Controlling the Diameter of Single Walled Carbon Nanotubes for Hydrogen Storage

-Carried in the “DOE Center pf Excellence on Carbon-Based Hydrogen Storage Materials”

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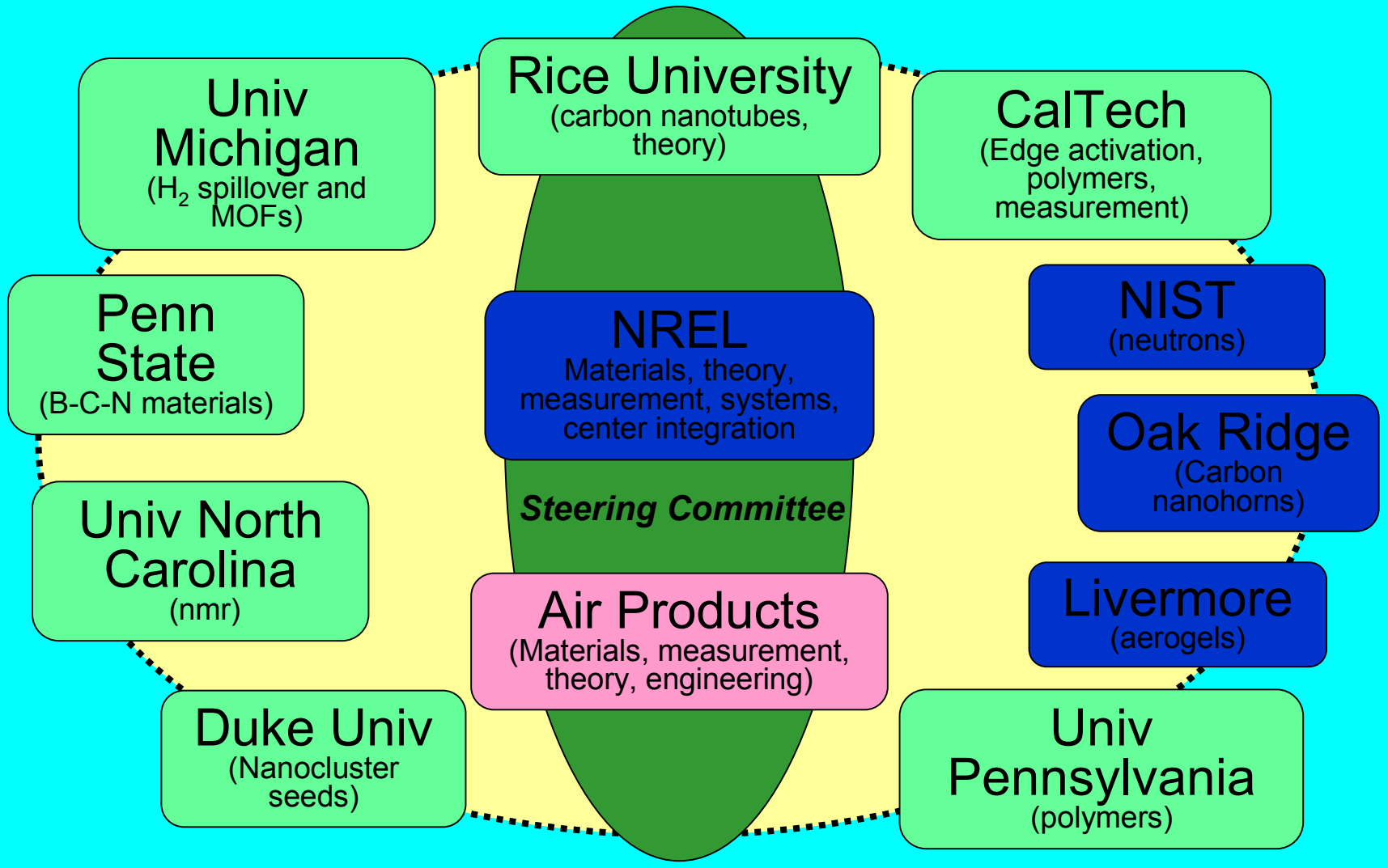
Project ID # STP35

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



Overview

Timeline

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

Budget

- Expected Total Funding
  - DOE share: $500,000
  - Contractor share: $125,000
- Funding for FY05
  - DOE Share: $100,000
  - Contractor share: $25,000

Barriers and Targets

- Barriers addressed

  A. Cost.

  B. Weight and Volume.

  C. Efficiency.

  M. Hydrogen Capacity and Reversibility.
- Targets

  Gravimetric capacity: >6%

  Volumetric capacity: >0.045 kg/L

Partners

- Interactions/ collaborations
  - NREL
  - Rice University
  - UNC
  - Oak Ridge
  - Livermore

Objectives of the research

- Study the effect of diameters of nanotubes on their hydrogen storage properties;
- Develop method to precisely control the diameter of the produced nanotubes
- Producing large quantity purified carbon nanotubes for the study of hydrogen storage;

Approaches

- Controlling the diameter of single walled carbon nanotubes using uniform catalyst nanoparticles;
- Controlling the diameter of single walled carbon nanotubes using existing nanotubes as templates (Cloning);
- Controlling the diameter of single walled carbon nanotubes using inorganic templates.

Overall Tasks and Timing

- Phase I: (FY05-FY06)
  - Demonstration of the synthesis of single walled carbon nanotubes with controlled diameter.
  - Go/No Go Decision I (Month 21):
    - Synthesis of gram quantity single walled carbon nanotubes with small (<1 nm) diameters and demonstrating the potential of the materials to meet DOE year 10 goal in hydrogen storage properties
- Phase II: (FY07-FY09)
  - Demonstration of the control of nanotube diameters as well as helicity.
  - Go/No Go Decision II (Month 33)
    - Demonstration of helicity through nanotube “cloning”
    - Establish 10g/day production capability for nanotube materials with controlled diameters.

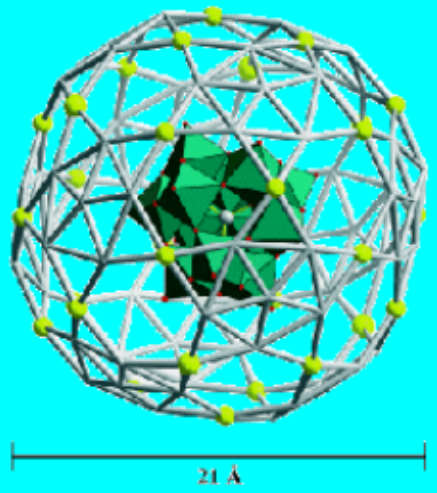
Approach 1: Using Molecular Cluster as Catalysts to Control the Diameters of SWNTs

Motivation:

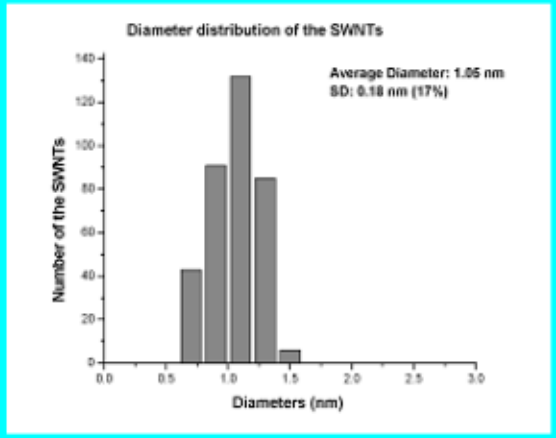
- The diameter of single walled carbon nanotubes is controlled by the size of catalyst nanoparticle during the initiation stage of the growth. If the diameter of the catalysts can be controlled, the diameter of the nanotubes can be controlled.
- Molecular clusters are molecules with identical number of metal atoms in each cluster, making them perfect catalysts for the growth of uniform nanotubes.
- The growth of uniform nanotubes were demonstrated before by our group using one type of clusters (Figures on the right).

Things to Do:

- Making smaller nanotubes using smaller cluster molecules (Next Page)
- Developing method to produce gram quantity of uniform nanotubes.



$[H_xPMo_{12}O_{40} \subset H_4Mo_{72}{}^{VI}Fe_{30}{}^{III}(CH_3COO)_{15}O_{254}(H_2O)_{98}].60H_2O$



L. An, J. M. Owens, L. E. McNeil, and J. Liu, *JACS*, **124**, 13688-13689, (2002).

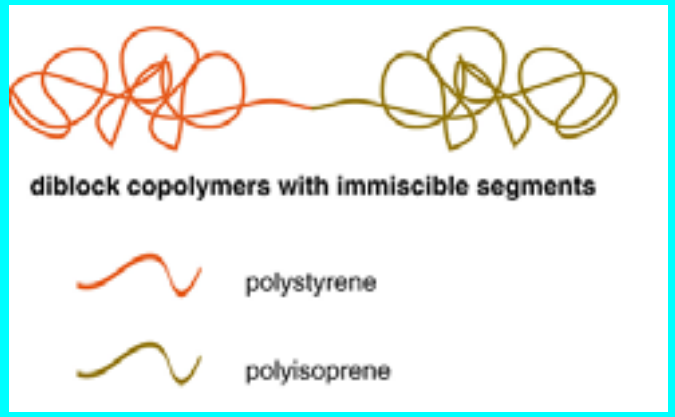
Cluster Molecules to Synthesis and Use as Catalysts for nanotube Growth

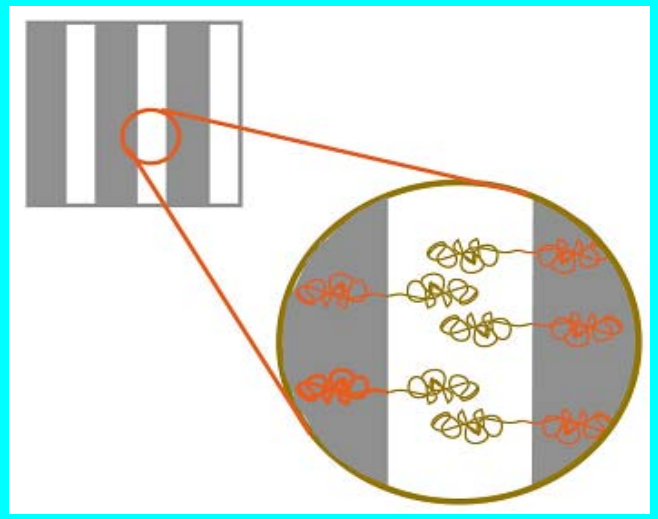
Formula	number of metal atoms
$H_xPMo_{12}O_{40} \subset H_4Mo_{72}{}^{VI}Fe_{30}(CH_3COO)_{15}O_{254}(H_2O)_{98}] \cdot 60H_2O$	84 Mo, 30 Fe
$Na_2[(Mo^{VI}(Mo^{VI})_5)_{12}(Mo_6{}^{V}Fe_{24}{}^{III})(CH_3COO)_{20}O_{258}(H_2O)_{84}] \cdot 150H_2O$	78 Mo, 24 Fe
$[((Mo^{VI})Mo_5{}^{VI}O_{21}(H_2O)_6)_{12}(Fe^{III}(H_2O)_2)_{30}] \cdot 150H_2O$	72 Mo, 30 Fe
$Na_{46}[Mo_{66}{}^{VI}Mo_{50}{}^{V}O_{331}(CH_3COO)_{30}(H_2O)_{56}] \cdot 300\ H_2O$	116 Mo
$(NH_4)_{42}[Mo_{72}{}^{VI}Mo_{60}{}^{V}O_{372}(CH_3COO)_{30}(H_2O)_{72}] \cdot 300\ H_2O \cdot 10CH_3COONH_4$	132 Mo
$Na_{26}[Mo_{142}O_{432}(H_2O)_{58}H_{14}] \cdot 300\ H_2O$	142 Mo
$(NH)_{28}[Mo_{154}(NO)_{14}O_{448}H_{14}(H_2O)_{70}] \cdot 350\ H_2O$	154 Mo
$[(MoO_3)_{176}(H_2O)_{80}H_{32}]$	176 Mo

Other Approaches in Obtain Uniform Catalysts

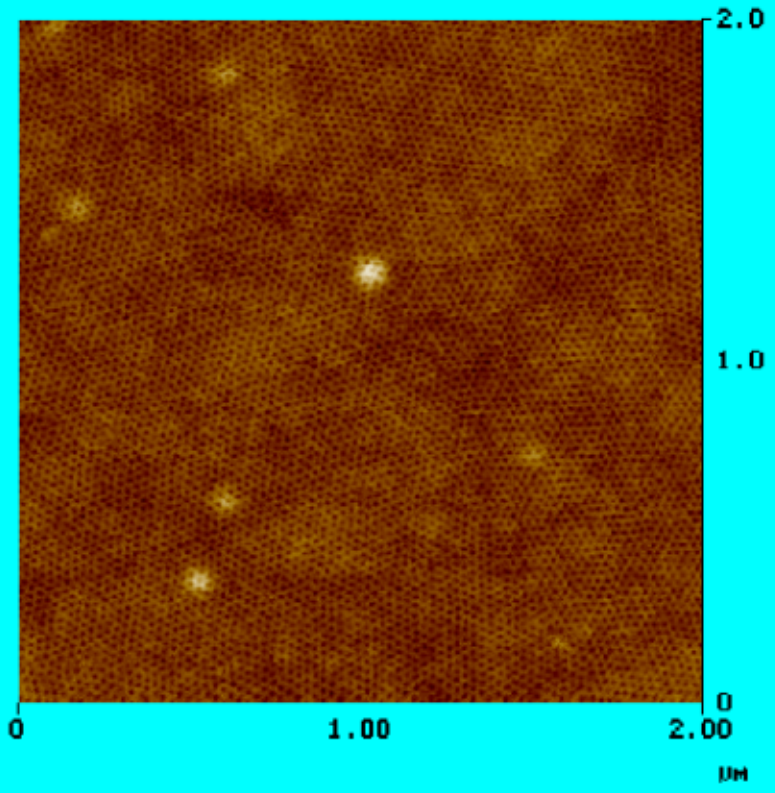
Approach:

Using diblock copolymer to control the size of catalysts. Diblock copolymer can self assemble into uniform domain structures at nanoscale (Figures on the right). If a controlled amount of metal atoms can be introduced into one of the polymer blocks, after removing all organic components using oxygen plasma, the metal atoms in each of the small domains will form a small uniform nanocluster as catalysts for nanotube growth.

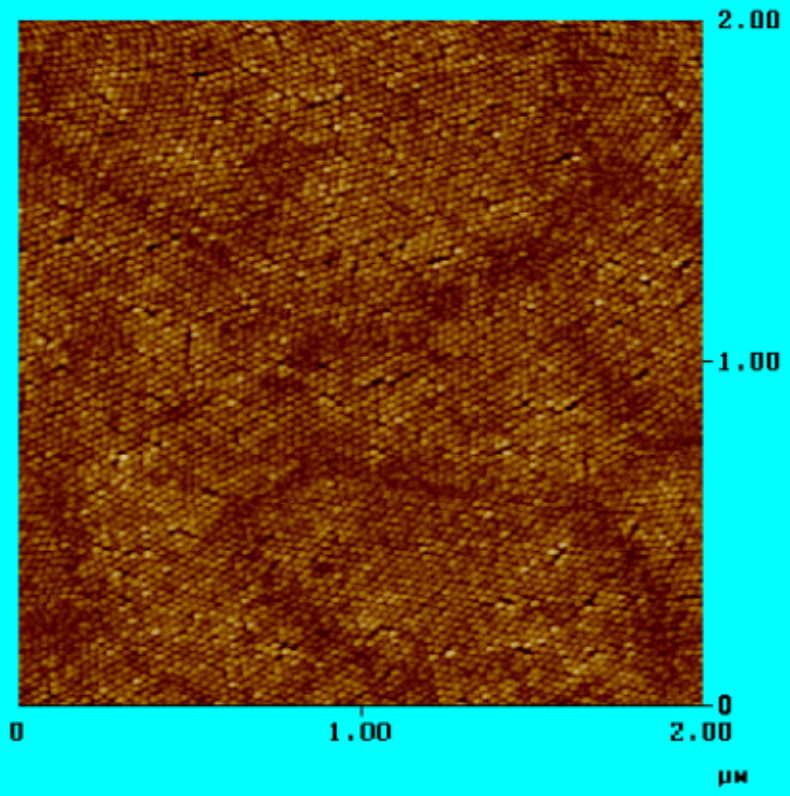




AFM Images of the Polymer Domain Structure and Uniform catalyst Particles

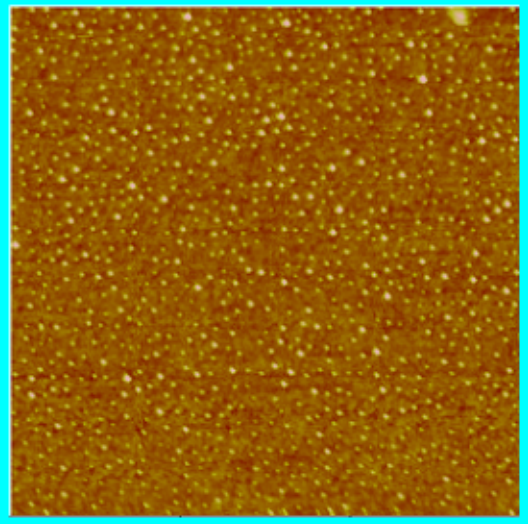


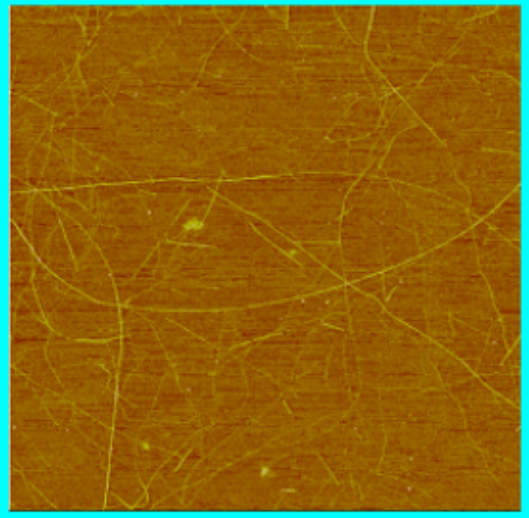
AFM Image of diblock copolymer domain structure in a thin film coated on a flat substrate.

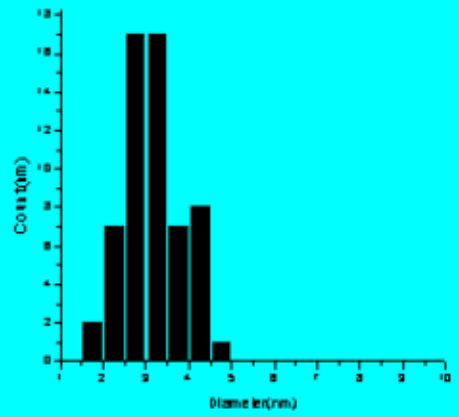


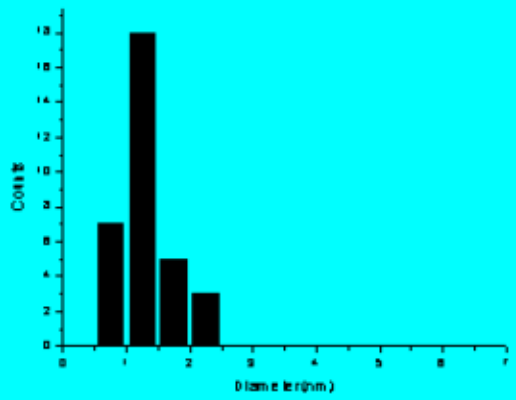
AFM Image of metal nanoparticle made from diblock copolymer domain structure after all organic components removed.

AFM Images and Size Distributions of Catalysts and Nanotubes Grown









Starting Catalysts

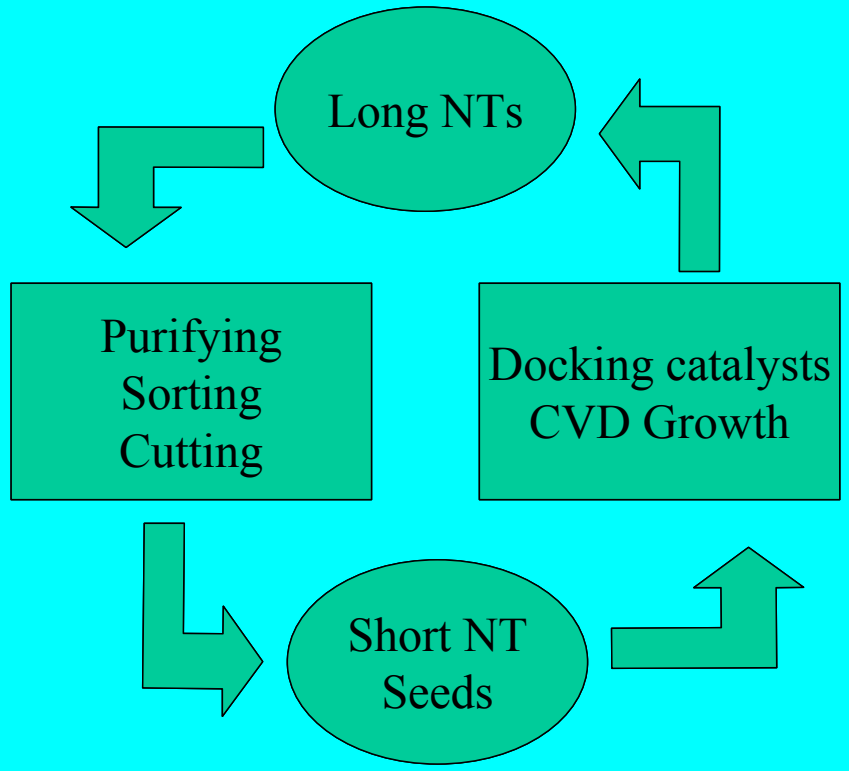
Prepared Nanotubes

Approach 2: Nanotube "Cloning"

(Collaboration with Rice University)

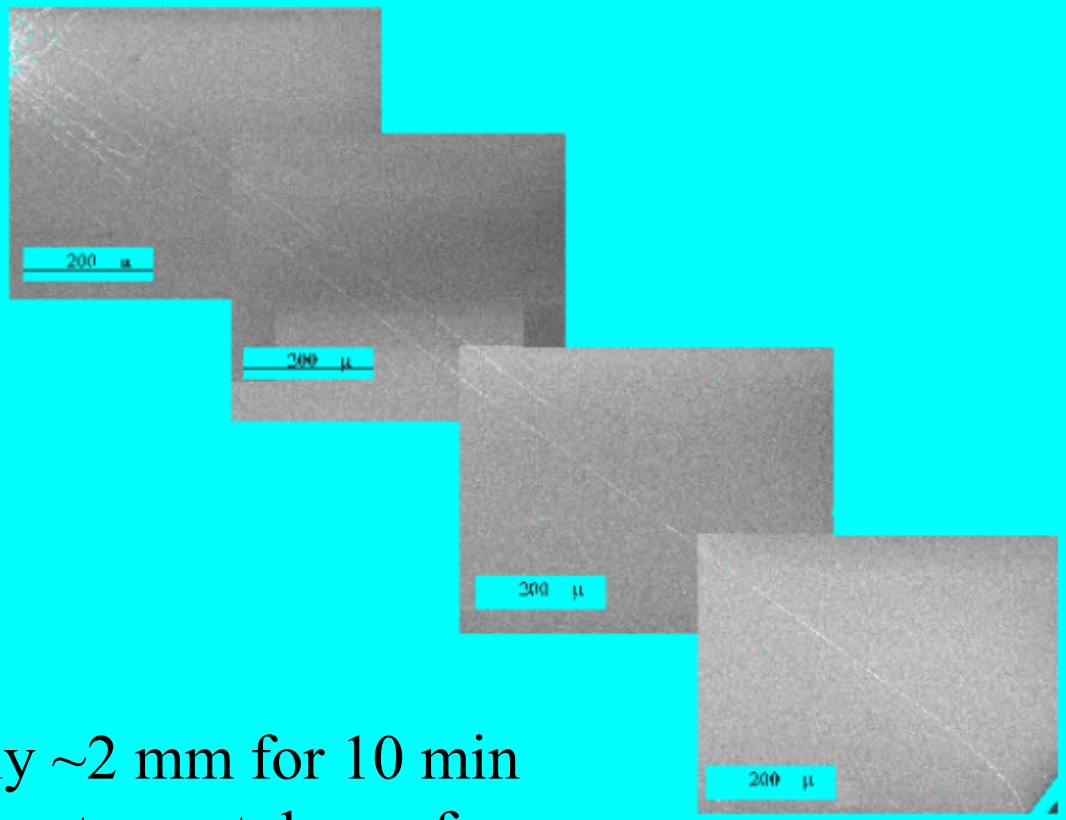
Motivation:

Using existing nanotubes as a templates to guide the nucleation of new nanotubes. Not only the diameters of the new nanotubes should be controlled by the nanotube templates, their helicities should also be the same as the nanotubes used as templates. After each cycle of "cloning", the amount of new nanotubes should be significantly "amplified" from the starting nanotube "seeds". The longer the nanotubes grow, the larger the amplification.



Nanotube "Cloning" Cycle

Long and Aligned SWNTs

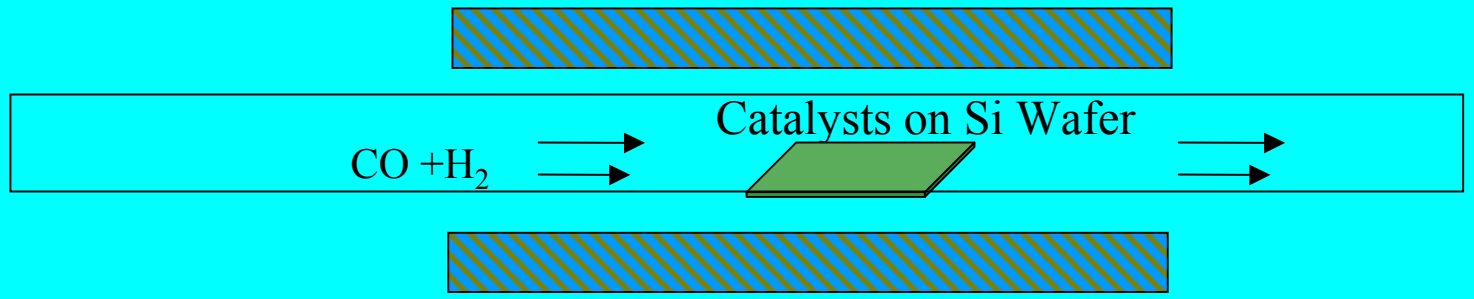


Length: Normally ~2 mm for 10 min growth; The longest nanotube so far reaches 3 cm.

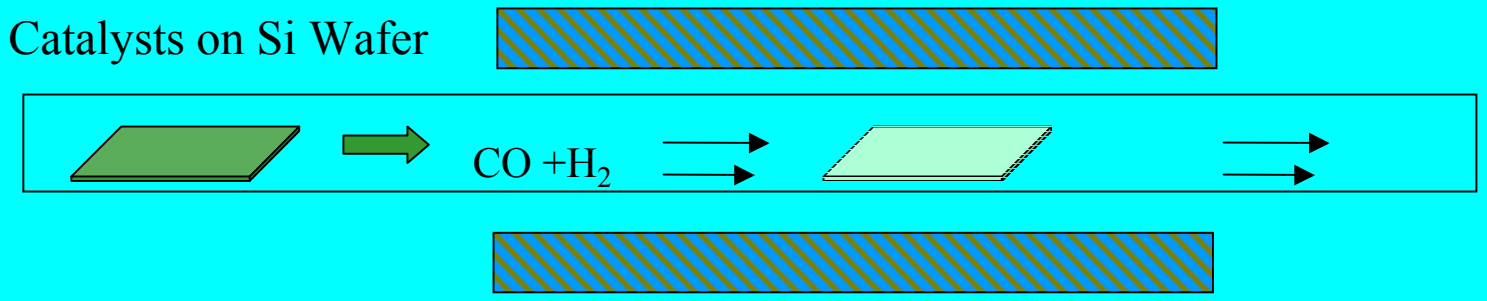
Growth speed: 12.5 microns/second

Scale Bar: 200 μM

Method to Grow Long Nanotubes

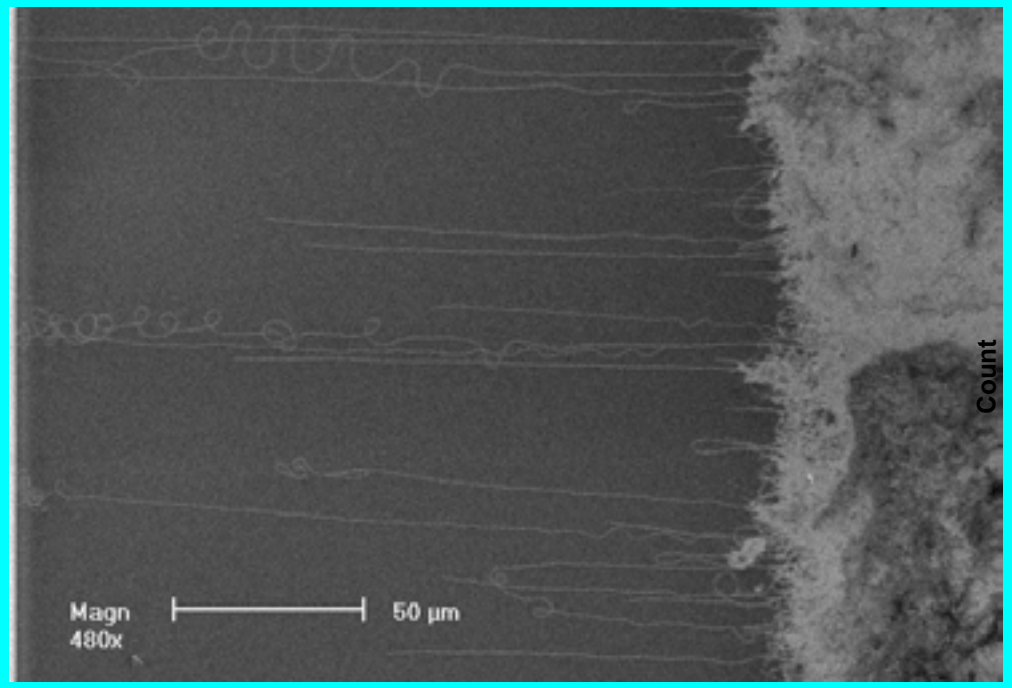


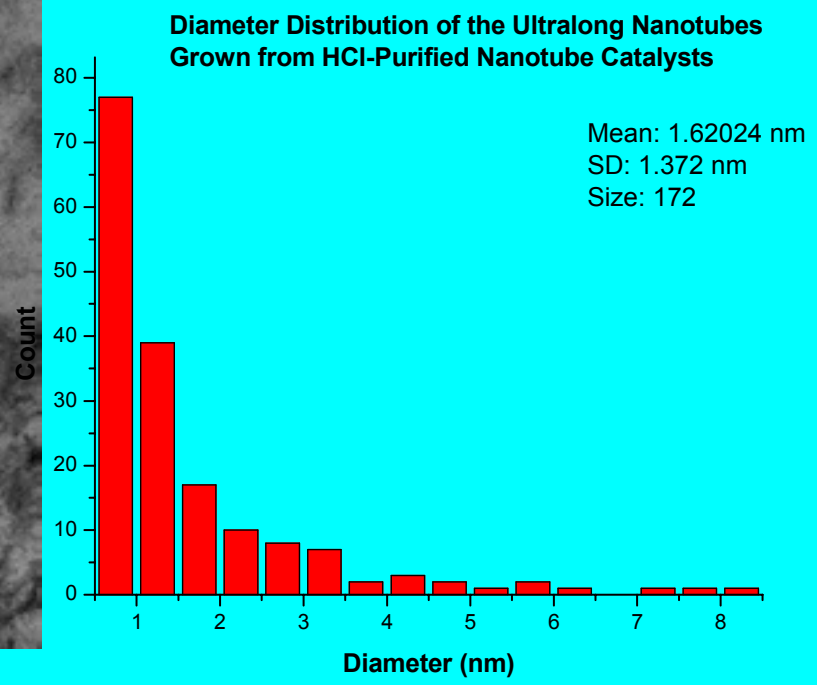
For Short and Random Nanotubes: Furnace heated from RT to 900C with sample inside



For Long and Oriented Nanotubes: Furnace heated to 900C before sample transferred into the furnace.

Long Nanotubes Grown from Nanotube Catalysts (Raw HiPCo Nanotubes Reacted with Acid)





SEM image and size distribution of nanotubes grown using catalysts supported on HiPCo Nanotubes.

On-Going and Expected Collaboration

- Rice University
  - “cloning” of nanotubes.
  - Nanotube structural and purity characterization.
- NREL
  - Characterization of nanotubes samples for their structures and hydrogen storage properties.
- UNC
  - Providing samples to UNC group for study on hydrogen storage properties using NMR
- Oak Ridge
  - Collaboration on nanotube growth and structure characterization
- Livermore
  - Preparation of carbon aerogel.

Hydrogen Safety

The major safety issue related to our research activities is the safe handling of flammable gases like Hydrogen, Methane and Carbon Monoxide.

Duke University has very strict rules on safety and has safety officers in all research labs. Regular walk through for all research labs is done on a regular basis with written comments on every potential safety hazard. For any of the gas, two or more of sensors and alarms are installed currently to detect any leakage of the gases.

Specific safety plan for this new research project supported by DOE is being developed together with Duke safety office.