CLONING SINGLE WALL CARBON NANOTUBES FOR HYDROGEN STORAGE

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May 23, 2005

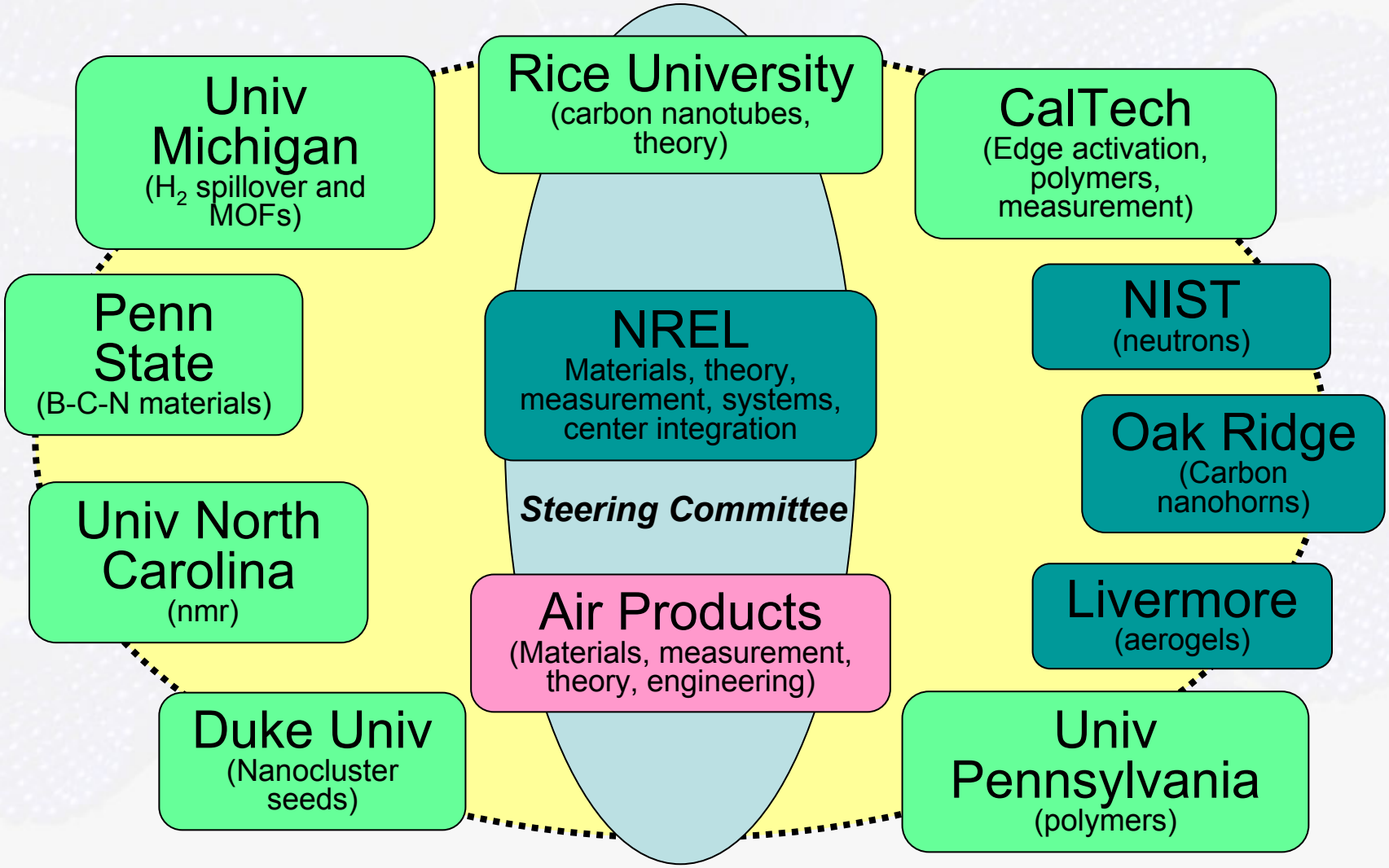
DOE 2005 Hydrogen Program Annual Review
Washington, D.C., May 23, 2005

Project ID
 # STP 37

This presentation does not contain any proprietary or confidential information

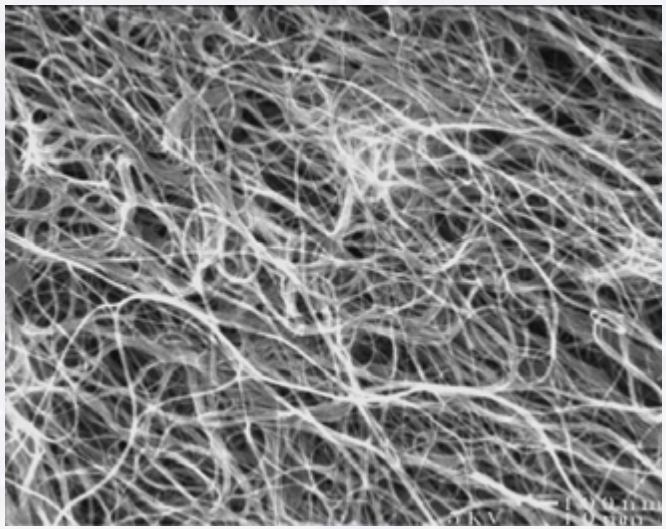
CbHS Center of Excellence Partners

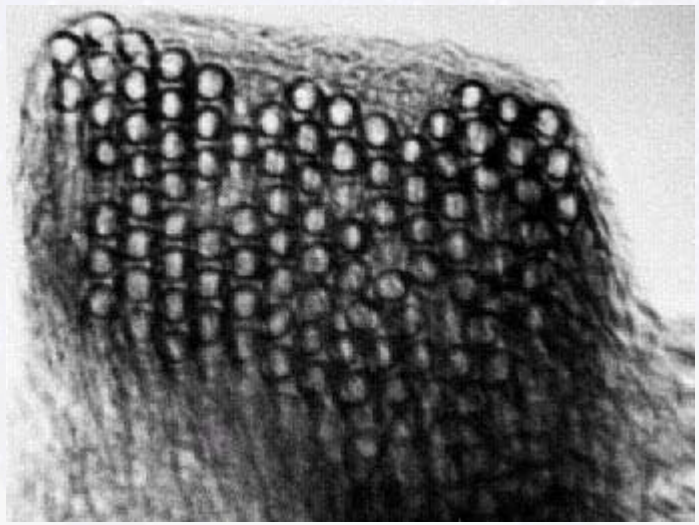
9 university projects (at 7 universities), 4 government labs, 1 industrial partner



Why SWNT?

- The Scale and Perfection of DNA
- The Strongest Possible Fiber
- Thermal Conductivity of Diamond
- The Unique Chemistry of Carbon
- Maximum Possible Surface Area
- Selectable Electrical Properties
  - Metallics Better Than Copper
  - Semiconductors Better Than InSb or GaAs
- *The Ultimate Engineering Material*





General Objectives:

Develop methods for producing type-selected SWNT

Produce particular SWNT types for hydrogen storage evaluation

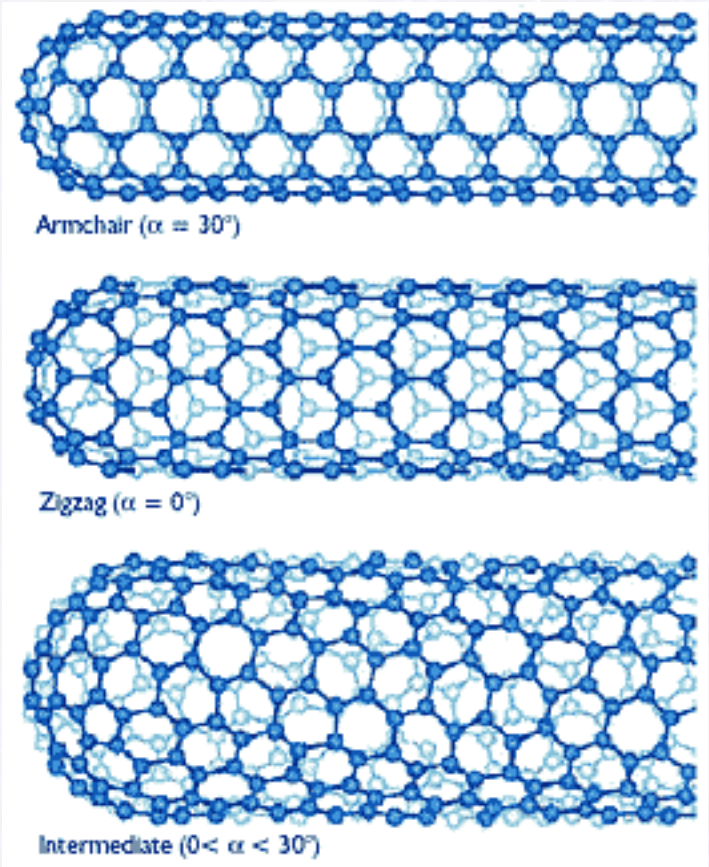
Scale production technology & deliver optimized SWNT material for prototype hydrogen storage system development

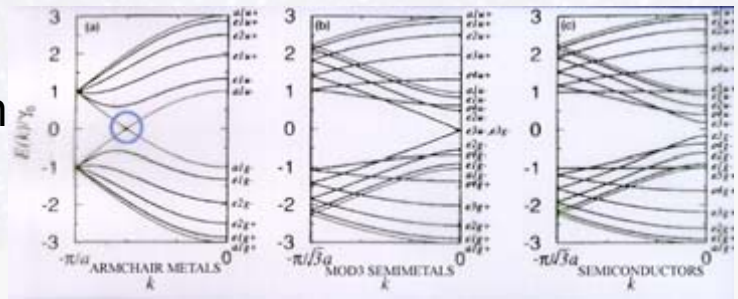
Objectives and Tasks

- Cutting single wall carbon nanotubes
- Sorting single wall carbon nanotubes
- Preparation of cut tubes and metal catalyst precursor for docking
- Attachment of catalysts to cut tubes
- Growth of seeds on supports
- Growth of seeds by injection into gas environment
- Evaluation of scaled up process that can be commercialized at a scale and price relevant to the DOE Hydrogen Storage task

Optimized SWNT Material

- Need Single-Type SWNT Production
- Current Growth Inadequate
  - Mixture of ~ 50/150 Types
  - Mixture of Metals, Semi-Metals & Semiconductors
  - Impure & Inefficient
- N,M Control Critical
  - Hydrogen Storage Media
  - Energy Conversion & Storage
  - SWNT Quantum Wire
  - Electronics & Sensors
  - Biomedical Therapeutics
- Seeded Growth Required
  - Separate Nucleation From Growth
  - Eliminate By-Products & Purification
  - Vastly Improved Efficiency
  - Sort Once at Small Scale



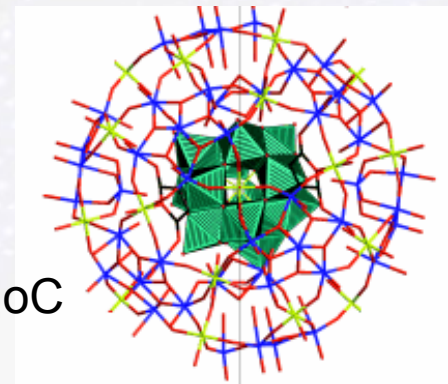


SWNT Seeded Growth

Current Results

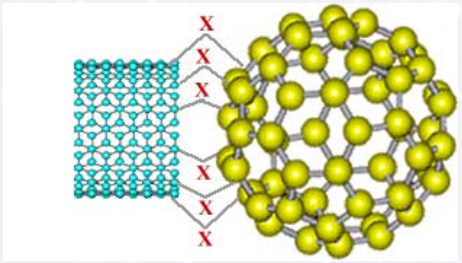
Key Starting Materials
- Have FeMoC Catalyst
- Have Short SWNT Seeds
- Have Soluble SWNT

Key Process Steps
- In-Solution Attachment
- Controlled Deposition
- Catalyst Docking
- Reductive Etching
- Limited Growth
- *Luxuriant Growth is Next !!*

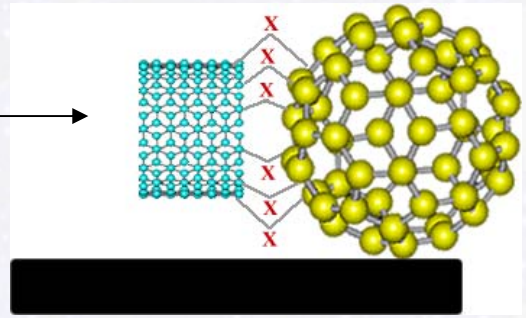


FeMoC

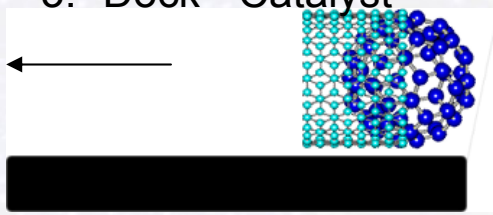
1. Attach Catalyst



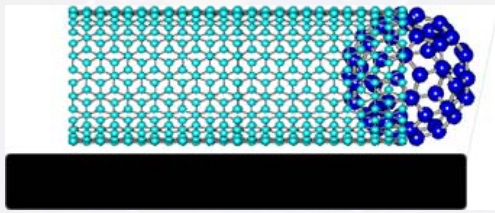
2. Deposit on Inert Surface

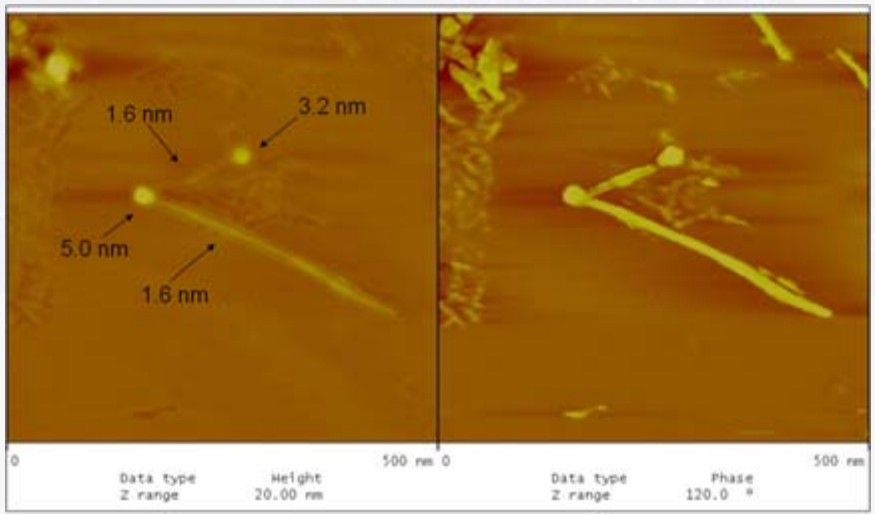


3. "Dock" Catalyst

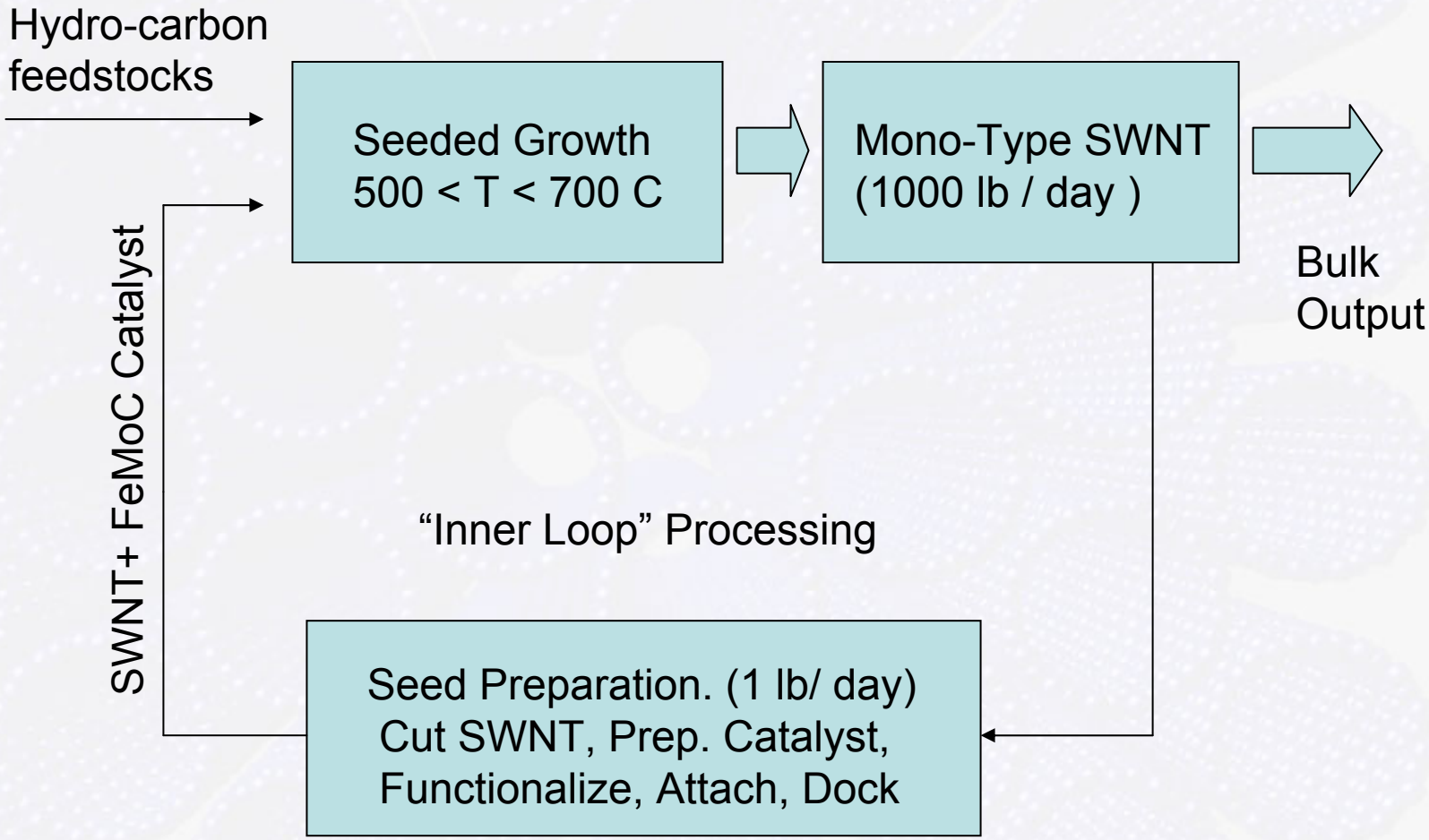


4. SWNT Growth





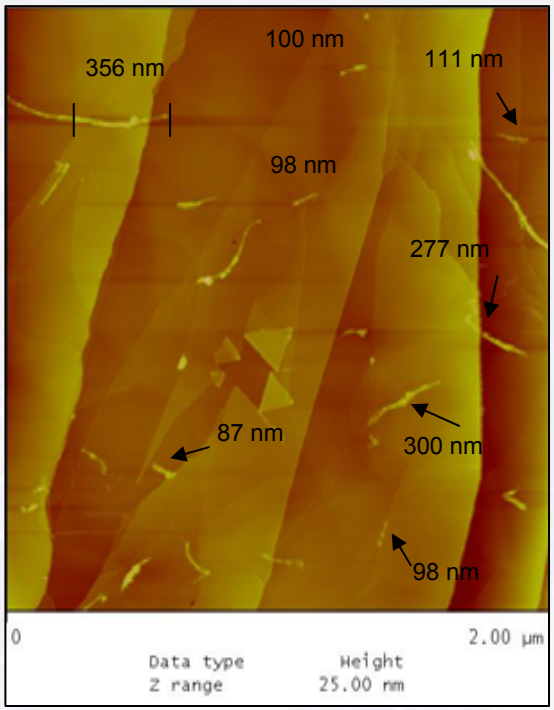
SWNTamp Production Concept



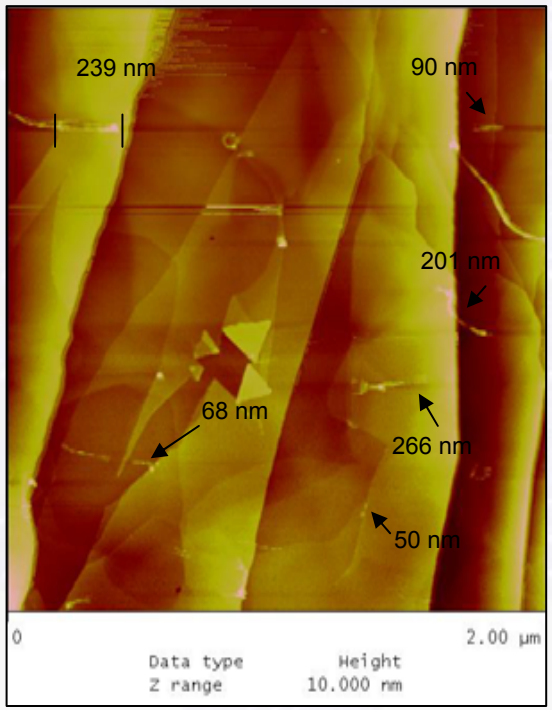
Controlled Docking / Etching

Controlled reductive docking with H2, varying temp. pressure & time.
Initial success @ 600°C, 760 Torr H_2,5 min.

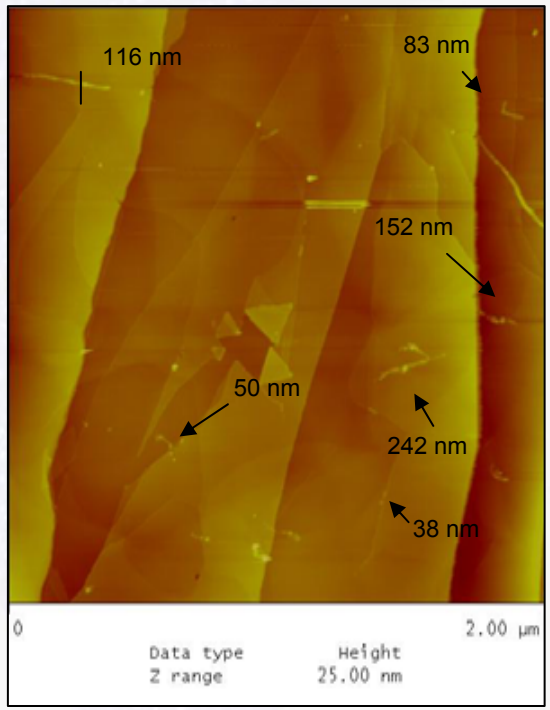
INITIAL



RUN 1
600°C, 760 torr H_2
5 minutes



Run 2
600°C, 760 torr H_2
5 minutes



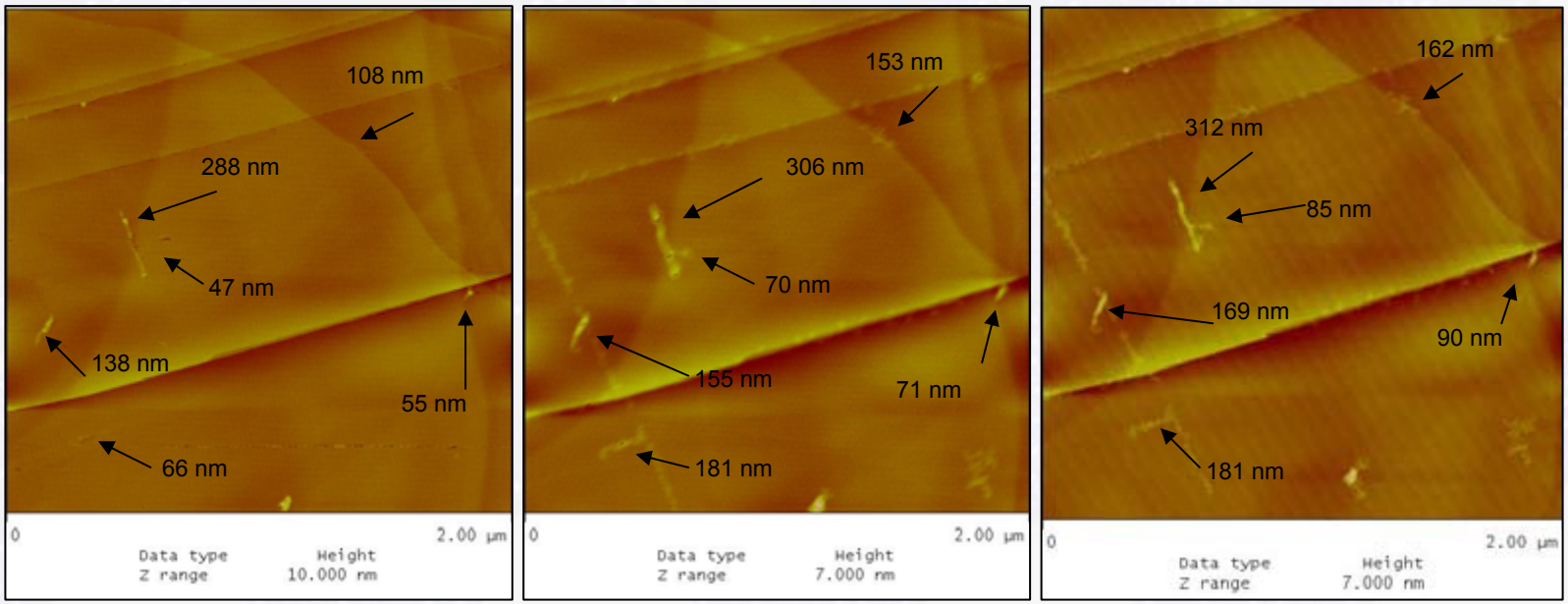
Controlled Growth

SWNTcat are produced by attaching catalyst to SWNT in solution, depositing on HOPG and placing in a growth environment. Initial success achieved with 60:1 Fe:SWNT ratio (based on 150 nm avg. SWNT length, and growth in methane.

INITIAL
$Fe(NO_3)_3$ – SWNT – dodecyl

RUN 1
700 °C, 1 torr CH_4
20 minutes

RUN 2
700 °C, 1 torr CH_4
20 minutes



Sidewall Covalent Functionalization of SWNT Permits:

1. Variable spacing between SWNTs with the spacing dependent on the size of the functional group. This permits the optimization of accessible surface area and the transport of molecular hydrogen throughout the sample

2. Choice of functional groups that enhance the adsorption of molecular hydrogen, for instance groups that facilitate the surface adsorption of selected metals that catalyze or strongly enhances the adsorption of molecular hydrogen.

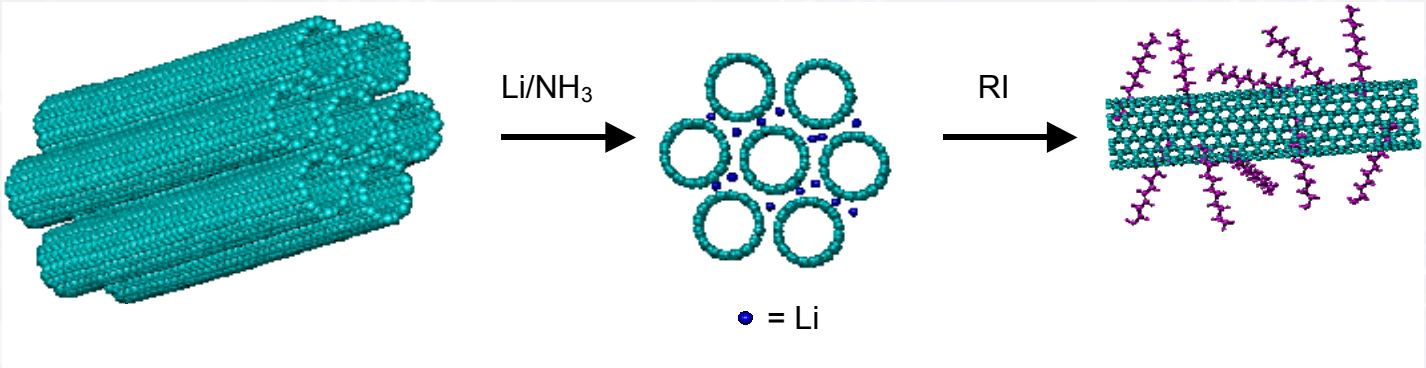
Functionalization Chemistries

Hydrophilic functionalizations developed and routine (for polars)

- diazonium/free radical chemistry in oleum
- phenyl sulfonate
- chloro-phenyl sulfonate
- phenyl-di-carboxylate
- amino-phenyl sulfonate

Lipophylic functionalizations developed and routine (for organics)

- Birch alkylation chemistry in liquid ammonia
- phenyl
- tert-butyl phenyl
- dodecyl



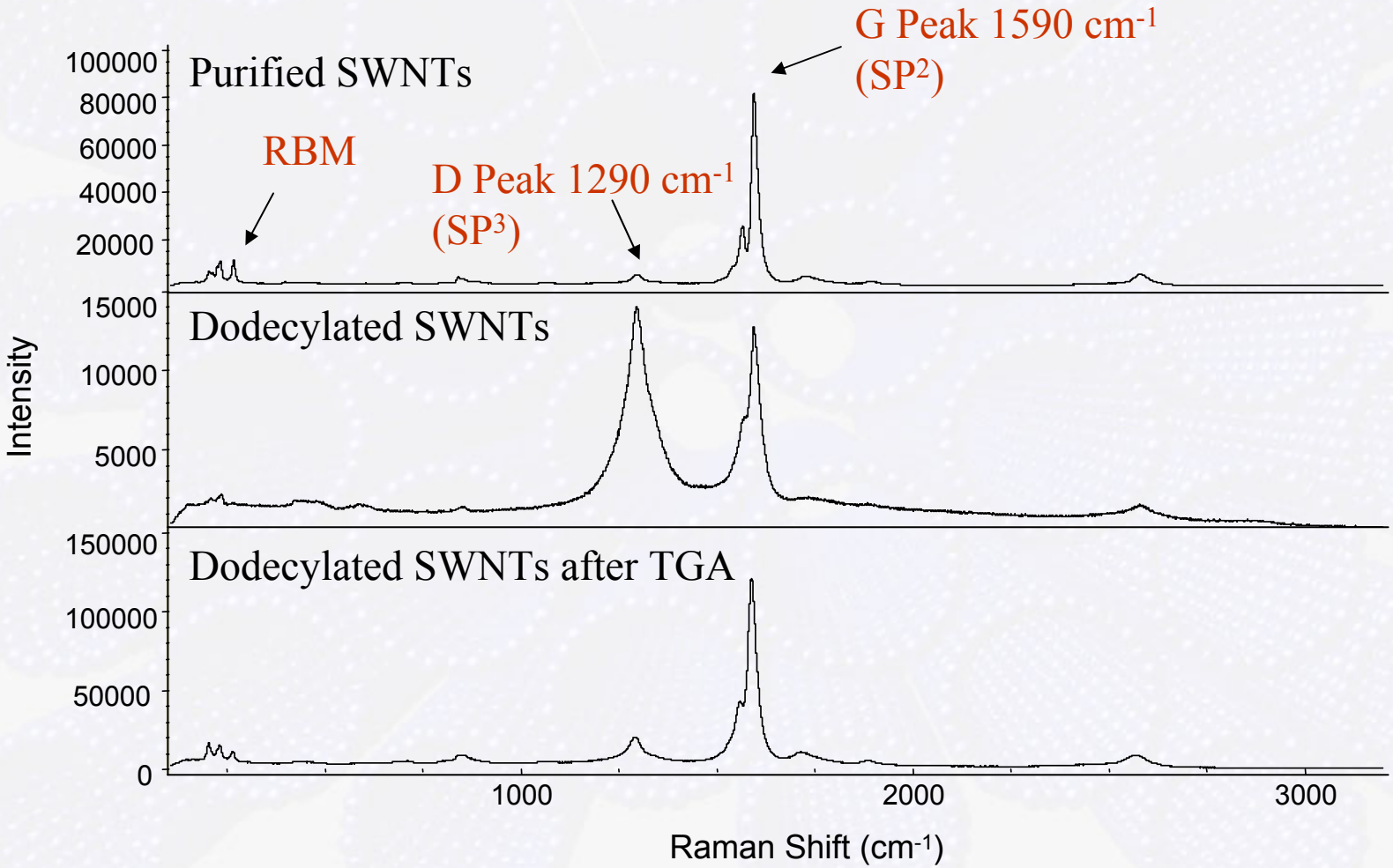
SWNT Bundles

Individual SWNTs soluble in organic solvents

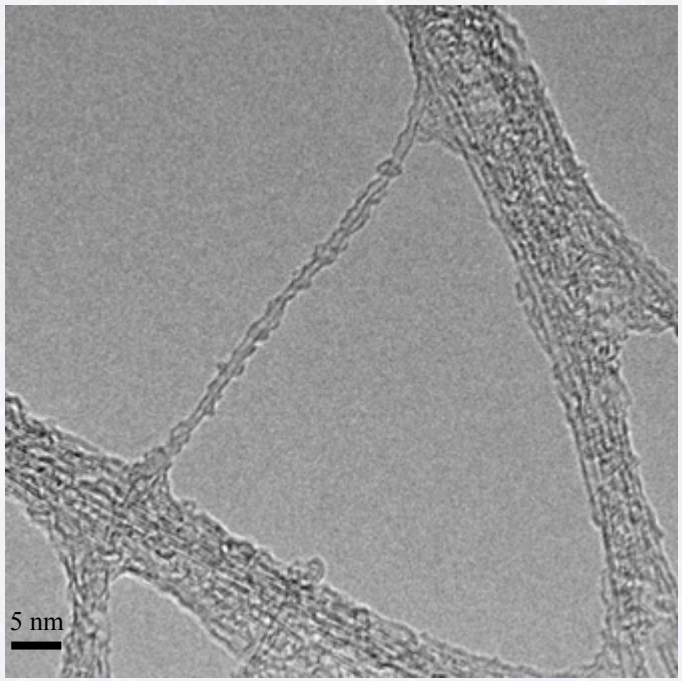
Reaction Setup

- Simple reaction setup
- Easy work-up
- Scalable

Raman Spectra (780 nm excitation)

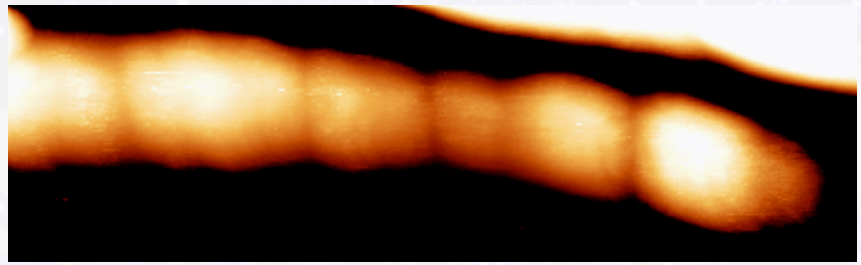


TEM Image of Dodecylated SWNTs



- Functionalization taking place in bands

STM Image of Dodecylated SWNTs



- Band structures
- Bright bands: Functionalized
- Dark bands: Unfunctionalized

Catalyst / Linker Systems

FeMoC & Fe Nanoparticles

- Developed high-purity, large-scale synthesis
- Determined ligand affinity sequence for in-solution attachment
- 4 nm Fe3O4 nanoparticles (reversed micelle)
- Fe3O oxo-clusters in solution

Developing generic linker chemistries

- Direct coordination to native –COOH groups
- Ester linkages to either –OH or –COOH on SWNT ends
- Terminal pyridine groups bind tightly to most metals and metal oxides

Developing additional Fe Clusters

- 1 nm Fe3O4 nanoparticles (polymer isolated)
- $FeNO_3$

SWNT Cutting Status

Developed controllable persulfate cutting chemistry

- Replaces piranha chemsitry
- Proceeds at lower temperatures
- More controllable reaction
- Determined preliminary kinetics for cutting vs. etching

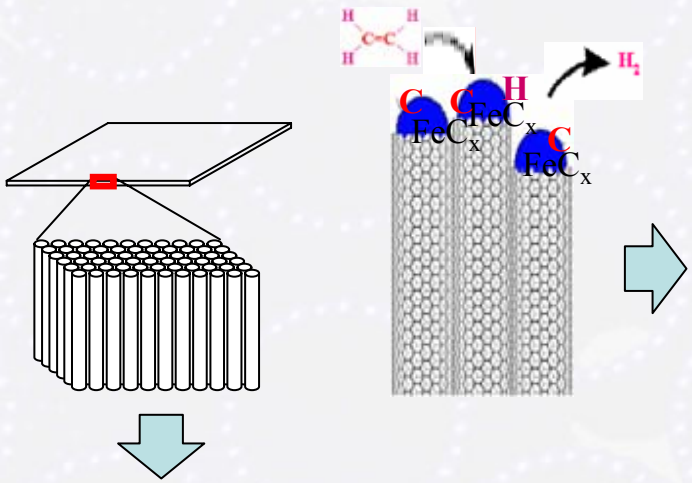
Other Activities

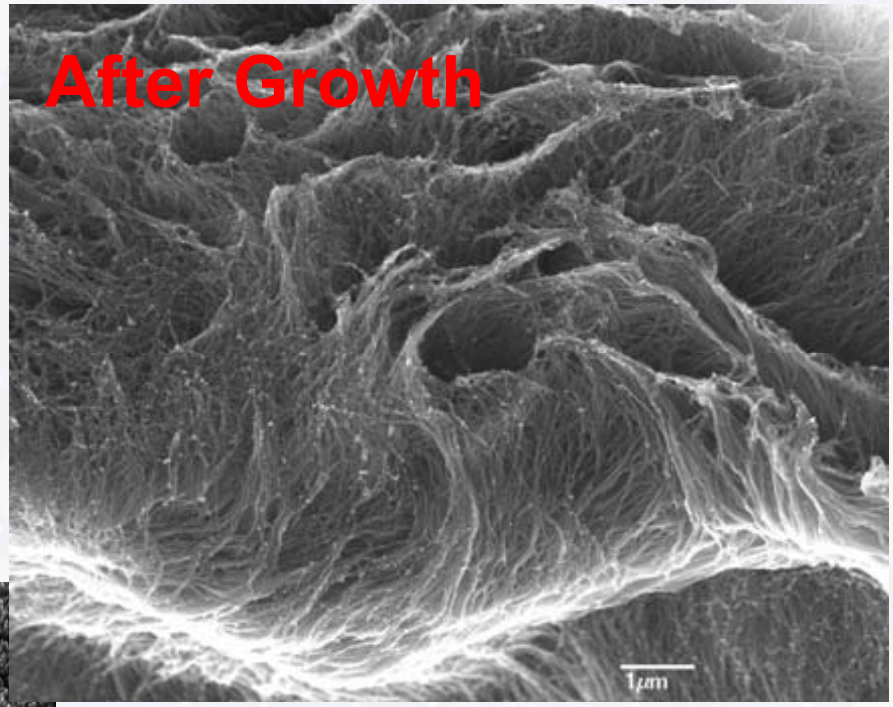
- Exploring ozone-based defect generation process
- Exploring radiolysis-based defect generation process
- Developed hybrid fluorine + persulfate cutting process

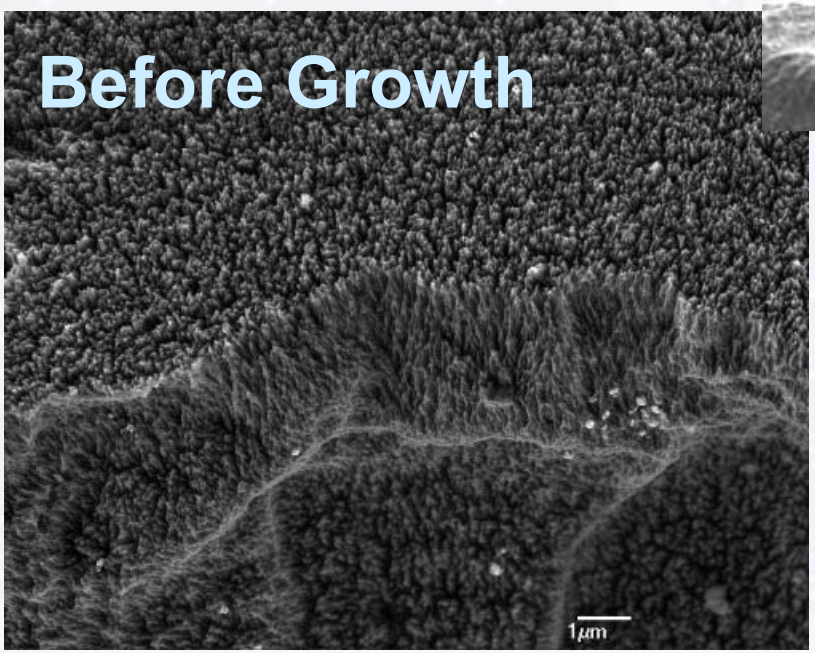
Short SWNT production

- Produced routinely at 100 mg levels
- Developed automated length measurement method
  - deposit SWNT on Mica + software image analysis

SWNT Continued Growth







Cut SWNT Fiber Substrate
Added one monolayer Fe/Ni
Growth with C_2H_4 0.47 Torr + H_2 @ 0.23 Torr, 820°C for 60 min.

Milestones, Interactions & Safety

- Milestones (fy05)
  - Demonstrate feasibility of significant SWNT growth under cloning conditions
  - Deliver gram quantities of cut SWNT (mixed types) for surface area measurements and hydrogen storage evaluation
- Milestones (fy06)
  - Deliver gram quantities of cut SWNT (optimized by type and surface functionalization) for surface area measurements and hydrogen storage evaluation

- Interactions
  - Interact with modeling groups as to ideal SWNT types for cloned growth / amplification
  - Interact with NREL, ORNL, Duke on materials growth processes
  - Interact with NREL, Air Products for materials characterization

- Safety
  - Sensors, high-flow exhaust and SCBA equipment around toxic gases (CO)
  - Sensors and high-flow exhaust around flammables gases (H2, CH4)
  - Negative pressure chambers and HEPA masks around light SWNT particles – densify rasw SWNT promptly
  - Basic lab precautions in wet lab and thin film activities
  - Concentrate and incinerate any water-soluble SWNT wastes

- Go/no-go decision
  - Go/no-go decision of the use of swnt as hydrogen storage material at the end of fy06

Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- New Start

Barriers

•Barriers Addressed

Reversible Solid-State Material Storage Systems:

Hydrogen Capacity and Reversibility

Lack of Understanding of Physisorption and Chemisorption

Test Protocols and Evaluation Facilities

Budget

- Expected Total Funding
- Total-$2,144,946
  - DOE share $1,715,989
  - Contractor share $428,997
- Funding for FY05 $400,000

Partners

- Interactions-NREL,Air Products
- Collaborations-Duke Univ.,ORNL