Hydrogen Storage in Carbon Nanotubes

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2003 DOE HFCIT Program Review Meeting

DOE Office of Energy Efficiency and Renewable Energy
DOE Office of Science, Division of Materials Science

Objective:

→ **Develop nanostructured carbon materials for vehicular H storage, focusing on carbon nanotubes**

- Reproducibly achieve 2005 DOE/FreedomCAR goals: 1.5 kWhr/kg (4.5 wt%) and 1.2 kWhr/L (0.036 kg H_2/L)

→ **Barriers:**

- Determine the hydrogen storage capacity of nanostructured carbon materials (Task 3)
- Develop cost-effective fabrication processes for promising materials (Task 3)
- Explore compressed gas/reversible storage material hybrid systems (Task 1)

→ **Permit Go/No-Go decision by 4th Quarter of FY 2005**

History & Problems with Activated Carbon (pre-1995)

- Coconut shell charcoal. (Kidnay and Hiza, 1967)
  Excess H of 2.15 wt% at 25 atm, 76 K. .
- "F12/350" carbon (Carpetis and Peshka, 1976)
  5.2 wt% for carbon at 41.5 atm, 65 K.
  Inverse relation between porosity and H wt%.
- Optimization (Schwartz, et al., 1980s, early '90s)
  Surface acidity, metal modification
  ~4.8 wt% at 59 atm and 87 K

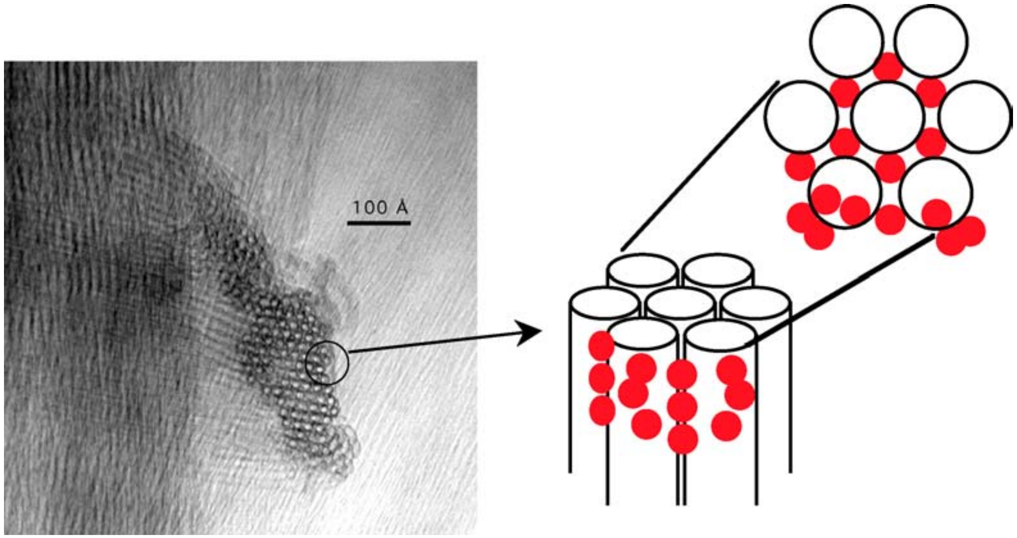
- Inaccessible volumes & heterogenous adsorption sites
- Difficult to control, study, and optimize
- Weak physisorption interactions (4-6 kJ/mol)

→ More H_2 stored in empty cylinders at T & P of interest.

A.C. Dillon and M.J. Heben, Appl. Phys. A 72, 133–142 (2001)

SWNTs: An Ideal Adsorbent for Hydrogen?

- Potential for higher binding energies, high volumetric packing, elimination of skeletal density, and maximum nanopore volume.
- SWNTs are tunable, modifiable materials, with variable electronic properties and controllable defect densities and sizes.
- Tunability offers possibility of designing P & T of operation, and capacity
- Scale-up production costs estimated to be ~ 1 $/kg



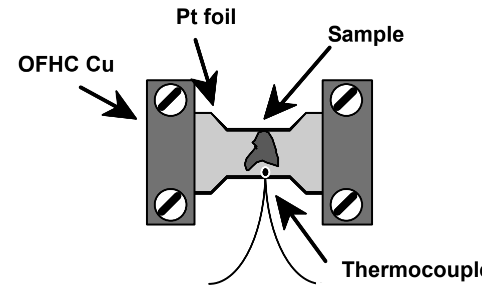
- Closed-packed crystals have densities of 1.3- 1.4 gm/cc
- 1 H:C ~ 7.7 wt%, which meets the 2005 goal
- 1 H:C in 1.3 gm/cc corresponds to ~ 0.1 kg H_2/L
- 36% of this “theoretical” maximum will meet the volumetric 2005 goal

M.J. Heben, Proc. 1993 DOE/NREL Hydrogen Program Review, 79-88, 1993.

H_2 Storage Measurement by TPD

(Temperature Programmed Desorption)

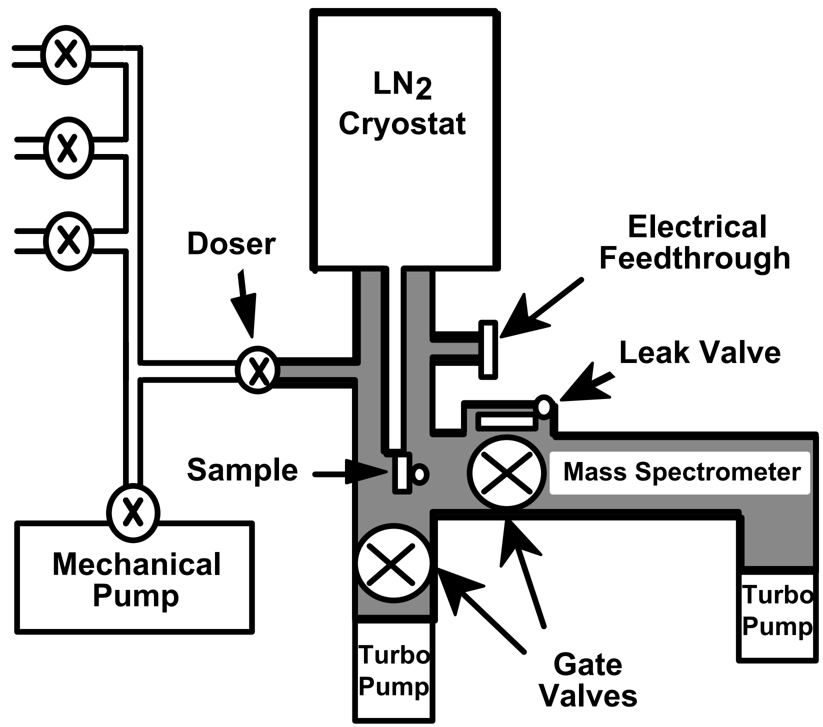
- Agrees with volumetric measurements on hydrides
- Water & gas purity detected by mass spectroscopy
- Small amounts of H are easily measured
- Cross calibration with three different standards



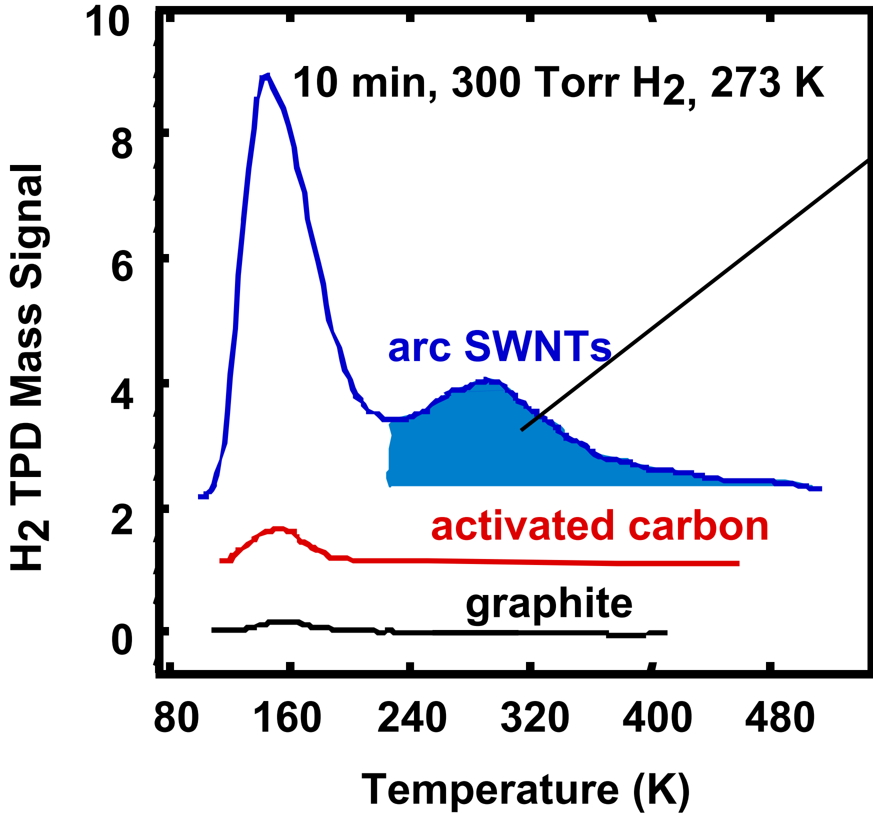
1 wt%H on 1 mg = 5 μgm H_2
≈ ΔP ~ 25 mtorr in 3 L

Capabilities:
- 90 to 1500 K
- 5 X 10^{-9} to 1000 torr
- Mass Spectra (0 - 300 amu)

1 mg samples reproducibly weighed with Mettler-Toledo UMT2 balance



Room Temperature Adsorption on Arc SWNTS



- After degassing in vacuum
- Not associated with catalytic metal particles
- Integrated H_2 ~0.01 wt% of total sample weight, between 5 and 10 wt% on SWNT basis
- 19.6 kJ/mol binding energy, higher than expectations for physical adsorption

A.C. Dillon, K.M. Jones, T.A.Bekkedahl, C.H. Kiang, D.S. Bethune, & M.J. Heben, Nature (386) 377, 1997.

6.5 -7 wt% H_2 on Ultrasonically Cut Samples

Laser-generated tubes are less-defective and require aggressive cutting techniques

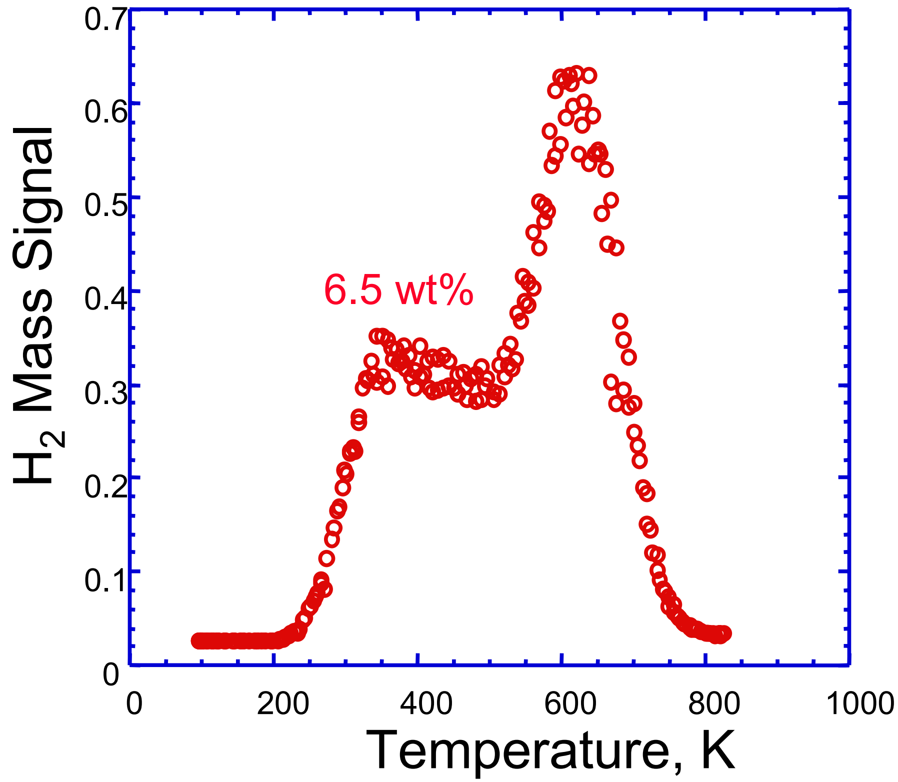
6.5 wt% H on total sample
Sample contains 26 wt% Ti-6Al-4V alloy (TGA)
Ti-6Al-4V alloy fraction stores < 3 wt%
Conclusion: 7 Wt% H stored on carbon fraction

Sonication:
16 hrs.
4 M HNO_3
50 W/cm^2

RT dose:

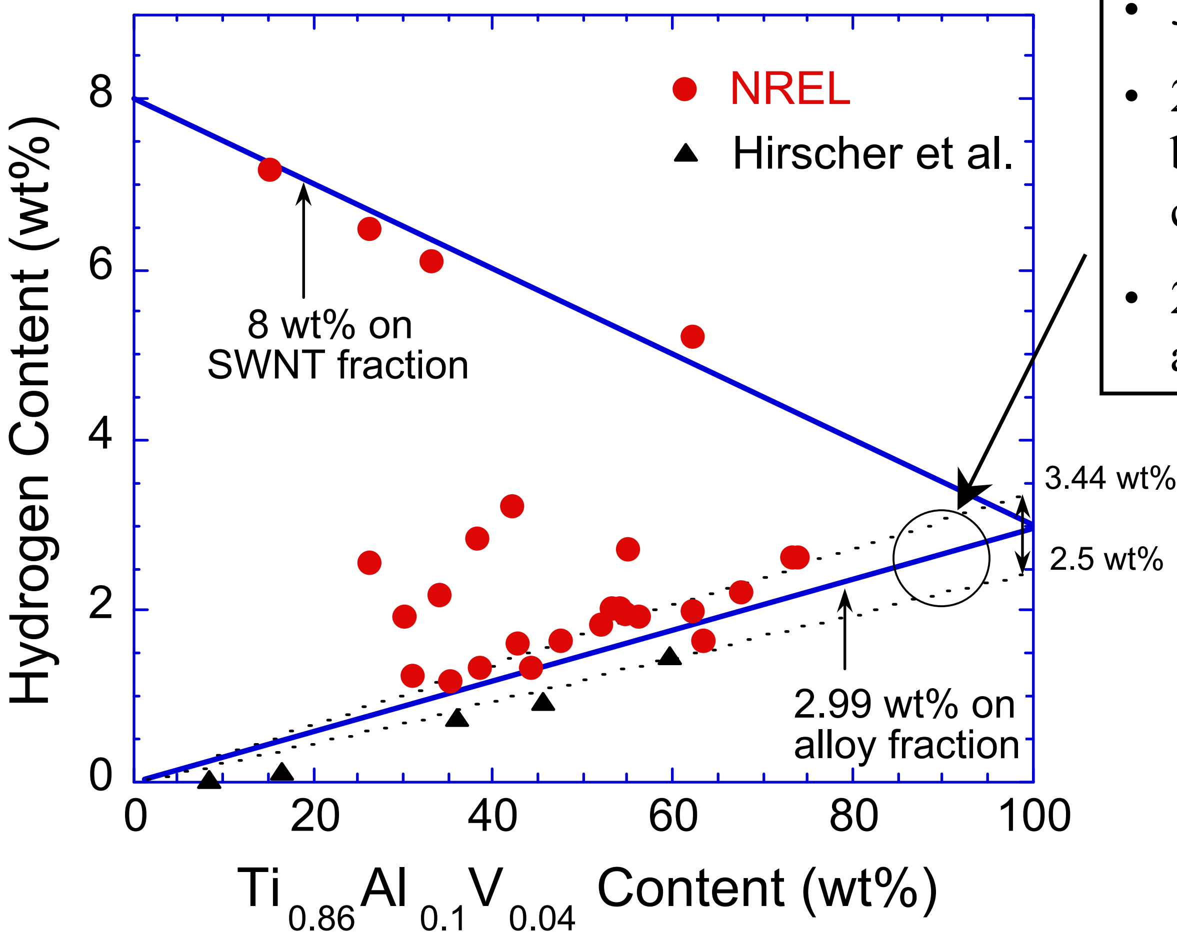
500 torr

Cool to 130 K prior to evacuation



Sample Prep Yields Scattered Results

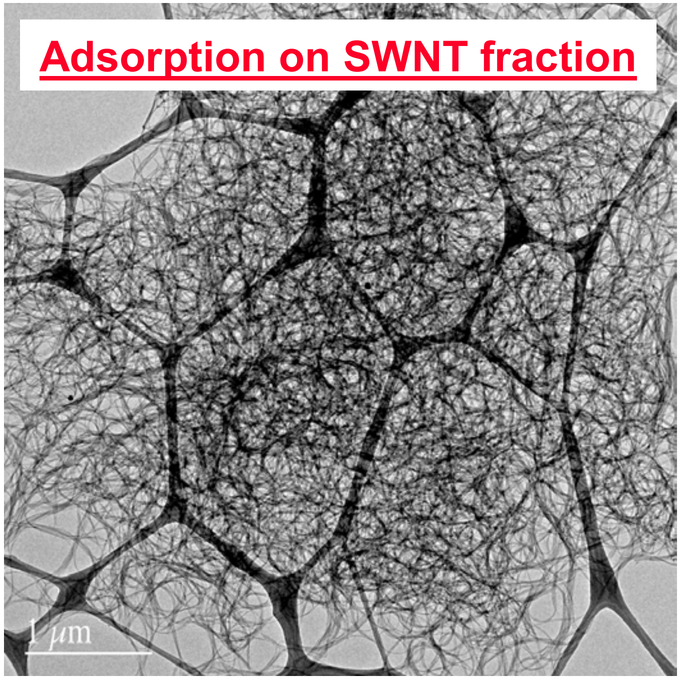
- Any data above metal hydride uptake is due to adsorption on tubes.
- ~ 50% of the data presented here shows significant SWNT uptake, up to 8 wt%.
- All of the Hirscher data falls below expectations for even alloy adsorption.

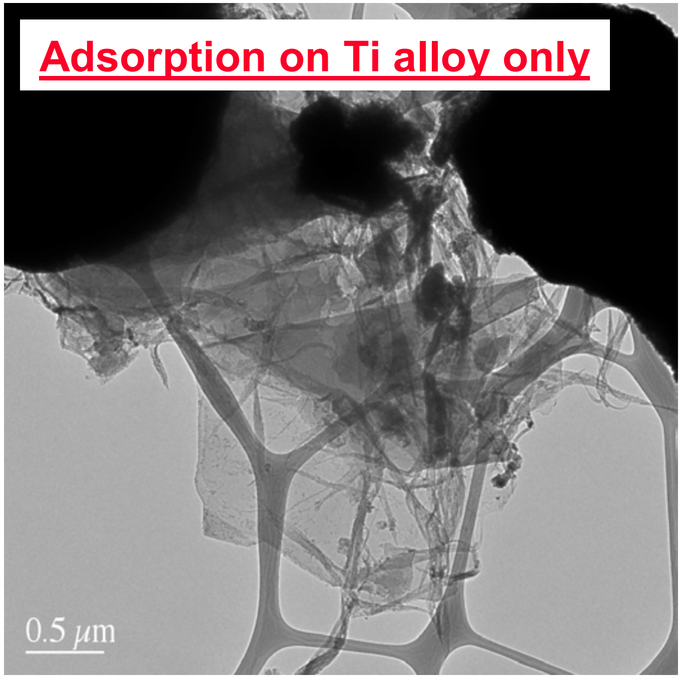


- 3.44 wt% for Ti portion to TiH_2
- 2.99 wt% on commercial alloy by volumetric method, consistent with literature.
- 2.5 wt% on probe-generated alloy by volumetric and TPD

Why is Current SWNT Activation Inconsistent?

Sonication produces differing degrees of cutting, amounts of metal, and metal particle sizes, in differing degrees of intimate contact with SWNTs, even with careful control of external parameters time such as sonication power, acid concentration, hydrodynamics.





Storage Results on Nanocarbons Vary Widely

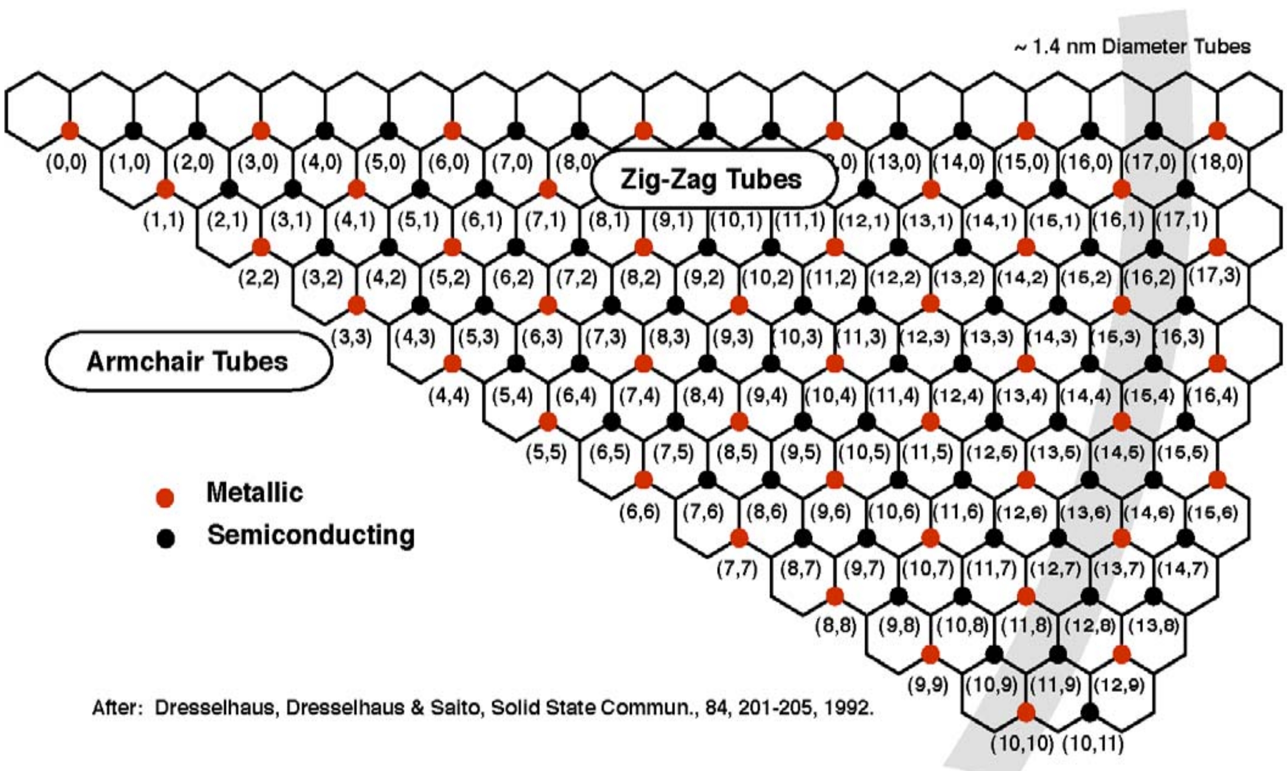
>10 wt%

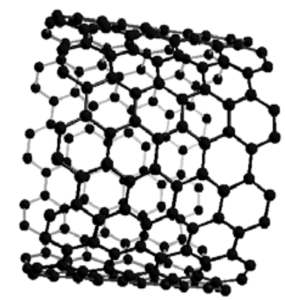
Material	Density wt%	Temp (K)	Pressure (MPa)	Reference	Year
GNFs (herring bone)	67.55	RT	11.35	Chambers	1998
GNFs (platelet)	53.68	RT	11.35	Chambers	1998
Li-MWNTs	20	~473-673	0.1	Chen	1999
K-MWNTs	14	< 313	0.1	Chen	1999
GNFs (tubular)	11.26	RT	11.35	Chambers	1998
CNFs	~10	RT	10.1	Fan	1999
Li/K-GNTs (SWNT)	~10	RT	8-12	Gupta	2000
GNFs	~10	RT	8-12	Gupta	2000
SWNTs (lo purity)	5-10	273	0.04	Dillon	1997
SWNTs (hi purity)	8.25	80	7.18	Ye	1999
CN nanobells	8	573	0.1	Bai	2001
Nano graphite	7.4	RT	1	Orimo	2000
SWNTs (hi p + Ti alloy)	6-7	~300-700	0.07	Dillon	2000
GNFs	6.5	RT	~12	Browning	2000
CNFs	~5	RT	10.1	Cheng	2000
MWNTs	~5	RT	~10	Zhu	2000
SWNTs (hi p + Ti alloy)	3.5-4.5	~300-600	0.07	Dillon	1999
SWNTs (50% purity)	4.2	RT	10.1	Liu	1999
Li-MWNTs	~2.5	~473-673	0.1	Yang	2000
SWNT (50% purity)	~2	RT	echem	Nutzenadel	1999
K-MWNTs	~1.8	< 313	0.1	Yang	2000
(9,9) array	1.8	77	10	Wang	1999
MWNTs	< 1	RT	echem	Beguin	2000
CNF	0.1-0.7	RT	0.1-10.5	Poirier	2001
(9,9) array	0.5	RT	10	Wang	1999
SWNTs	~0.1	300-520	0.1	Hirscher	2000
Various	< 0.1	RT	3.5	Tibbets	2001
SWNT (+ Ti alloy)	0	RT	0.08	Hirscher	2001

< 1 wt%

Variability Compounded by Differences in Materials

- *Only recently have methods been developed to determine the identities of tubes in a given sample (Bachilo, et al., Science, p2362, Dec. 2002)*
- *Purities and properties vary widely, especially from commercial suppliers*

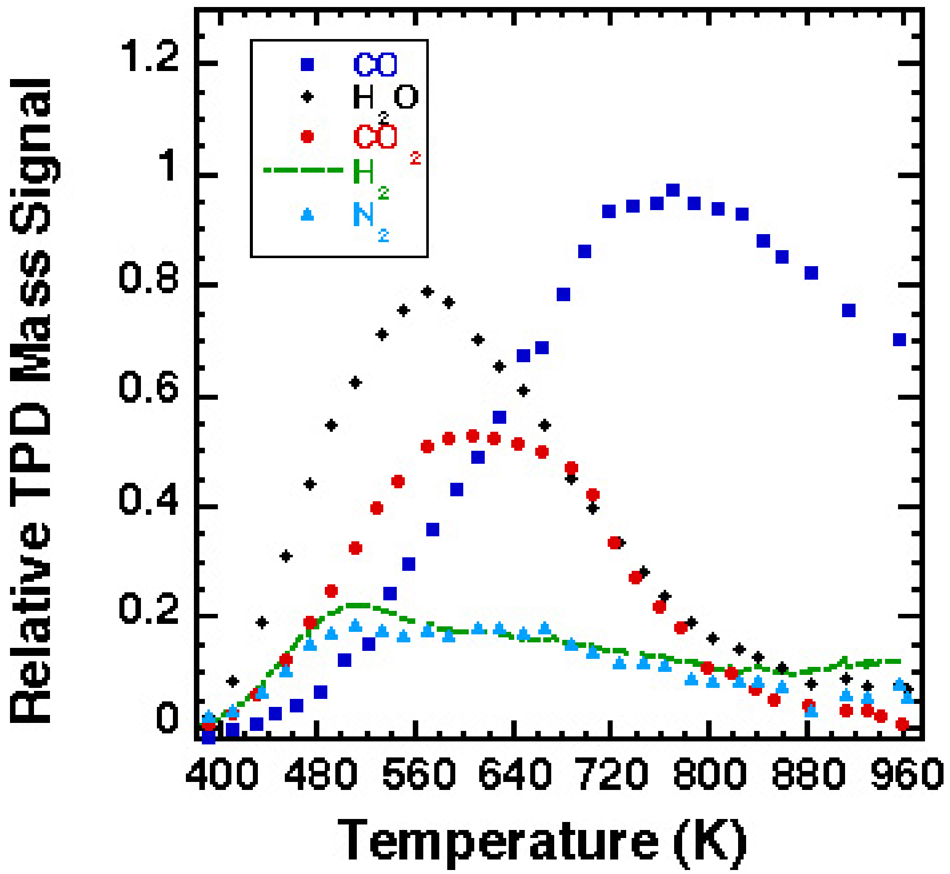




(10,10) - metallic

(17,0) - semiconductor

In Most Published Work, Samples are not Cleaned in Vacuum by Degassing



A.C. Dillon, M.D. Landry, J.D. Webb, K.M. Jones and M.J. Heben
Proceedings of the Electrochemical Society, Vol. 97-4, pp. 916-929, (1997).

What is the Mechanism?

- Ti, and other metals, may assist in the addition of H either via thermal effects due to immediate contact, or by a catalytic effect
- Raman and thermopower experiments at NREL offer evidence for partial electron transfer from SWNT to H_2.
- Sp^2 bonded carbons have sp^3-like character due to curvature of tubes
  H. Cheng, et al., JACS 123, 5845 (2001); Kostov, et al., PRL 89, 146105-1(2002).
- Emerging literature on carbon / metal Hybrids

  Mechanical milling of Mg and graphite lead to enhanced physical and electrochemical properties for H adsorption.

  e.g. Imamura et al., Int. J. Hydrogen Energy **25** (2000) p. 837.

  US patent publication 2002/0096048A1 (Cooper & Pez)

  "….carbon-metal hybrid materials…display an H_2 adsorption capacity that is greater than the sum of the capacities of the hybrid's individual components…"

SWNT materials may only be a special case, offering an opportunity for optimization / study through structural control.

Time-line from Beginning

- 1993 — Introduced concept
- 1994 — MWNT microbalance @ 82 K
- 1995 — TPD on arc-discharge SWNTs
- 1996 — Surface chemistry of arc SWNTs; synthesis of laser materials
- 1997 — binding energies w arc SWNTs; Nature publication
- 1998 — chemical cutting of laser SWNTs
- 1999 — hi-purity materials; ultrasonic cutting/alloy introduction; 4.5 wt%
- 2000 — 6.5 wt%; mechanistic studies Raman / IR neutrons
- 2001 — attempted scale-up; CVD growth; beginnings of controversy
- 2002 — multiple calibrations; alloy contribution; defect and cutting analysis with Raman

Going Forward: Carbon Materials Working Group

- Bring community together to establish characterization and measurement protocols for round-robin testing and verification, discuss and vet findings

  NREL, Air Products, Caltech, HRL Laboratories, ORNL, Phillips / Conoco, U. Pittsburgh, U. Pennsylvania, Max Planck Institute, U. Quebec - Trois Rivieres, NETL, Southwest Research Institute

- 1st meeting at Argonne H_2 storage Workshop, 8/15/2002
- 2nd meeting via telecon, 1/5/03
- Worked with C. Ahn to establish plan to purify (by J. Vajo) 10 grams of commercially available material for distribution to group
- Materials will be measured at NETL, UQTR, ORNL, NREL, MPI, Air Products, HRL Labs by agreed upon protocols
- Next meeting to occur this week

Improving Understanding of Activation Process

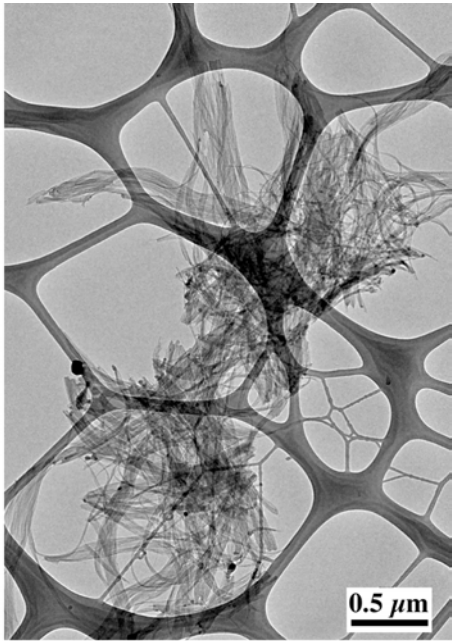
Limit the number of independent variables under study

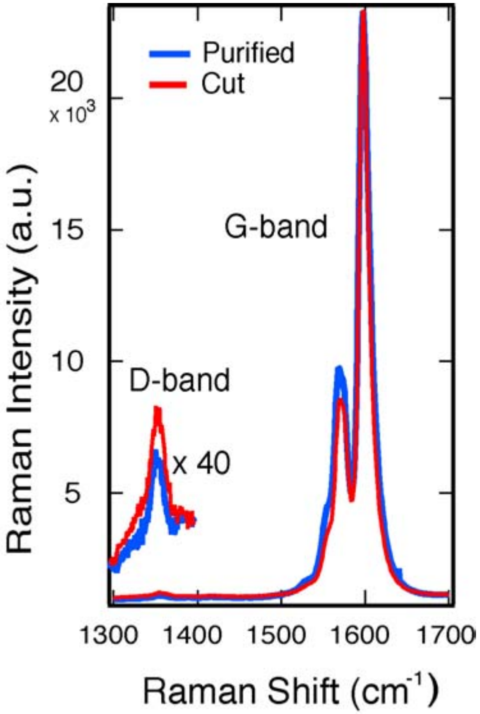
- Control tube types (chirality and diameter) during synthesis
  Chemical vapor deposition, laser growth, hot-wire deposition
- Measure tube types and defect densities
  Infrared photoluminescence excitation and Raman spectroscopies
- Develop cutting methods than do not introduce metal species
  D-band spectroscopy can assess the degree of cutting
- Introduce metals in known quantities, sizes, and locations
  Vapor transport, electrodeposition, chemical treatments, evaporation, mechanical methods

Approach to Cutting and Ti Incorporation with TiO_2

- Carbo-reduction of TiO_2 is possible at elevated temperatures and produces cutting, but the following reaction is favored:

  $TiO_2 + 3C \rightarrow TiC + 2\,CO$: Ti metal is not produced





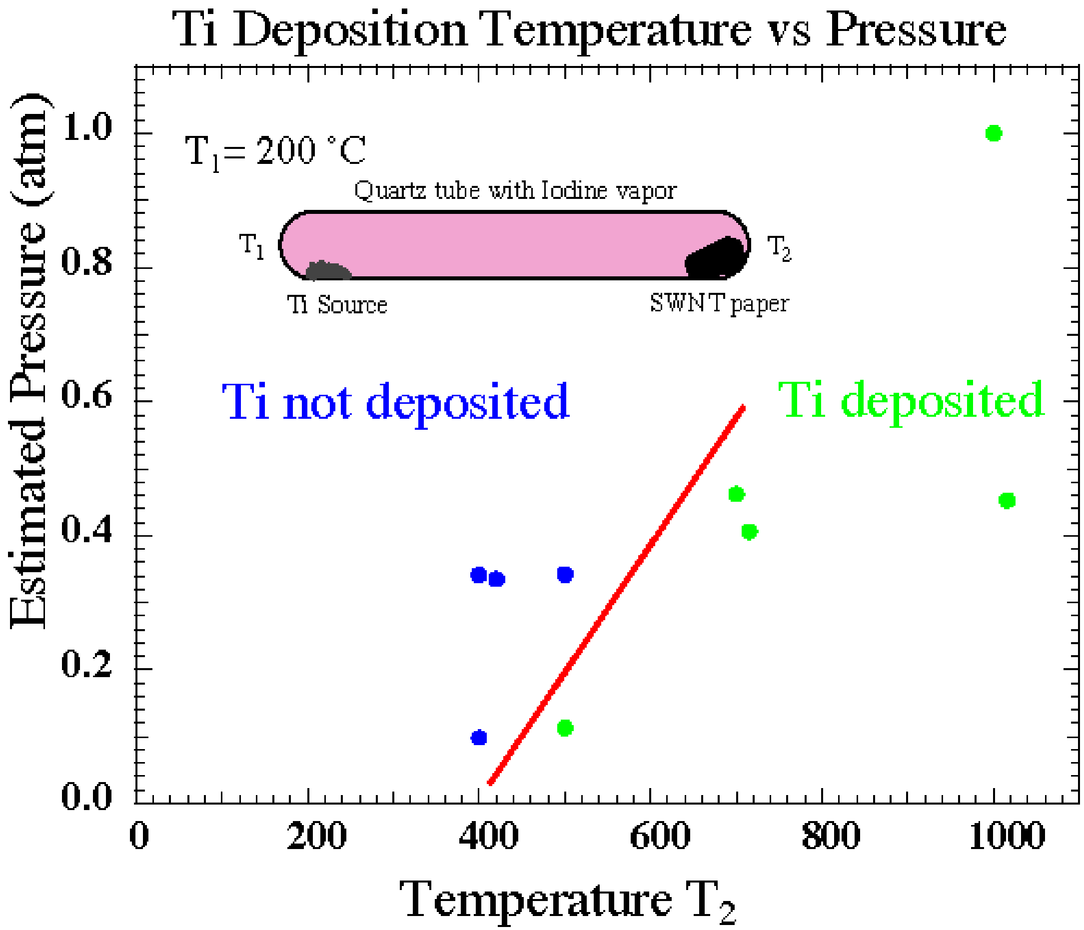
Degree of cutting can be followed by observing an increase in the D/G intensity ratio

Lower Temperature Routes to Ti Incorporation

Using well known Iodine transport reaction: $Ti + 2I_2 \leftrightarrow TiI_4$

- TiC favored over Ti & C at all temps
- Kinetics inhibit formation at low temps
- At typical transport conditions, TiC will form

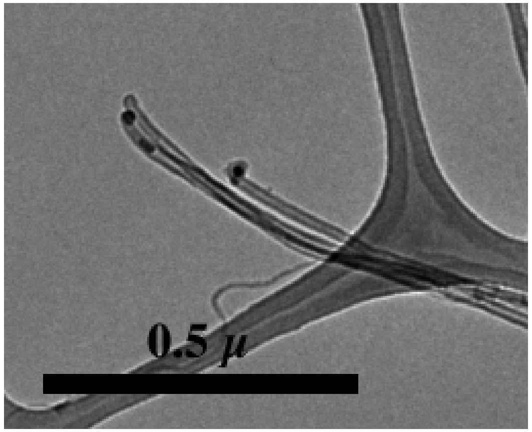
Ti metal has been incorporated by evaporation, but H adsorption has not yet been fully evaluated

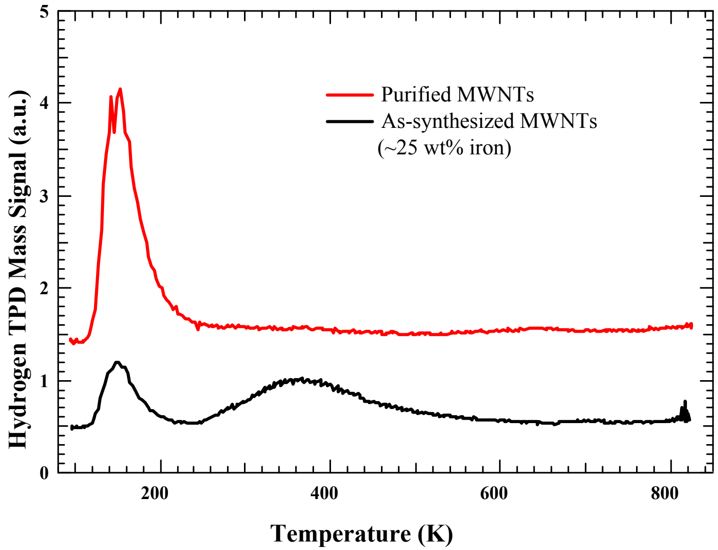


Placing Metal Particles in Specific Locations

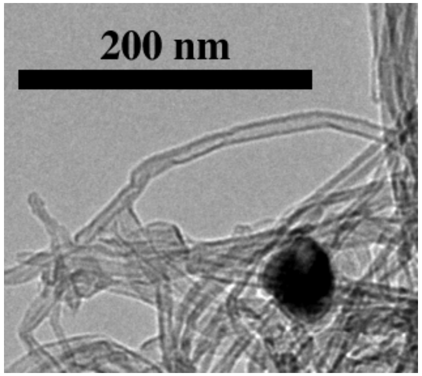
Hot-wire growth of multi-walled nanotubes with metals at tips

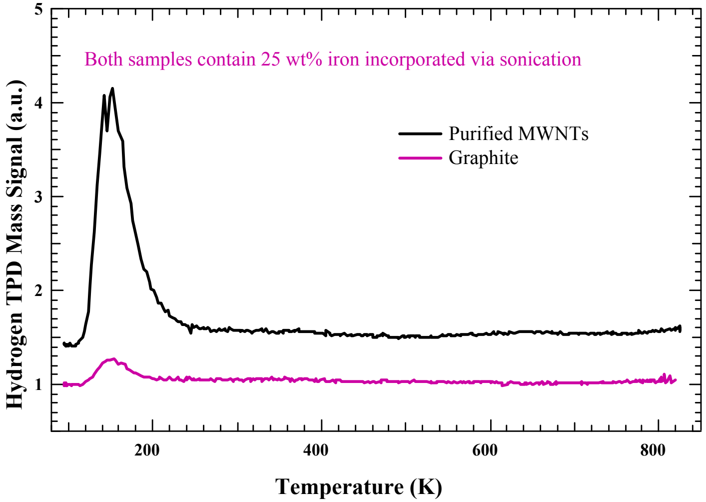
As grown, ~10-30 nm Fe particles at tube tips





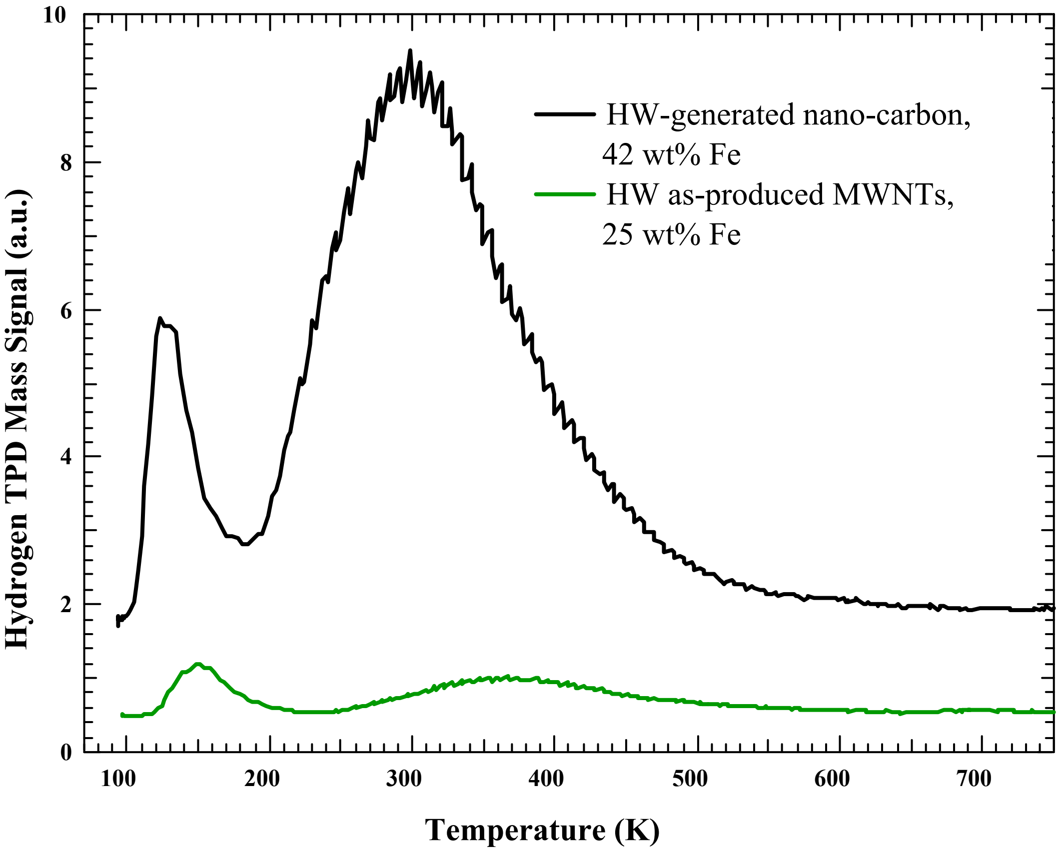
Fe particles added via sonication.

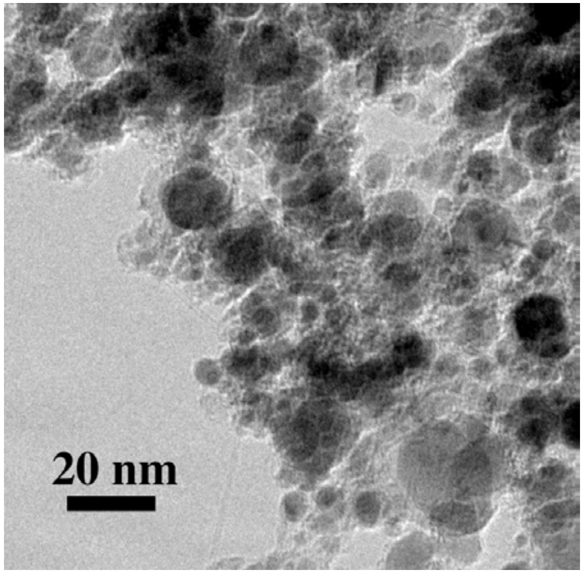




Hydrogen Storage in Nanocarbon Materials

HWCVD-generated Nano-carbon with Fe nano-particles



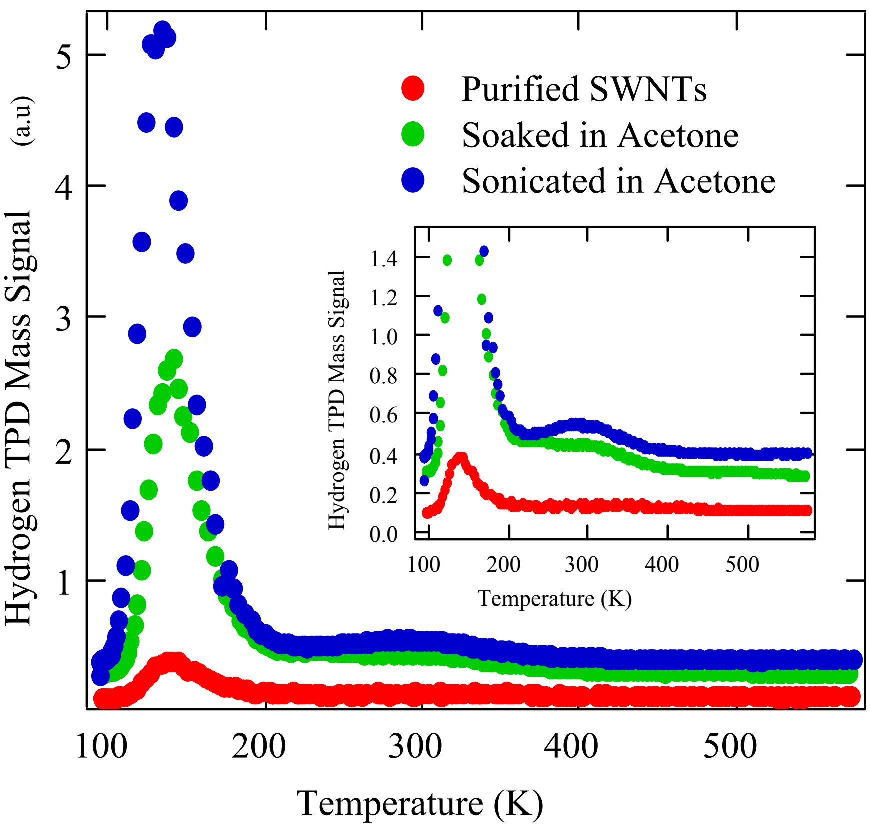


500 torr dose at room temperature

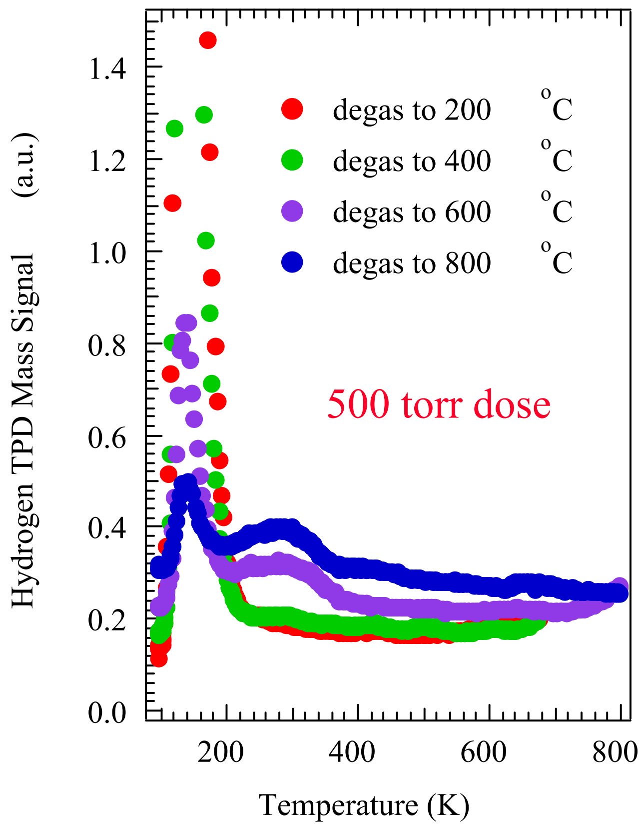
Effect of Bundle Delamination

Incorporation of acetone lowers the degas temperature needed to activated ambient hydrogen adsorption

Degas to 550 ˚C, Sonication is 1 min.



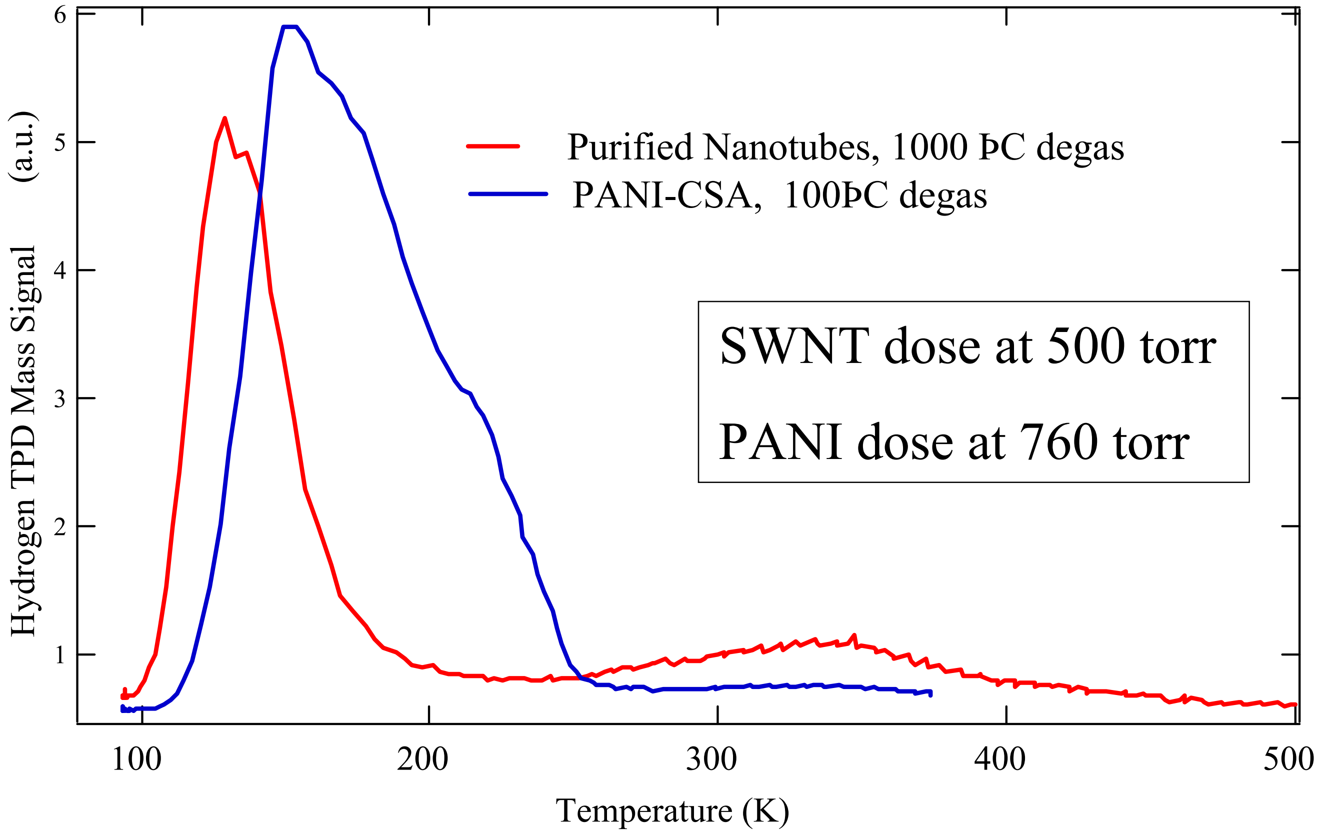
Soaked in Acetone 10 min.



Comparison of SWNTs to Conducting Polymers

Conducting polaniline samples from MacDiarmid Group (U. Penn/ UT Dallas)

Investigating the report By Cho et al. of 8 wt% storage in PANI



PANI-CSA (Camphorsulfonic Acid) one phase w/Triton X100 and stirring doped 031703

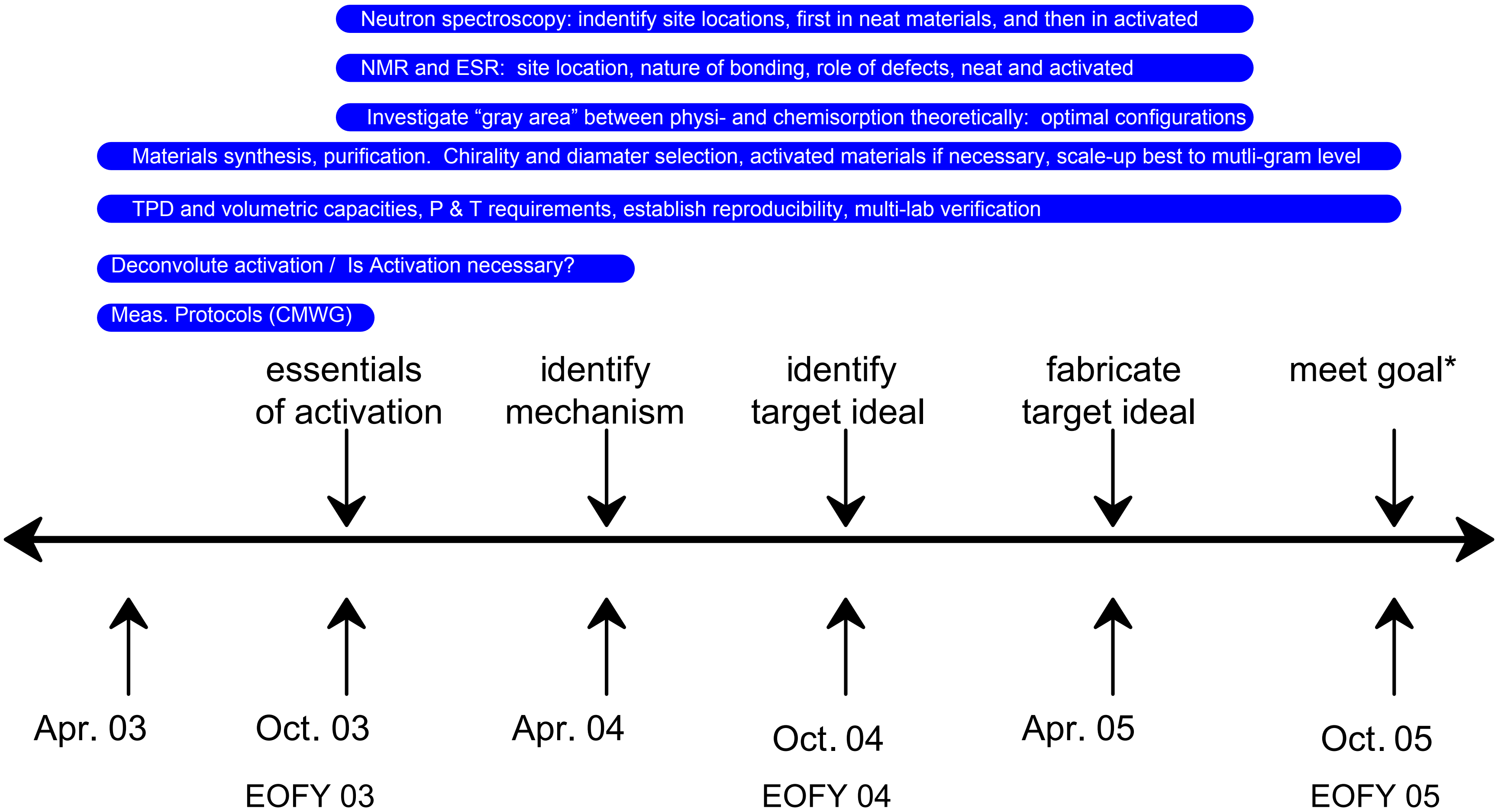
Other Interactions / Output

- Office of Science, Division of Materials Science: CO_2 sequestration
  - Gas transport, separation, purification in SWNT-based membranes

    CVD synthesis, dispersion in polymers, competitive adsorption & transport, impurity effects
- Office of Science, Division of Chemical Science: Nanotechnology initiative
  - Managing charge and energy transfer between semiconductor quantum dots with SWNTs.

    Cutting SWNTs, chirality and diameter selection, derivitization
- Five peer reviewed publications this year
- Several invited talks
- 1 graduate student from Colorado School of Mines (Gilbert)
- Five undergraduates researchers at NREL this summer
- Mechanical milling of nanotubes with hydrides shows that desorption temperatures can be modified

Time-line for Project



*1.5 kWhr/kg (4.5 wt%) and 1.2 kWhr/L (0.036 kg H_2/L)