U. S. DOE Hydrogen Program Annual Review May, 2003

Doped Carbon Nanotubes for Hydrogen Storage

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Objectives

Develop reversible high-capacity hydrogen storage material:

- **Hydrogen capacity greater than 6 wt.%**
- **Favorable thermodynamic and kinetics suitable for transportaion applications**
- **Stable with hydriding/dehydriding cycling**

(DOE goals for a H2 storage system)

Approach

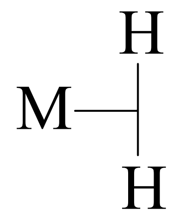
Produce large quantities of consistent structure carbon nanotube systems

- Not restricted to physisorption or chemisorption (weak covalent bond-dihydrogen is sought)
- Doped with transition metals and alloys
- Doped with other elements and metal clusters
- Material tuned for hydrogen sorption to occur at desired temperature and pressure

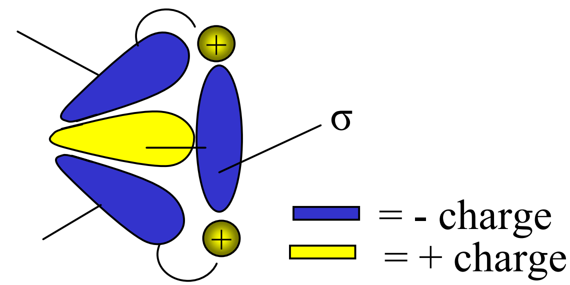
APPROACH Based on C-H bond

Physisorption= 2Kcal/mol, Chemisorption=17.5Kcal/mol

Weak covalent bond
Dihydrogen bond

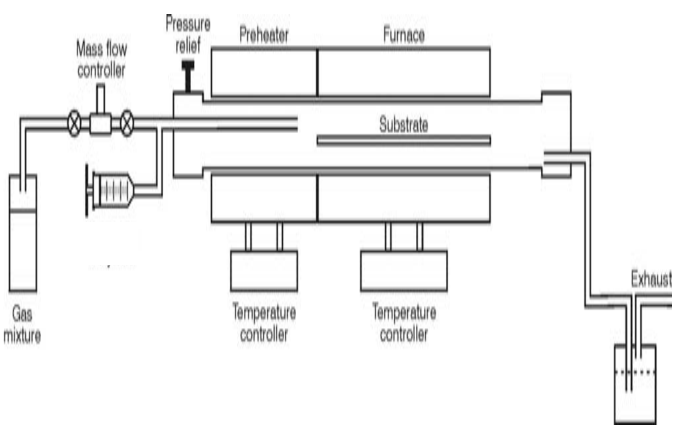


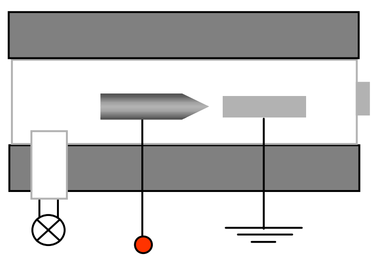
Example
$W(CO)_5RR_3(H_2)$

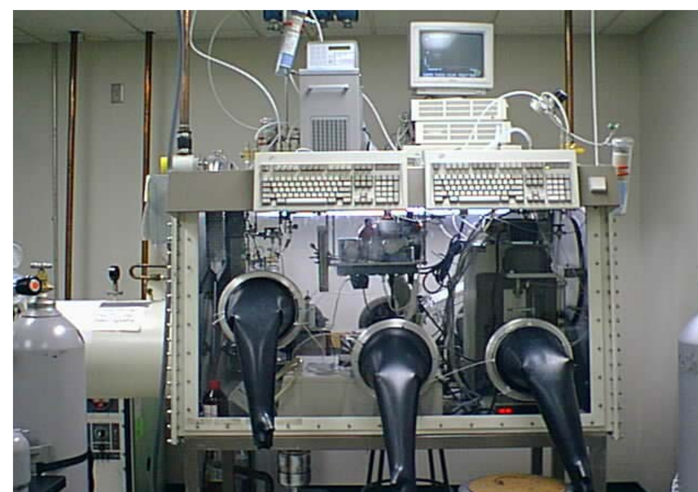


METHODOLOGY:

Developing a new method for producing consistent structures of doped carbon nanotubes







Status and Progress

1- Synthesis of material

1a- Different dopants

1b- Different quantities of dopants

1c- Different diameters and configurations

2-Thermodynamic characterization

2a. Set up a high pressure TVA system

2b. Hydriding and dehydriding

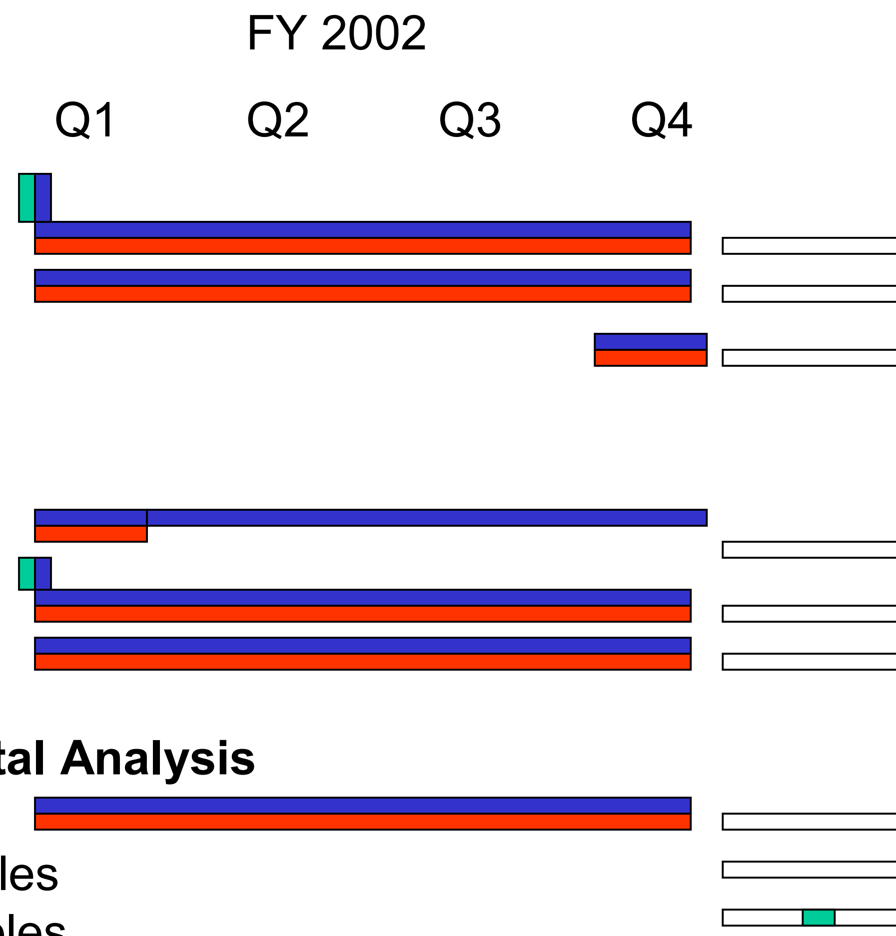
2c. Examine nanotubes with cycling

3-Material Characterization and Elemental Analysis

3a. Spectroscopic analysis of product

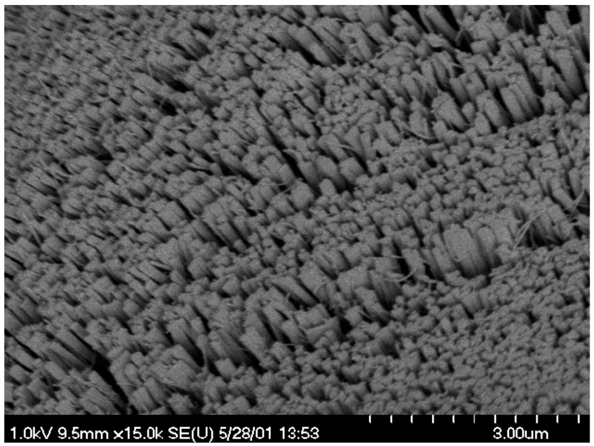
3b- Spectroscopic analysis of cycled samples

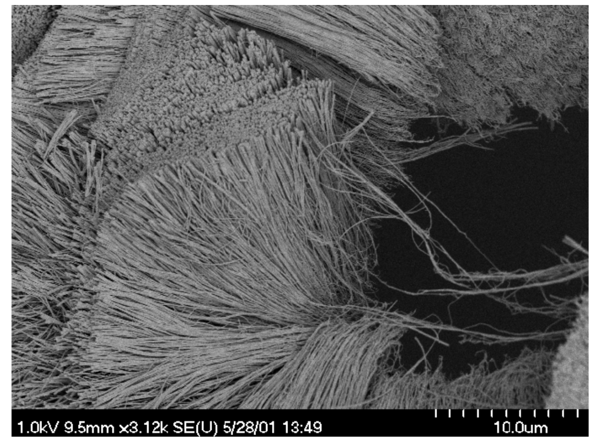
3c- Spectroscopy of H2 reaction with samples

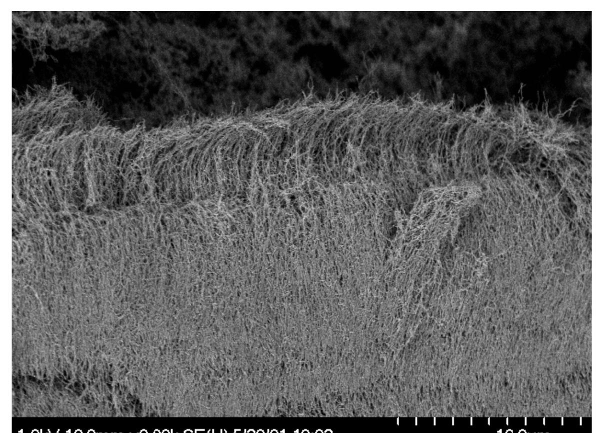


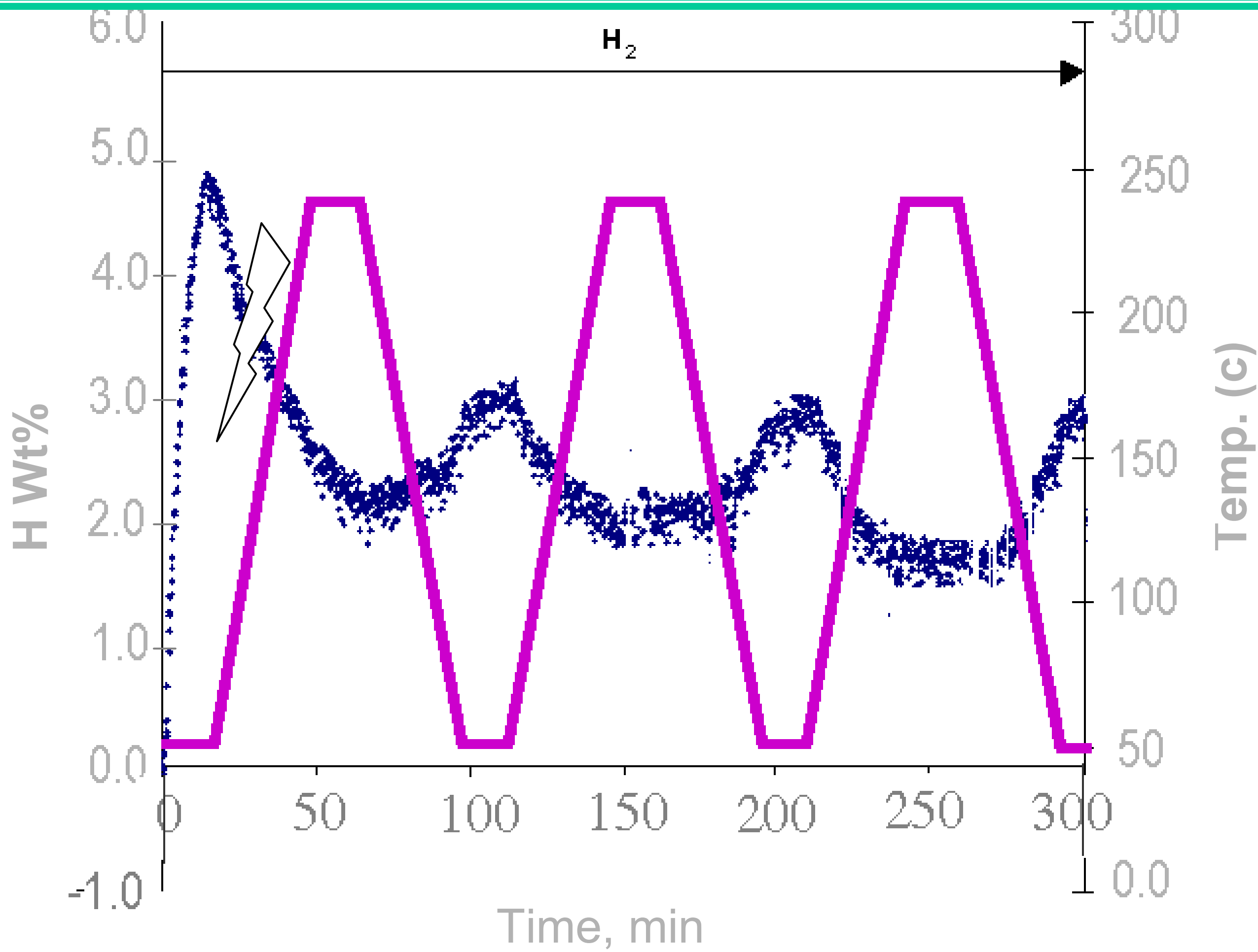
Planed Achieved Key Milestone

Consistent structure doped carbon nanotubes









Hydrogen uptake and release by doped nanotubes

Proposed Future Work

- Continue production of nanotubes with different dopants
- Determine thermodynamic characteristics of hydrogen uptake and release
- Identify the type and size of nanotubes and clusters that result in a reversible, high hydrogen capacity material (barrier)
- Tune conditions that result in a high yield of material possessing favorable characteristics
- Utilize theoretical modeling to guide the experiment
- Set up a YAG laser system for producing C-nanotubes

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Savannah River Technology Center SRTC We Put Science to Work

Leadership and Collaborations

Collaboration between the Savannah River Technology Center (SRTC) and :

- Clemson University, Dr. Apparao M. Rao,
- University of South Carolina, Dr. James Ritter

- Patent disclosure has been submitted on producing and controlling the characteristics of doped carbon nanotubes
- Effort is part of IEA
- Paper in *J. of Nanoscience and nanotechnology,*

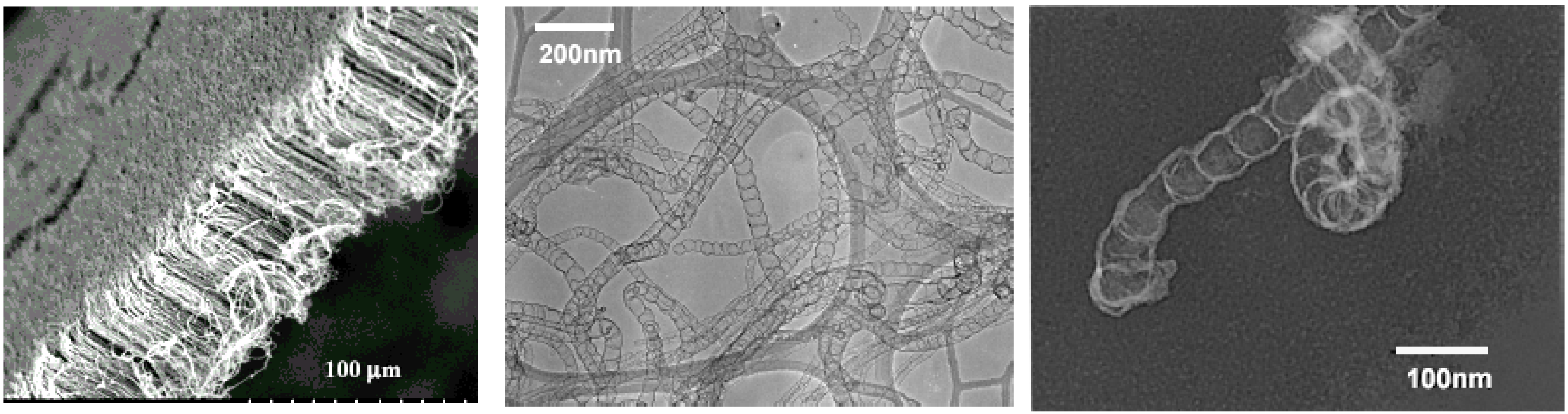
  Department of Physics and Astronomy,Clemson University, NASA Ames Research Center, Department of Materials Science and Engineering, Georgia Tech., Savannah River Technology Center

Continued work

One of our goals has been to synthesize nanotubes containing other elements such as boron or nitrogen largely due to the possibility of fabricating nanotube materials with tailored electrical and mechanical properties. *

Nitrogen Doped Carbon Nanotubes, with average nitrogen content of about 5 at. %, were synthesized

*B.Sadanadan a, T. Savage a, S. Bhattacharya a, T. Tritt a, Alan Cassell b, M. Meyyappan b, Z.R. Dai c, Z. L. Wang c, R. Zidan d and A. M. Rao a, J. nanoscience and nanotechnology accepted
"Synthesis and Thermoelectric Power of Nitrogen Doped Carbon Nanotubes"



a b c

(a)- SEM images of a film containing nitrogen-doped tubes

(b)& (c)- TEM images of the nanotubes prepared under identical conditions in the presence of melamine (($C_3H_6N_6$)

Nitrogen-doped nanotubes

- Individual nitrogen-doped nanotube exhibited a bamboo-like structure and comprised of 6-16 tube walls

- Electron Energy Loss Spectroscopy (EELS) measurements yielded an average nitrogen content of ~5 at % in the doped tubes.

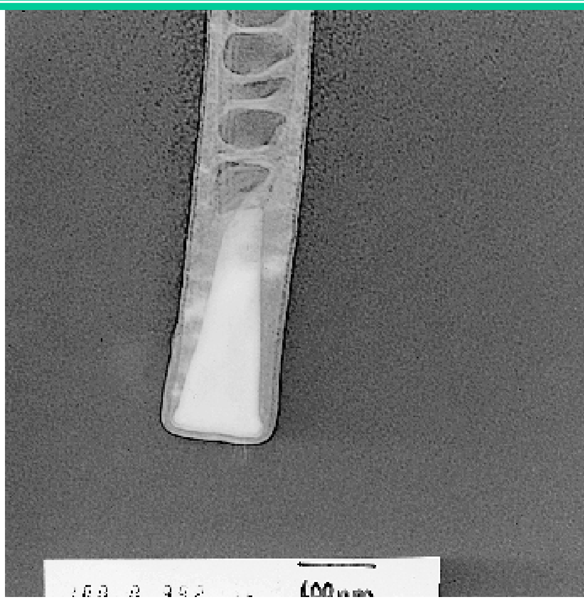
- Thermoelectric power data of nitrogen-doped tubes remained negative even after exposure to oxygen for an extended period of time suggesting that nitrogen doping of carbon nanotubes renders them *n*-type (stable electronic structure)

Model and Growth factors

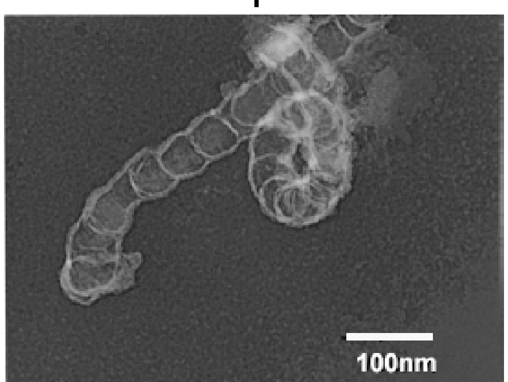
These tubes best fit Blank *et al.* model of a spheroidal catalyst particle in which the number of inner graphene layers depends on the velocity of the particle.
These inner walls terminate when the particle slides away from the graphite sheath upon sufficient accretion of stress while the outer layer is continuous.

- The size and structure of an individual bamboo-like tube is largely dependent on the velocity, size, shape, and composition of the catalyst particle.
- The growth temperature influences the nanotube morphology

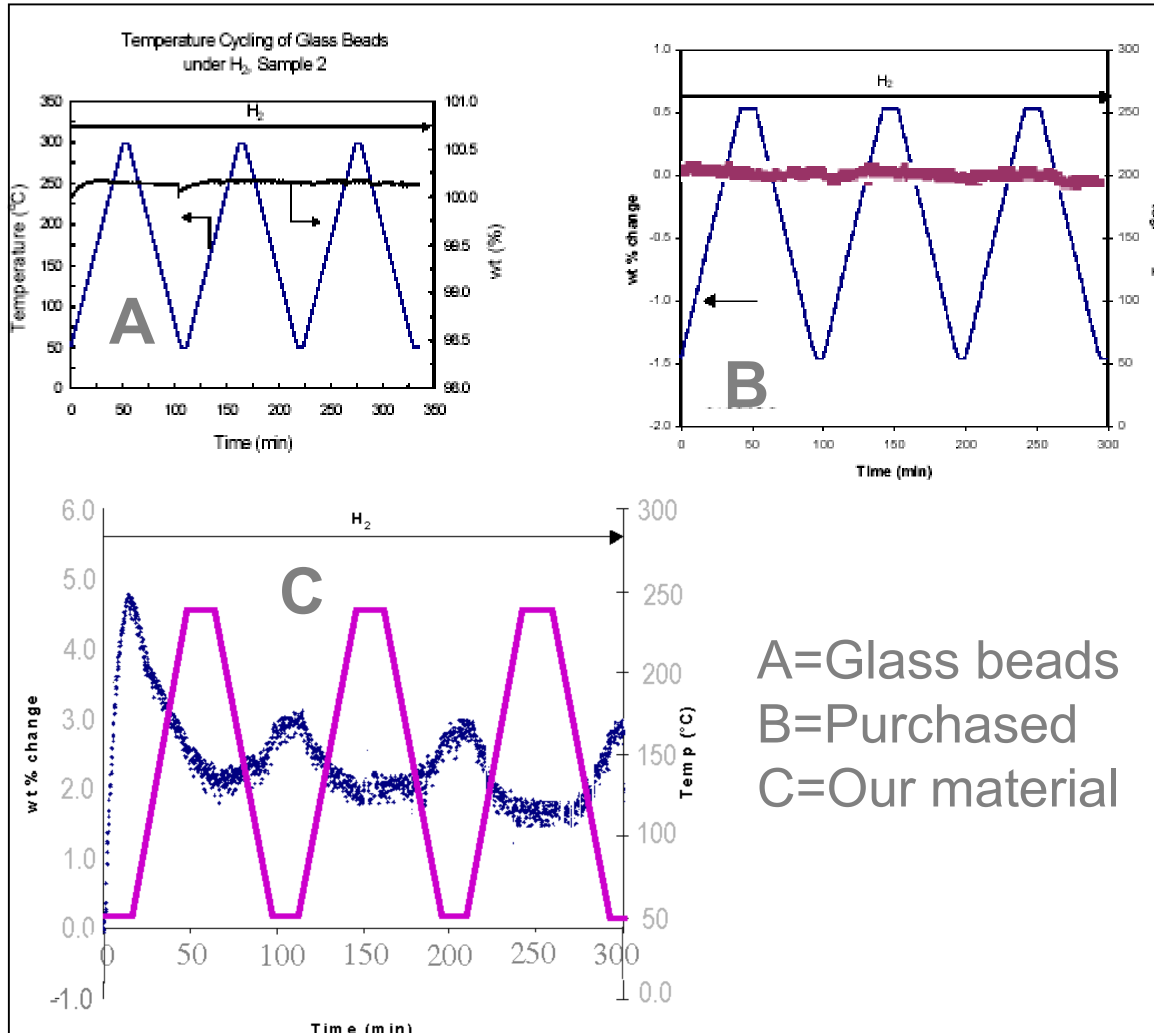
Summary



Tip of a nanotube with impeded metal particle



Nitrogen-doped tube



Conclusion

- High Risk High Reward
- Preliminary results *demonstrated* hydrogen uptake and release
- Developed a novel method of encapsulating metal, doping and controlling morphology and structure of C-nanotubes
- Further investigation of hydrogen sorption in doped C-nanotubes is needed

Reviewers 2002

- Produced large quantities of consistent structure carbon nanotubes is a good approach.
- Adopted DOE's goals for a hydrogen storage system
- Realized that neither physisorption nor chemisorption models will achieve this goal and were looking at weak covalent bond-dihydrogen as the mechanism for enhanced storage.
- Preliminary data showed only 1% wt. However their system has not been optimized and so further improvements are possible with doping.
- At the very minimum they have a model to guide their investigation. "**The Panel saw good progress and recommends continued funding**"

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