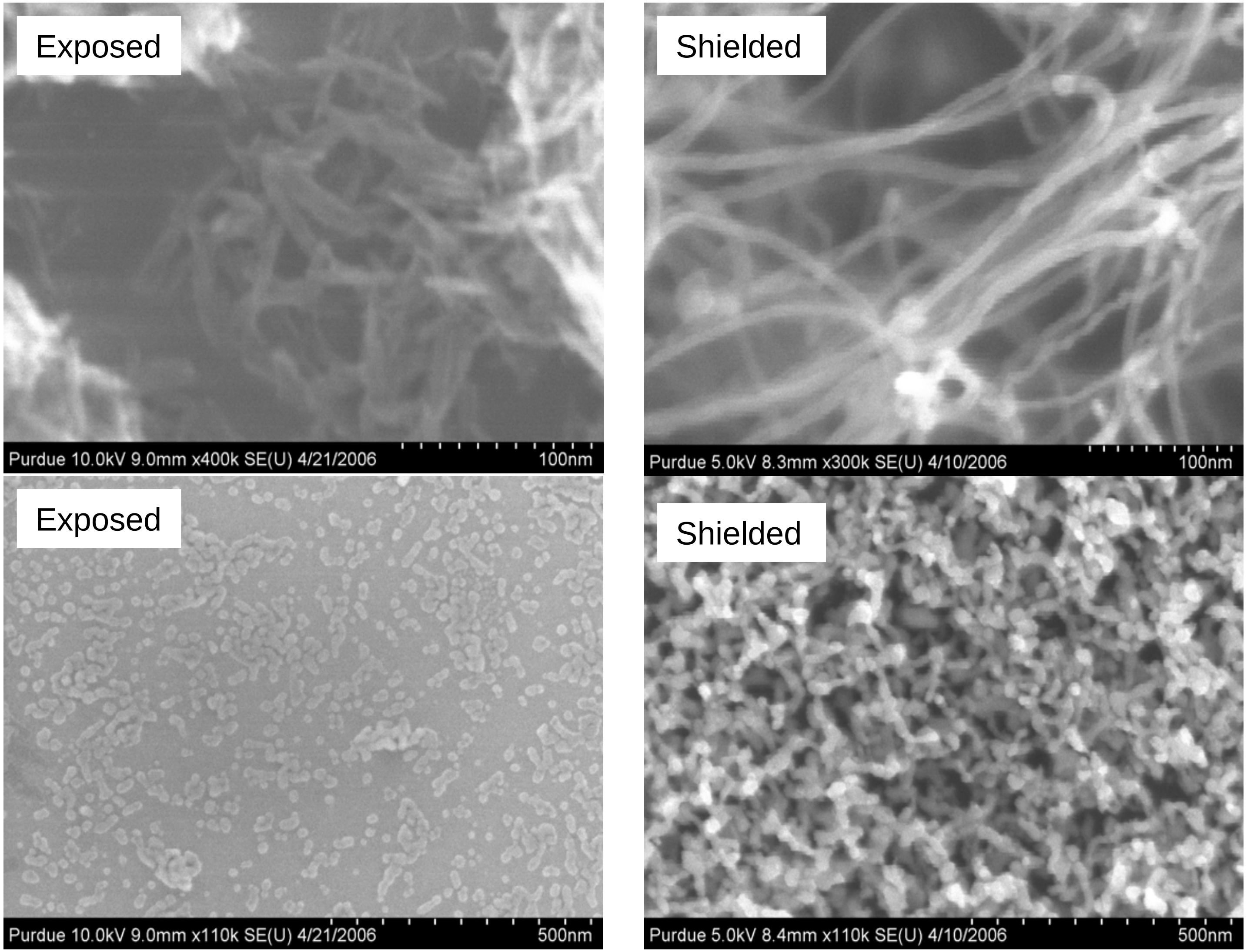


Experimental setup for low-temperature growth from shielded and exposed SiO_2/Si-supported Fe_2O_3 nanoparticles in the PECVD reactor

Dendrimer-Assisted Low-Temperature Growth

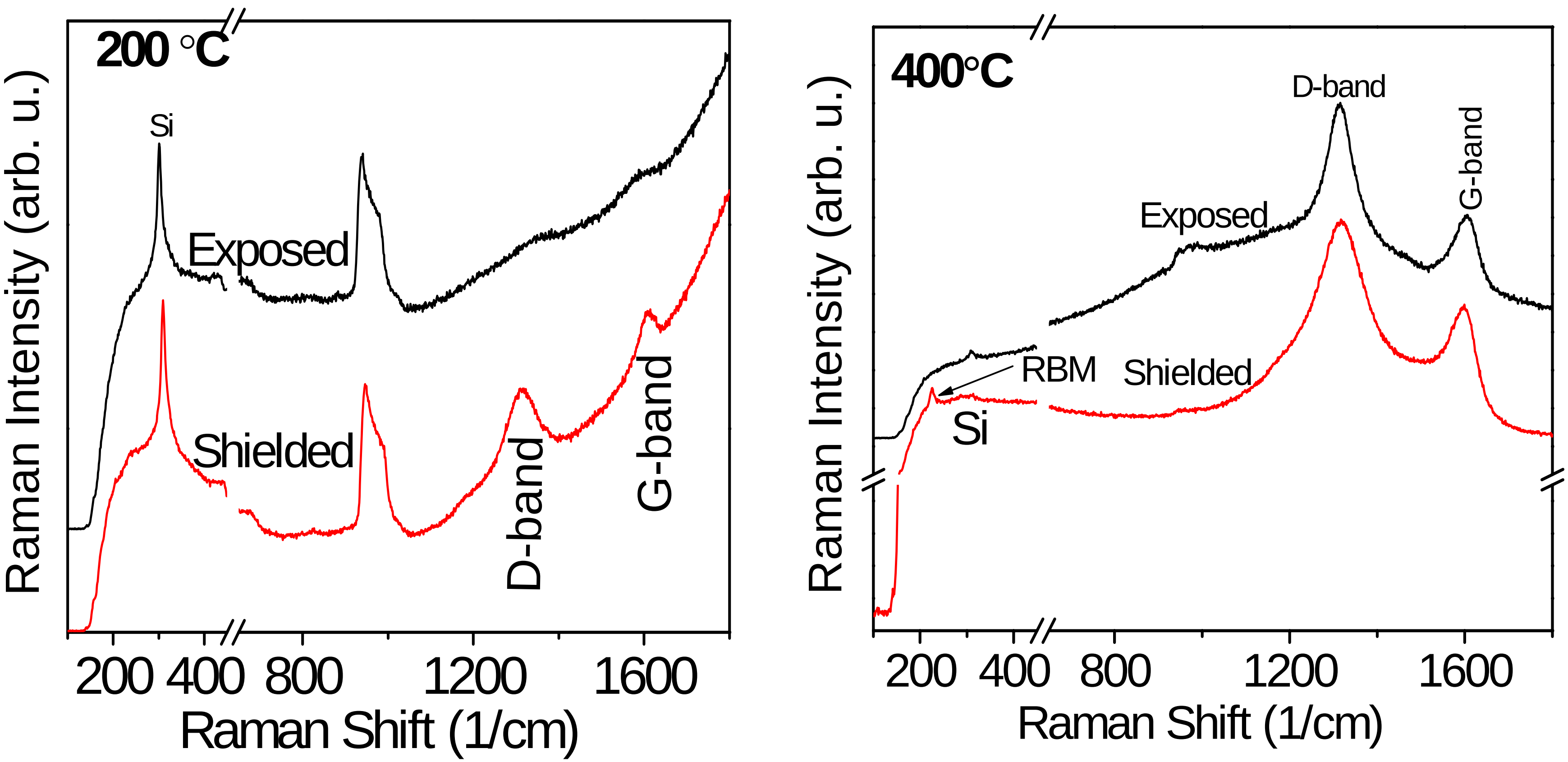
400 ^{o}C

200 ^{o}C



P.B. Amama, O. Ogebule, M.R. Maschmann, T.D. Sands, T.S. Fisher, *Chem. Commun.* **2006**, *27*, 2899.

Low-Temperature Growth



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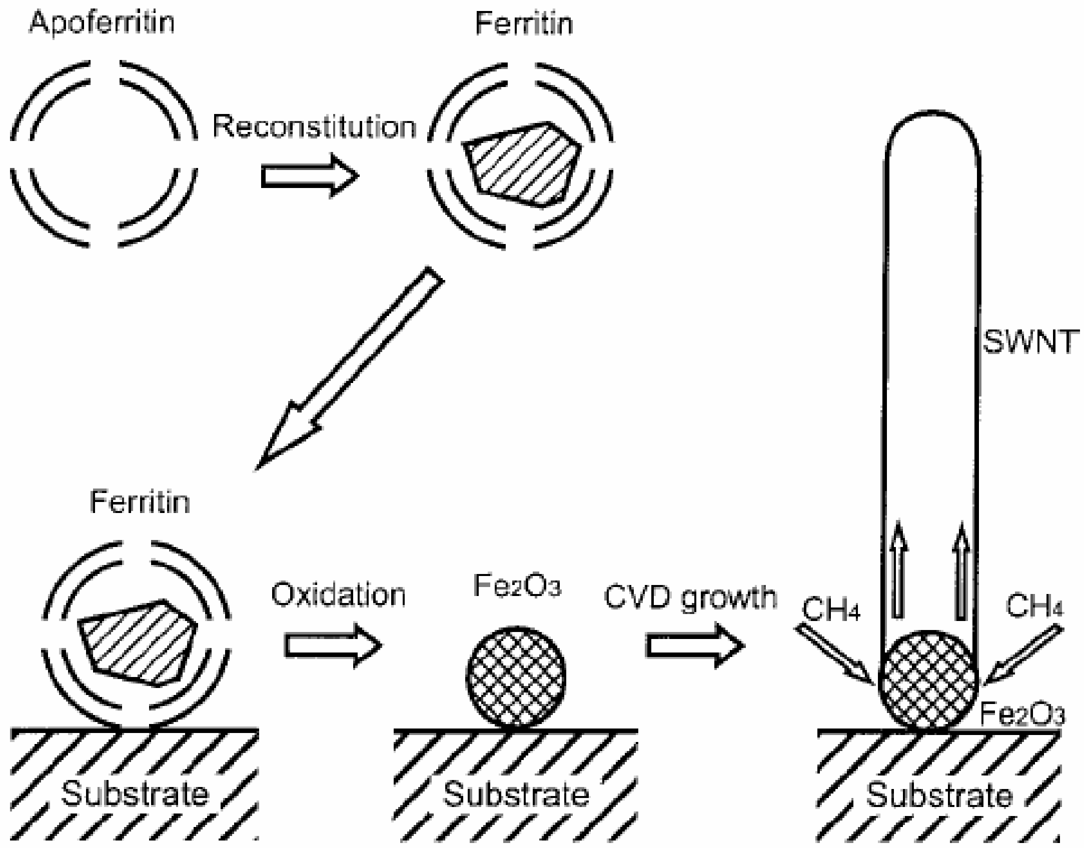
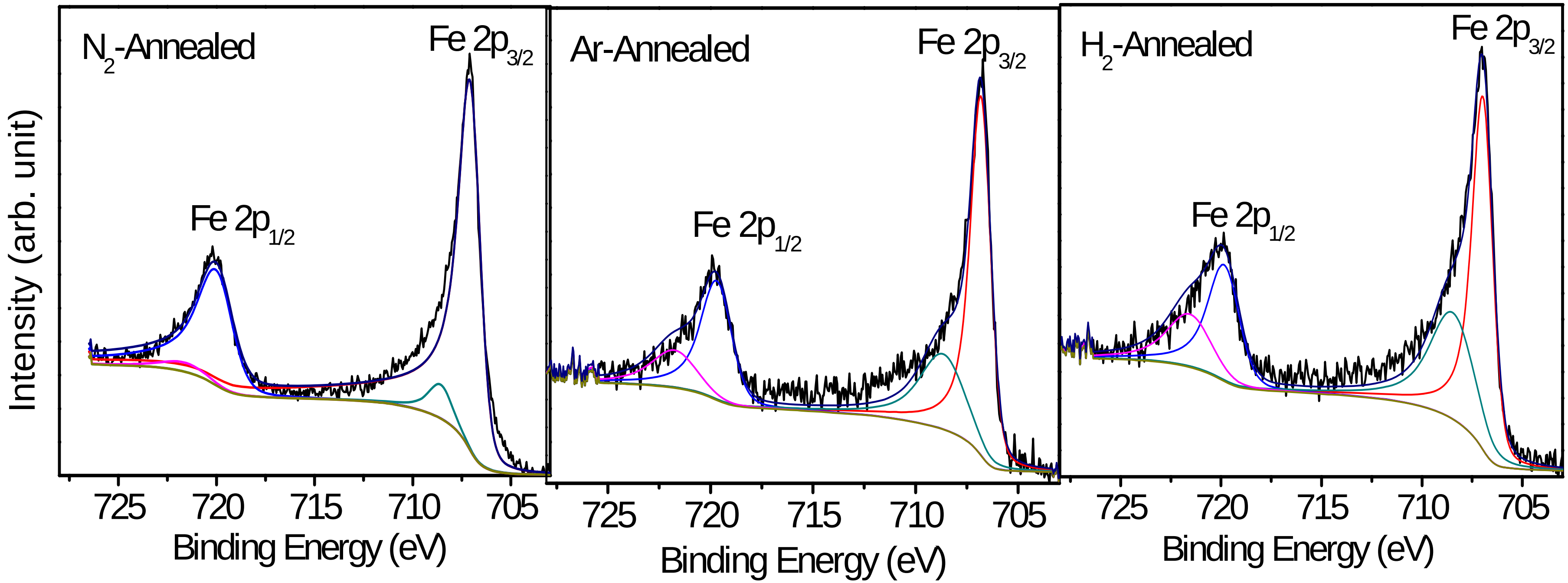
Process Flow for SWNT Synthesis from Discrete Nanoparticles by CVD



Y. Li, W. Kim, Y. Zhang, M. Rolandi, D. Wang, H. Dai, *J. Phys. Chem. B* **2001,** *105,* 11424-11431

XPS Spectroscopy: After Carbon Deposition



Ambient	Binding Energy (eV)	
	Fe $2p_{1/2}$	Fe $2p_{3/2}$
N_2	720.2	707.1
Ar	719.9	706.7
H_2	719.9	707.0

- Fe 2p peaks with BEs corresponding to 720 and 707 eV are ascribed to metallic Fe
- Metallic Fe appears to be the active specie during CNT growth

P.B. Amama, D. Zemlyanov, D.N. Zakharov, R.S. Katiyar, T.D. Sands, T.S. Fisher, *manuscript in preparation*

Summary

- Growth conditions in the PECVD chamber that favor stabilization of Fe_2O_3 nanoparticles and the chemical specie that nucleates CNT growth have been determined.
- The findings have enabled the growth of SWNTs of narrow diameter distribution, and the increase in SWNT selectivity and quality.
- The application of dc bias voltage during SWNT growth improves vertical alignment, quality, and selectively removes metallic SWNTs leaving larger-diameter semiconducting SWNTs.
- Low-temperature growth (200-400^{o}C) of MWNTs has been demonstrated using a shielded growth approach, which also shows promise for SWNT growth.

Acknowledgements

- **Prof. Tim Sands**
- **Prof. Tim Fisher**
- **NASA-Purdue Institute for Nanoelectronics and Computing** (INaC)
- **Birck Nanotechnology Center**, Purdue University
- **Dr. Dmitry Zemlyanov**, Purdue University
- **Dr. Matt Maschmann,** Intel
- **Prof. Katiyar**, University of Puerto Rico
- **Prof. Lynne Taylor**, Purdue University
- Members of Fisher Group
- Members of Sands Group

Questions and Answers

Ex-situ XPS Analysis: Raw Data

Al_2O_3 supports

The standard binding energy (BE) for CNTs is 284.3 eV

Observed shift in BE = 1.3 eV

FWHM of C 1s peak
N_2 = 1.03 eV
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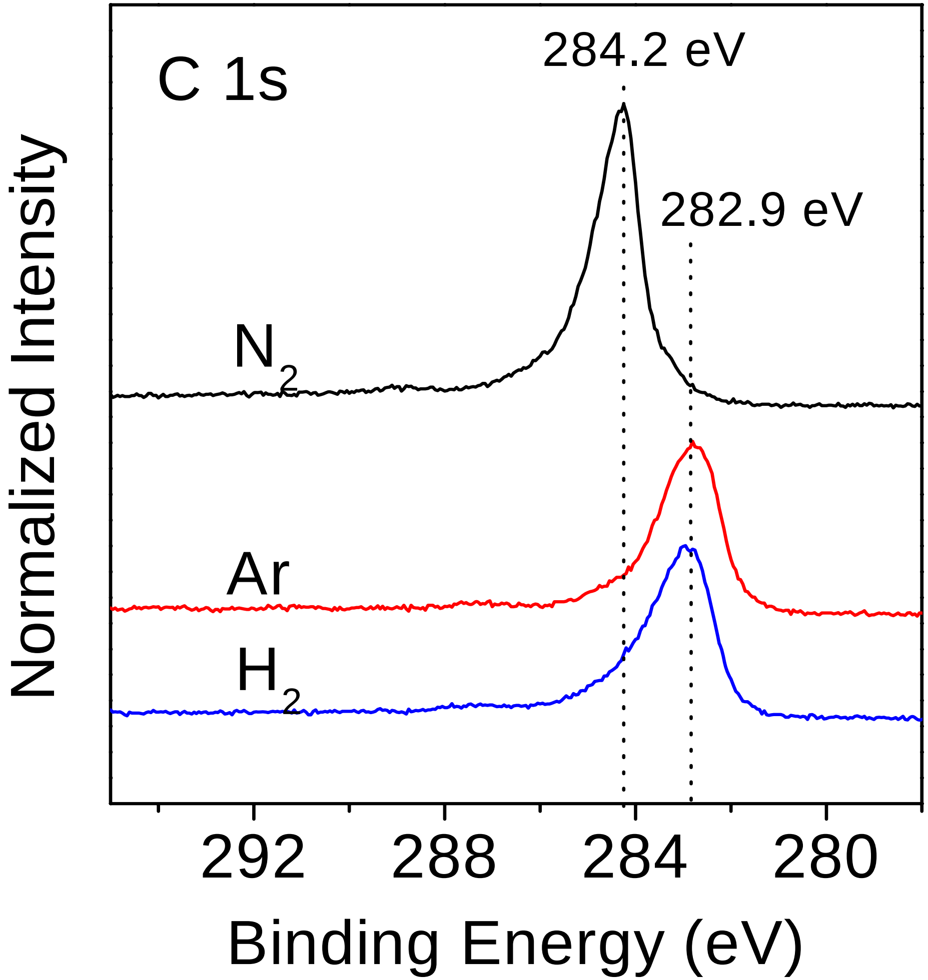

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Questions and Answers

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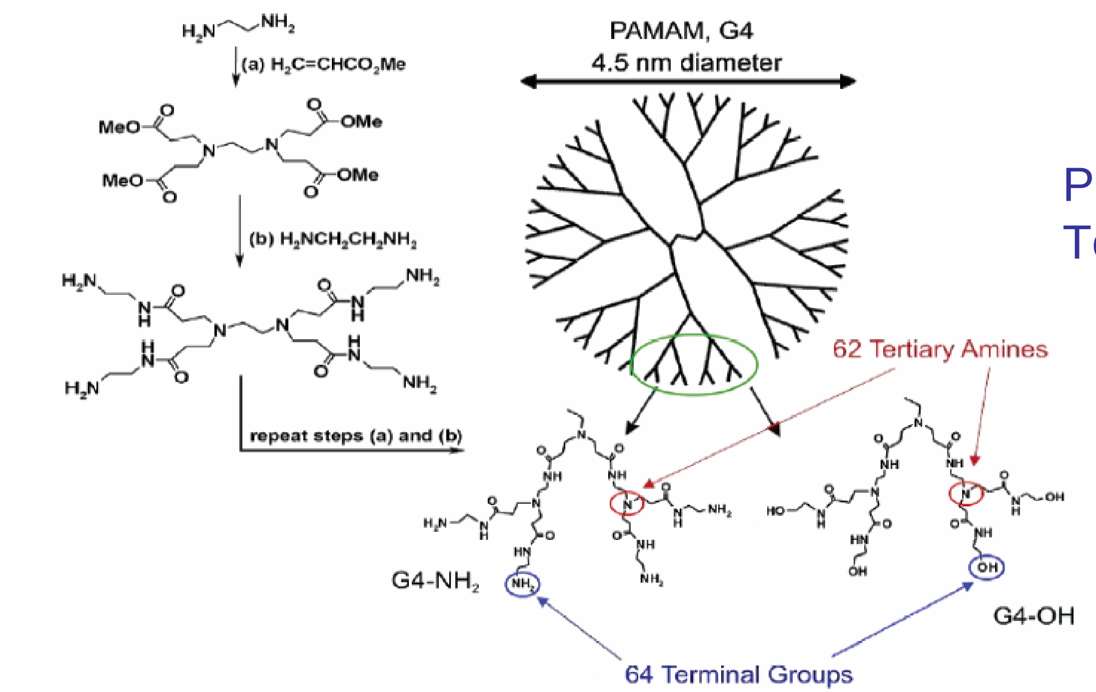

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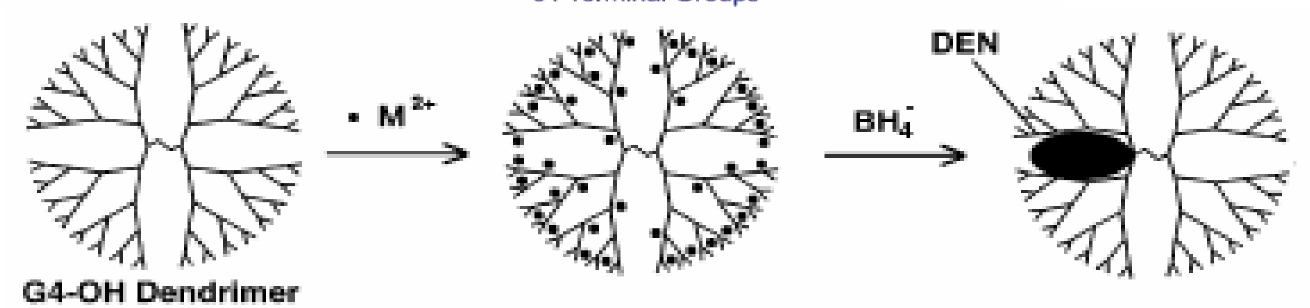
Tertiary NH_2 (pK_a = 6.30)



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