Aug 20th, 3:15 PM - 3:45 PM

Hydrogen Fuel Cells and Storage Technology (FCAST) Project

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Hydrogen Fuel Cells and Storage Technology (FCAST) Project

Clemens Heske (lead PI-experiment)

Balakrishnan Naduvalath (lead PI-theory)

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University of Nevada, Las Vegas

Project manager: Robert F. D. Perret

UNLV Research Foundation

sponsored by the DOE EERE Hydrogen Research Program through the UNLV Research Foundation, contract number *DE-FG36-05GO85028*

FCAST partners

UNLV Experiment

- Chulsung Bae – Chemistry
- Andrew Cornelius – Physics
- B.J. Das - Electrical Engineering
- David Hatchett – Chemistry
- Clemens Heske – Chemistry
- Wayne Stolte, Oliver Hemmers, Dennis Lindle – Chemistry

UNLV Theory

- Changfeng Chen – Physics
- Eunja Kim – Physics
- Steven Lepp – Physics
- Bala Naduvalath – Chemistry
- Tao Pang – Physics
- Bernard Zygelman – Physics

External Partners

- United Technologies (UTC) Power
- Rice University
- Lawrence Berkeley National Lab
- Air Products
- Hahn-Meitner-Institute, Berlin
- Shanghai Jiatong University
- Penn State

Why Hydrogen Economy?

Why Hydrogen Economy?

- We need a new fuel! (sooner or later)

Why Hydrogen Economy?

- We need a new fuel! (sooner or later)
  - This could be:
    - Biodiesel
    - Hydrogen
    - Electricity
    - Uranium
    - ...

What would a Hydrogen Economy need?

- Hydrogen Production
- Hydrogen Storage
- Hydrogen Delivery
- Hydrogen Consumption

What would a Hydrogen Economy need?

- Hydrogen Production
  - Solar (thermal, photoelectrochemical)
  - Nuclear
  - Currently: natural gas reforming
- Hydrogen Storage
  - Nanomaterials, Metal Hydrides, Chemical Hydrides
- Hydrogen Delivery
  - Pipelines, Trucks, Tanks, ...
- Hydrogen Consumption
  - Fuel Cells, Internal Combustion Engine

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Objectives of FCAST

- Perform closely-coupled theoretical and experimental investigations of
  - hydrogen adsorption/desorption in various matrices to establish a solid understanding of optimal storage concepts
  - the electronic and geometric structure of metal hydrides, nanomaterials (C, B, N, transition metals, alloys), metal adatoms, and adsorbed hydrogen molecules/atoms
  - Fuel cell membranes and catalytic materials

  to predict optimized materials and structures for hydrogen storage and fuel cells in the DOE Hydrogen program

- Collaborate closely with external partners

Approach

Task 1: Theory and Experiment of Nanomaterials for Storage Applications (New Materials, Hydrogen Uptake, Local Electronic Structure, Adsorption Energies and Geometries, …)

Task 2: Metal Hydrides (Structure, Reversibility, T- and P-Dependence, …)

Task 3: Mesoporous Polymer Nanostructures (Synthesis, Hydrogen Uptake, …)

Task 4: Improved Fuel Cell Membrane

Task 5: Design and Characterization of Improved Fuel Cell Catalytic Materials

Hydrogen storage in/on nanomaterials

Titanium-decorated Carbon Nanotubes as a Potential High-capacity Hydrogen Storage Medium

T. Yildirim and S. Ciraci, Phys. Rev. Lett. **94**, 175501 (2005)

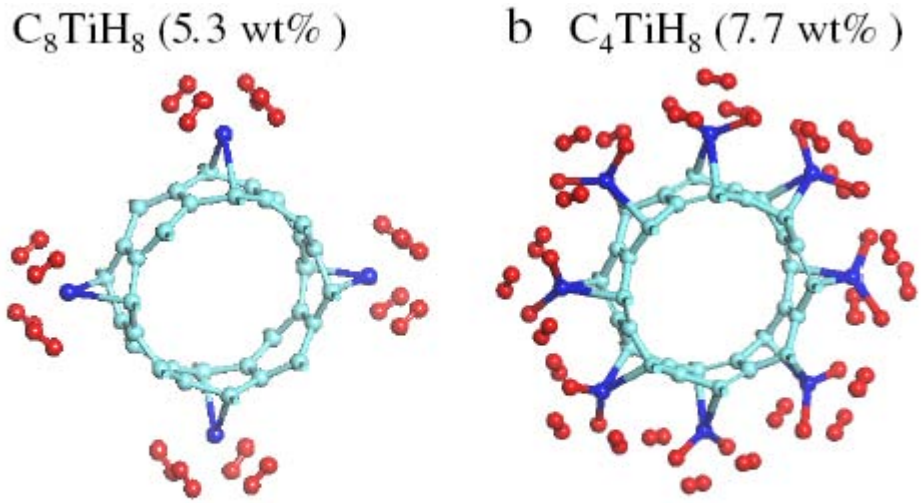
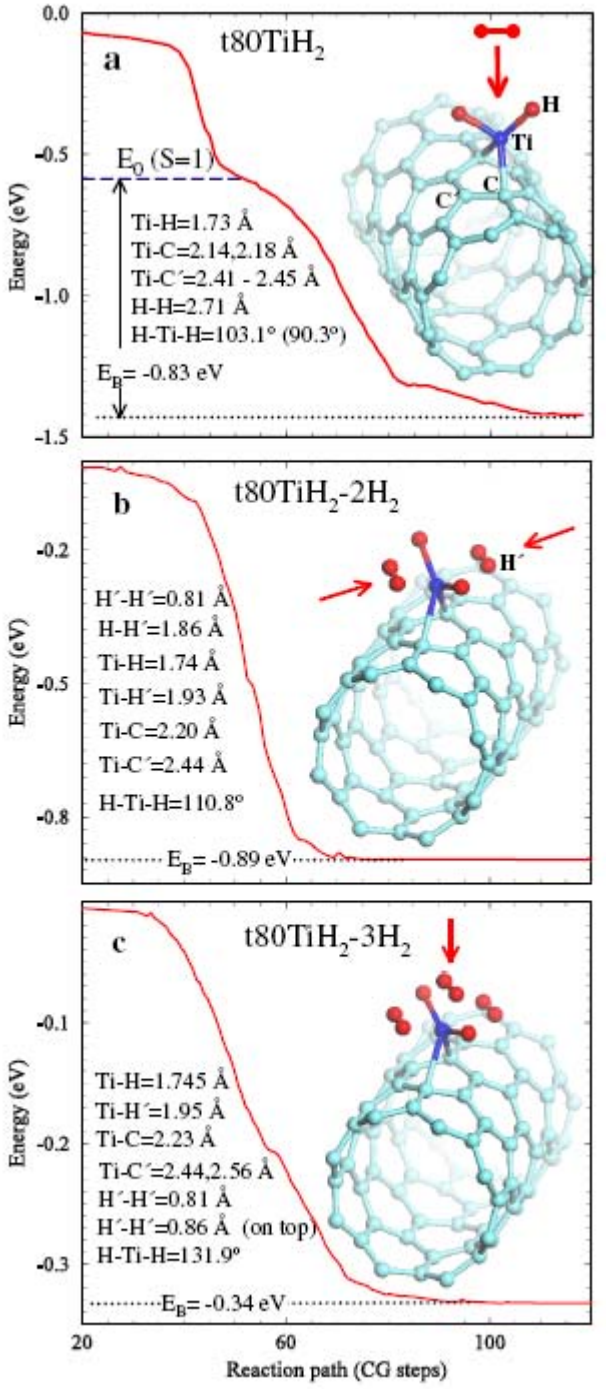
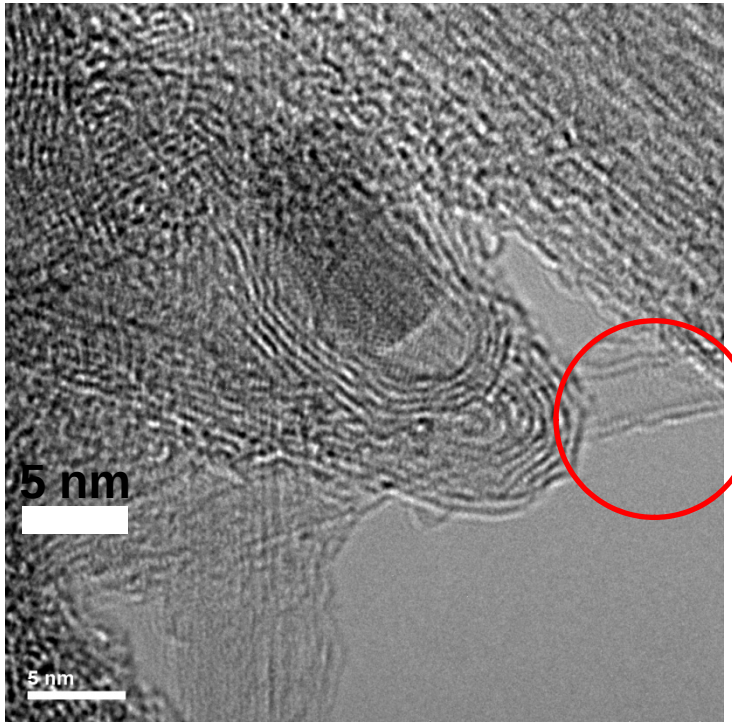


FIG. 3 (color online). Two high-density hydrogen coverage on a Ti-coated (8, 0) nanotube.



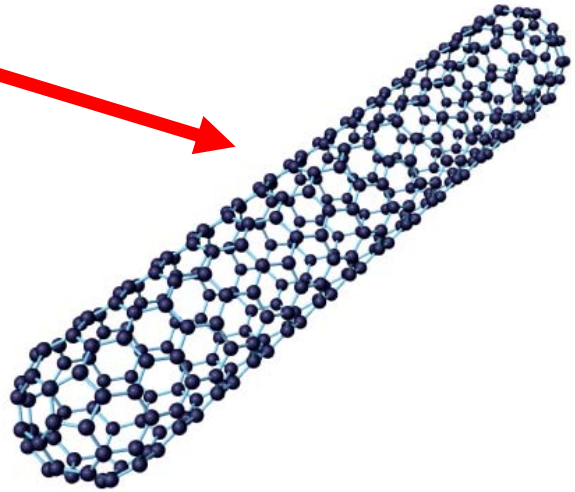
Single-Walled Carbon NanoTubes (SWNT)



TEM of SWNT

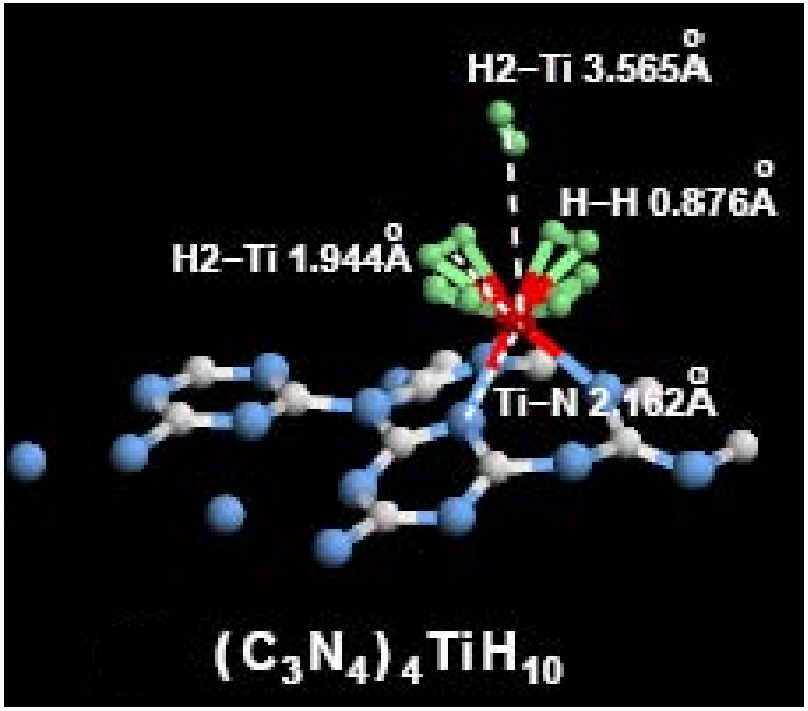
- nanotubes come in bundles
- Samples have a size distribution
- Samples contain impurities

A local experiment on
one individual nanotube would be ideal!



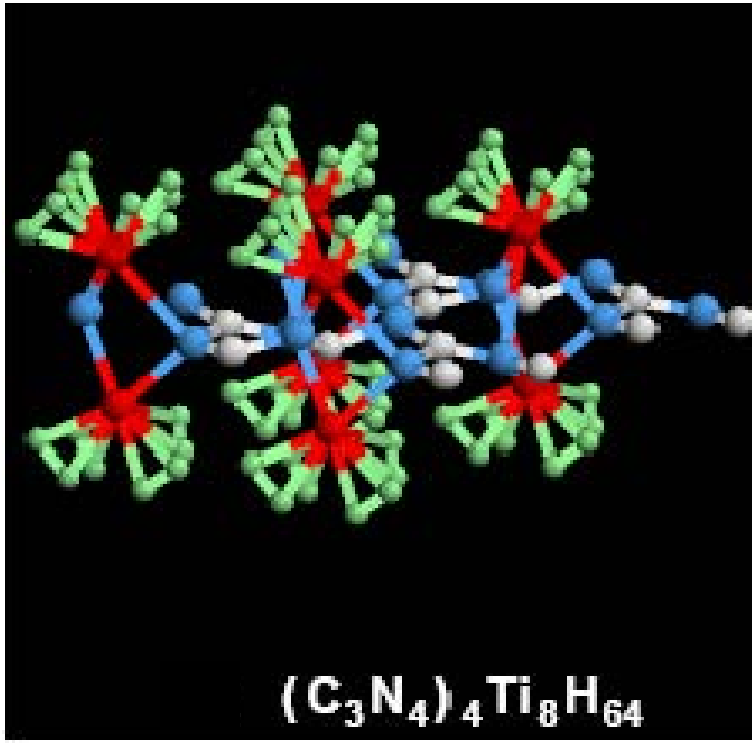
Which is the best nanotube for hydrogen storage ?
How does hydrogen adsorption/desorption work ?
How can we improve it ?

Transition-metal decoration and hydrogen storage (Changfeng Chen, Physics, Task 1)



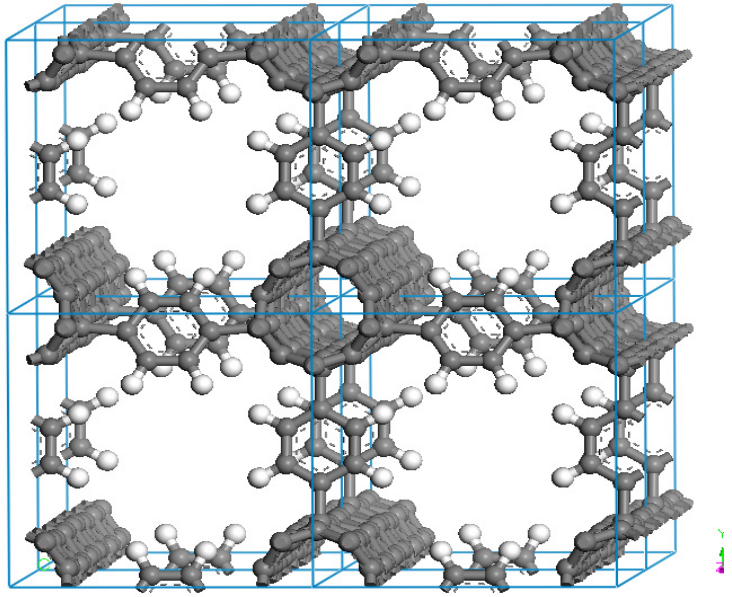
Ti	$1H_2$	$2H_2$	$3H_2$	$4H_2$	$5H_2$
E (eV/H_2)	0.60	0.36	0.39	0.09	0.02

The binding energy of H_2 on Sc is slightly lower than that on Ti.



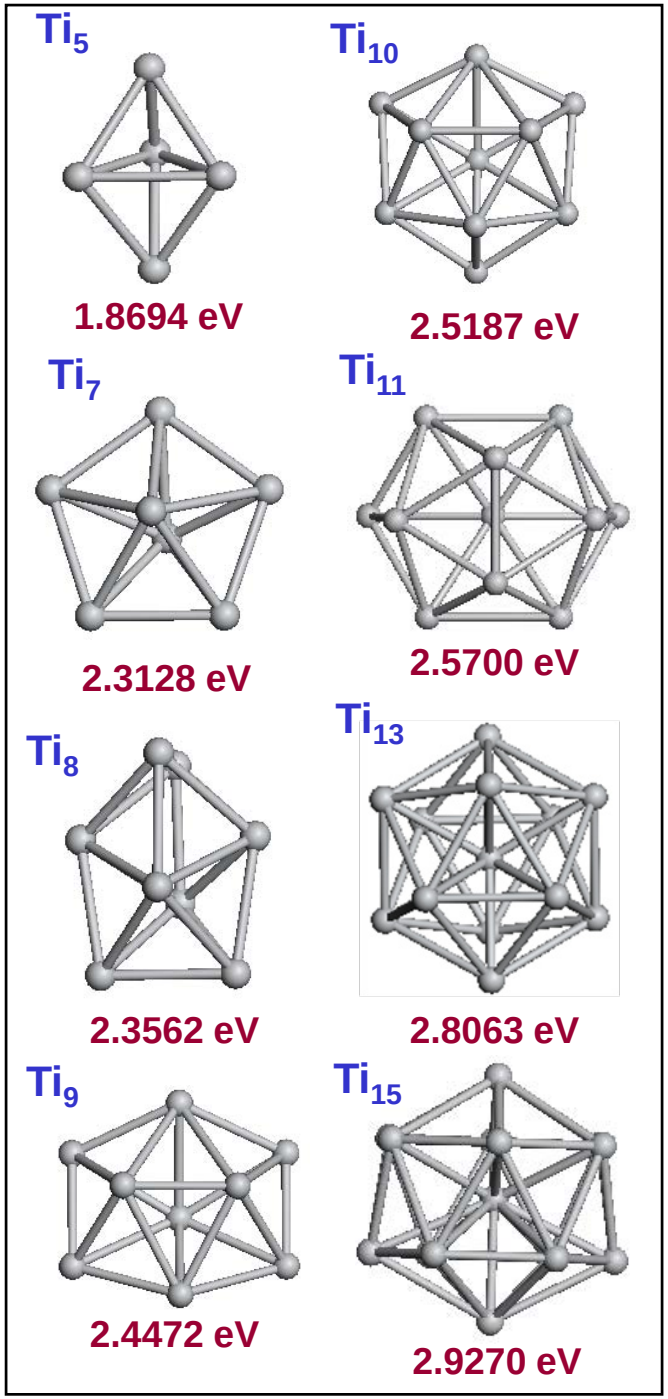
• Up to 4 H_2 are adsorbed on each Ti atom with the binding energy ranging from 0.1 eV to 0.4 eV per H_2. (7.8wt% for double side coverage)

A novel class of 3D nanoframeworks based on CNTs (Balakrishnan Naduvalath, Chemistry, Eunja Kim, Physics, Task 1)



- Car-Parrinello molecular dynamics simulations indicate that the proposed frameworks are thermodynamically stable up to 20 ps at 300 K and 2 ps at 600K
- Preliminary results indicate that Li-decorated 3D nano-frameworks are promising for hydrogen storage

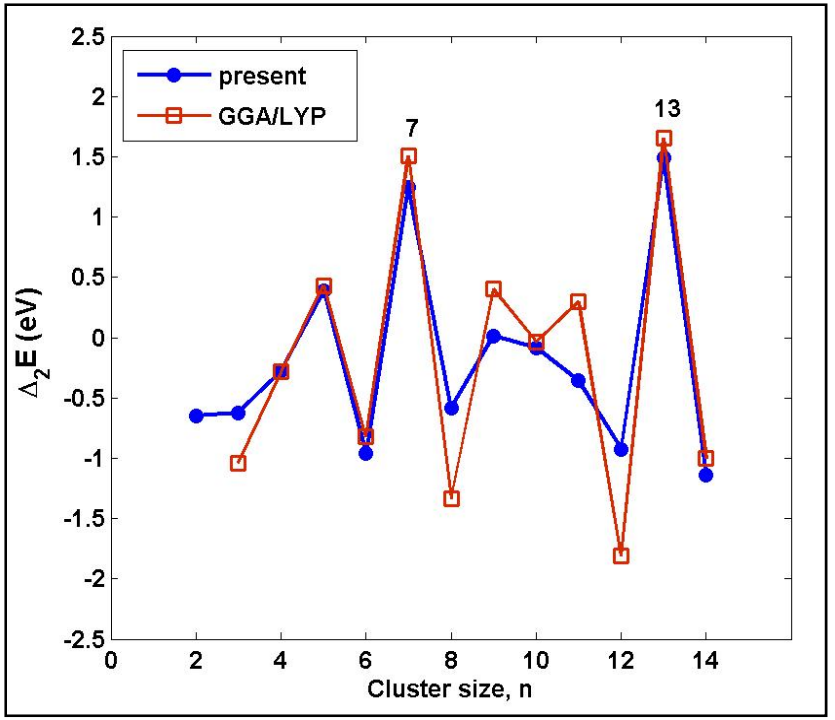
Electronic structure of Titanium clusters (B. Naduvalath, Task 1)



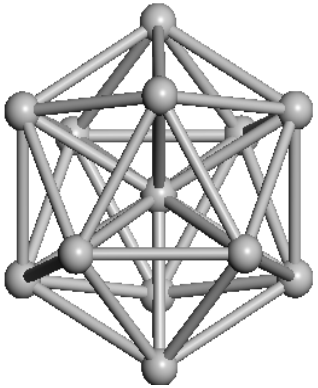
- Ti_n clusters evolve on **Pentagonal** growth pattern
- Second energy difference indicates Ti_7 and Ti_{13} clusters are highly stable, which agrees well with the experimental results

Second Energy Difference

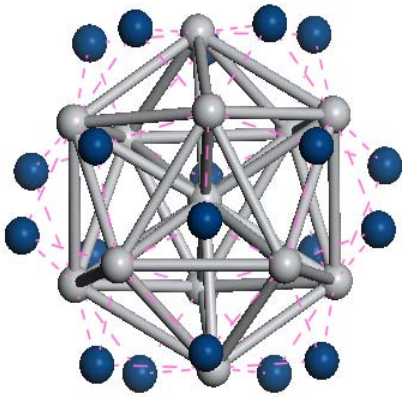
$$\Delta_2 E = E(n+1) + E(n-1) - 2E(n)$$



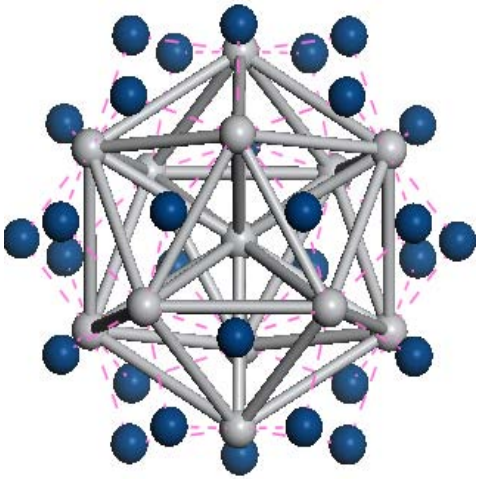
Ti_{13} cluster and H_2 saturation (B. Naduvalath, Task 1)



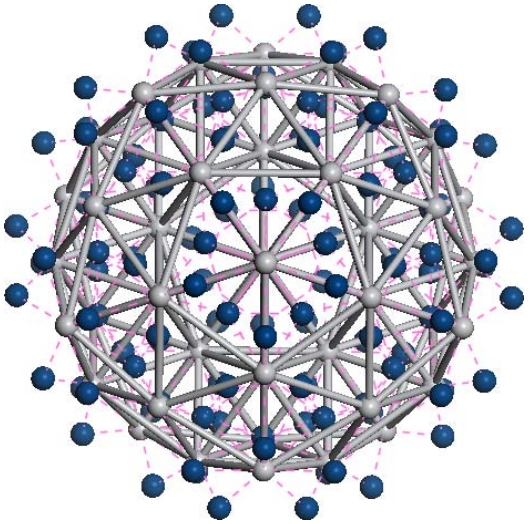
Ti_{13}



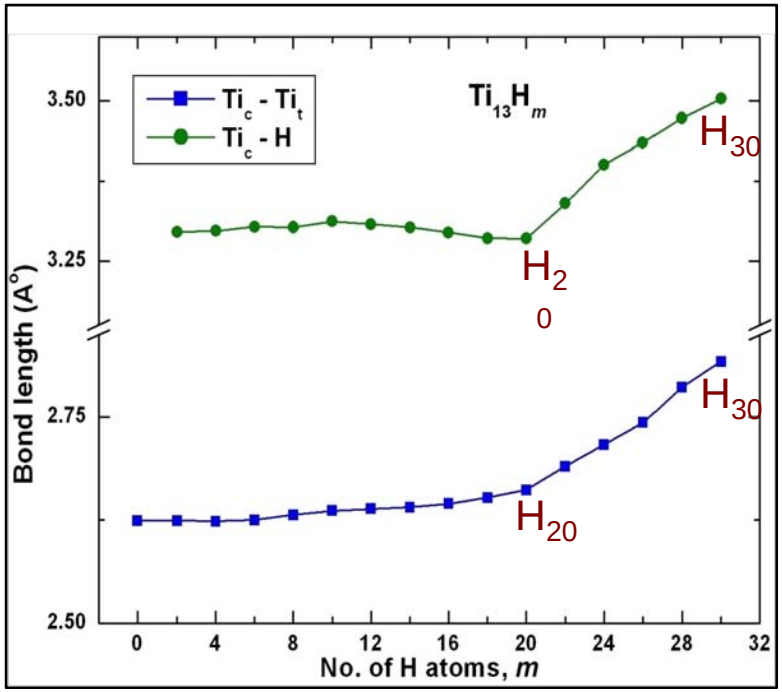
$Ti_{13}H_{20}$ (μ_3)

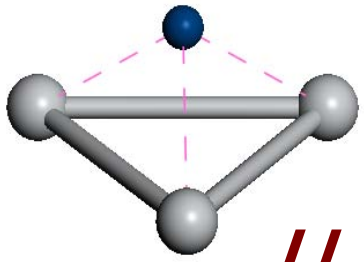


$Ti_{13}H_{30}$ (μ_2)

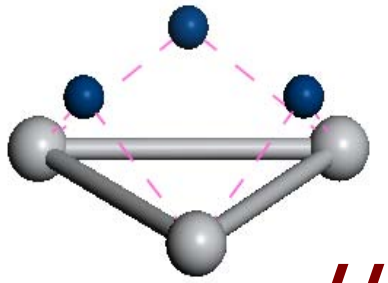


$Ti_{55}H_{120}$ (μ_2 & μ_3)





μ_3



μ_2

- Hydrogen multi-center bonds in $Ti_{13}H_m$
- μ_3 for m ≤ 20 and μ_2 in $Ti_{13}H_{30}$
- Cage expansion due to saturation from m = 20 – 30 by 6%

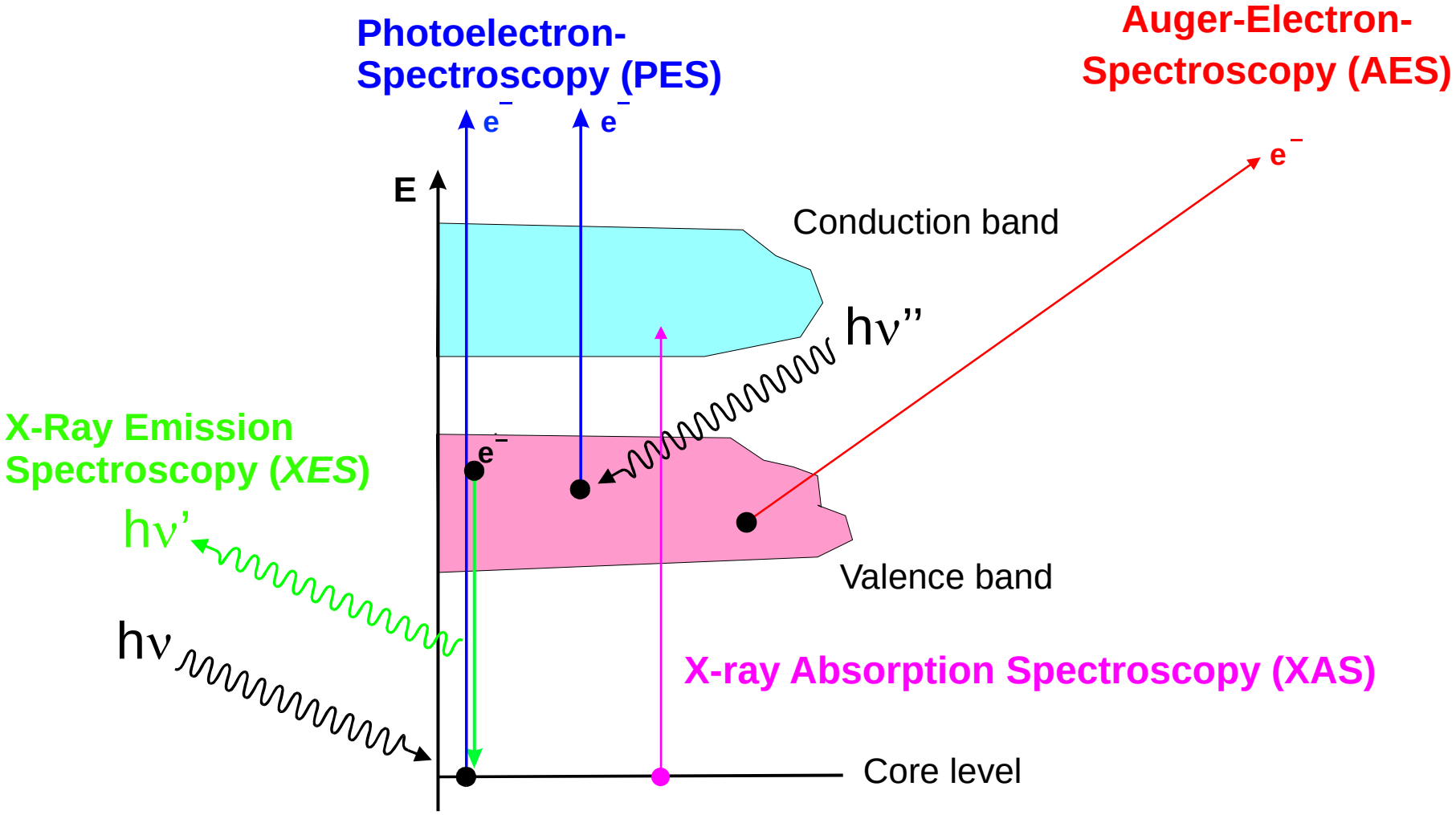
Surface and interface spectroscopy/microscopy of nanomaterials for hydrogen storage (Clemens Heske, Chemistry, Task 1)

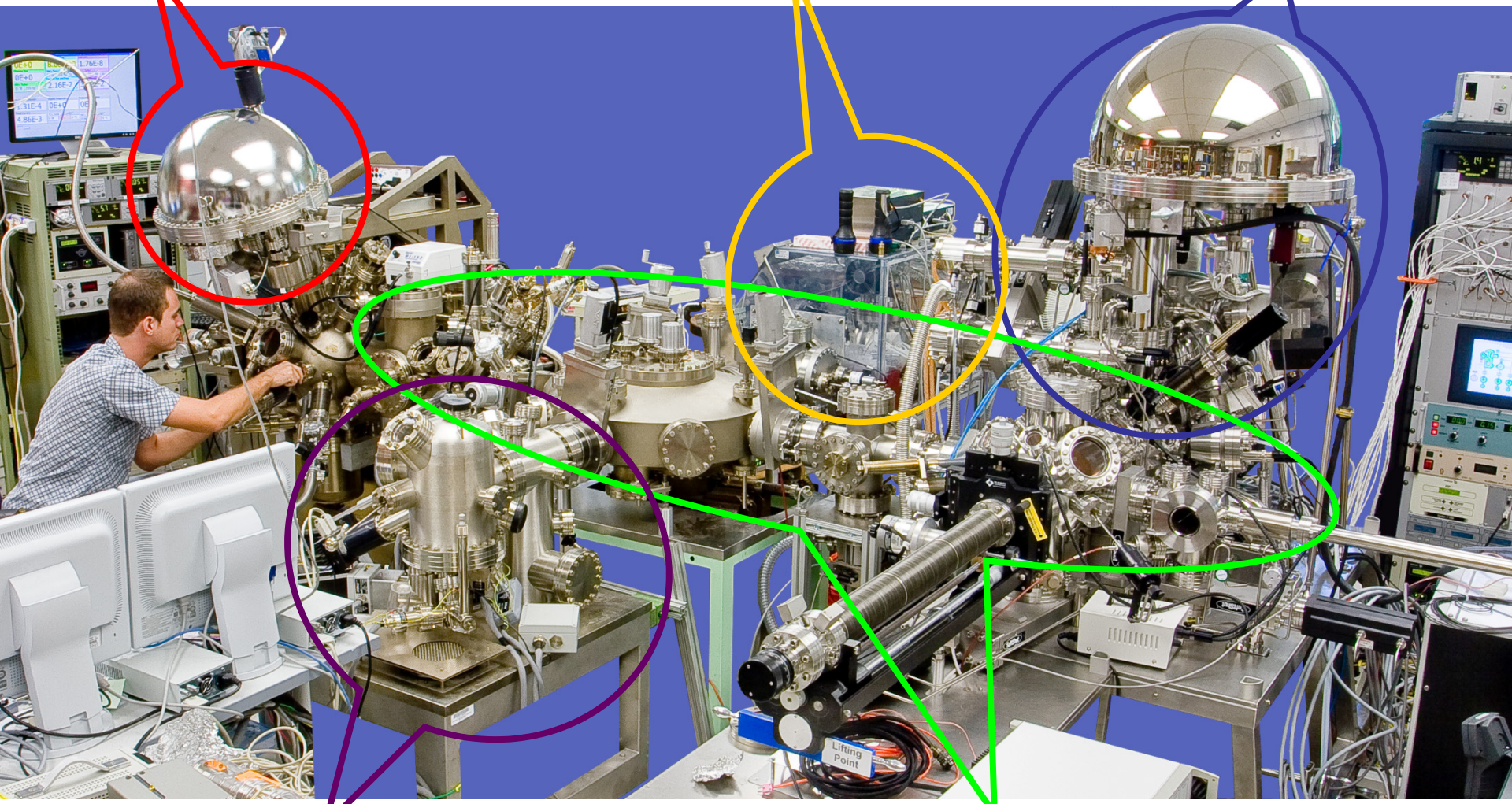
Experiment matrix for Hydrogen storage on (metal-decorated) carbon nanomaterials:

- Carbon (nano)materials: C_{60}, SWNT, HOPG
- Metal (co-)adsorbates: Ti, Li
- Hydrogenation: molecular, atomic

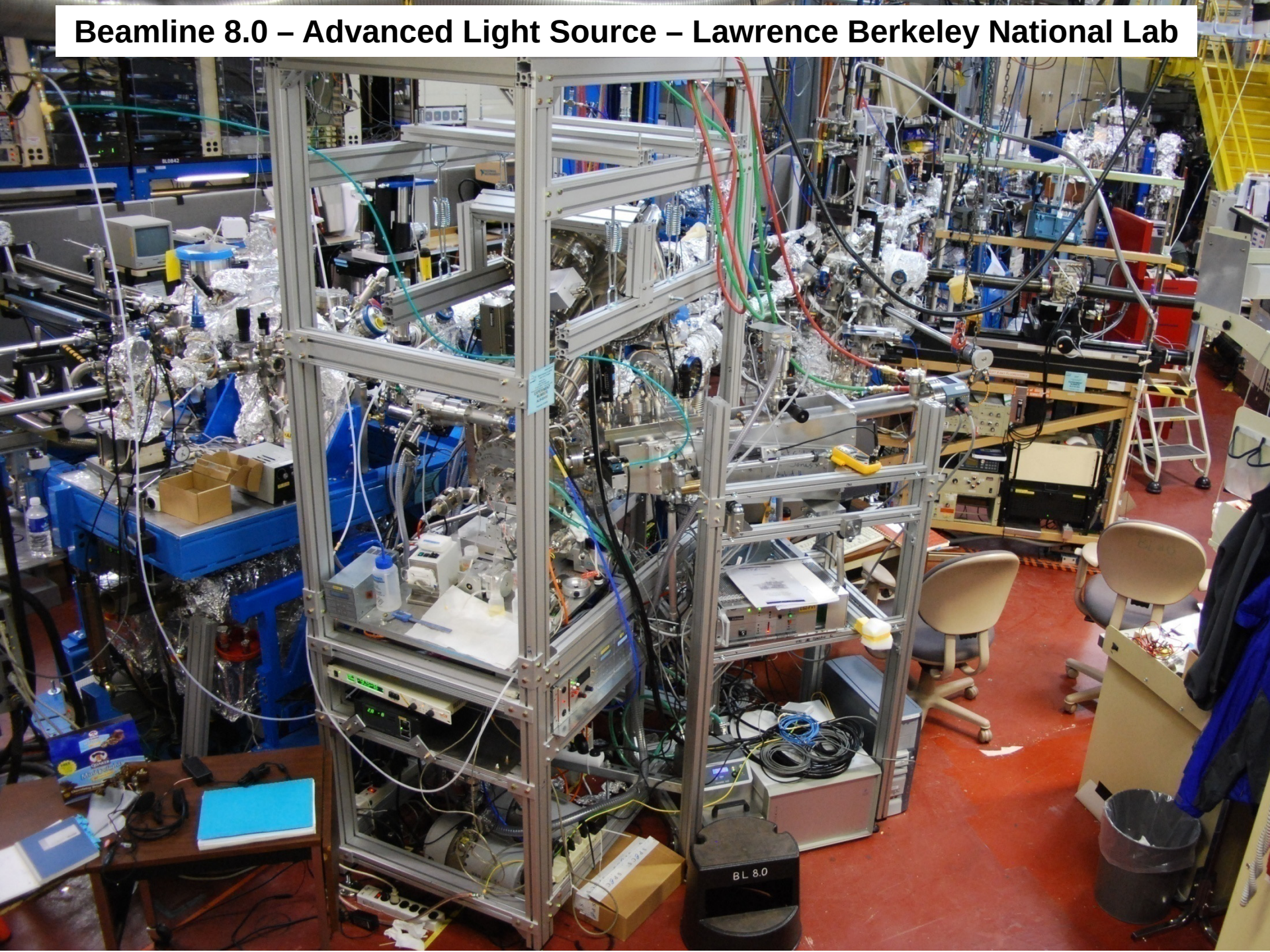
- How does Hydrogen interact with carbon-based nanomaterials?
- Why is there a “gap” between theory and experiment?

Soft X-ray spectroscopies

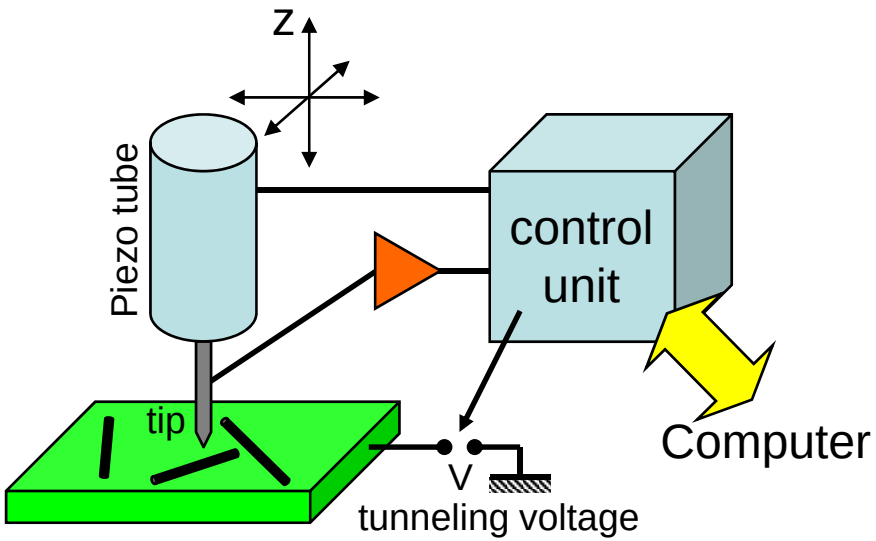



High dynamic range
XPS, UPS, Auger, IPES
Glovebox
High resolution
XPS, UPS, Auger
Scanning Probe
Microscope
Sample preparation
and distribution

Beamline 8.0 – Advanced Light Source – Lawrence Berkeley National Lab



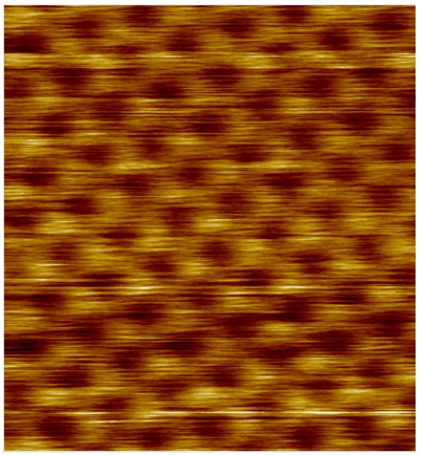
Scanning Tunneling Microscopy (STM) / Spectroscopy (STS)



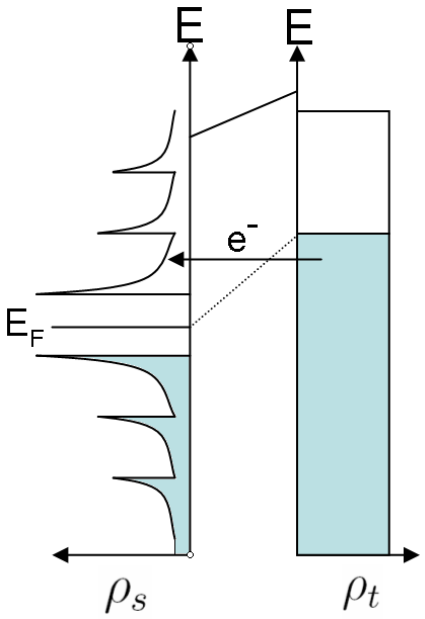
Microscopy

- Tunneling tip can be scanned over the sample by piezos
- Tunneling current is measured at a tunneling voltage V and kept constant by a feedback controlling the z-direction
  → "topography of electron density"

z-range 150 pm



HOPG 2x2 nm^2



Spectroscopy

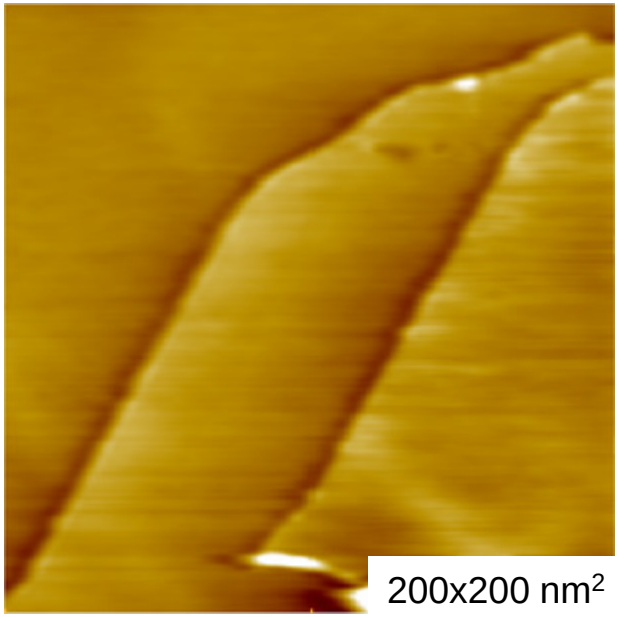
- Tunneling voltage V is varied at one spot with constant tip-sample distance
  → density of states around E_F

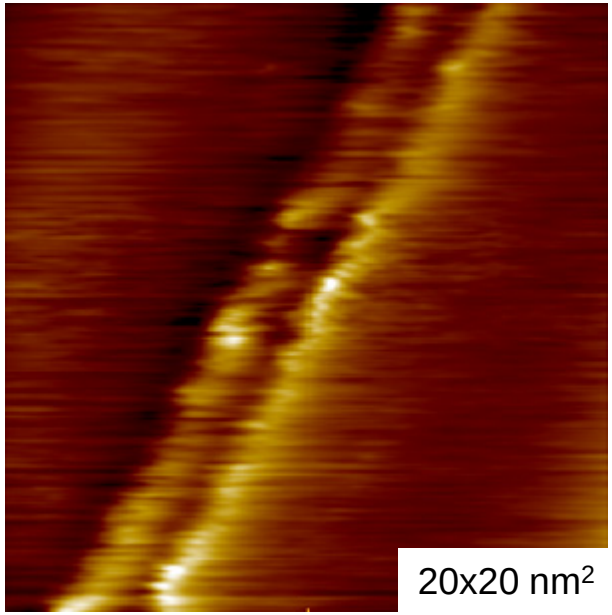
$$I(V) = \int_0^{eV} \rho_s(E) \cdot \rho_t(E - eV) \cdot T(E, eV, d) dE$$

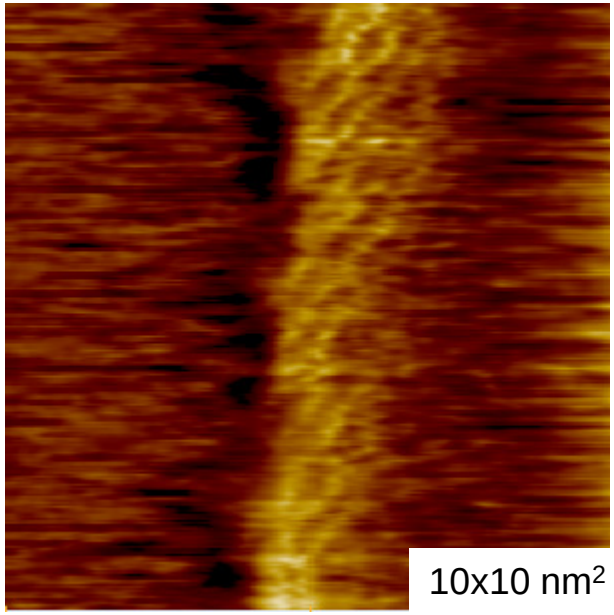
$$\rho_s(eV) \approx c \cdot \frac{dI(V)}{dV}$$

STM on SWCNT – 2

- Electro-deposited (6 min, upside down) on HOPG, SWCNT (not cut)

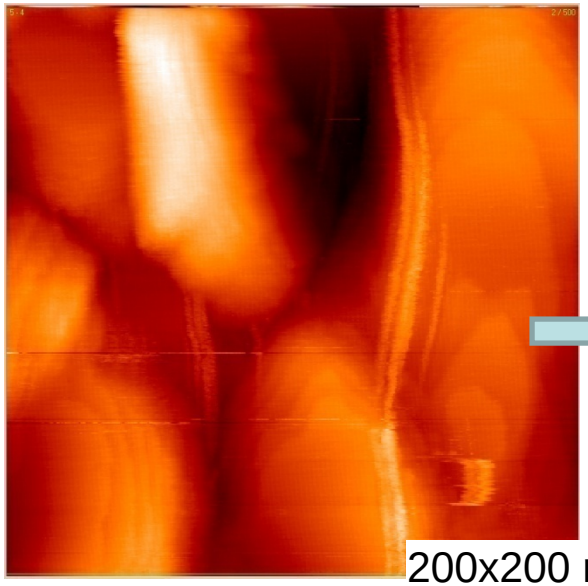




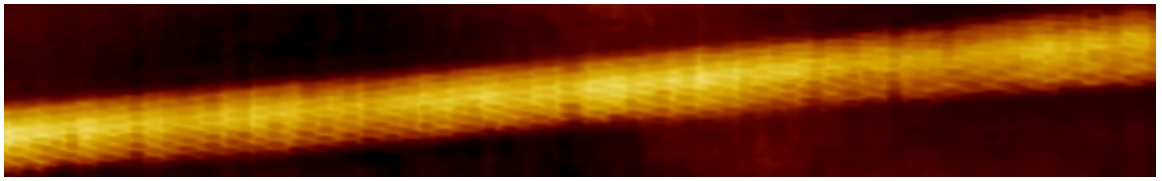


- Electro deposition worked
- Low coverage with long SWCNT
- “Small” bundles (e.g. two bundled tubes) and individual tubes are observed
- Atomic resolution can be achieved

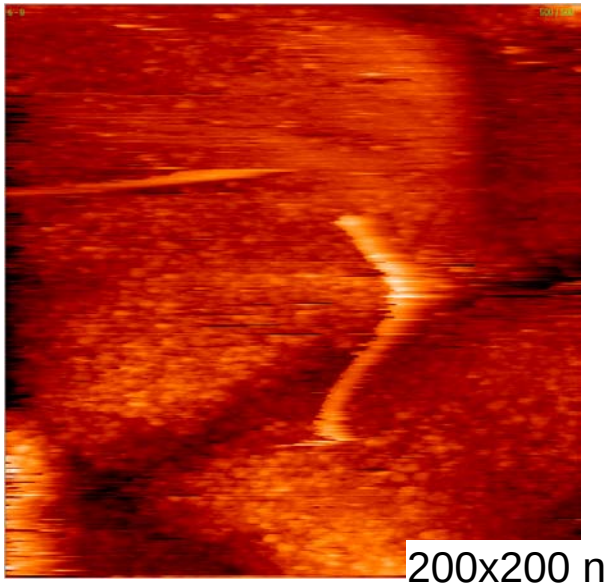
Scanning Tunneling Microscopy/Spectroscopy of SWNT with/without Ti decoration (Task 1)



200x200 nm^2

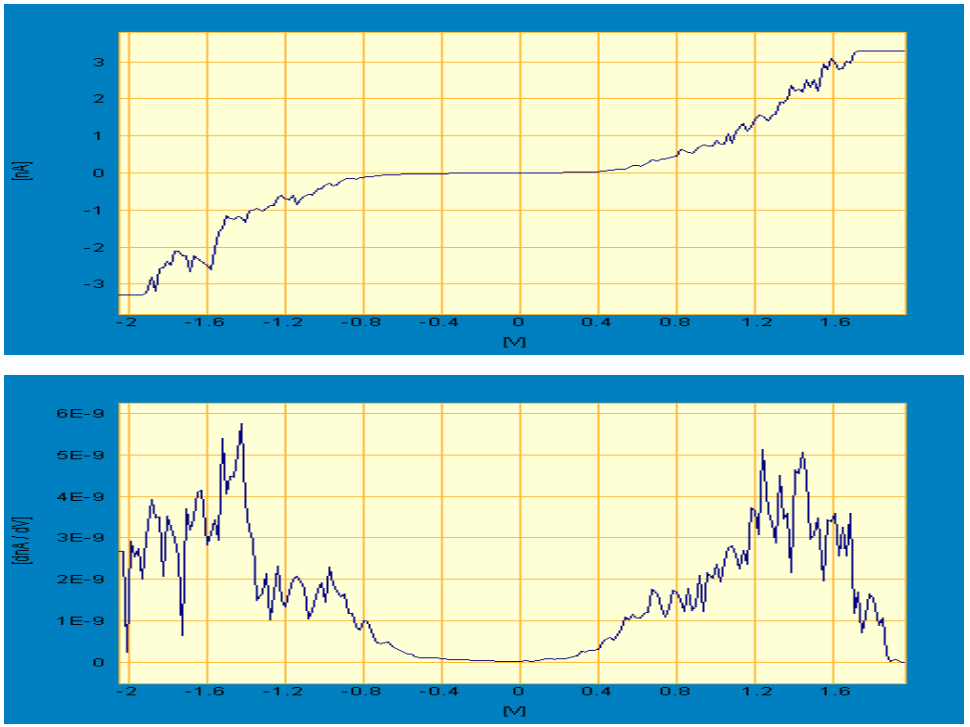


STM image of SWNT on Au with atomic resolution



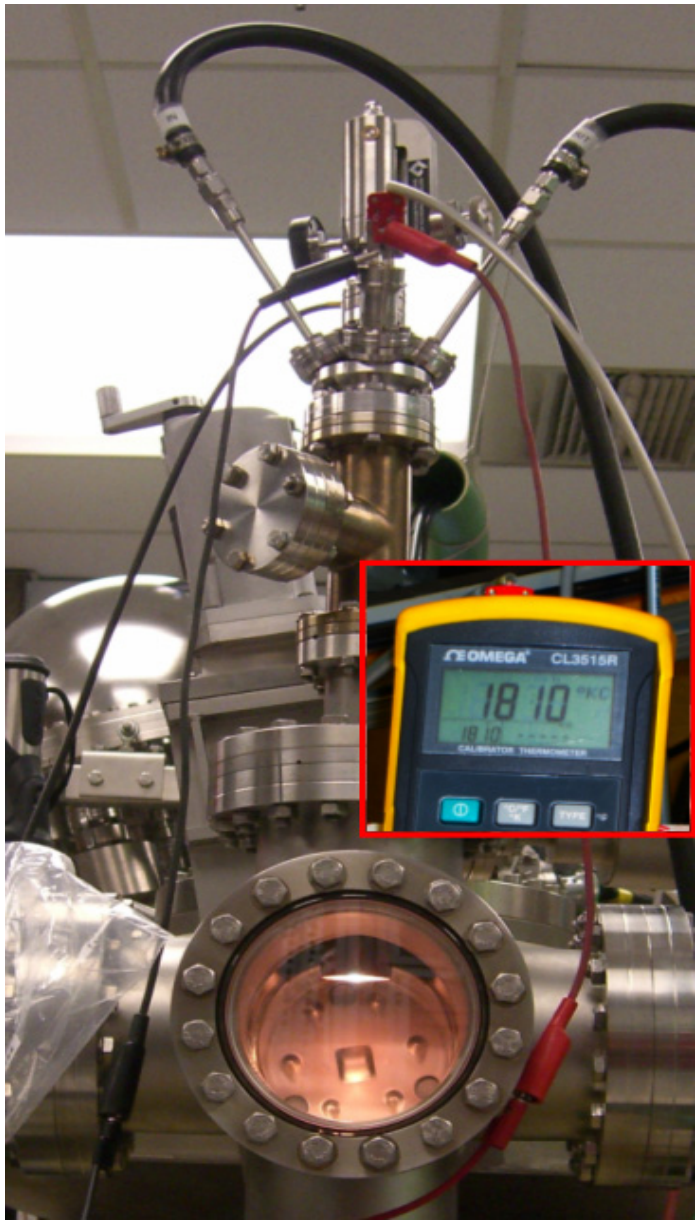
200x200 nm^2

Ti deposited on top of SWNT/Au



I-V curve and STS of SWNT on Au

Atomic Hydrogen Source (AHS)

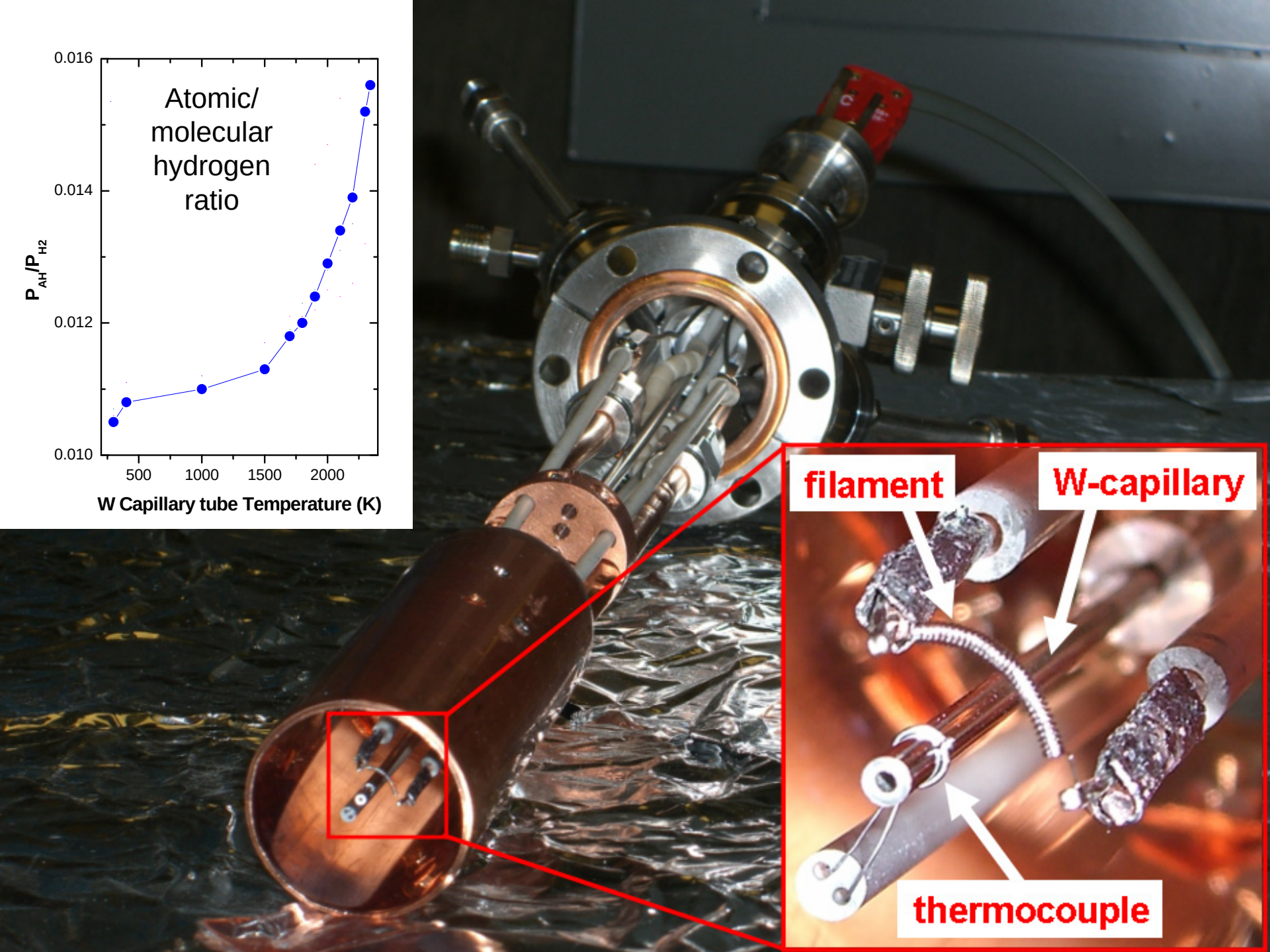


Based on U. Bischler, J. Vac. Sci. Technol. A 11, 458 (1993)

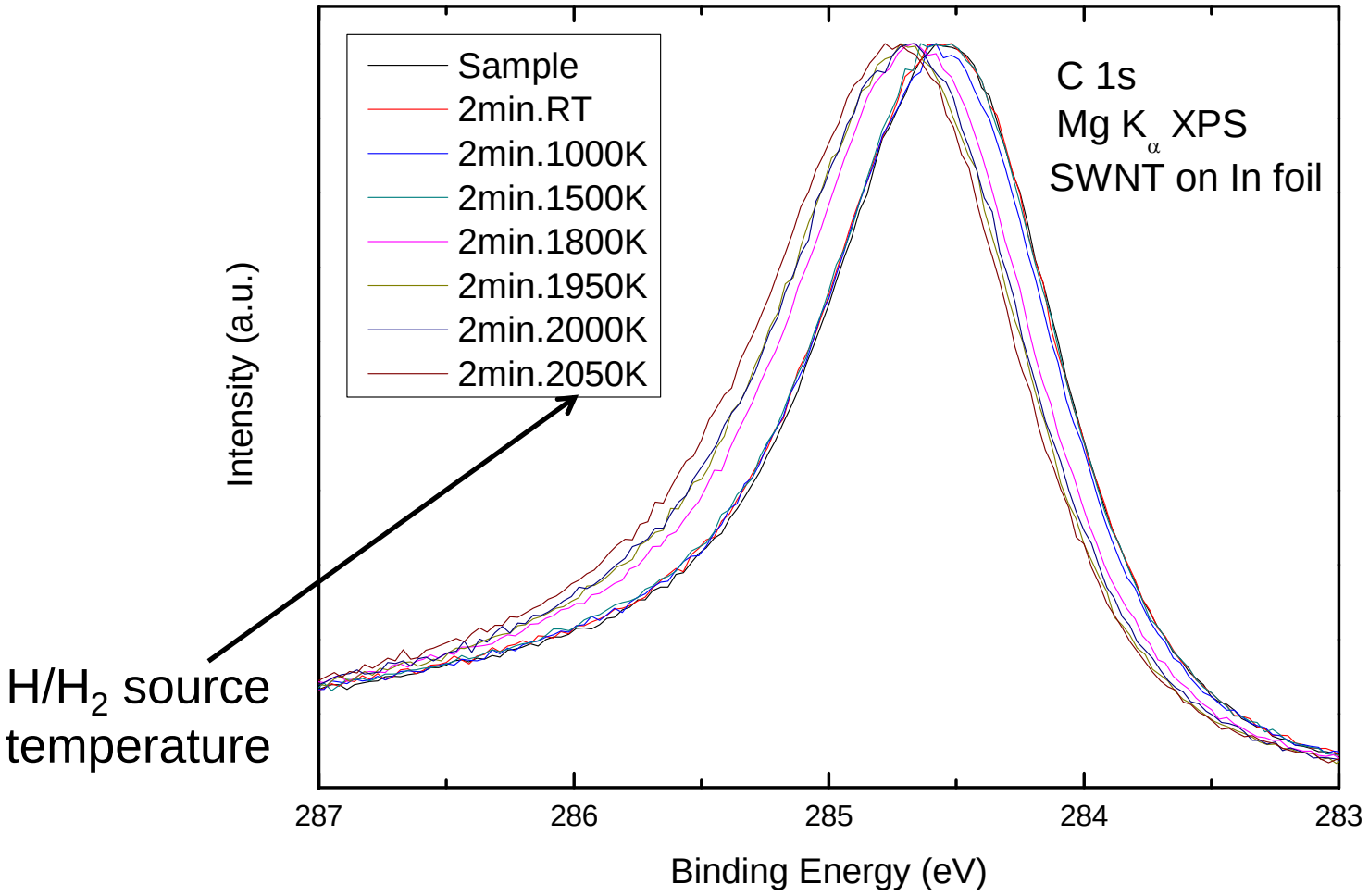
Atomic hydrogen is produced by high temperature thermal cracking of molecular hydrogen via a W capillary tube, submitted to HV and electron bombardment

Atomic Hydrogen Source components:

- Gas Reservoir
- Tungsten Capillary Tube
  - 50-mm long, 1.6-mm O.D, 0.6-mm I.D.
  - Acceleration Voltage of ~+3 kV
- Tungsten Filament
  - 1.7 A, 7.0 V, 12 W


Atomic/
molecular
hydrogen
ratio
0.016
0.014
0.012
0.010
P_{AH}/P_{H2}
500
1000
1500
2000
W Capillary tube Temperature (K)
filament
W-capillary
thermocouple

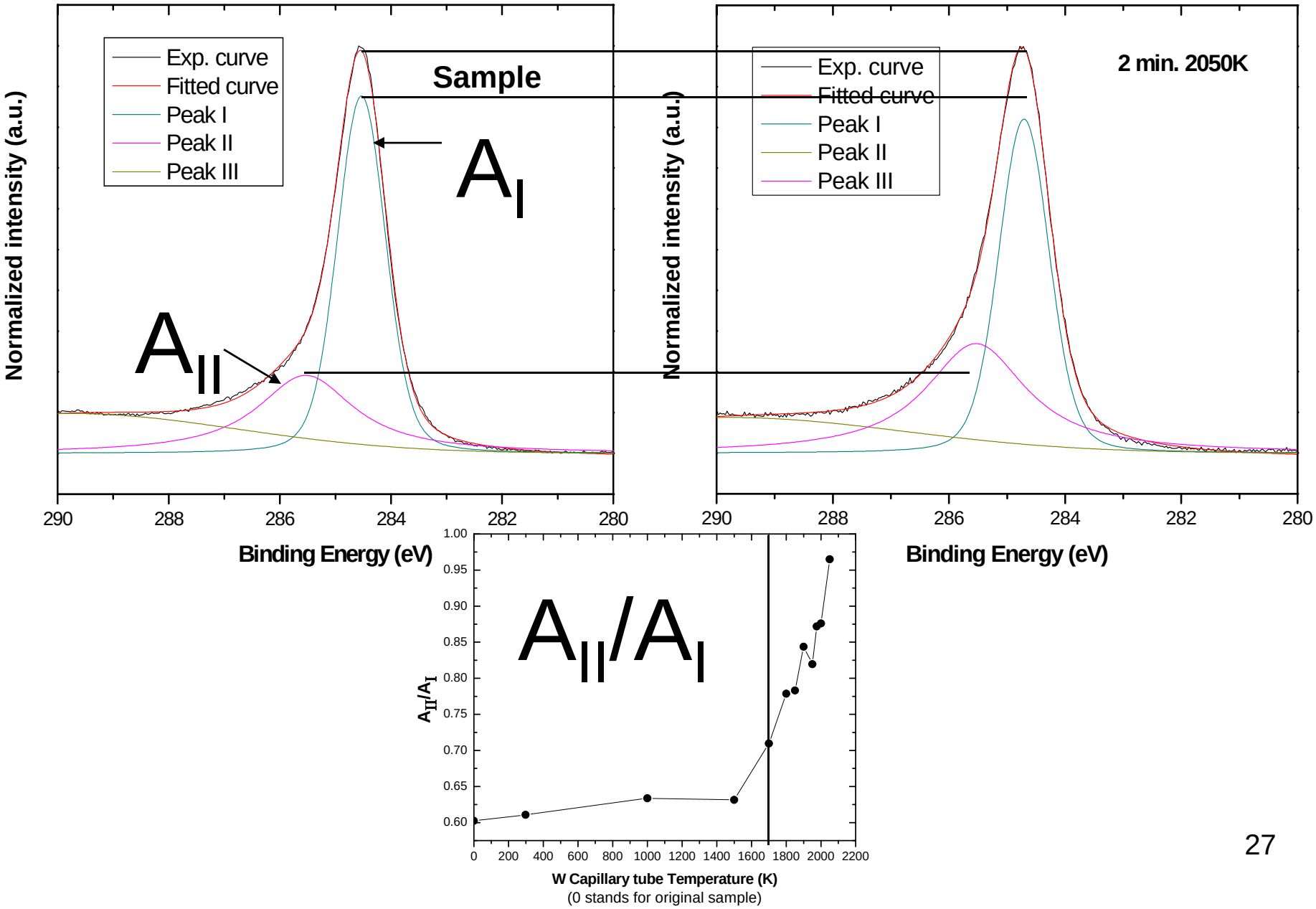
XPS: Hydrogenation of SWNT (Task 1)



1. No shift in C 1s for molecular hydrogen adsorption (at RT)

2. C 1s shifts to higher binding energy for atomic hydrogen (along with capillary temperature), indicating H adsorption

XPS: Hydrogenation of SWNT (Task 1)

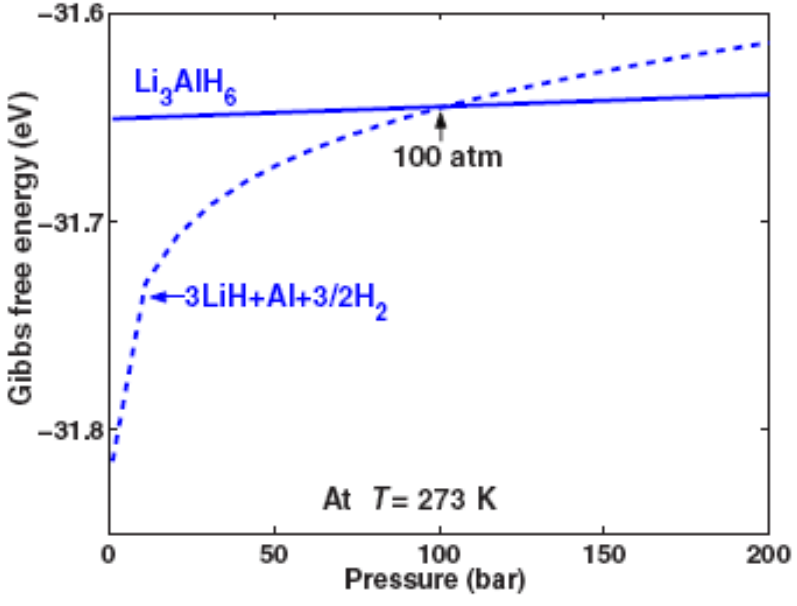


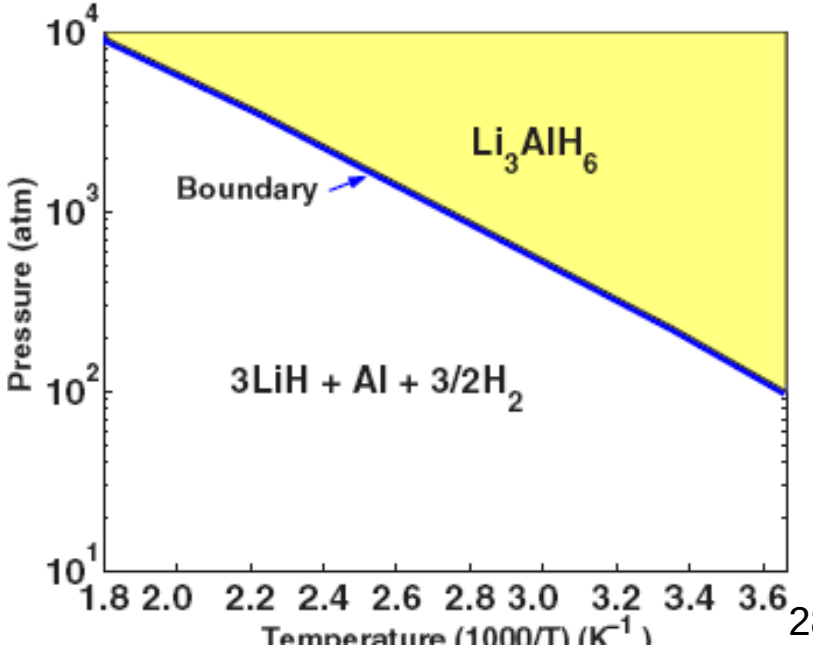
Gibbs free energy and temperature-pressure phase diagram of lithium alanates (Changfeng Chen, Task 2)

Apply first-principles electronic structure and lattice dynamics calculations within and beyond the harmonic phonon approximation to examine the thermodynamic phase stability of lithium alanates and predict their reaction pathways and reversibility

Results:

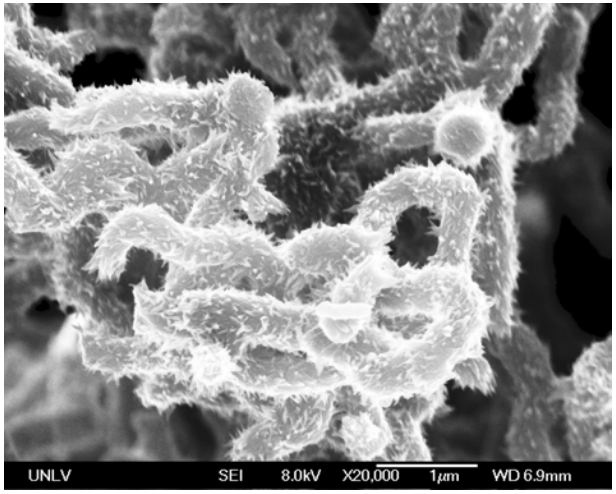
- Obtained a comprehensive set of thermodynamic functions over a wide temperature range for $LiAlH_4$, Li_3AlH_6 and LiH.
- Evaluated decomposition reactions to determine reversibility and suitability for practical use in mobile applications.
- Established the thermodynamic (temperature-pressure) phase diagram for lithium alanates and identified key operating physical parameters for hydrogen storage and reversible release-recharge process.

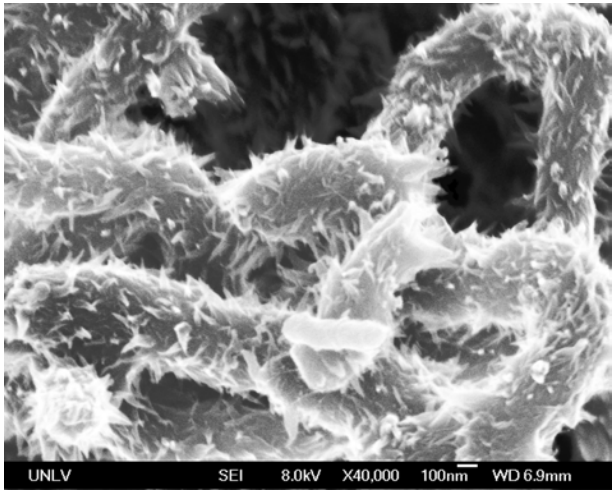




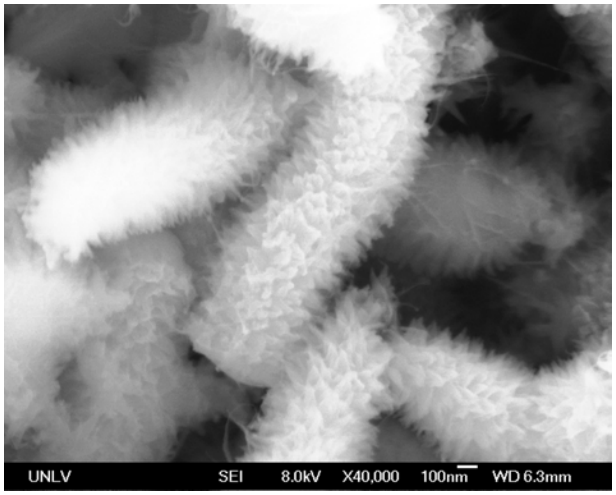
Polyaniline (PANI)/Pd Composites for Hydrogen Storage (David Hatchett, Task 3)

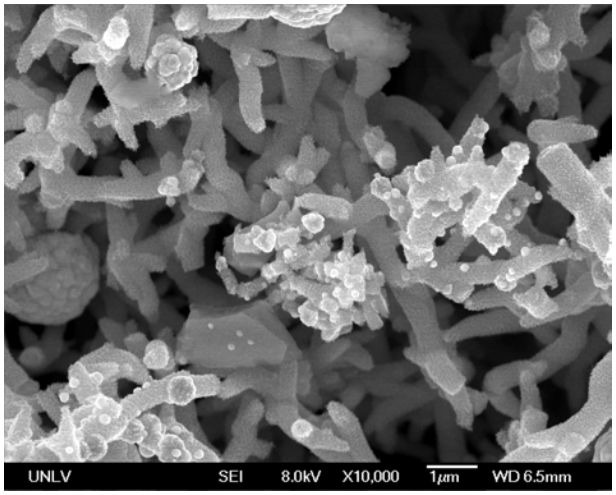
Pd(ii) reduction in PANI





Pd morphology is a function of the number of voltammetric cycles

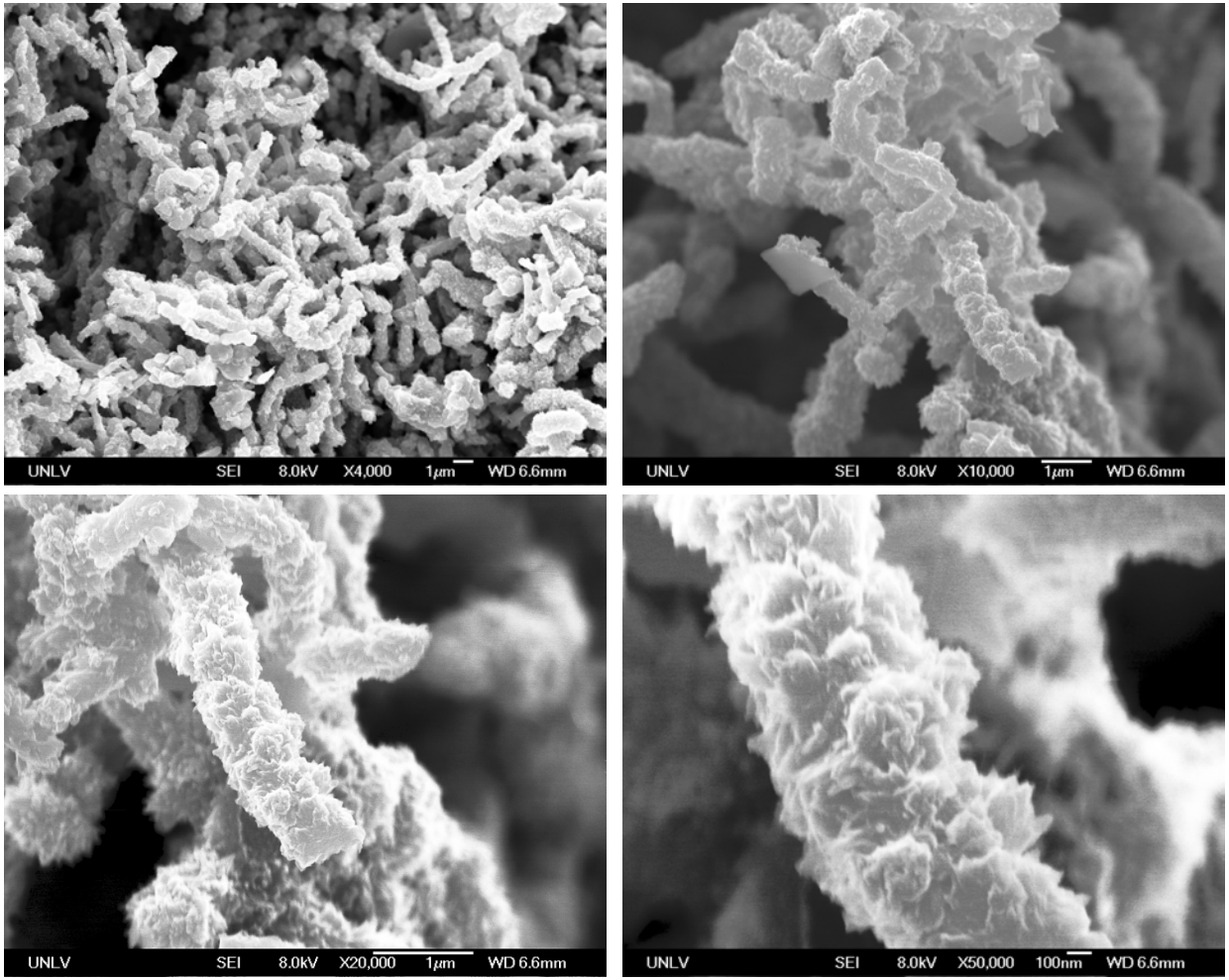




Pd aggregation also possible with potentiometric growth

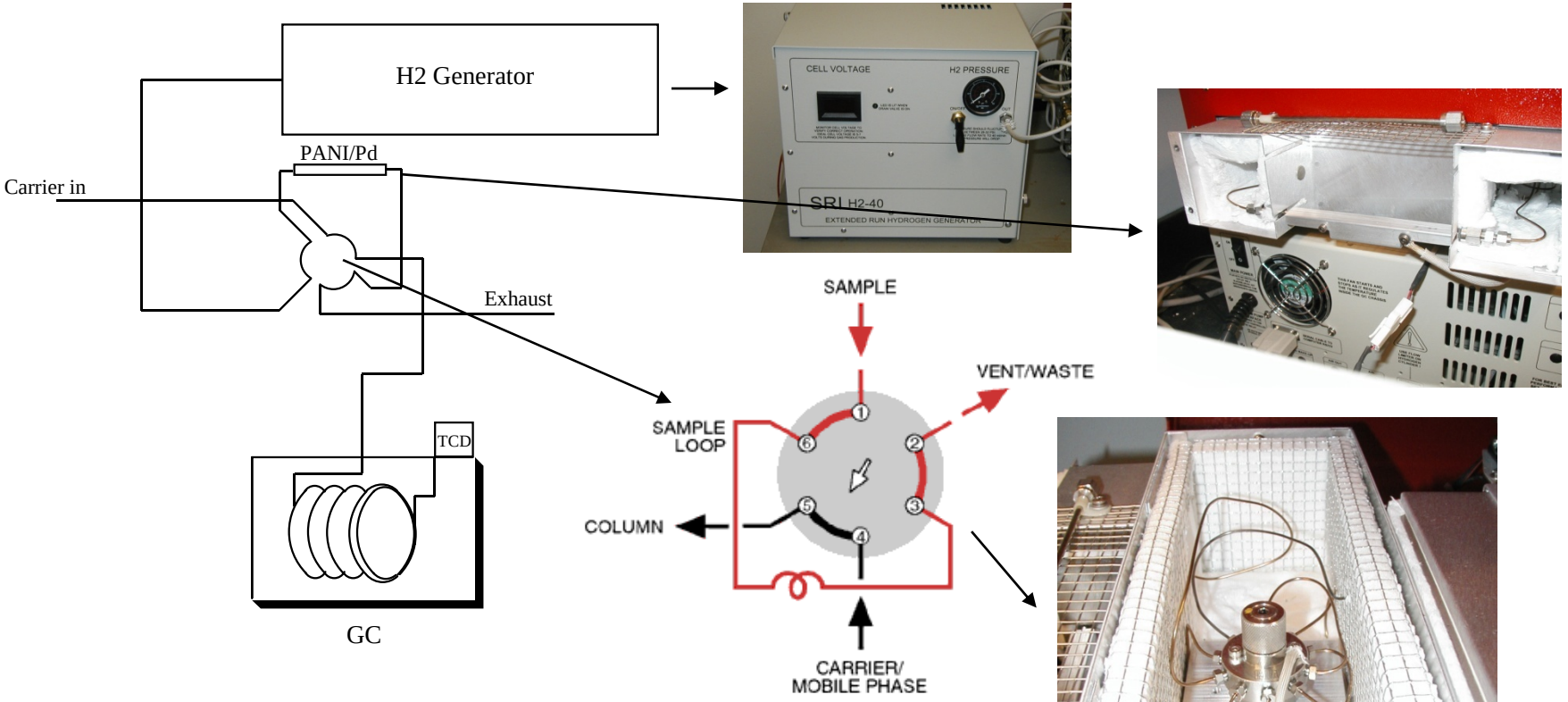
PANI/Pd Composites (Task 3)

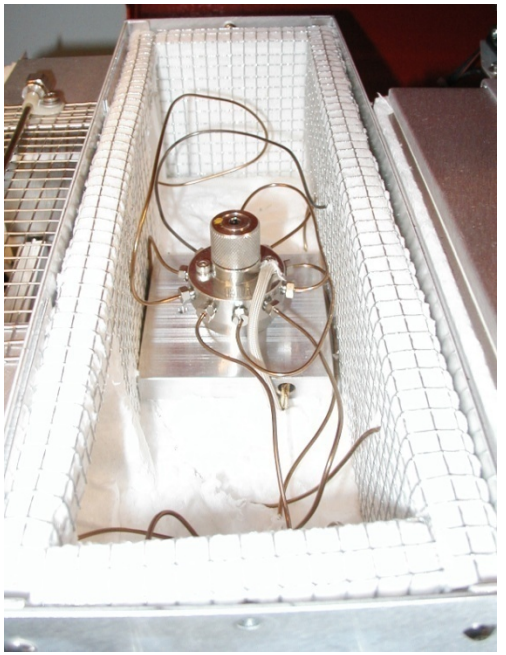
Pd(iv) Reduction in PANI



Pd thickness is a function of the number of voltammetric cycles

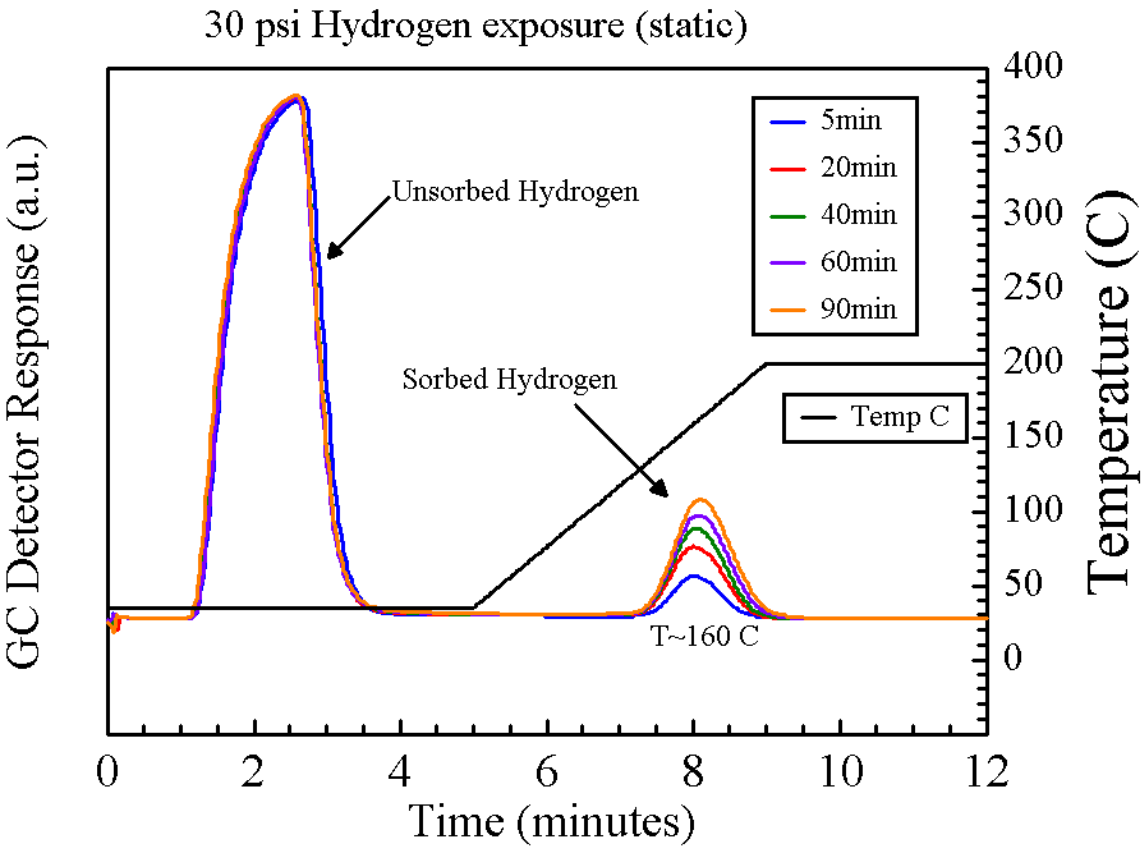
H Sorption Apparatus (Task 3)





Hydrogen Sorption in Chemical Composites (Task 3)

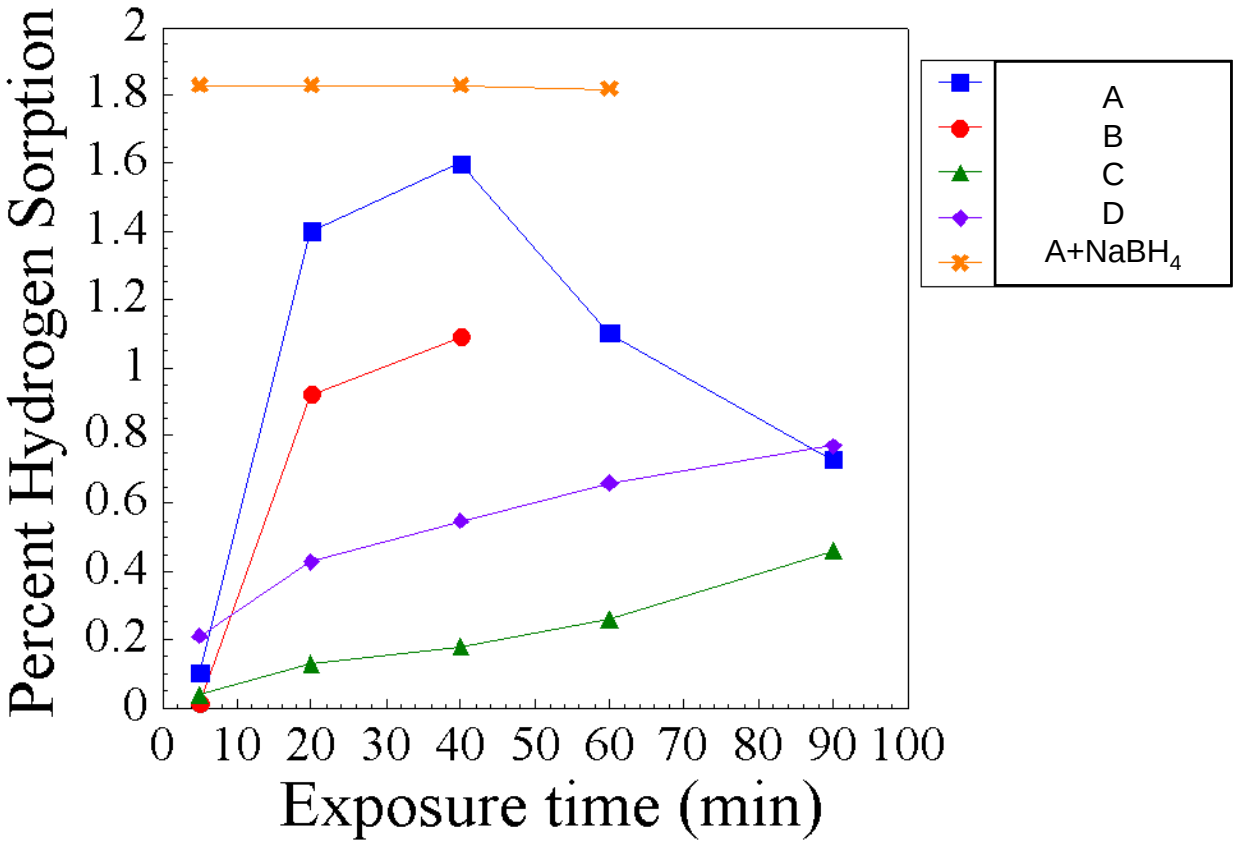
Material A



Sorption is obtained using a normal GC with a hydrogen generator

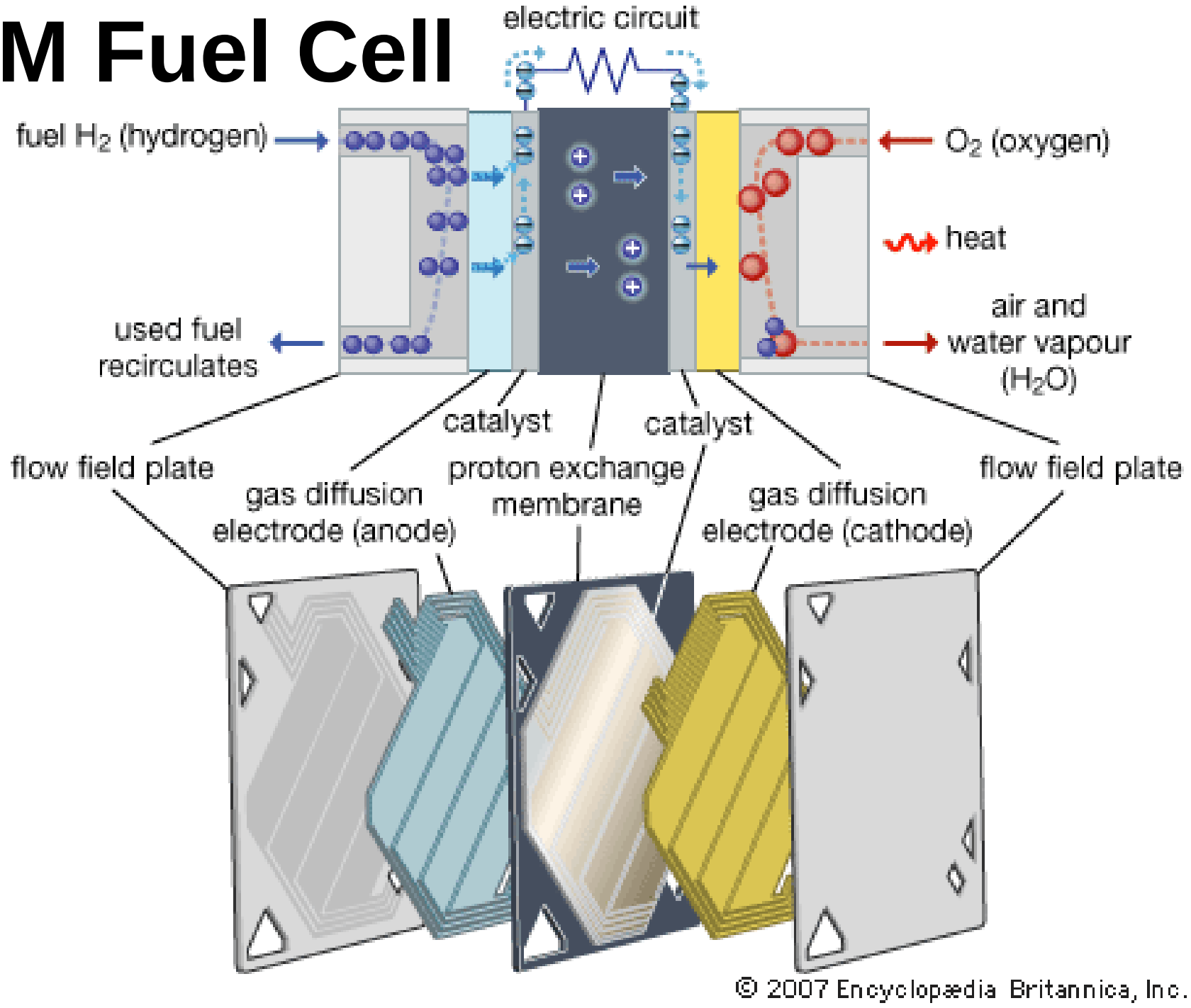
- **The first peak remains unchanged relative to the second because it represents the void volume of hydrogen in the tube rather than sorbed hydrogen**
- **The second peak represent sorbed hydrogen**
- **A temperature ramp is used to observed desorption**

Hydrogen Sorption Results and Conclusions (Task 3)



- Five composite materials have been produced that show promise for Hydrogen sorption
- Preliminary measurements have been made to verify the sorption properties
- Variations in the chemical composites have been eliminated by treatment with $NaBH_4$ thus reducing any unreduced species
- This material shows the highest sorption suggesting that treatment of the other chemically prepared composites may increase sorption properties

PEM Fuel Cell



Summary

FCAST is a joint experimental and theoretical project to enhance the understanding of hydrogen fuel cells and storage materials

- Joint experimental and theoretical work performed on electronic structure of carbon nanoclusters
- Stable structures of graphitic-BC_2N as potential hydrogen storage media identified
- The electronic structure of Ti decorated SWCNTs explored using X-ray and electron spectroscopy. Significant oxidation of Ti leading to TiO_2 formation is observed
- Systematically explored hydrogen uptake of transition metal-bonded organometallic systems (Sc, Ti, V) using DFT methods
- Proposed new class of carbon nanoframeworks (thin SWCNTs linked by phenyl spacers) as potential hydrogen storage media
- Investigated electronic structures and bondings in hydrogen saturated Ti and Ti-Al clusters and identified novel bonding motifs which may be harnessed to design novel hydrogen storage systems
- Synthesized bulk quantities of mesoporous PANI/Pd composites for hydrogen storage

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