# Hydrogen Storage in Metal-Modified Single-Walled Carbon Nanotubes (start 9/15/01)

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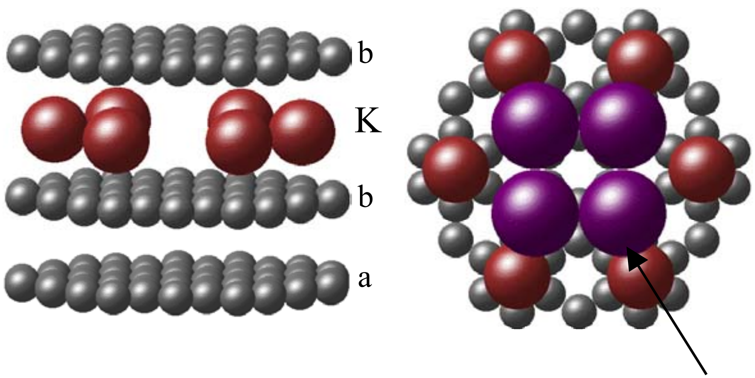
## Relevance and Objectives:

- Hydrogen physisorption for reversible solid-state material storage systems.
- Investigate effect of potassium (alkal-metal) additions to single-walled nanotubes on $H_2$ adsorption.
  Potassium intercalated graphite long known to absorb $H_2$
  (both physisorption, as in $KC_{24}$ and chemisorption, as in $KC_8$).
- Increase effective surface area of single-walled nanotubes through intercalation.
- Understand charge redistribution mechanisms, improve temperature/pressure behavior.

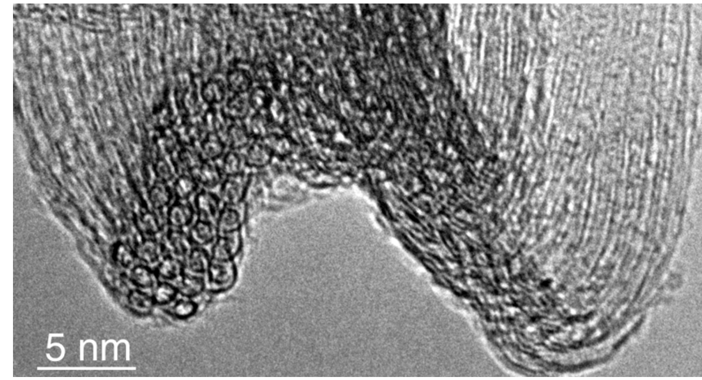
# Rationale for approach

Stage 2, K-intercalated graphite ($KC_{24}$) accommodates $H_2$ through both chemisorption[1], 0.1 wt% at RT and physisorption[2] at 1.2 wt% absorption at 77K, <1 atm.

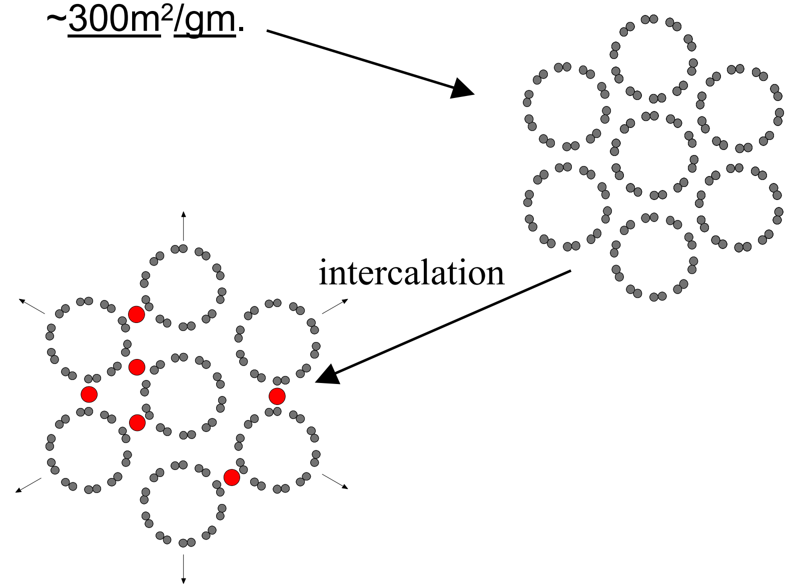



[1] M. Colin and A. Herold, CR Acad. Sci. Paris, Serie C, 269, 1302 (1969).
[2] K. Watanabe, M. Soma, T. Onishi and K Tamaru, Nature 233, 160 (1971).

Normal activated carbon dependent on surface area (# of available adsorption sites) to accommodate $H_2$. (Chahine criterion, 1 wt%/500m$^2$) at 77K.




(10,10) SWNT theoretical outer surface area 1638m$^2$/gm, inner surface area of 978m$^2$/gm (based on van der Waals diameters). But SWNTs form ropes, limiting surface area to ~<u>300m$^2$/gm</u>.

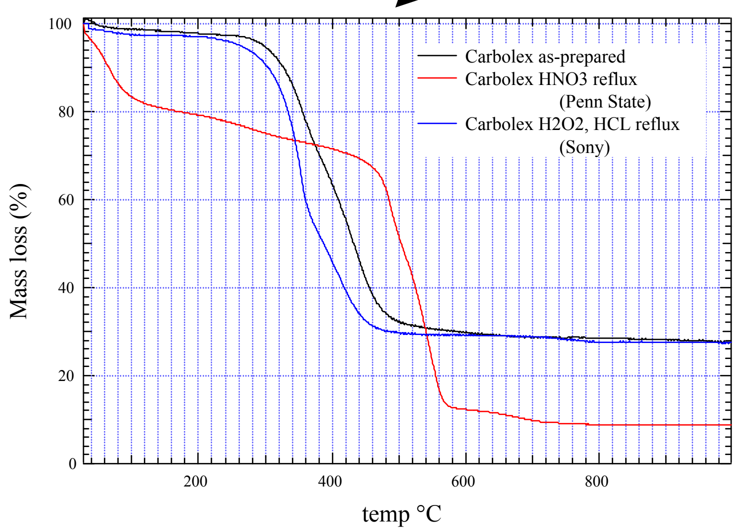


# Project timeline

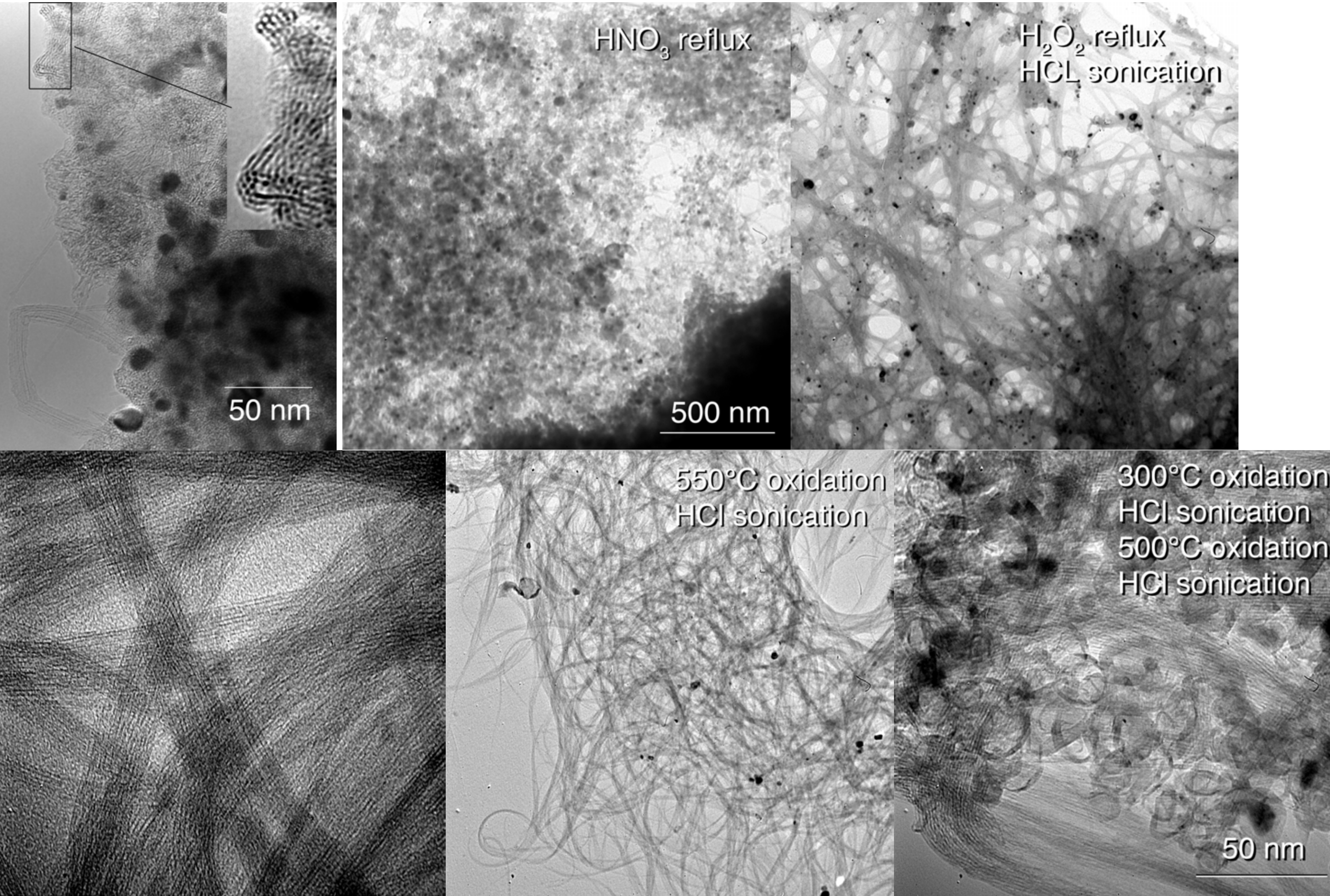
| | | FY2002 | | | | 2003 |
|---|---|---|---|---|---|---|
| Task Designation/Milestone | | Qtr1 | Qtr2 | Qtr3 | Qtr4 | Qtr1 |
| Single Walled Nanotube Procurement | | ♦ | | | | |
| Characterization of as-received material | | ♦ | | | | |
| Intercalation of carbons | | ♦ | ◊ | | | |
| Characterization of intercalated single walled nanotubes | | | | ★ | | |
| Gravimetric and volumetric dens evaluation | | | | | ☆ | |

Only commercial vendor of laser-oven material is Carbolex
-sells as-prepared nanotubes only

Commercial Madagascar graphite provided by Superior Graphite

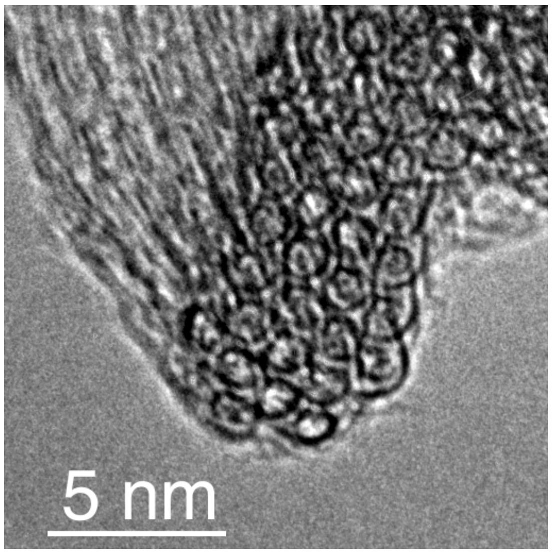


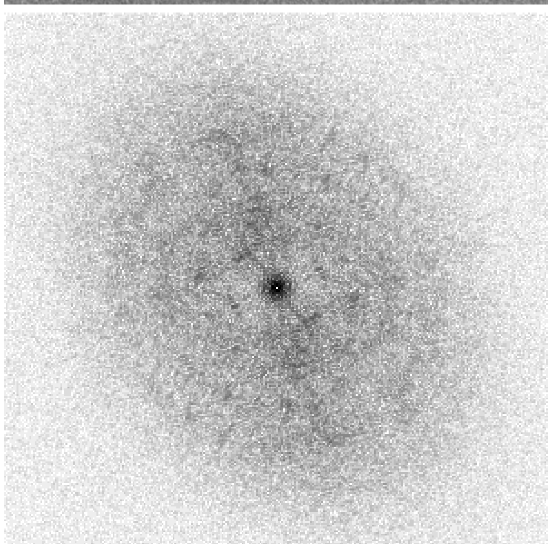
# Accomplishments: Purification, microstructural evolution (Carbolex)



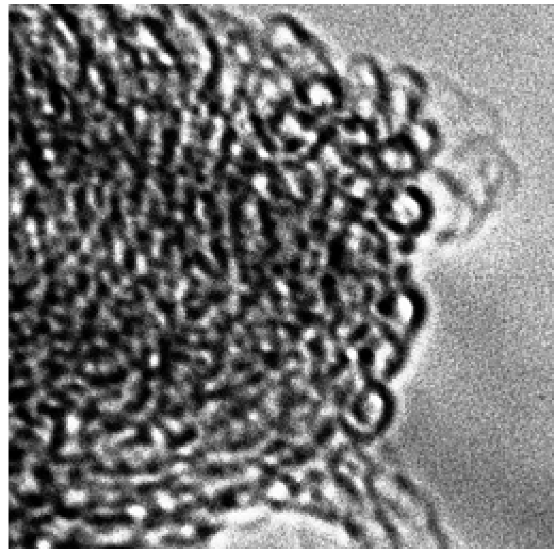
# Accomplishments/Progress: Nanotube analysis Transmission Electron Microscopy

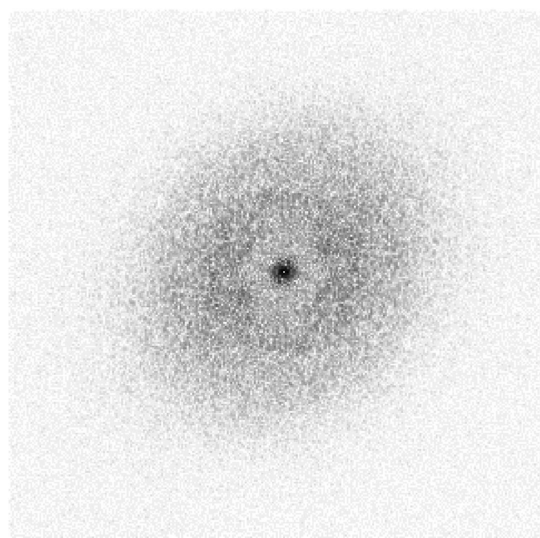
“Bucky” paper, laser-oven, Rinzler prepared



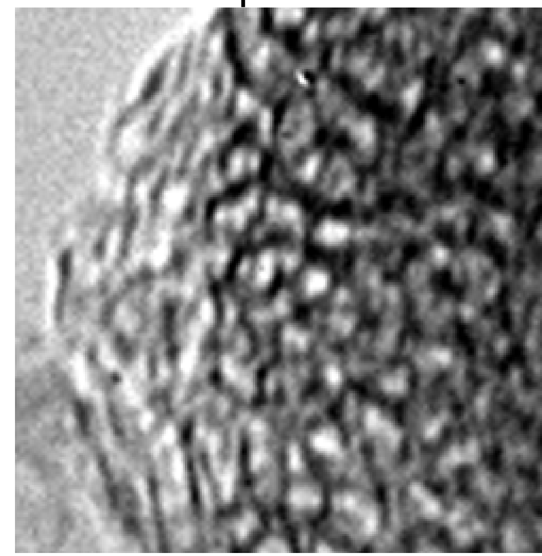



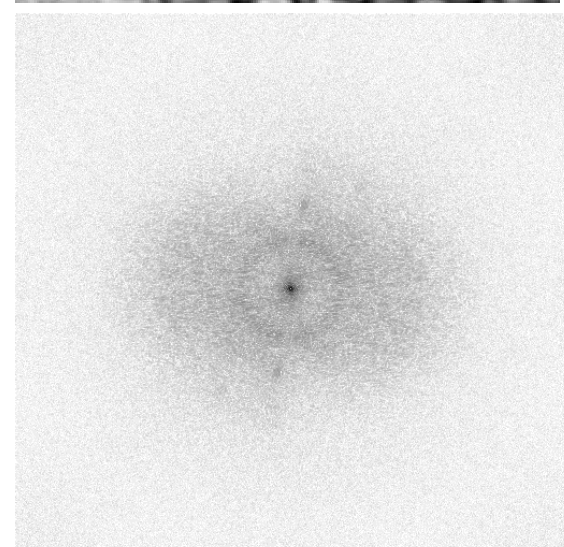
Carbon Nanotechnologies Hipco material (HRL purified)





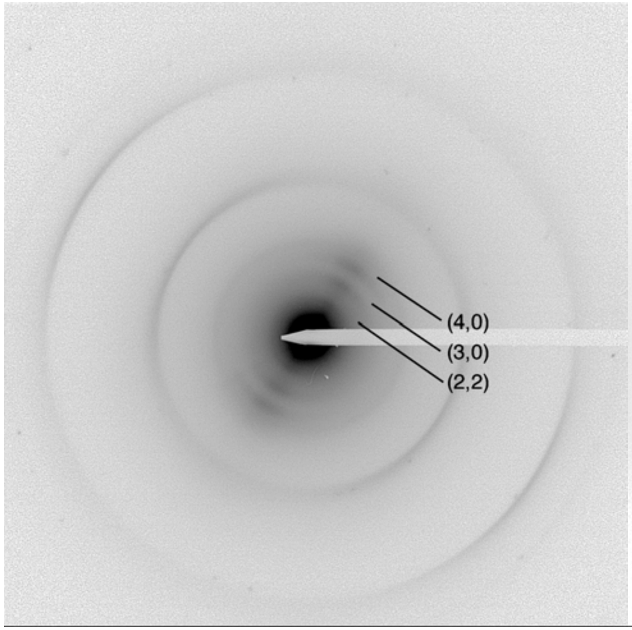
Carbolex laser-oven Caltech purified



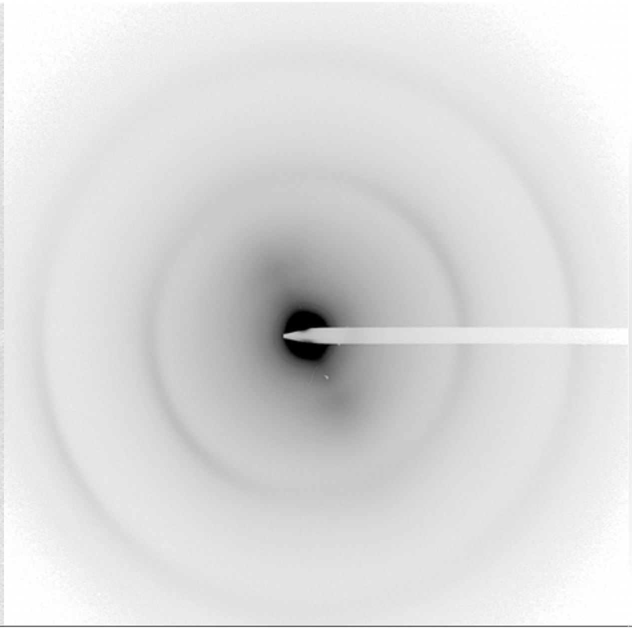


# Accomplishments/Progress: Nanotube analysis Transmission Electron Microscopy (diffraction)

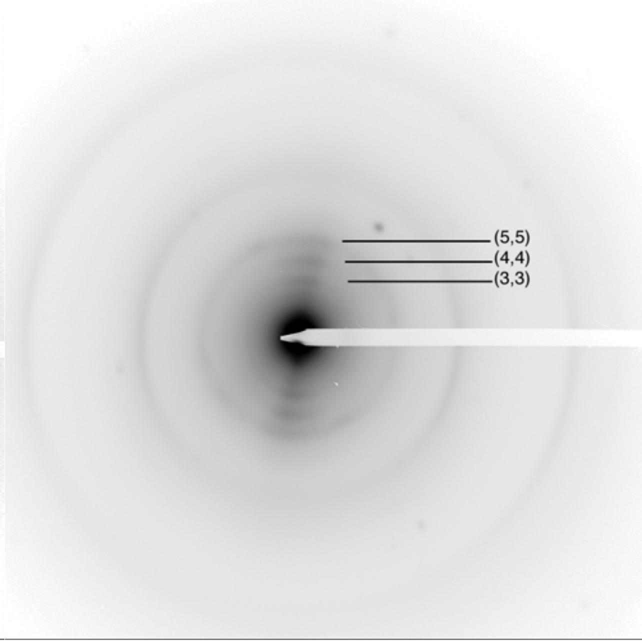
"Bucky" paper, laser-oven, Rinzler prepared




Carbon Nanotechnologies Hipco material (HRL purified)



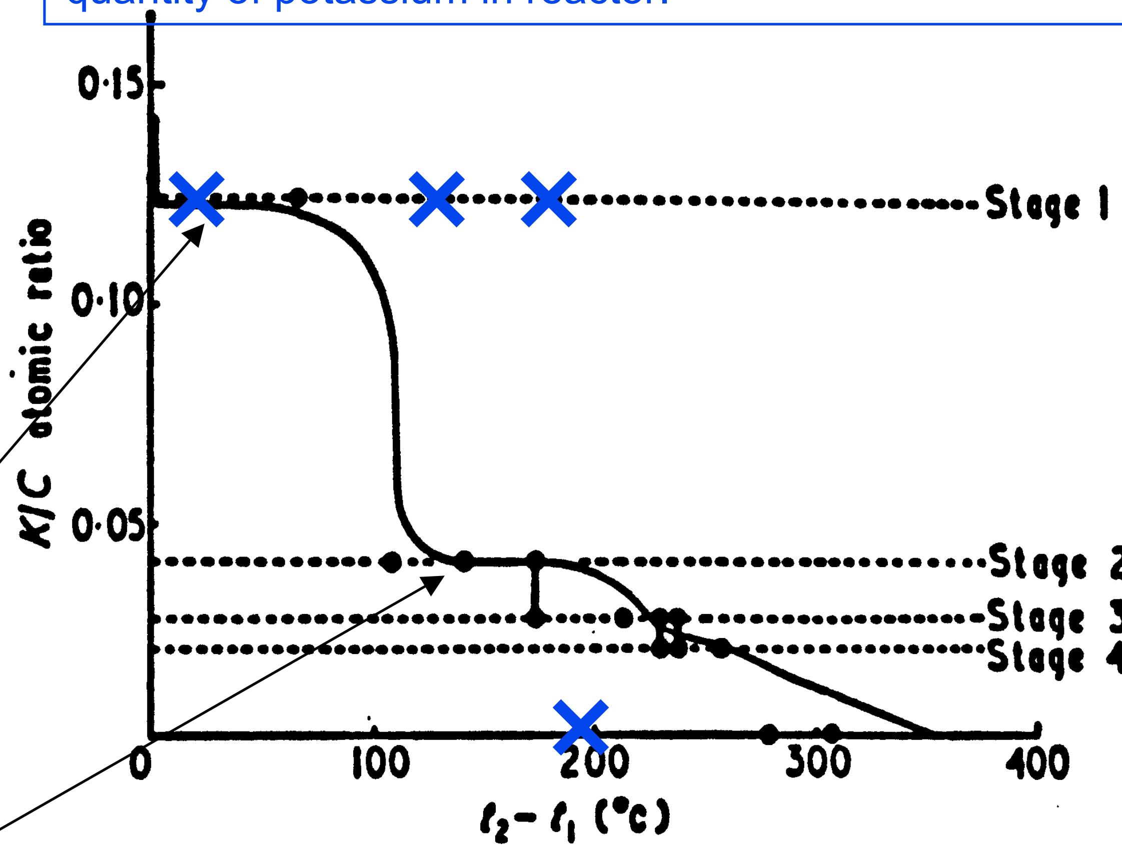
Carbolex laser-oven Caltech purified



# Accomplishments: Potassium intercalation synthesis routes for graphite and single walled nanotubes

Potassium interaction using any 0<Δt<170°C yields stoichiometry ~$KC_8$

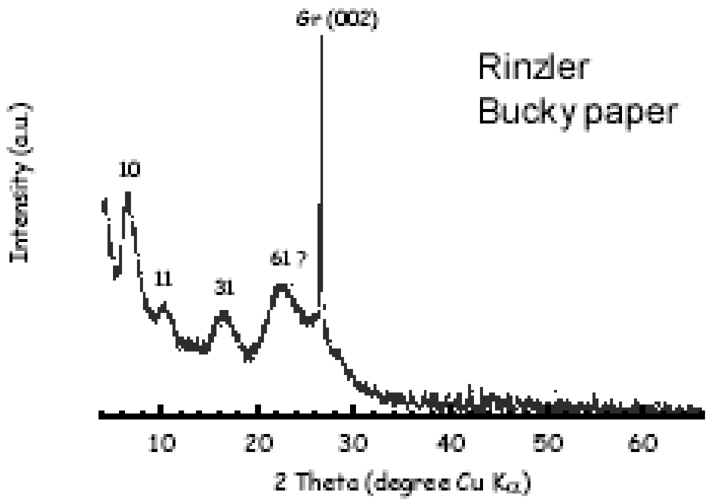
Solution for limiting nanotube stoichiometry is limiting quantity of potassium in reactor.



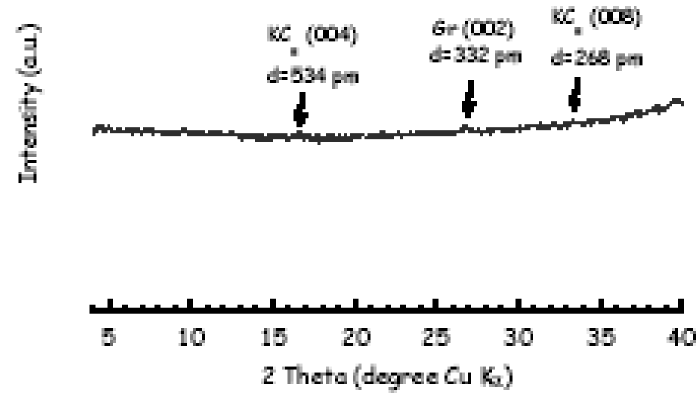

$KC_8$ $KC_{24}$

D. E. Nixon and G. S. Parry, J. Phys. D, 1, 291 (1968).

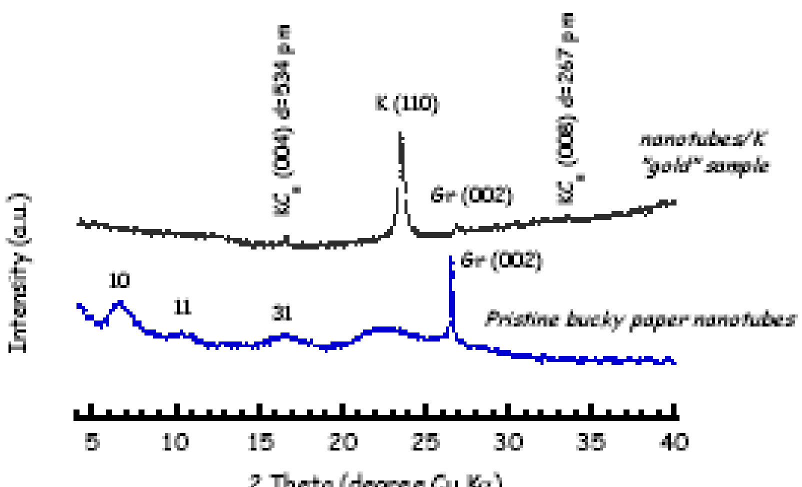
# Accomplishments/Progress: Nanotube analysis, X-ray diffractometry



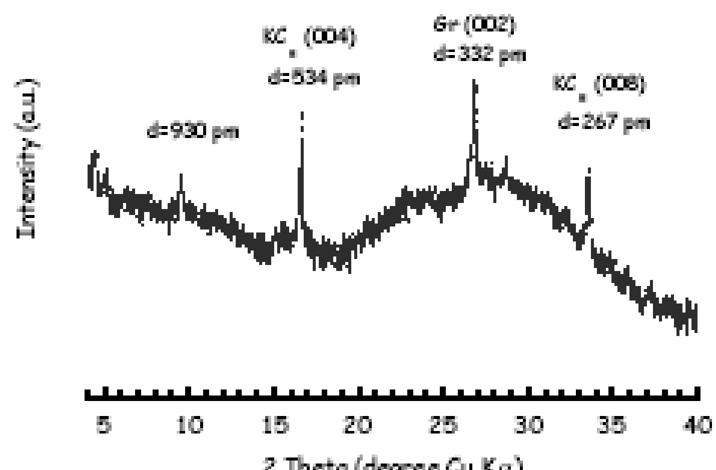

200 C, 190 C reactor temps.



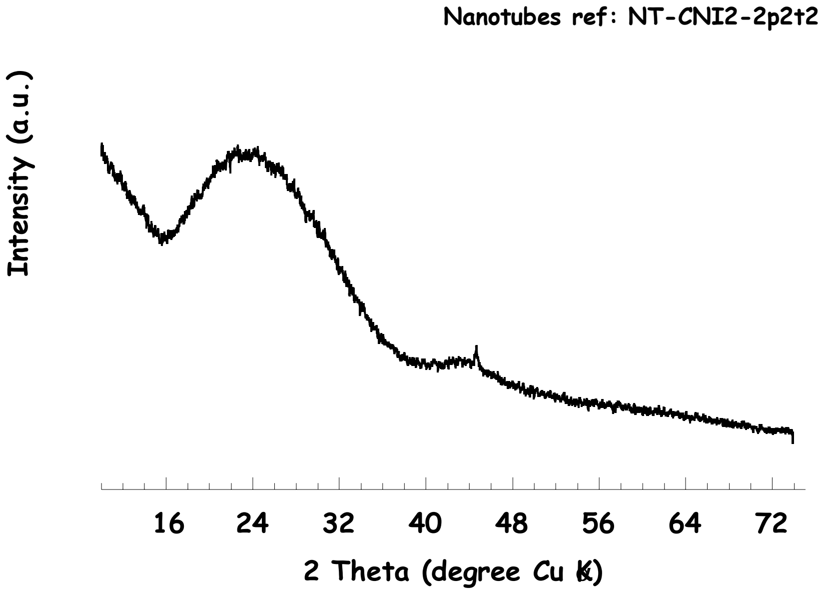

Condensed K reaction product 250 C

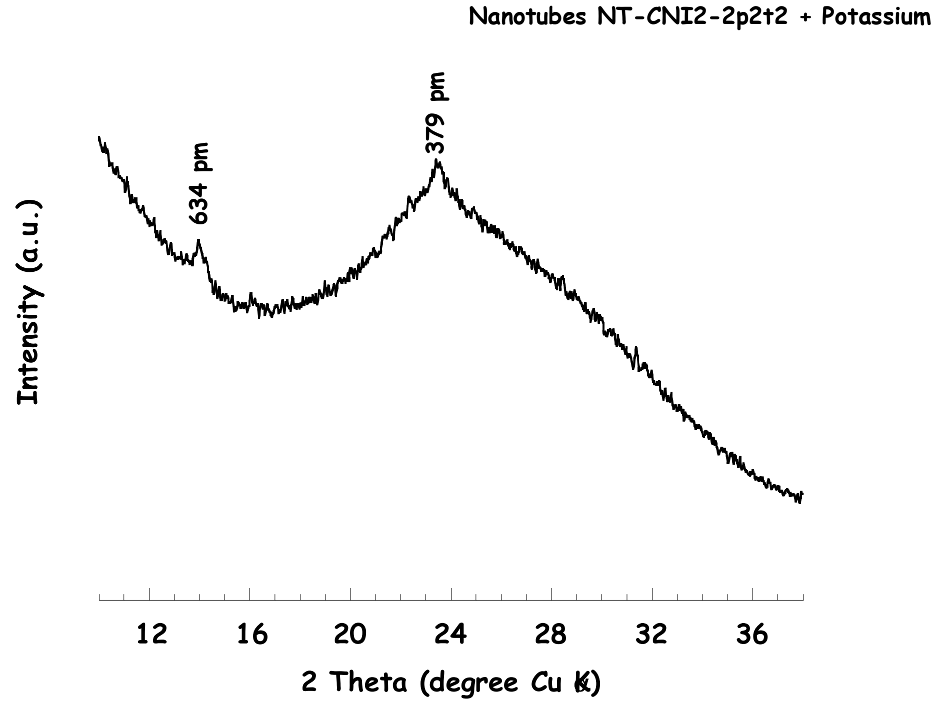



"KC19" 241 C, 248 C reverse temp.



# Accomplishments/Progress: Nanotube analysis, X-ray diffractometry (cont'd)



# Single point adsorption isotherm results

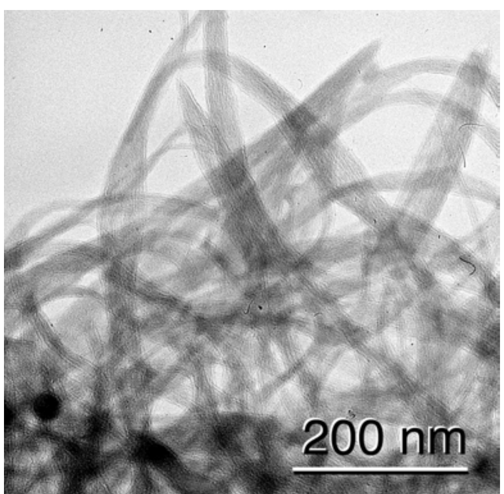
## From $KC_9$ intercalated "Hipco" nanotube

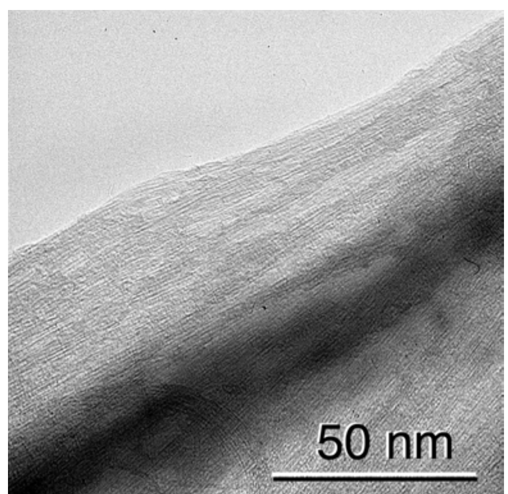
Initial introduction of $H_2$ at room temperature highly exothermic (dissociation reaction resulting in KH formation).
Assuming density = 2.0 g/cm$^3$, Capacity(25°C, 70 bar) = 0.69 wt%
Capacity (77 K, 50 bar) = 1.05 wt%
Assuming density = 2.5 g/cm3, Capacity(25°C, 70 bar) = 0.63 wt%
Capacity(77 K, 50 bar) = 0.90 wt%

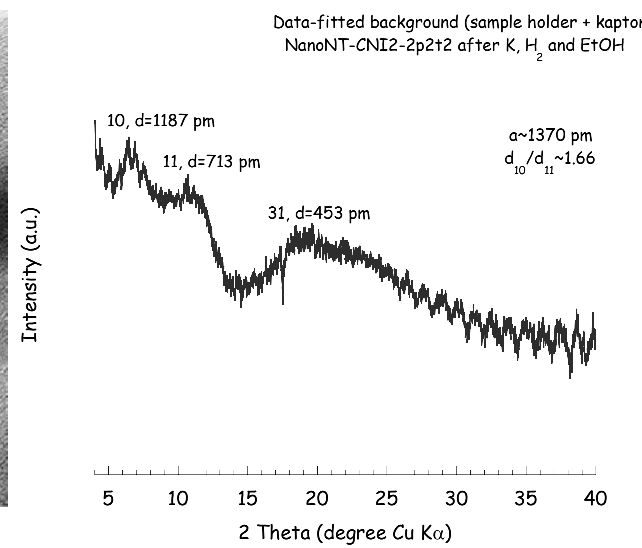
## From restored $KC_9$ "Hipco" nanotube after K removal

0.35% at 25°C
2.36% at 77 K (90% of the as-purified results).

## No unzipping from K interaction with nanotubes, (as is seen with Li)



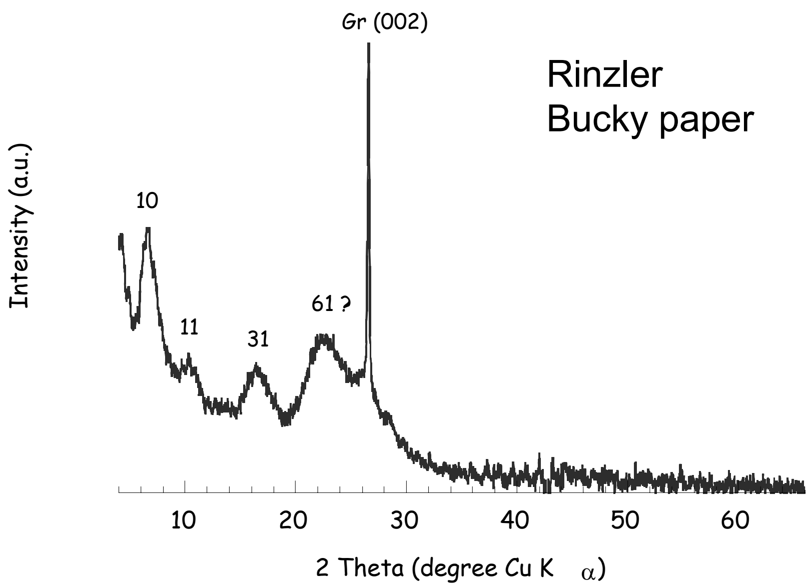
# Single point adsorption isotherm results (cont'd)

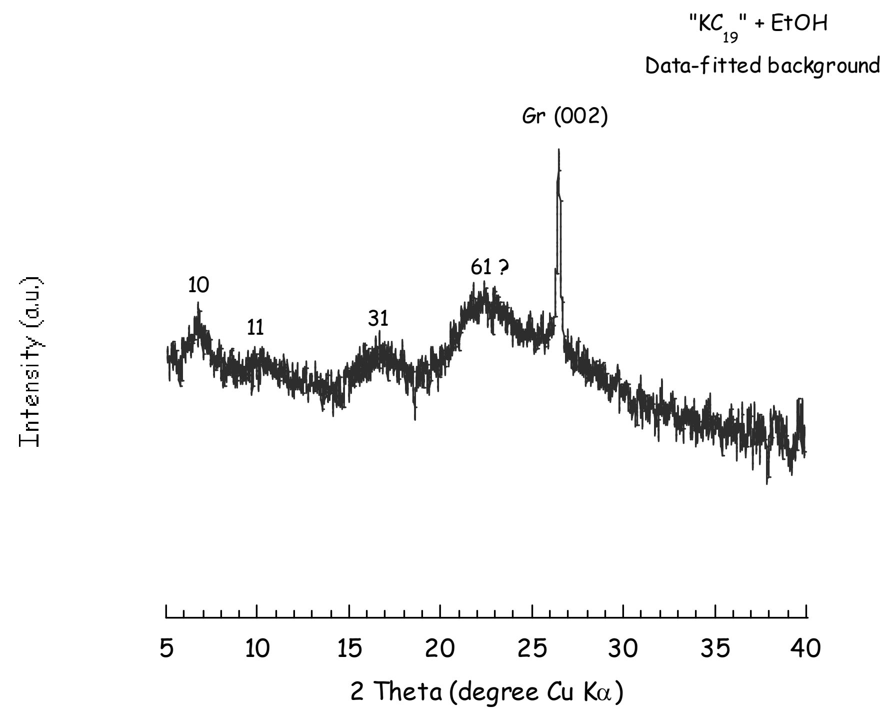
## From $KC_{19}$ intercalated "Bucky" nanotube

2.0 g/cm³, capacity (25°C, 70 bar) = 0.06-0.11 w %
0.54-0.69 wt % at 77 K (depending on the density).

similar to results from Tubes@Rice nanotubes after recovery from the surfactant suspension purification to remove the catalyst.

## No unzipping from K interaction with nanotubes.



# Collaborations

J. J. Vajo, HRL Laboratories, LLC
Sievert's volumetric hydrogen sorption measurements (single point adsorption isotherms).
T. Proffen and D. W. Brown, Los Alamos National Laboratory
Neutron Diffraction measurements, pair distribution function analysis.
Igor Barsukov, Superior Graphite
Purified and milled Madagascar graphite

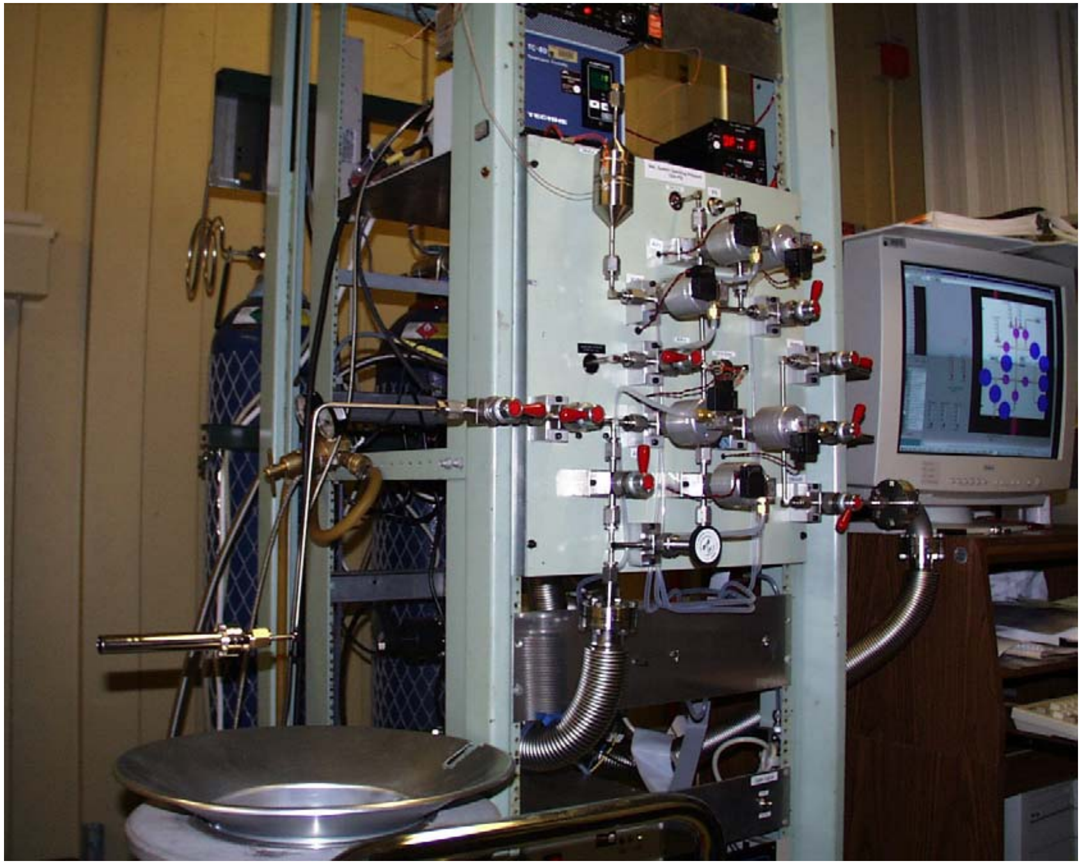
(David Eaglesham, Lawrence Livermore National Laboratory
Nanotube synthesis)

# Jet Propulsion Laboratory Sieverts apparatus (R. C. Bowman, Jr.)

• New Sieverts apparatus being completed at JPL for use on Caltech campus.

• Originally intended for He cryo-cooler studies on carbons for flight detector applications (Christian Lindensmith).

Construction completion underway by Dean Johnson and Phil Wilson (JPL).



# Plans/Future Milestones:

- Refinement of Intercalation procedures
  more structure analysis
- Electron Spin Resonance experiments to study charge transfer
- Sieverts apparatus set-up, testing and complete isotherm measurements
- Study other carbons (activated carbons, nanofibers).

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HRL Laboratories:
John Vajo

Jet Propulsion Laboratory
Robert C. Bowman, Jr.