Synthesis and Processing of Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

a participant in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials
DOE Hydrogen Program Annual Review, Washington, D.C., May 23, 2005

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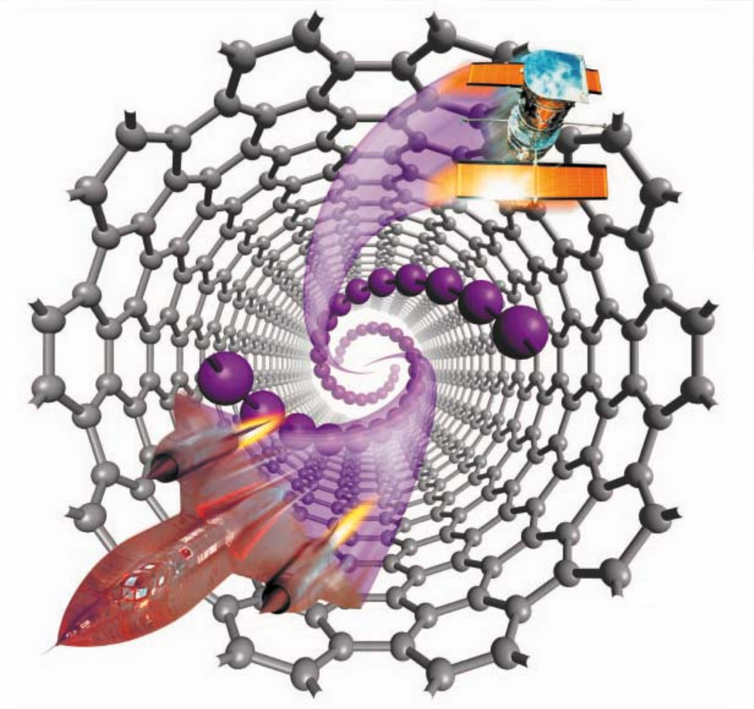

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Project ID# STP32

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CbHS Center Key Questions

1) How do the diameter, degree of curvature, and interstitial pore size of nanostructured carbons affect hydrogen adsorption in proximity with metal nanoparticles?

2) What is the role of metal atoms and nanoparticles in anomalously high hydrogen adsorption measured on nanoporous carbon supports?

Objectives

- To controllably synthesize and process a novel new form of carbon - *single walled carbon nanohorns* - as a hydrogen storage medium

- To work interactively with CbHS Center members to optimize these materials and their composites for maximal hydrogen storage consistent with DOE targets

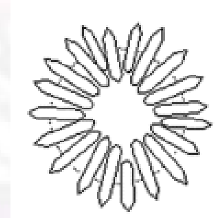
Approach

- Carbon nanohorns are single-walled carbon structures and may be synthesized free of metals. They may be used to support finer metal nanoparticles than any other carbon. They are already being used in laptop fuel cells, and provide a versatile material to understand and optimize the carbon-metal interaction which is key to hydrogen storage in our CbHS Center project.

- Their formation process is not well understood and a great variety of nanohorn structures are known.
  - We will synthesize SWNHs with controllable structure in gram quantities using a unique *in situ diagnostics-based* laser vaporization facility at ORNL.
  - We will develop unique methods to optimally load them with clean catalysts.

Why Single-Wall Carbon Nanohorns (SWNH)?

- **SWNH excellent as both storage vessels and catalyst supports**
  - **single-walled carbon structures like single-walled carbon nanotubes**
    - **huge surface area**
    - **visible in TEM**
    - **can be produced *without* metals**
    - **can be produced mixed with SWNT and metals to probe spillover mechanism**
  - **Two modes of storage**
    - **outer surface - initially exposed**
    - **inner surface accessible by opening pores**
    - **tiny "bottles" for storage**
  - **Excellent catalyst supports - for gas storage, fuel cells**
    - **nanohorn structure restricts catalyst aggregation, supporting finer catalysts at lower weight loadings**
    - **demonstrated by Iijima's group at NEC**
      - first commercial methanol fuel cell now in production for laptops



Schematic diagram of nanohorn aggregates. [Bekyarova'02]

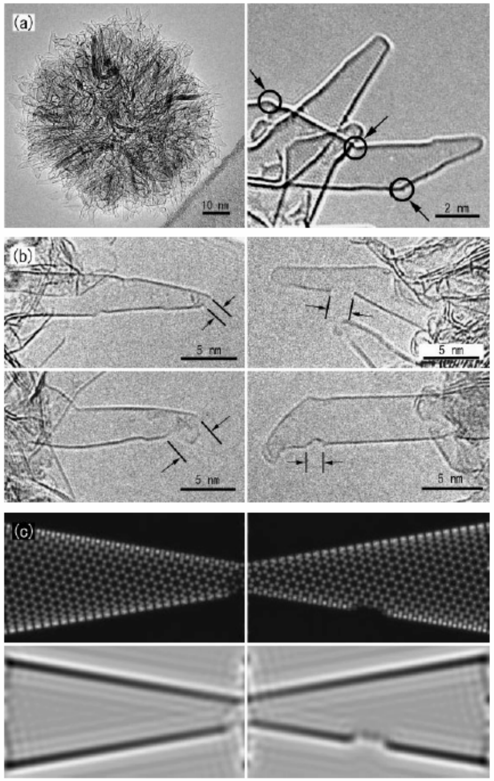


Figure 1. HRTEM images of the porous nanocarbon. a) A dahlia-like aggregate of carbon nanohorns before the heat treatment. Bumps and dips are occasionally found as indicated by arrows (Scale bars= 10 nm and 2 nm). b) HRTEM images of the carbon nanohorns after the heat treatment. The pathway holes introduced are clearly visible, as indicated by arrows. c) Image simulations for the structures of the path at the tip (left) and at the side wall (right) of the carbon nanohorns, simulated with atomic models.

TEM of SWNH as produced and after heat treatment [Aijima AM'04]

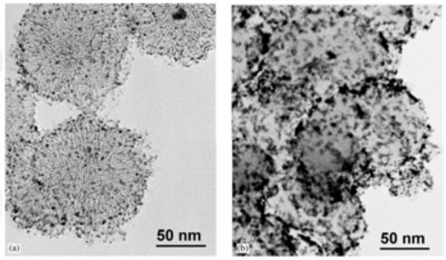
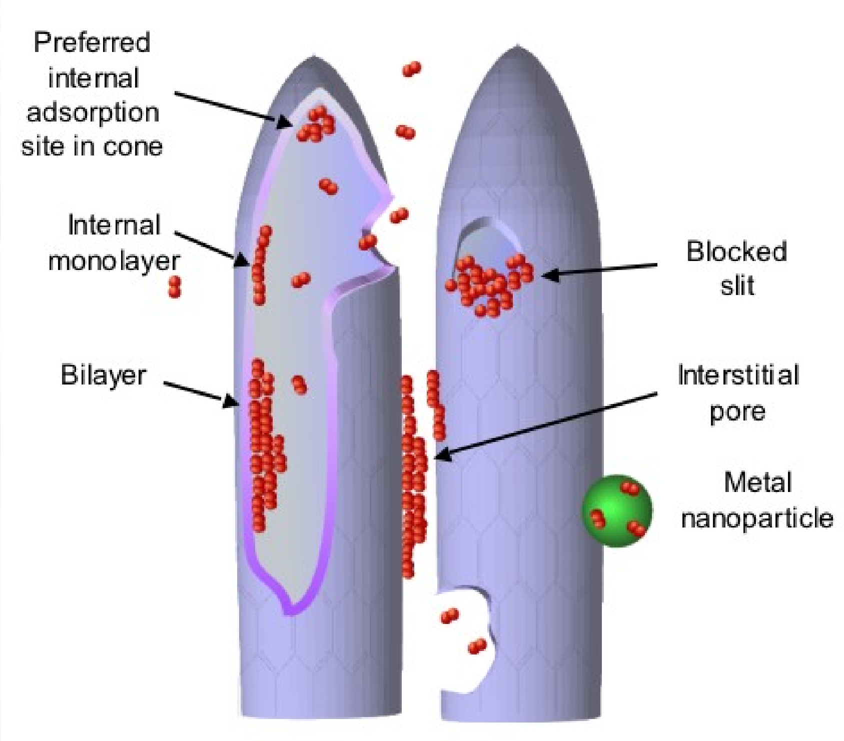


Fig. 1. TEM micrographs of the Pt catalyst supported on SWNHs (a) and on carbon black (b).

Pt nanoparticles on nanohorn aggregates (left) vs. carbon black (right). [Yoshitake PRB'04]

Hydrogen Storage in Carbon Nanohorns

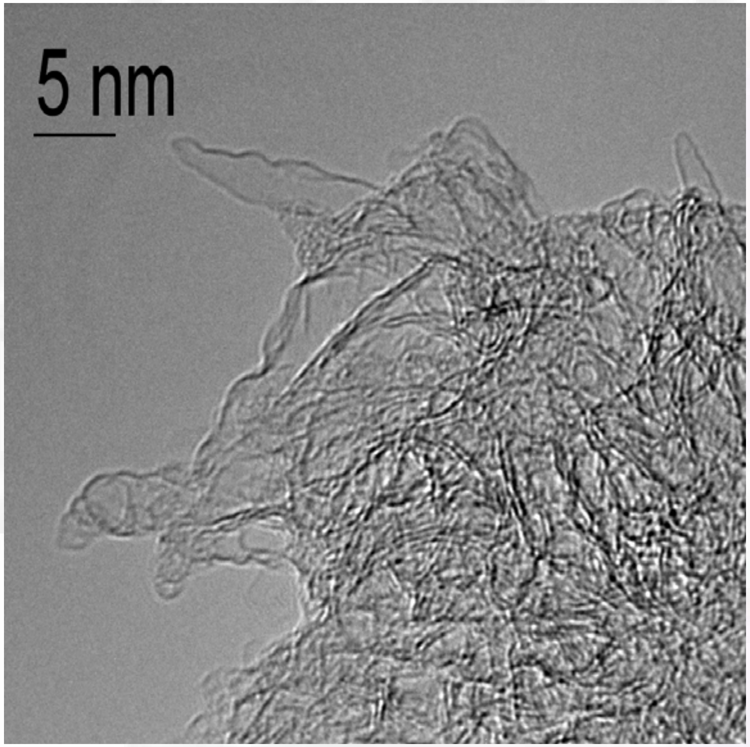
- <u>Idealized Geometry of a Nanohorn</u>
  - A nanohorn can be idealized as a circular cylinder of 2-3 nm diameter, plus a conical endcap with a cone angle of 20°.
- <u>Three hydrogen physisorption sites identified*</u>:
  - 1) Internal: Conical region, 7% of internal area
    - Preferred due to charge density at pentagon tips [Berber, 2000]. Numerous wall defects offer similar points in real (non-idealized) nanohorns
  - 2) External: Interstitial pores (next preferred site)
  - 3) Internal: Monolayer and bilayers along walls (self-stabilization of hydrogen by adsorbed hydrogen)
- <u>Open Question</u>:
  - How can metal nanoparticles inside and outside the nanohorns affect hydrogen adsorption at these 3 sites?



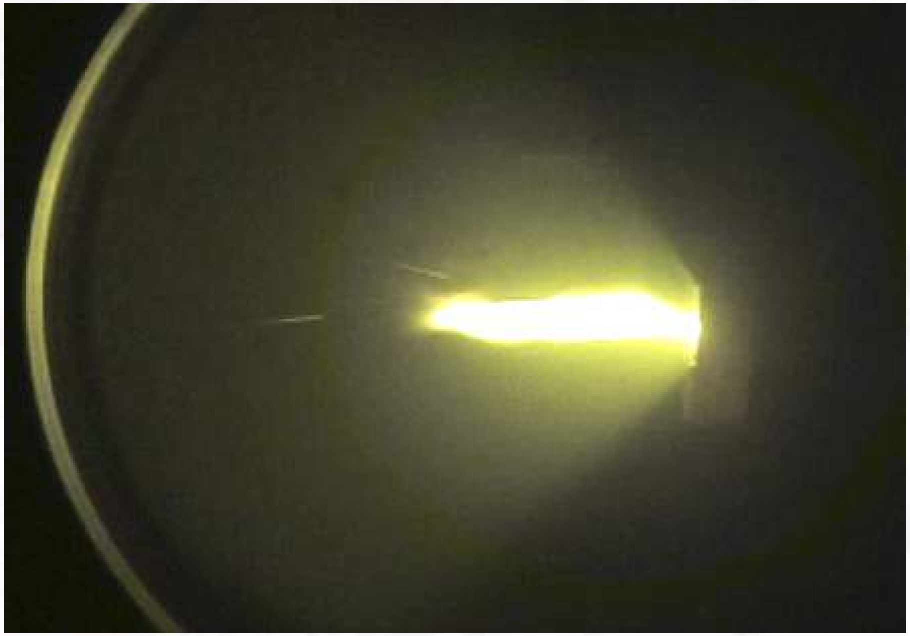
Schematic diagram of an idealized pair of single-wall carbon nanohorns - illustrating preferred adsorption sites

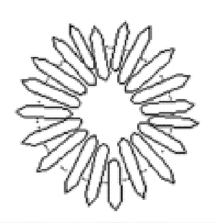
*Murata, K., K. Kaneko, et al. (2000). "Pore structure of single-wall carbon nanohorn aggregates." J. Phys. Chem. B **331**(1): 14-20

Carbon Nanohorns - How are they produced?



SWNH produced with high-power 600W ORNL Nd:YAG laser vaporization





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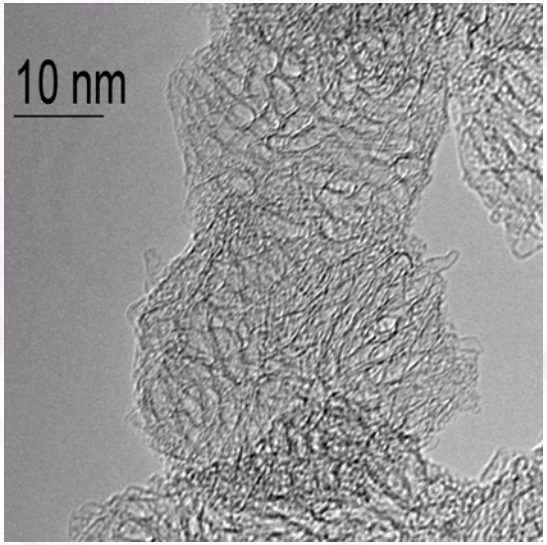


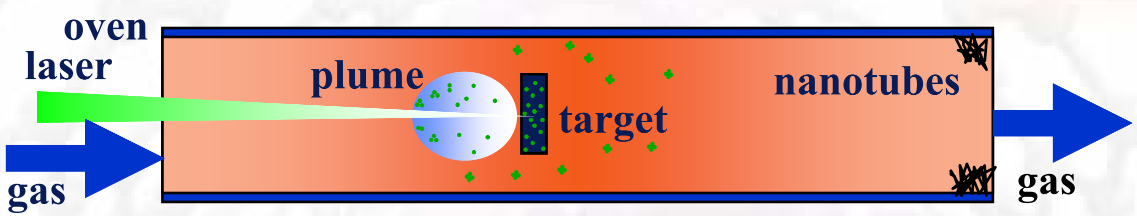
Why do single-walled carbon structures form naturally by laser vaporization of pure carbon targets?

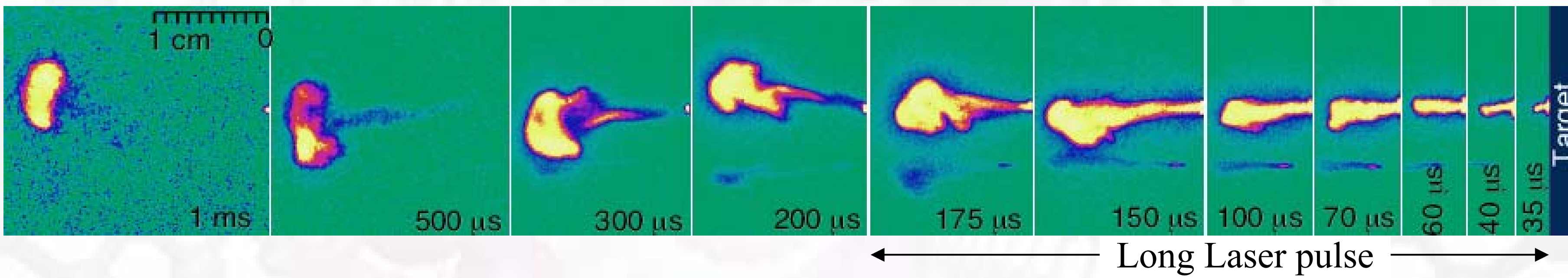
Answer:

The synthesis process is poorly understood at present

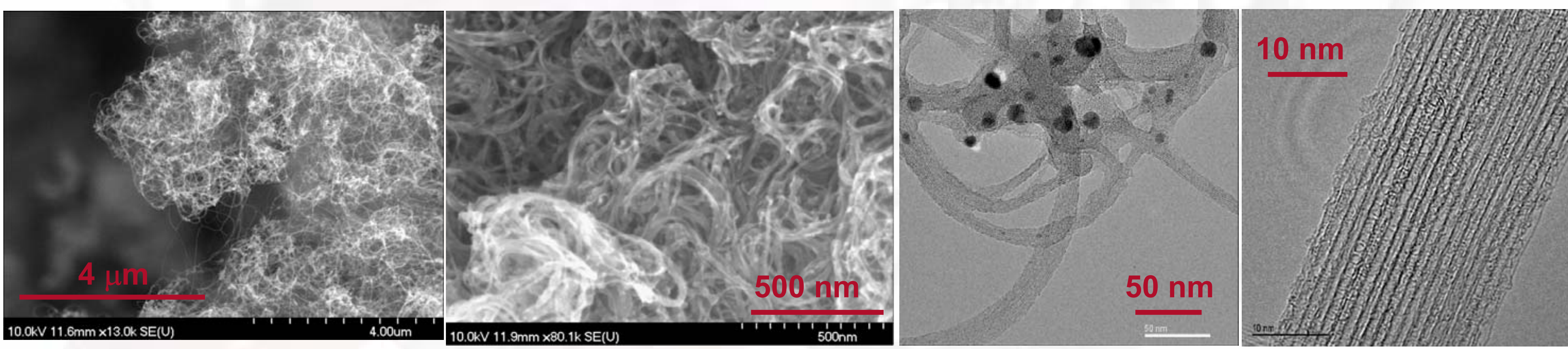
Unique Diagnostic Facilities Available for this Work

Laser Synthesis of SWNT and SWNH at ORNL



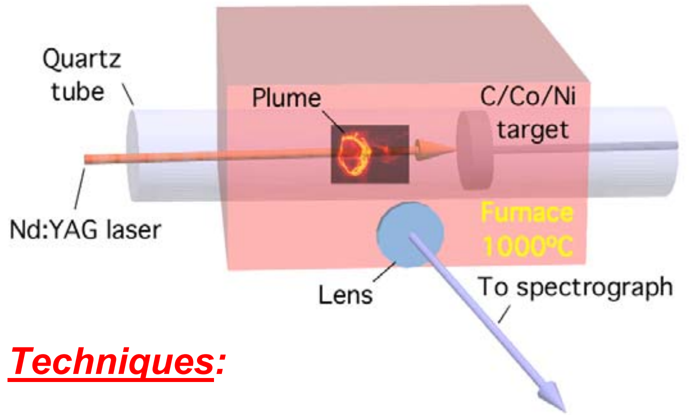


Laser vaporization to produce high-quality SWNTs has been extensively studied at ORNL using time-resolved in situ diagnostics. The same techniques will be applied to understand nanohorn formation.



As-grown nanotubes at high temperatures - 1 nm fibers, form ropes, metal/carbon impurities

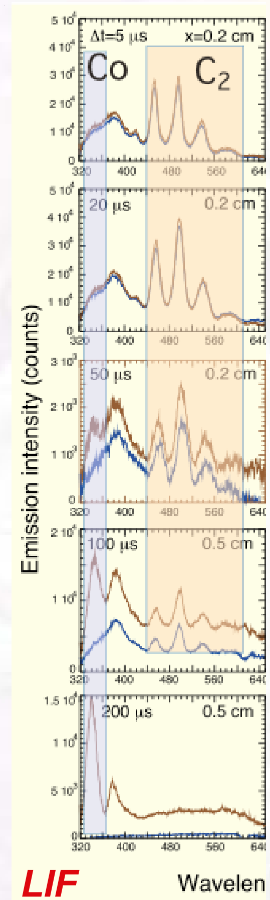
In situ diagnostics facility to understand and control growth

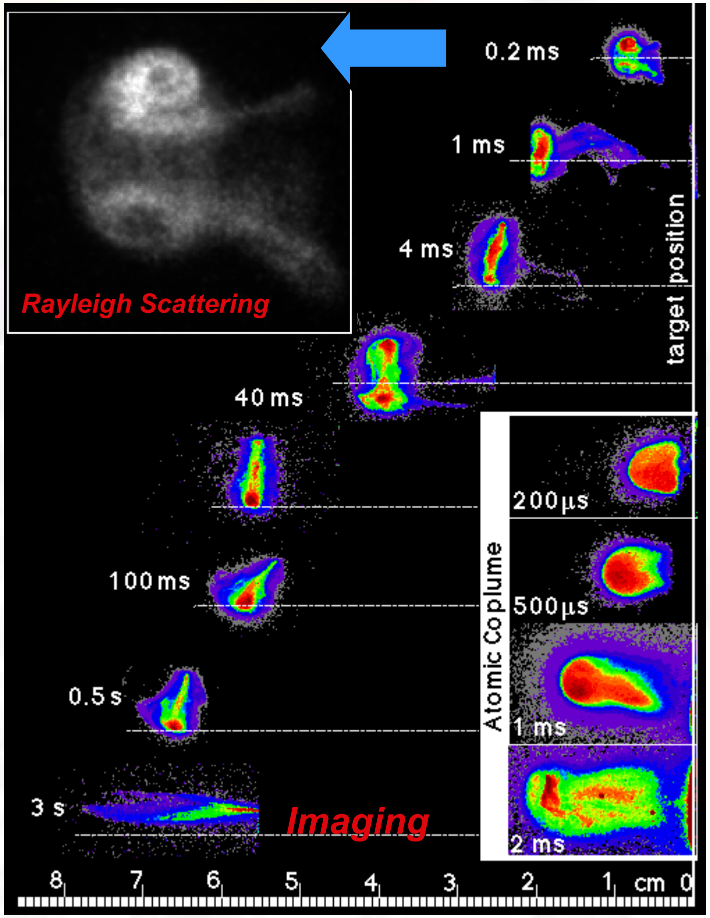


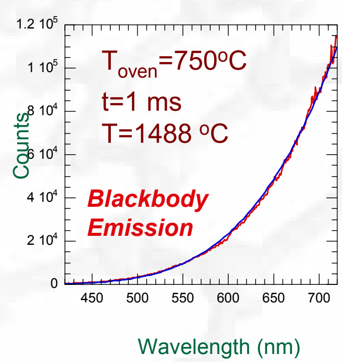
***Techniques*:**

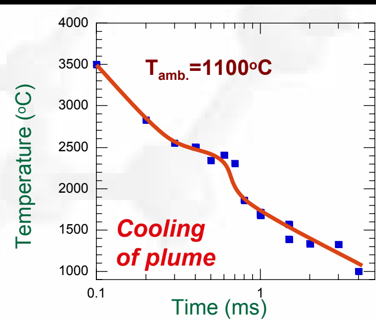
- First imaging of plume dynamics and spectroscopy of plume at extended times during SWNT synthesis
  - First growth rates measured (1 – 5 μm/s)
  - Mechanism of growth deduced
- Position and dynamics
  - Gated ICCD imaging using 2nd laser
- Composition of the plume
  - Laser-induced fluorescence spectroscopy
- Temperature vs. time
  - Blackbody emission
  - Laser-induced incandescence
- Particle sizes
  - Rayleigh scattering
  - Optical absorption spectroscopy

Appl. Phys. Lett. **76**, 182 (2000). *Appl. Phys. A* **70**, 153 (2000).
Appl. Phys. Lett. **78**, 3307-3309 (2001). *Phys. Rev. B* **65**, 245525 (2002).









Milestones - Year One

- ***Apparatus Construction and Testing for SWNH Production***
  - Build and test SWNH synthesis chamber for production of nanohorns
  - Characterize SWNH synthesized under different processing conditions (e.g. gas type, pressure, temperature) by HRTEM, TGA, Raman ...
  - Load-lock chamber constructed for fast sampling of products
  - Determine optimal collection techniques consistent with safety - Thermophoresis, electrostatic, filters.

- ***Optimization of SWNH Synthesis Conditions Through in situ Diagnostics and Feedback and Production of Bulk Samples for Adsorption Measurements***
  - In situ diagnostics started
  - Methods of metal catalyst loading during laser vaporization studied, and effects on yield and loading
  - <u>Gram quantities of SWNH produced</u>

Go, No-Go Decision Points

Year One and Beyond

- **Year 1: Synthesis - SWNH production by laser vaporization**
  - Can SWNH be produced and collected safely in gram quantities, with reproducible structure?
  - End of first year

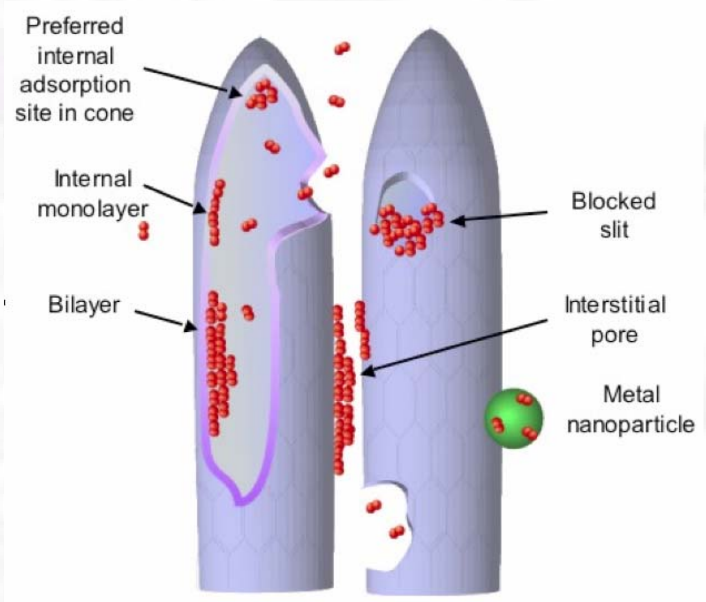
- **Year 2: Optimize metal loading techniques, correlated with hydrogen uptake**
  - Can methods be developed to load metals reproducibly on SWNH?
  - Assessment of hydrogen uptake capability
  - End of 2nd year

- **Years 3-5:**
  - Optimization of metal loading for maximal hydrogen uptake
  - Scaled-up production assessed.

Tasks - *year one*

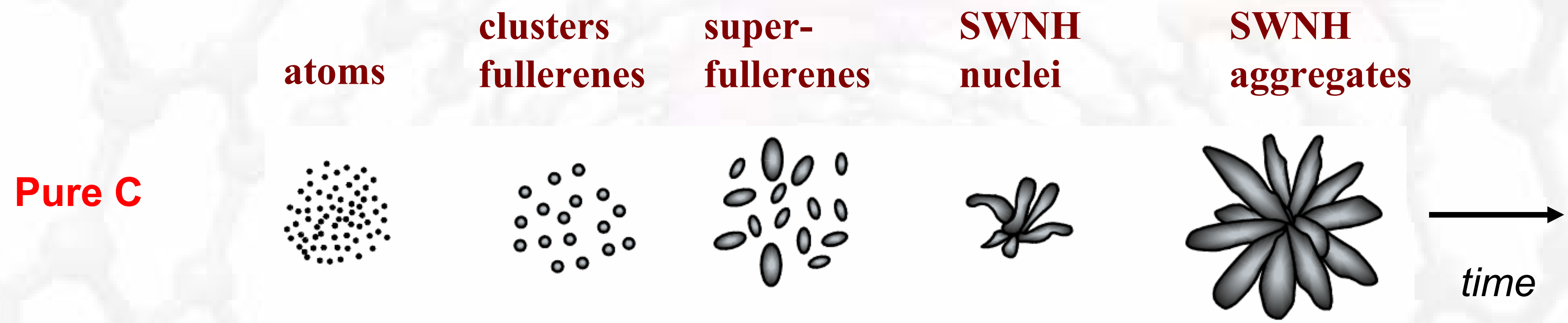
Single-Wall Carbon Nanohorn Synthesis and Catalyst Loading

1. **Synthesis and Characterization of SWNH vs. Laser Vaporization Processing Conditions**
   A. Produce SWNH using different gases, at different pressures, at different temperatures, and with different laser powers to determine how the nanohorn nanostructure and yield can be controlled.
      A. Design and build nanohorn production chamber
      B. Implement rapid sampling apparatus
      C. Perform HRTEM, Raman, and TGA analyses of products
   B. Implement *in situ* diagnostics to understand how SWNH's grow, and how their growth may be controlled
      1) Plume imaging, temperature measurements, spectroscopy performed.
   C. Explore catalyst addition to graphite targets to probe the transition between SWNT and SWNH formation at elevated temperatures for the production of SWNT/SWNH composites
   D. Design, test, and implement techniques for the safe collection and handling of carbon nanohorns
   E. Produce gram quantities of SWNHs for supply to partners



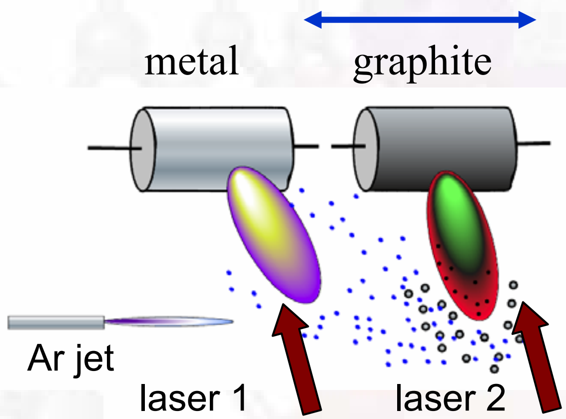
2. **Catalyst Loading**
   1. Assess and develop methods of loading SWNH with catalyst nanoparticles
      1. In situ vaporization of composite targets
      2. Ex situ dry evaporative coating technology
      3. Wet chemistry approaches

Possible Nanohorn Synthesis Pathway
- *and approach for SWNH/SWNT structure control*



Nanohorns form at high pressures from pure C in hot plasmas. Are they formed from large fullerenes?

Now add metal - adjust temperature and timing



- Metal-atom coated fullerenes
- Metal nanoparticles on SWNH aggregates
- Metal nanoparticles or atoms in superfullerenes/ nanohorns

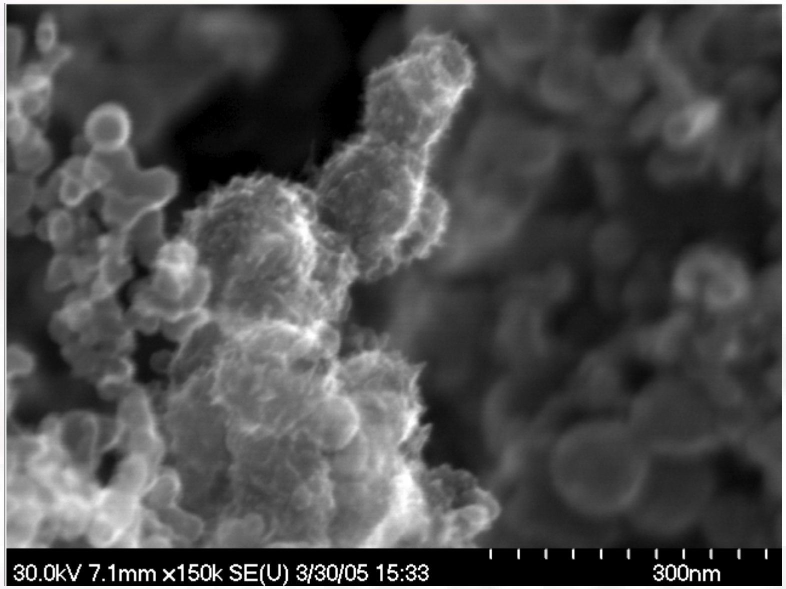
Co-vaporization of metal and carbon produces nanotubes in high temperature gas, and metal-coated nanohorns in room temperature gas.

Approach: Vary the timing between fullerene and metal nanoparticle condensation at different temperatures to understand the synthesis process and produce a wide variety of nanohorn/nanotube/metal materials for hydrogen storage studies

Nanohorn Aggregates - *How are they formed?*

Preliminary Results

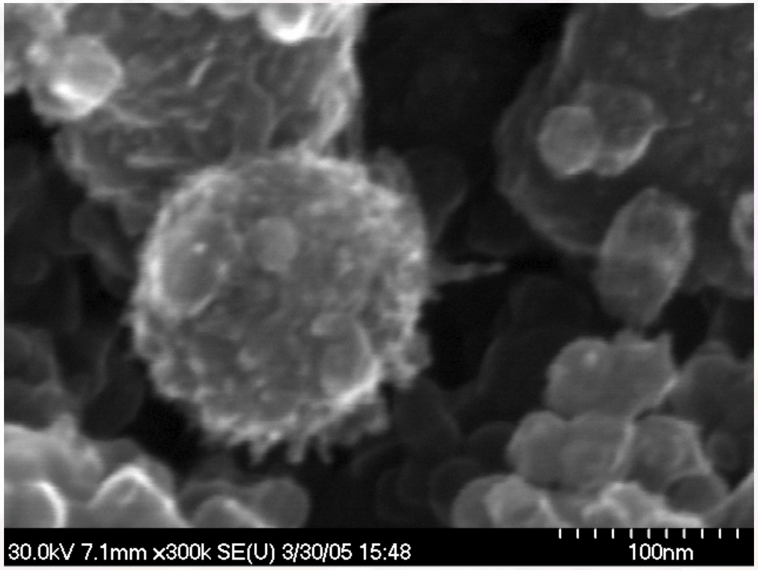
Scanning Electron Microscopy images of SWNHs formed by high power laser vaporization in this project

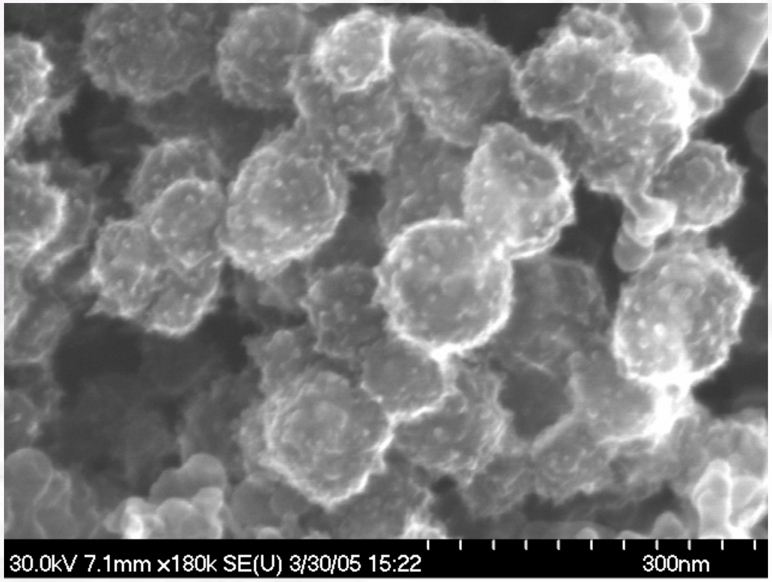


Questions:

Are nanohorn aggregates welded together at a central core?

How do they nucleate and grow?





Nanohorn/SWNT at Elevated Temperatures

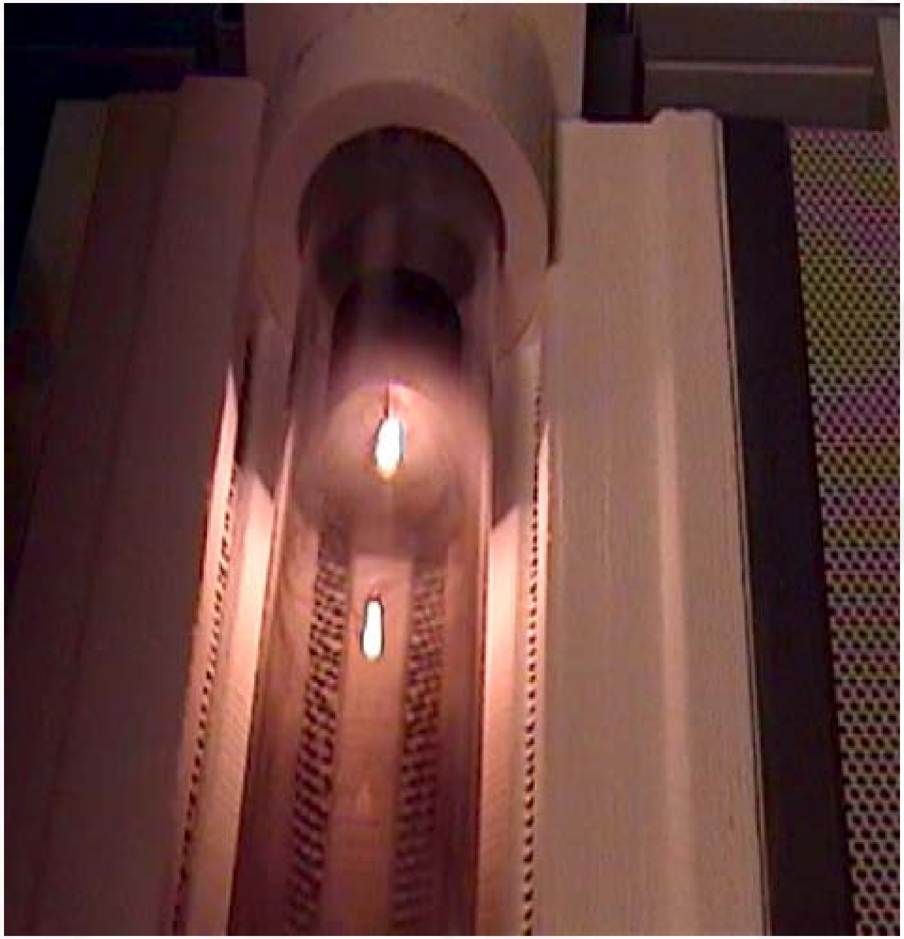
- Variable pulse widths
  - 0.5 ms minimum

- Laser parameters:
  - Avg. power : 500 - 600 W
  - e.g. 25 J @ 20 Hz
  - e.g. 1J @ 500 Hz

- Nanohorns created into RTP argon

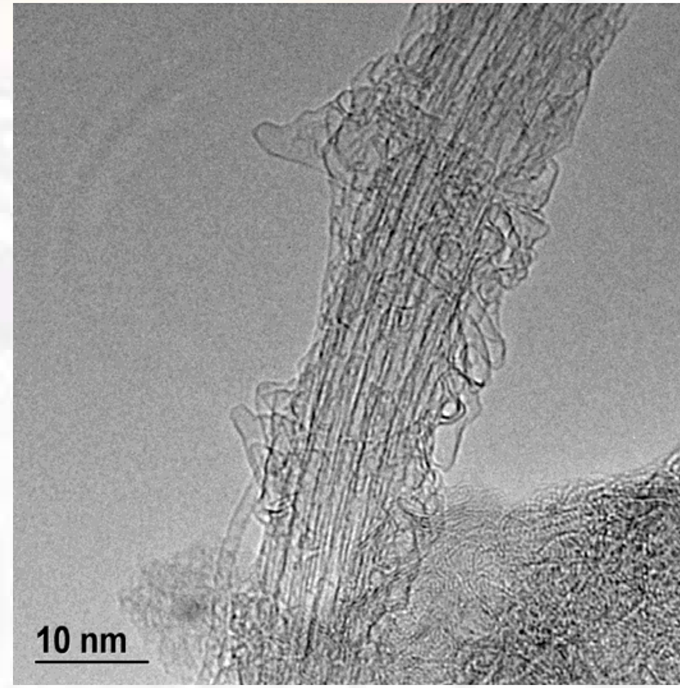
- Nanotubes at elevated temperatures

- Huge range of parameter space to explore
  - Laser heating of target and local area of gas



Laser plume during nanohorn production inside tube furnace

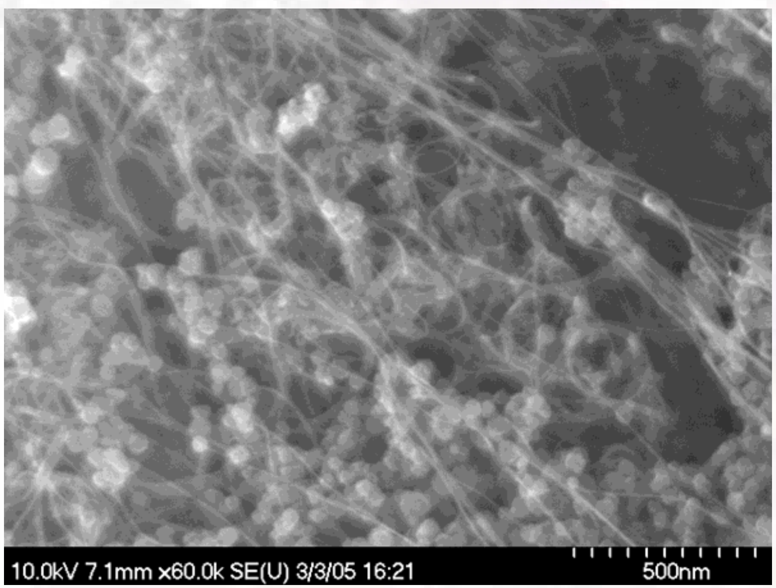
SWNH/SWNT at Elevated Temperatures

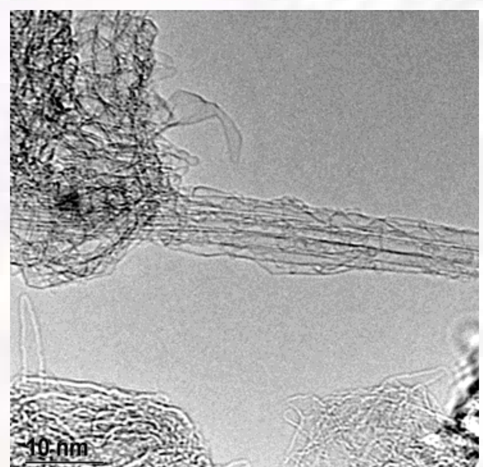


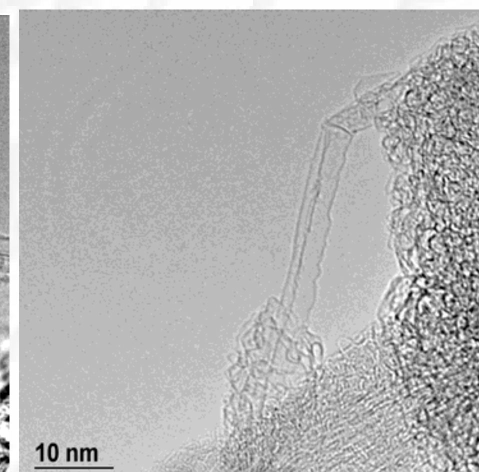
Preliminary Results

SWNT and SWNH are formed together by ablation at elevated temperatures of catalyst/carbon targets.

What is the role of the catalyst in nanohorn vs. nanotube formation?



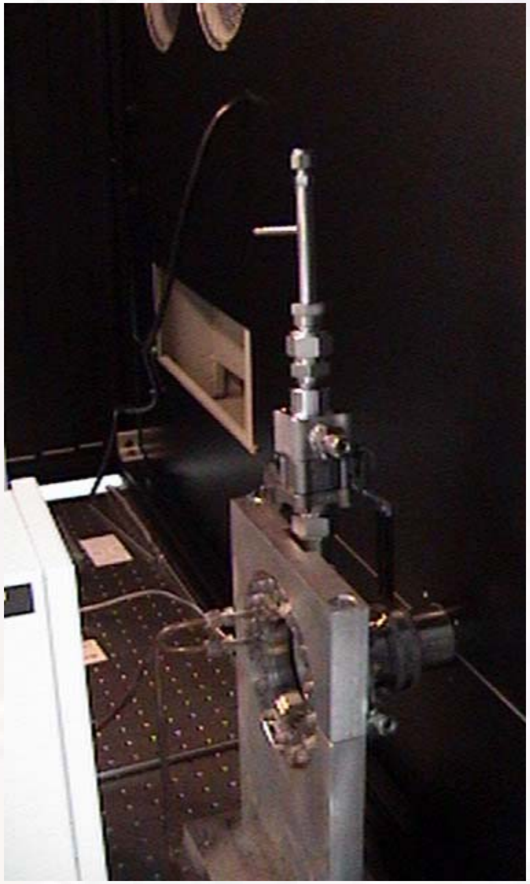


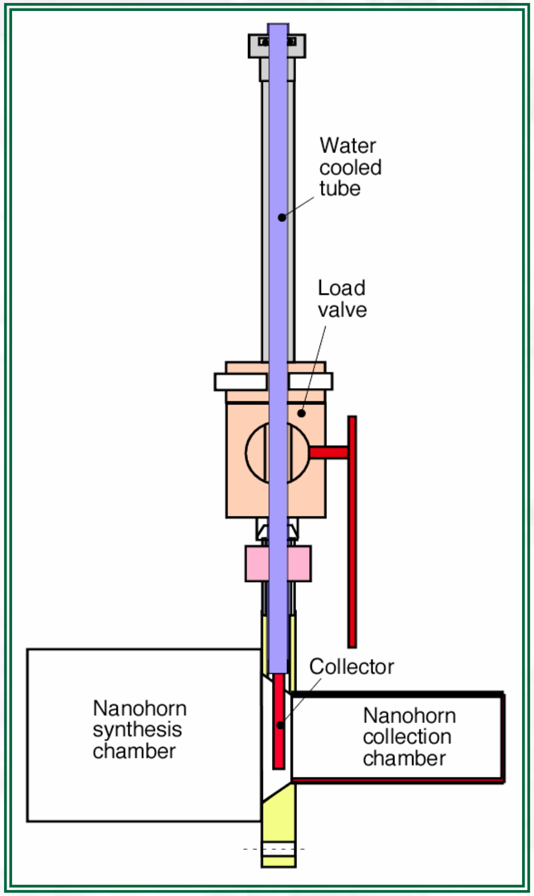


Rapid Sampling Apparatus

Preliminary Results

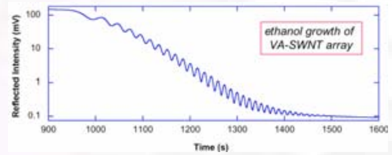
Water cooled thermophoretic rapid-sampling apparatus constructed for rapid sampling and optimization of synthesis products vs. processing conditions



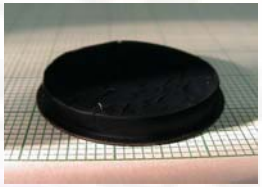


Advances
in Nanotube and Nanohorn Synthesis Worldwide

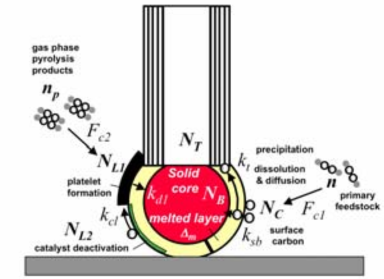
- **Synthesis of SWNTs**
  - Our work in nanotube synthesis
    - CVD growth of aligned SWNT arrays to mm's lengths
    - Growth model for nanotubes by CVD based upon *in situ* diagnostic measurements of growth rates
    - High-power laser synthesis rig for SWNT production at CNMS



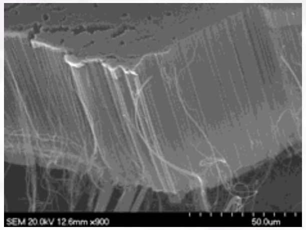
in situ reflectivity - first direct kinetics of nanotube growth

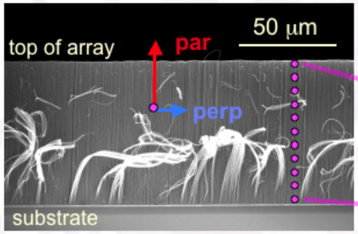


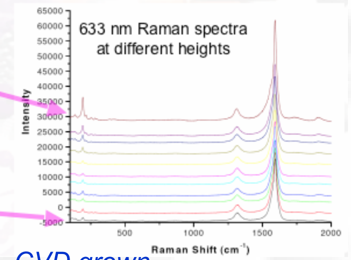
up to mm's long



growth model



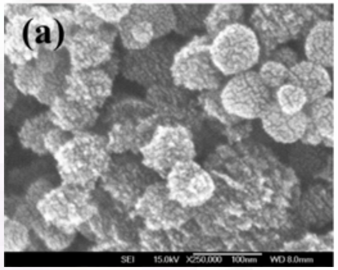




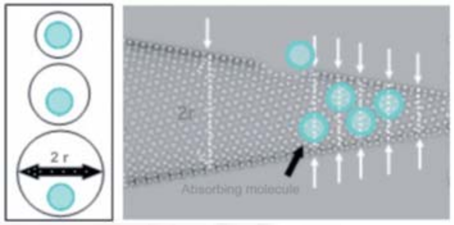
vertically-aligned arrays of carbon nanotubes - CVD grown

- **Preliminary SWNH synthesis tests with high power laser**

- **Japanese work on SWNHs - Iijima**
  - Growth of metal catalyst clusters, fullerenes inside SWNHs
  - Methane storage
  - Commercial fuel cell
  - Drug delivery



SEM of NH assy's. [Yang JPCB'04]



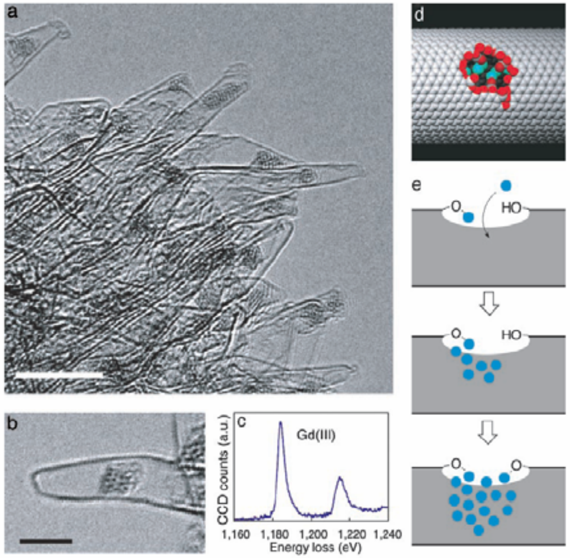


Fig. 2. Oxygen-bridged Gd(III) cluster trapped in the interior of oxNH580 (GdoxNH580). (a) A low-magnification TEM image of GdoxNH580. (Scale bar, 5 nm.) (b) A cluster in a single-wall tube. (Scale bar, 3 nm.) (c) EELS of the Gd(III) M-edge (1,185 and 1,216 eV) of a cluster in a NH (for the data of carbon and oxygen atoms; see Fig. 4). (d) A model of a 1.5-nm hole opening in a NT of 3.0-nm diameter containing a Gd cluster inside. (e) A scheme of the cluster growth in the interior of NH.

Gd clusters grown in opened SWNH [Aijima Advanced Materials (2004)]

NEC's Nanohorn Fuel Cell

OUTLOOK

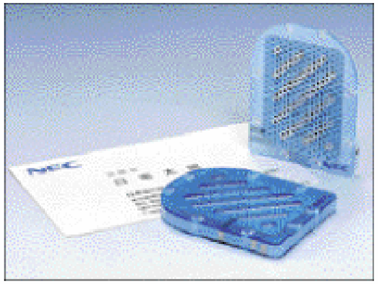
Miniature fuel cell employs carbon nanotubes

Micropolymer electrolyte cell has smaller catalyst particles than other technologies

By using carbon nanotube structures, a miniature polymer electrolyte fuel cell promises to provide up to 10 times the energy capacity of Li-based battery technologies. The use of these structures will enable the continued development of advanced portable and personal devices.

Carbon nanotube structures called nanohorns are used in a micropolymer electrolyte fuel cell from NEC (Tokyo, Japan). Made of a material superior to the activated carbon currently used, carbon nanohorns enable the cell to have an energy density up to 10 times that of lithium-based battery technologies.

Related to buckminsterfullerene nanotubes, a primary characteristic of carbon nanohorns--so named because of their irregular hornlike shape--is that when many are grouped together, they form an aggregate roughly 100 nm in diameter. When the aggregate is used as an electrode in a fuel cell, not only is its surface area large, but gas and liquid can easily permeate it , increasing electrode efficiency.



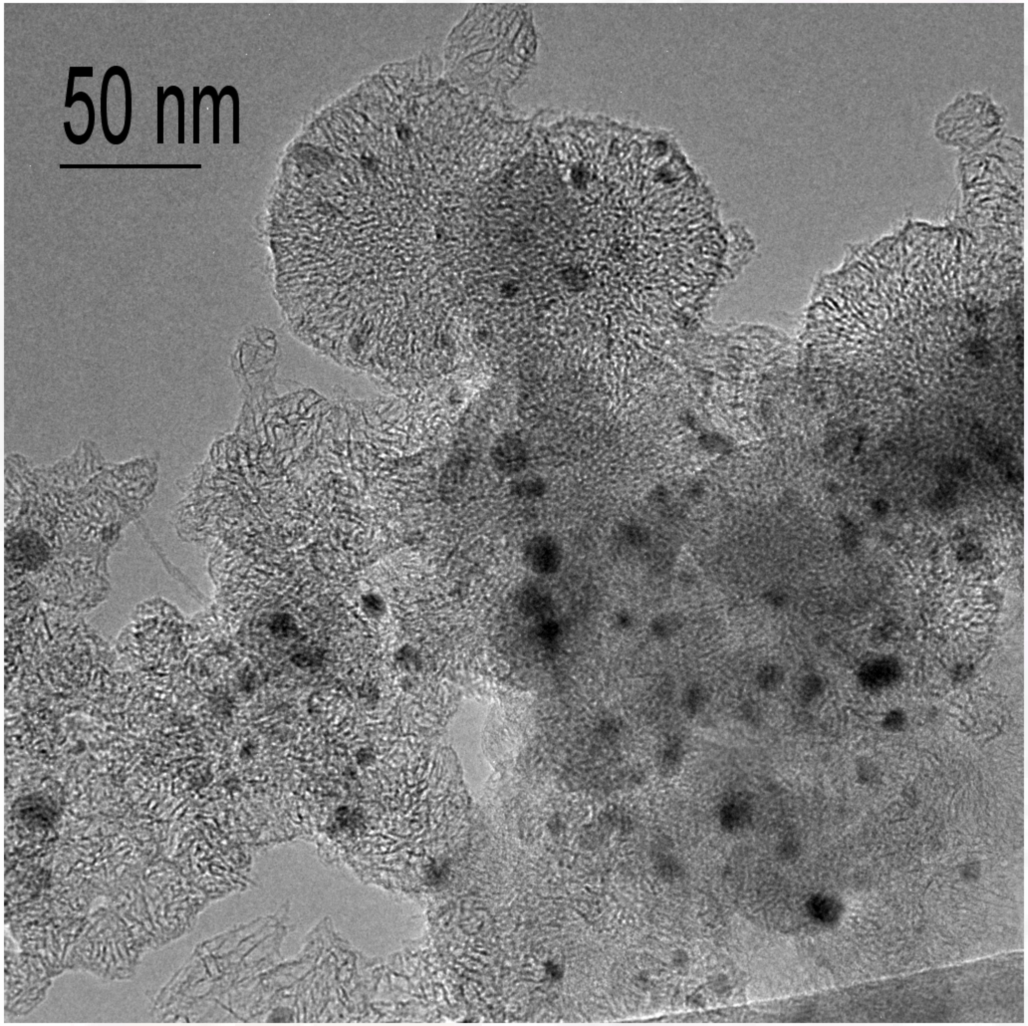
This miniature fuel cell uses carbon nanotube technology to provide up to 10 times the energy capacity of Li-based batteries.

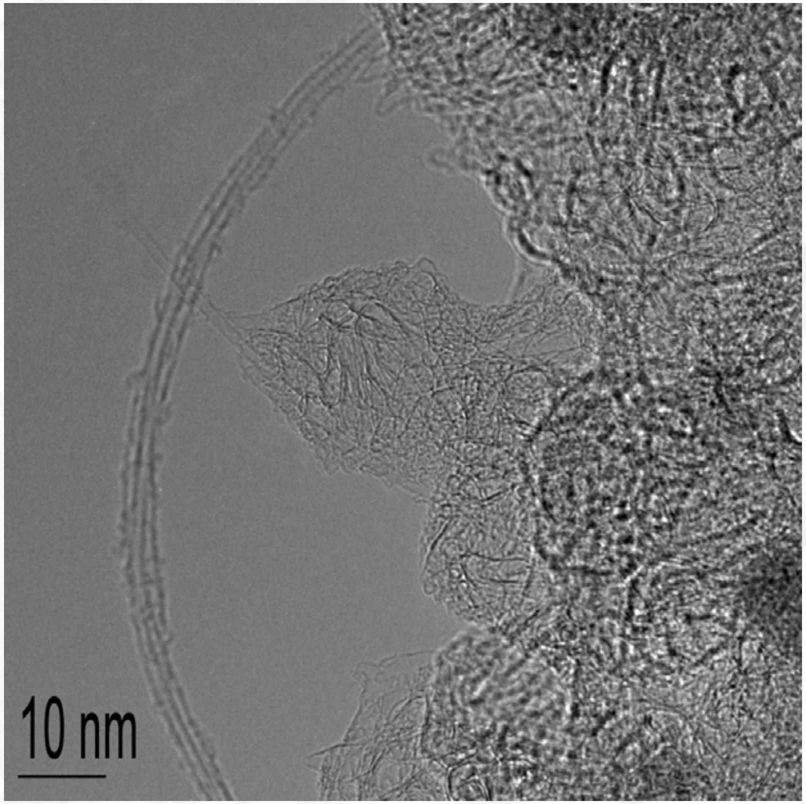
The size of the nanohorn structure's constituent platinum catalyst particle--a significant factor in fuel cell performance--is less than half of that supported by ordinary activated carbon . When the platinum catalyst is simultaneously evaporated in the laser ablation process that creates the carbon nanohorns, platinum particles tend to adhere to the nanohorn surface. With this method, the complicated conventional wet process can be omitted.

NEC's development not only represents an advance in fuel cell technology, but also the first practical use of carbon nanotube structures and nano-self-assembly. For more information from NEC, visit http://www.nec.com

--Alix L. Paultre

Carbon Nanohorns + Metal Catalysts



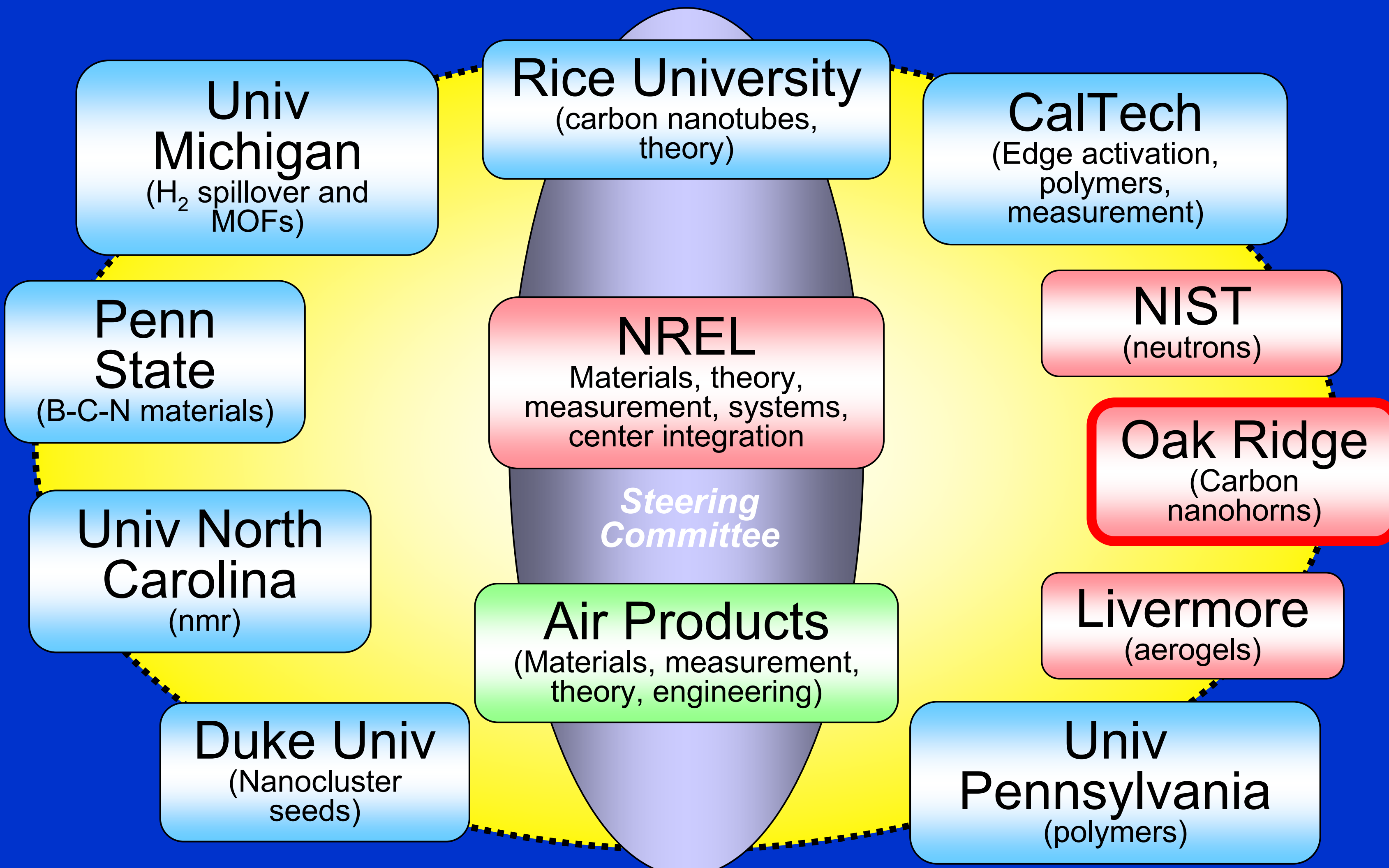


How do metal nanoparticles grow on nanotubes and nanohorns?

How are they stabilized?

CbHS Center of Excellence Partners

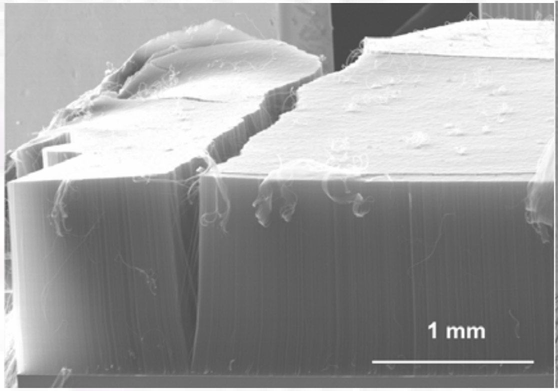
9 university projects (at 7 universities), 4 government labs, 1 industrial partner



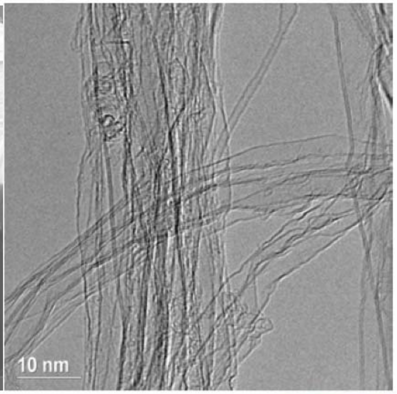
Anticipated Interactions
With Center of Excellence Participants

- SWNH are excellent comparators with nanotubes - *but can be made catalyst free*
  - Provide to participants
  - Work with participants for best catalyst loading procedures
  - Best material for NMR studies to determine mechanism for sp^2 - hybridized carbon/metal composites - NREL/Dillon/Davis
  - Plan for highly interactive tuning of SWNH and metal catalyst loading based upon emerging results

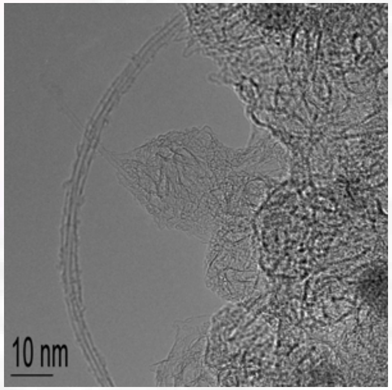
- We synthesize SWNT and MWNT also
  - Ultrapure SWNT by LV
    - Purification procedure based on NREL's
      - Existing collaboration !
  - CVD growth of mm-long NT arrays
    - Existing collaboration with R. E. Smalley group
    - CNMS collaboration with Jie Liu



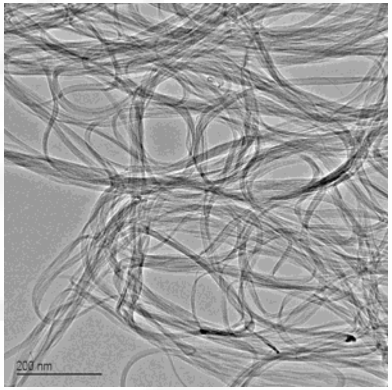
CVD VA-MWNTs grown to mm heights - walls 1-20



CVD VA-SWNTs grown at ORNL - so similar to SWNHs



Nanotube/Nanohorn composites



Ultrapure SWNT grown by LV at ORNL and purified (<0.02 wt.% metal)

Interactions

Catalyst-Assisted Growth of Single-Walled Carbon Nanotubes at High Rates

- **DOE Basic Energy Sciences research on fundamentals of nanotube growth**
  - *Aligned nanotube project*
  - *Rice University participating*
- **Several collaborations with other CbHS participants**
  - *Duke Univ. (Jie Liu) - CNMS user project on rapid growth*
  - *NREL (Anne Dillon) - Chemistry/purification of nanotubes*
- **Many other universities, national labs, NASA, AFRL**

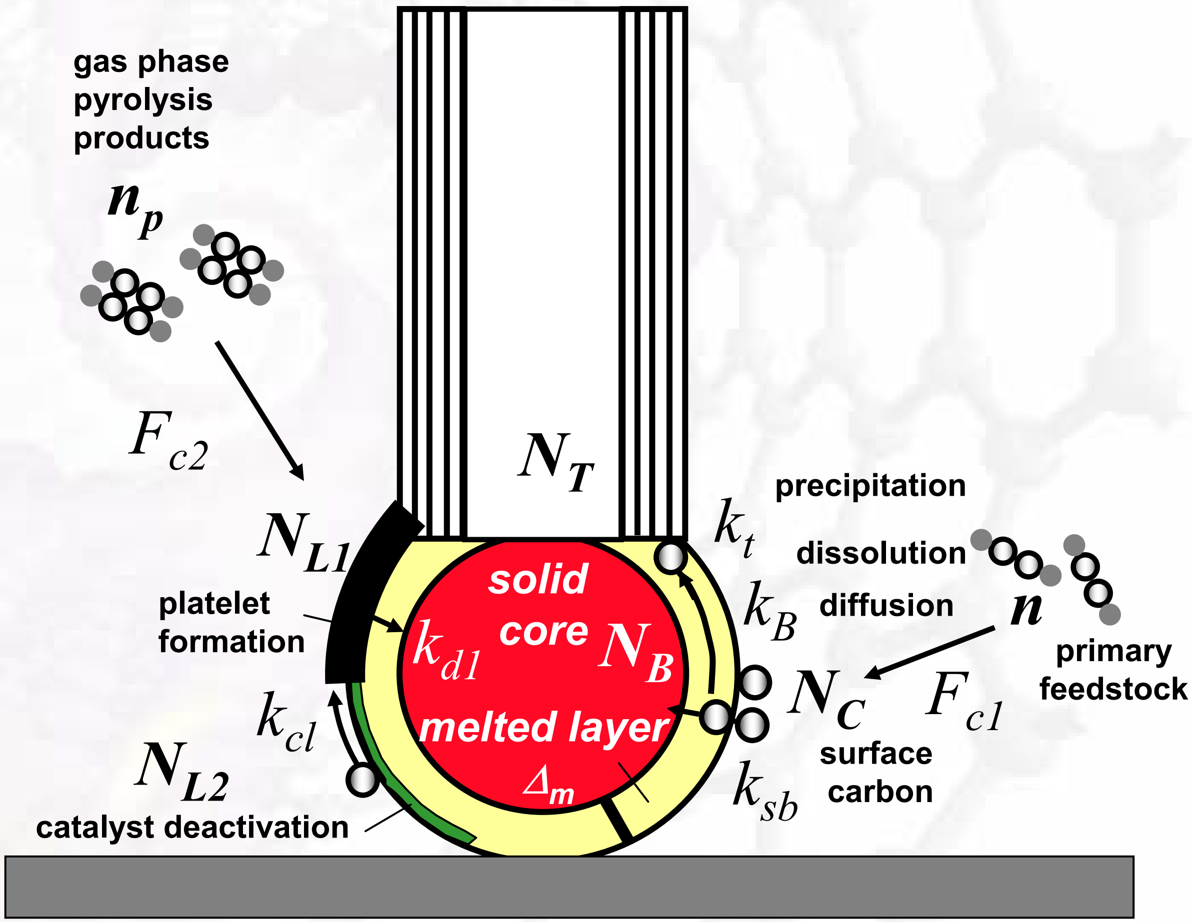


Figure from Puretzky et al, Appl. Phys. A (invited review) (2005, in press).

Interactions - BES Nanoscience Centers and Users

- **CNMS**
  - **Center for Nanophase Materials Sciences (CNMS)**
  - **A collaborative "user" facility**
  - **Will open this fall**
  - **Already collaborating with over seventy users**
  - **Our team is leading the *"Functional Nanomaterials"* research focus area**

- **Developing unique tools to explore**
  - **nanomaterial synthesis**
  - **advanced characterization techniques**
  - **catalysis**
  - **nanoscale magnetism and transport**
  - **nanofabrication**
  - **macromolecular materials**

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

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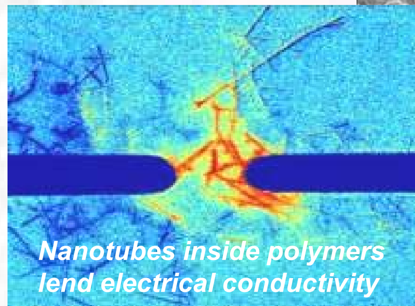
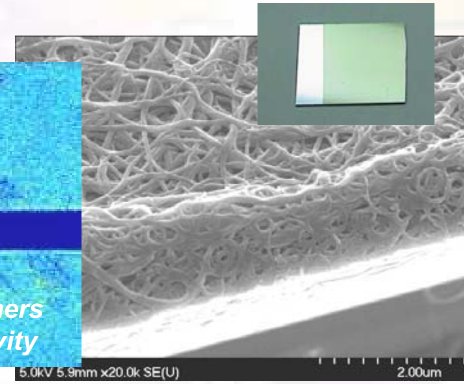
A highly interdisciplinary DOE-BES research facility which encourages synthesis and characterization of nanomaterials fulfilling *"Nanoscience Research for Energy Needs"* goals

http://www.cnms.ornl.gov

Interactions - Synthesis of Nanotubes and Processing of Nanotube-Based Composites at ORNL

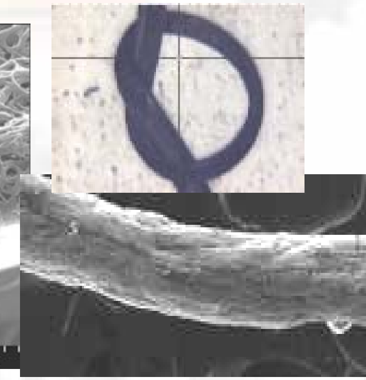
- **Loose SWNTs**
  - Single-wall carbon nanotubes
  - **Grown by laser vaporization**
  - Purified to ultra-high levels (< 0.02 wt.% metals)
  - Spun into fibers
  - Membranes, coatings
  - Multifunctional polymer composites





Films, sheets, coatings

Nanoscale Electronics

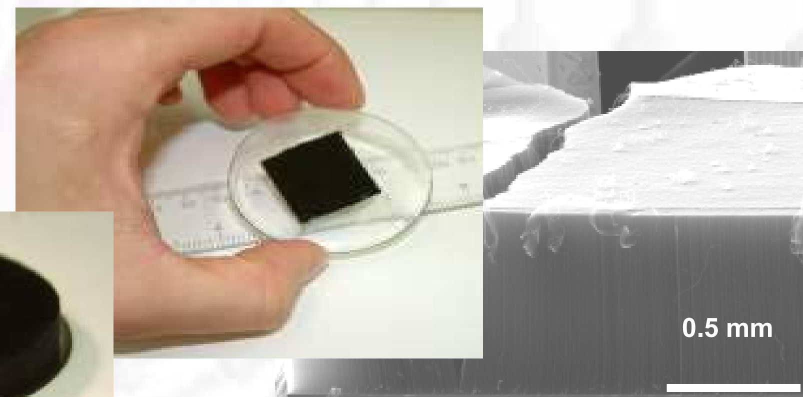


Fibers

- **Vertically-Aligned Nanotube Arrays (VANTAs)**
  - **Grown by CVD** rapidly to millimeters heights on substrates
  - Continuous nanotubes from substrate to the top
  - *in situ diagnostics* of nanotube growth
  - Defect density control
  - Infiltrated with polymers preserving their alignment
  - Developed for thermal management applications

Thermal Management

3mm



Nanotube arrays inside polymer composite

Exploring Electrical, Mechanical, and Thermal Properties of Carbon-Based Nanomaterials with Many Collaborators

Safety

Procedures in Place at ORNL - And Beyond Them ...

- **Two safety concerns - *<u>other</u> than hydrogen***
  - **Laser safety - *high power laser used to make nanomaterials***
  - **Nanotoxicology - *Nanomaterials are highly mobile, are they toxic via inhalation?***

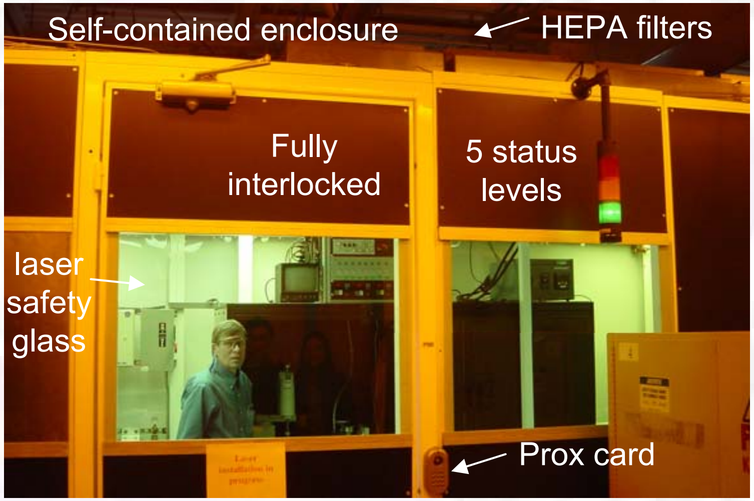
- **Laser Safety - *Triple protection***
  - **Isolated room-within-a-room**
    - **proxcard restricted access to authorized users**
  - **Fully interlocked, completely shielded laser facility**
    - **Laser will not operate without enclosure completely shut**
  - **Laser goggles worn at all times as a final precaution**
  - Lab policy: http://sbms.ornl.gov/sbms/sbmsearch/subjarea/Lasers/sa.cfm
  - Contact points in my (Condensed Matter Sciences) Division:
    - Laser Safety Officer: Jay Jellison (865) 576-7309
    - General Safety Officer: Dave Poker (865) 576-8827

- **Toxicity of Nanohorns - *A proactive approach***
  - Nanohorns are very small, highly mobile - one task: efficient collection
  - We are using our Environmental Sciences Division's expertise at ORNL to measure our particle size distribution and our collection efficiency - to insure that we are collecting them all
  - We will monitor airborne concentrations to insure safe handling
  - We are supplying these materials for nanotoxicology studies on living lung cells
  - We will know if they are toxic and take appropriate measures long before the NTP establishes guidelines.

Safety:
High-Power Laser Vaporization Nanomaterial Synthesis Facility

Advanced Laser Processing and Synthesis Laboratory

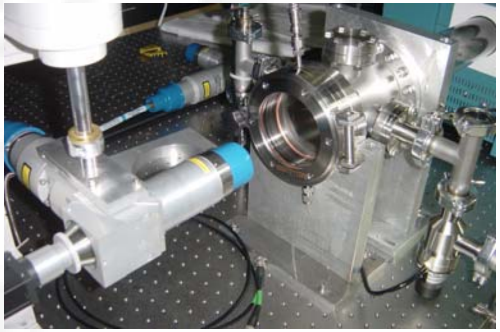
- ALPS Facility in Bldg. 3150 at ORNL
  - Built for high volume SWNT production at CNMS for JumpStart program
  - Will be utilized for SWNH production
- ORNL's top laser-safe lab?
- HEPA filtered recirculating air inside



600W Nd:YAG laser

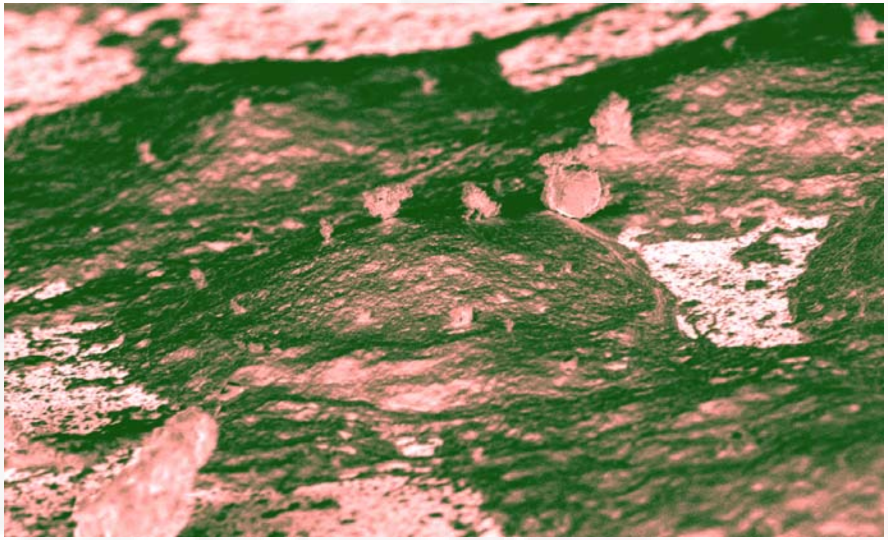
Robot

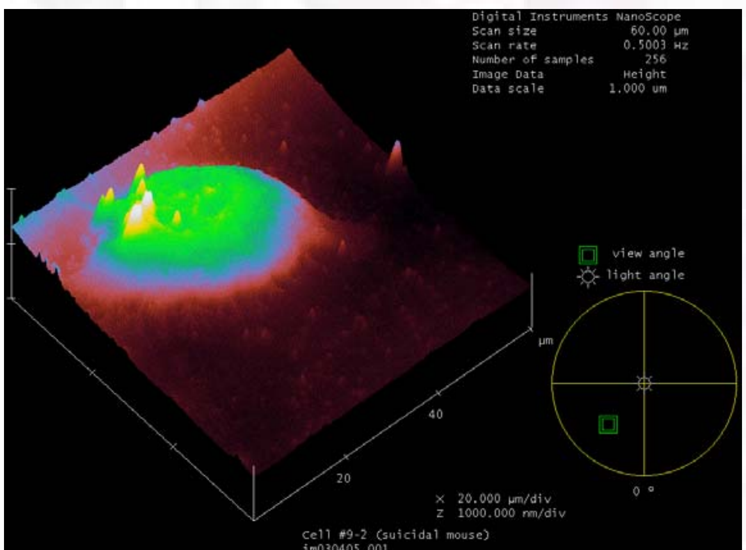
Vacuum apparatus for nanotube collection

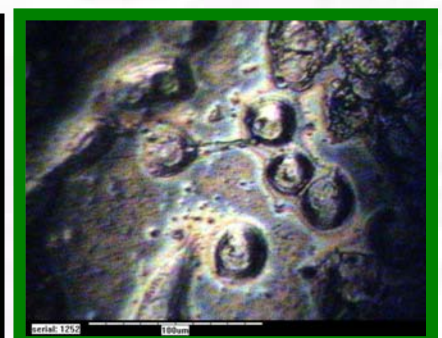


Robot-controlled laser head

Safety: Nanotoxicology of Carbon Nanohorns - *Interactions between nanohorns and living lung cells*







Lung cells and nanoparticles
SEM, AFM, microscopy imaging

- **Are SWNH's toxic? Are we collecting them safely?**
  - **SWNHs are highly mobile and difficult to filter**
  - **In order to prove that we are safely collecting the nanohorns, and evaluate their toxicity, an internally-funded ORNL LDRD project has teamed environmental sampling experts and biologists with us to evaluate the methods of collection we are employing and the toxicity of the materials we are producing**
  - **Gene expression assay techniques will attempt to determine what effects, if any, nanohorns have on living cells**
  - LDRD: M.-D. Cheng team leader

Project Overview - STP32
Single Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

Timeline

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

Budget

- Total project funding
  - DOE share 1.2M$
  - Contractor share 0k
- 200k received in FY05
- 250k expected in FY06

Barriers

- Barriers addressed
  - Cost
    - Scalable production
  - Weight and Volume
    - Reduced catalyst weight
  - Efficiency / Thermal Management
    - Composites
  - Durability
    - Catalyst stability

Partners

- Interactions/Collaborations
  - NREL, Rice Univ., Duke Univ.
    - Synthesis and purification of SWNHs vs. SWNTs
  - LLNL
    - NMR Characterization techniques