UNLV
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DOE Hydrogen Program

Hydrogen Fuel Cells and Storage Technology Project

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UNLV Research Foundation

4/13/2007

Project ID #
STP17

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Overview

Timeline

- Project start: Sept. 2005
- Project end date: Sept. 2007
- Percent complete: 75%

Budget: Five tasks at UNLV (3 on storage, 2 on fuel cells)

- Total project funding: $7,927,500
  - DOE: $6,342K
  - UNLV: $1,585,500
- Funding in FY05: $3,720,000 ($2,976K Federal; $744K UNLV)
- Funding in FY06: $4,207,500 ($3,366K Federal; $841,500 UNLV)

Barriers

Primary:

M. Hydrogen Capacity and Reversibility

N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Secondary: B. Weight and Volume

Partners

- Collaborations with UTC, Stanford, Shanghai Jiaotong U, U Oslo, U Hawaii, Penn State, Air Products, Rice U, Berkeley Lab, Hahn Meitner Institute, LANSCE
- Project management: Bob Perret, UNLV Research Foundation

Objectives

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

Synergy between Experiment and Theory

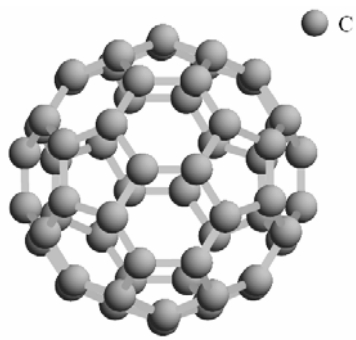
- Joint experimental and theoretical studies of carbon nanoclusters and stable graphitic BC_2N structures for hydrogen storage (Chen, Heske)
- Joint experimental and theoretical development of improved membranes for PEM fuel cells (Bae, Naduvalath)
- Joint experimental and theoretical work on metal hydrides (Cornelius, Kim)
- Closely integrated experimental and theoretical work on fuel cell membranes and catalyst development with an industrial partner (UTC; UNLV: Heske, Naduvalath, Bae)

Hydrogen adsorption on functionalized and pristine carbon nanoclusters (Task 1)

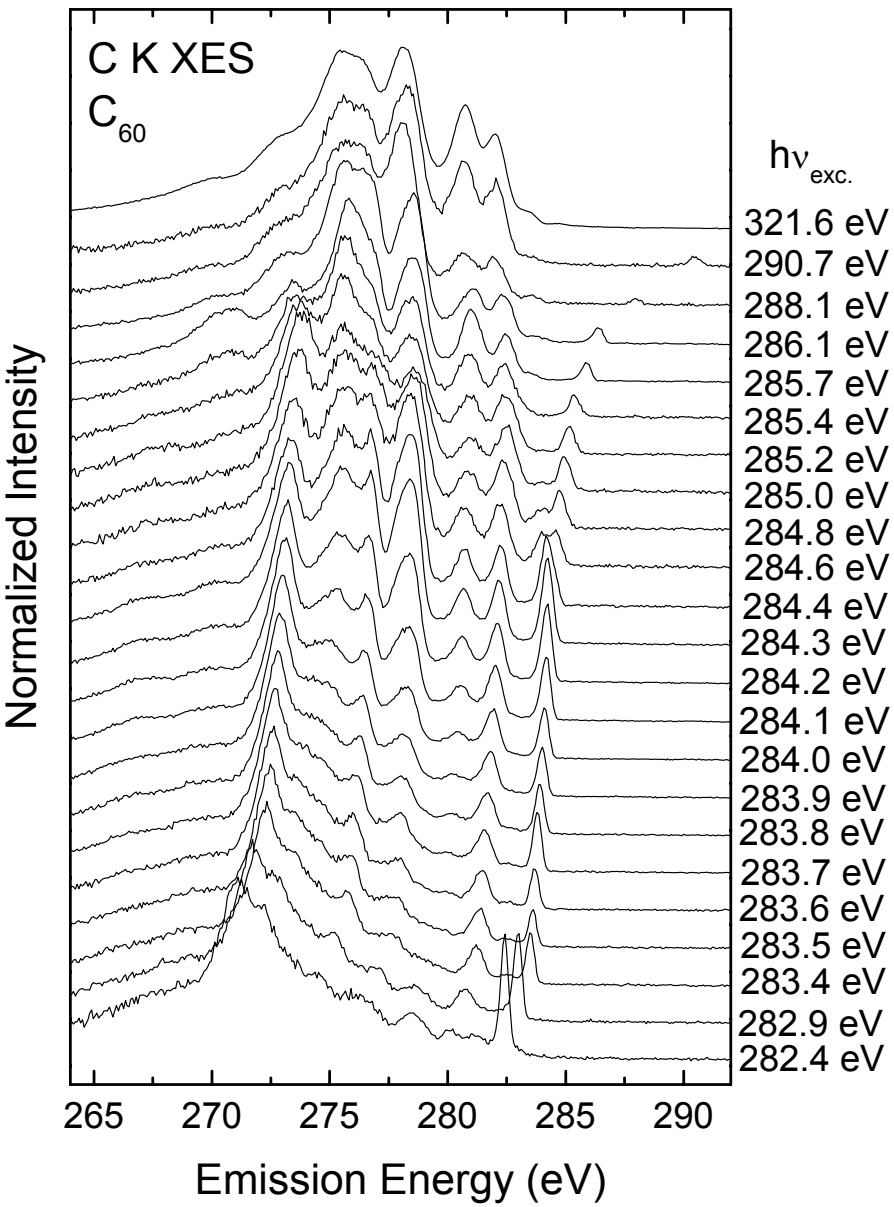
- ***Goal***:
  understand and clarify the mechanism and capacity of hydrogen adsorption on carbon nanoclusters with and without transition metal doping

- ***Approach***:
  - first-principles band structure calculations using the GW method
  - Calculations of electronic structure and lattice excitations for comparison with experiments
  - Experiments: local and non-local electronic structure measurements to compare with theory

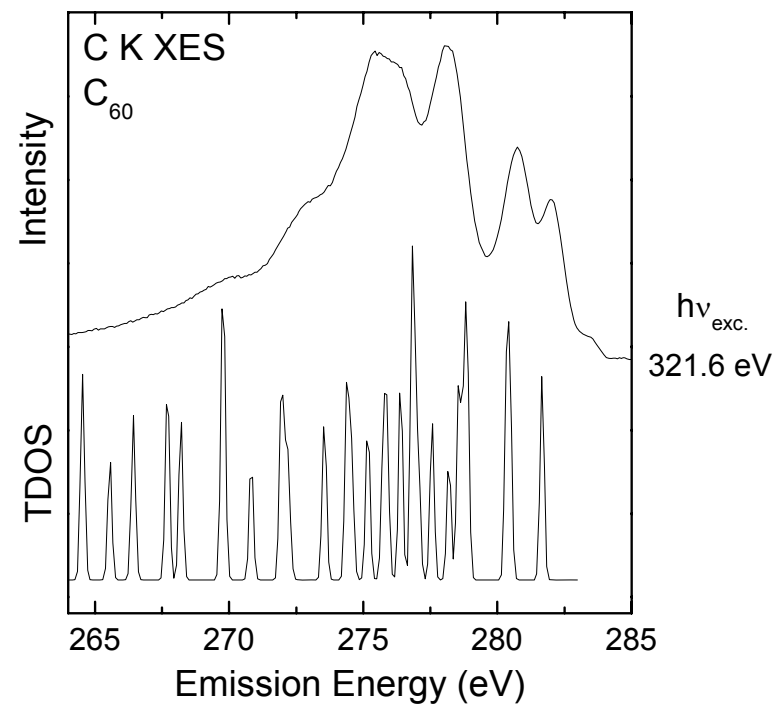
- ***Current Status:***
  - Electronic structure calculations in progress
  - Spectroscopy calculations being implemented
  - Experiments ongoing
  - Regular meetings between theory and experiment groups



Comparison of experimental and theoretical electronic structure of C_{60} (Task 1)

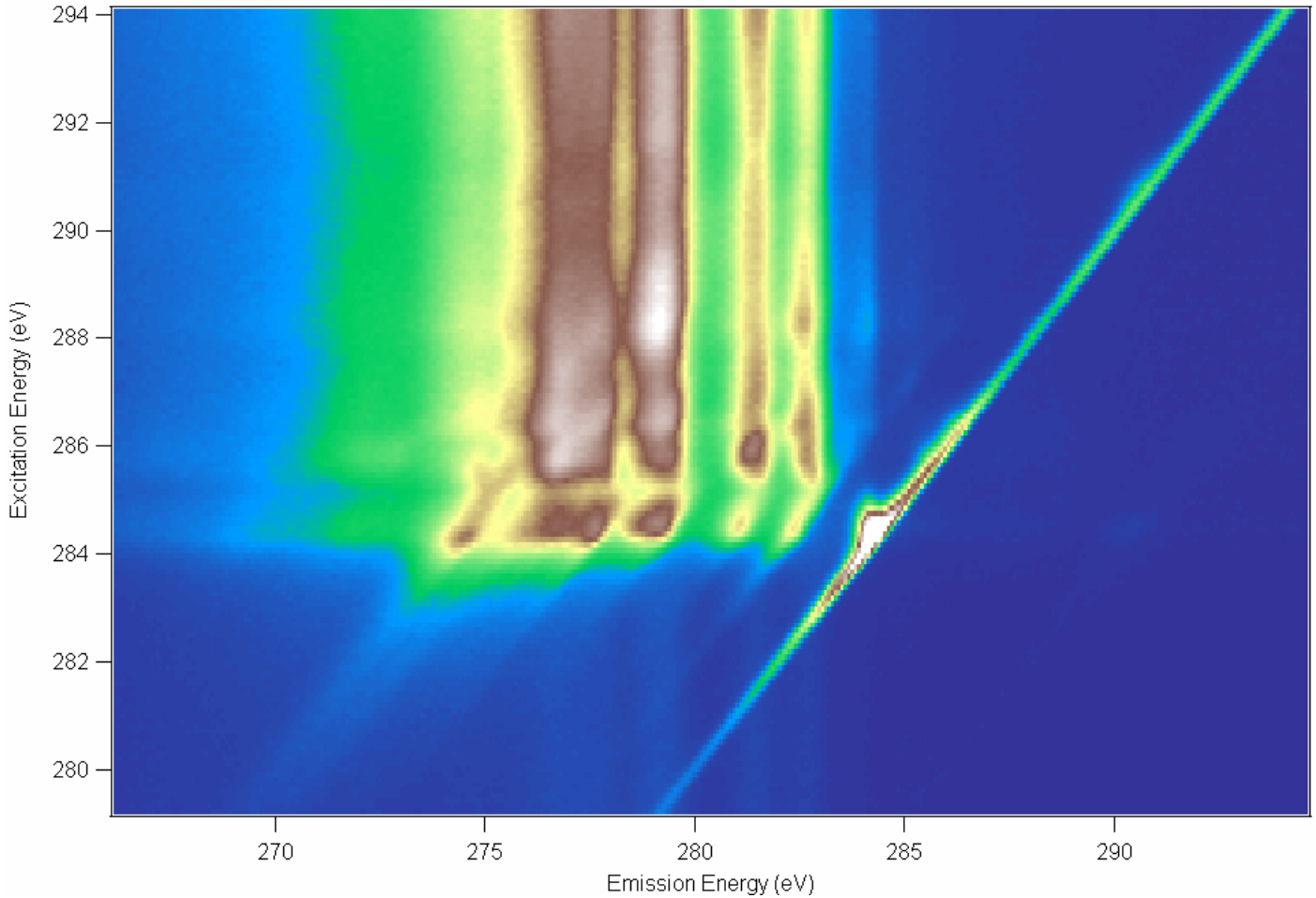


- Strong resonant effects in X-ray emission spectroscopy (XES) can be observed
- Raman-like behavior below $h\nu_{exc.}$=284.0 eV
- Increase in the intensity of the elastic scattered peak (Rayleigh line)
  → formation of a core exciton



- First DFT calculations (Total DOS) of C_{60}
- Complete GW band structure calculations in progress

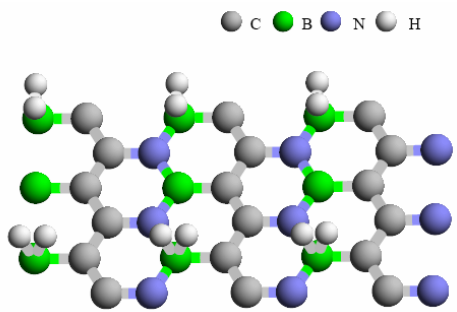
Rapid resonant XES mapping of C_{60} with new spectrometer (Task 1)



New spectrometer allows complete resonant XES mapping with unprecedented detail in substantially reduced time (30 minutes vs 8 hours)

Graphitic BC_2N as a hydrogen storage medium (Task 1)

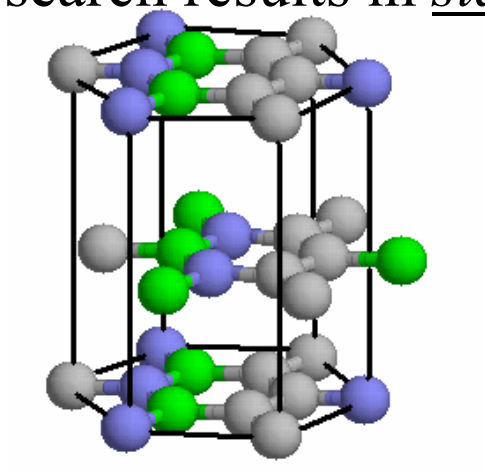
- ***Goal***: explore g-BC_2N as a potential high-capacity hydrogen storage medium. *Why BCN?* – binding energy enhancement by B-doping in C_n
- ***Approach***: determine hydrogen binding energy and capacity based on first-principles structural and electronic calculations
- ***Current status:***
  - Extensive search has been conducted and identified the stable structure synthesized in experiment
  - Electronic band structures with the GW correction have been obtained
  - Calculations of hydrogen adsorption in g-BC_2N are in progress; a large variety of configurations are being examined
  - Experimental probe planned

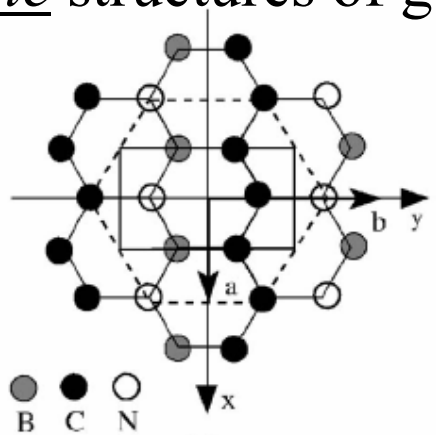


The structural form of g-BC_2N (Task 1)

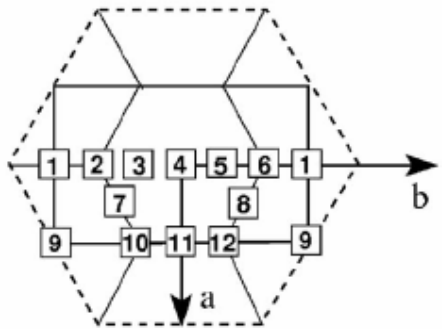
Extensive search results in *stable* structures of g-BC_2N:

3D View



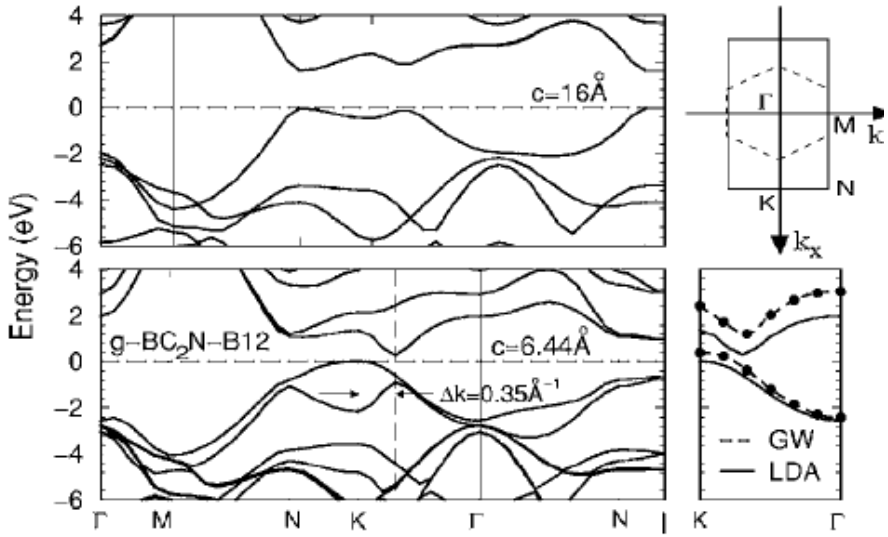


Top View

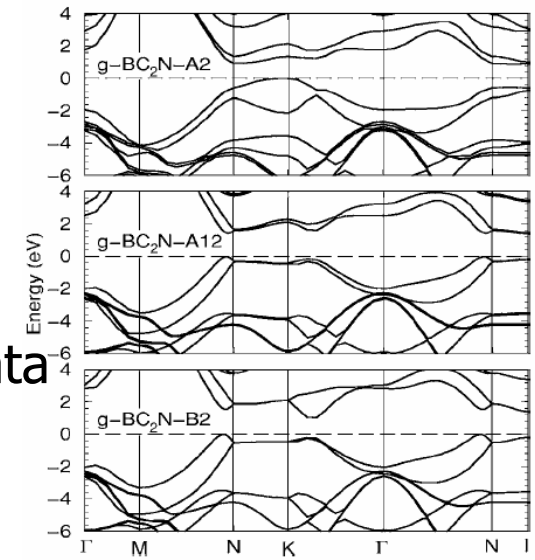


Interlayer stacking positions

The band structure of g-BC_2N



Calculated band dispersion and direct gap (2.05 eV) in excellent agreement with experimental data (2.1 eV).



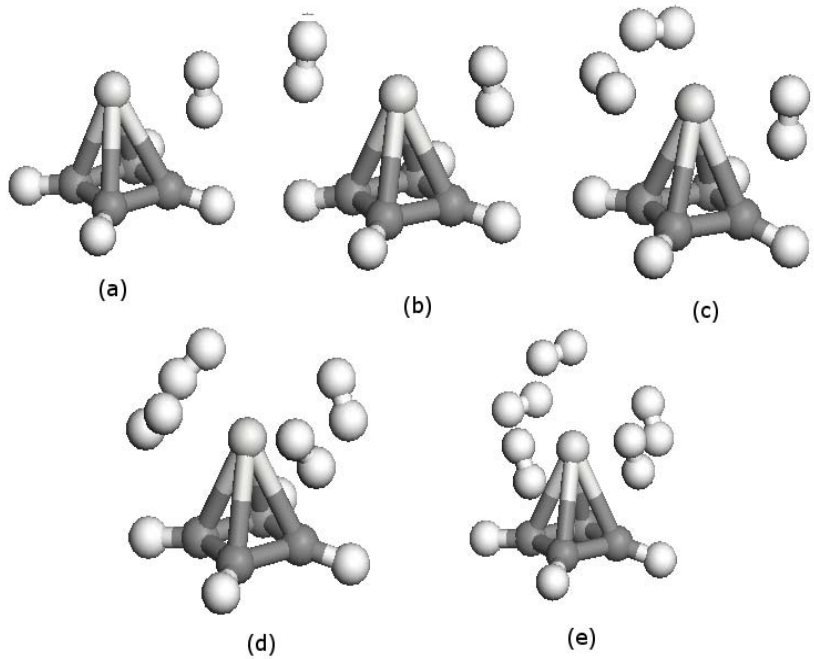
Computational study of organometallic compounds found that ScC_4H_4 can achieve 9.3 wt % H_2 storage (Task 1)

- Systematic study of hydrogen storage capacity of model organometallic systems consisting of **Sc**, **Ti** and **V** transition-metal atoms bound to C_mH_m rings (m=4-6).
- Calculations were performed using the density functional theory (GGA, PW91).
- The maximum retrievable H_2 uptake predicted is **9.3 wt %** using **ScC_4H_4**, slightly better than the **9.1 wt %** hydrogen using **TiC_4H_4** and much larger than the **7.2 wt %** hydrogen with **VC_4H_4**.
- Average binding energies:

  $ScC_4H_4(H_2)_n$: 0.33 eV/H_2

  $TiC_4H_4(H_2)_n$: 0.64 eV/H_2

  $VC_4H_4(H_2)_n$: 0.77 eV/H_2
- For **$ScC_4H_4(H_2)_n$** the average binding energy is close to the binding energy of individual H_2 molecules to the complex.



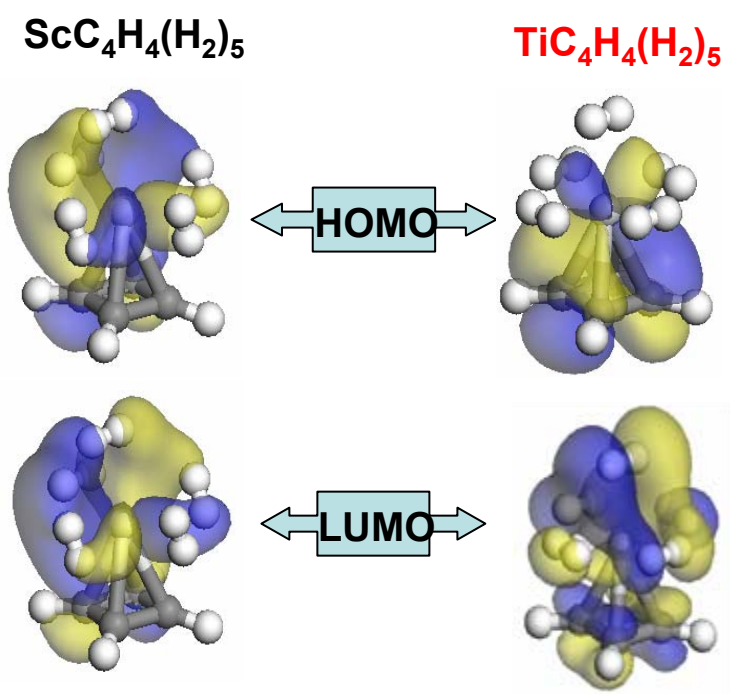
Optimized geometries of $ScC_4H_4(H_2)_n$ (n=1-5)

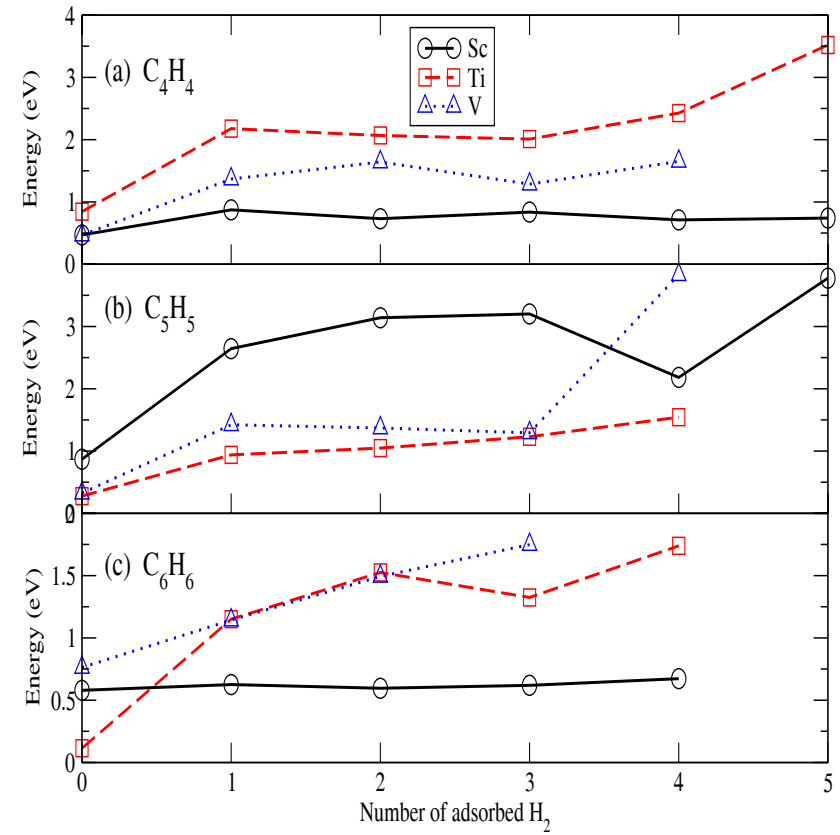
Calculated HOMO-LUMO gaps distinguish performance of similar compounds (Task 1)

$TiC_4H_4(H2)_n$ and $VC_4H_4(H_2)_n$ are found to be energetically more stable than $ScC_4H_4(H_2)_n$, in terms of the HOMO-LUMO gap.

Future theoretical effort:

Design of practical multidecker systems based on our findings.

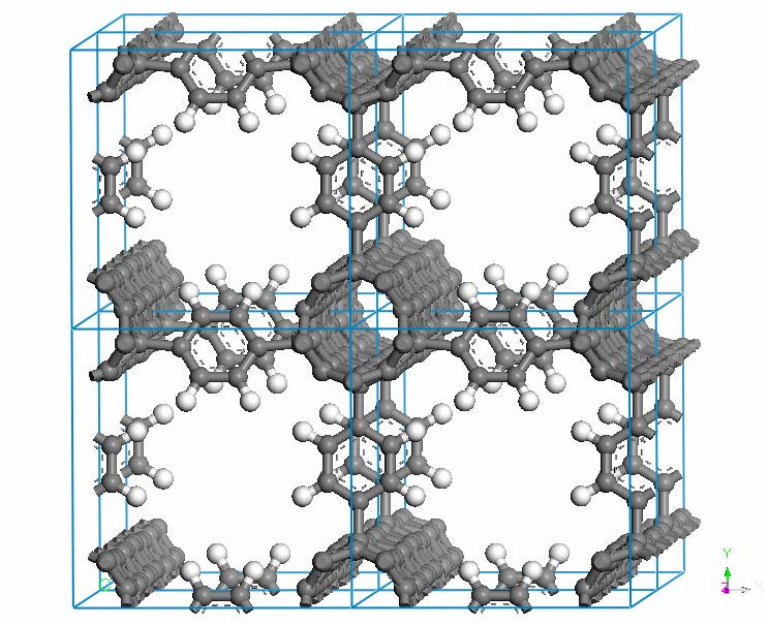




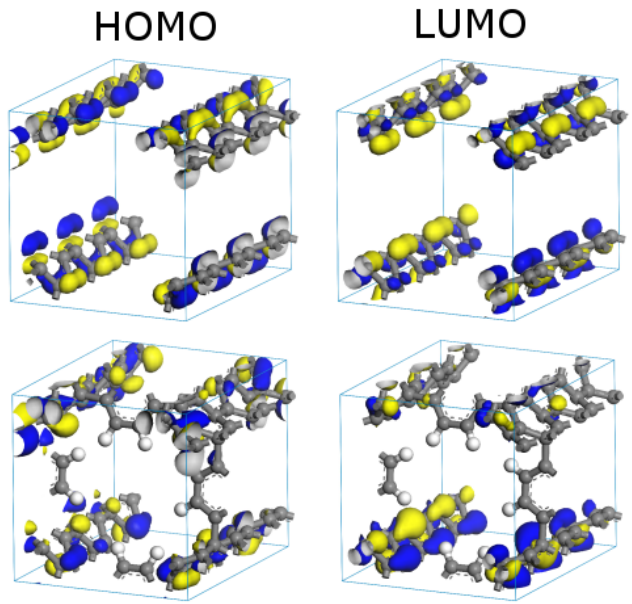
HOMO-LUMO gaps for $TMC_mH_m(H_2)_n$ (TM: Sc, Ti, V; m=4-6)

Carbon nanoframeworks are being designed and evaluated for hydrogen storage (Task 1)

- Novel class of 3-D materials consisting of small diameter single-walled carbon nanotubes (SWCNTs) functionalized by organic ligands are proposed, based on DFT calculations, as potential hydrogen storage media.
- Nanoframeworks consisting of (5,0) and (3,3) SWCNTs constrained by phenyl spacers are constructed.



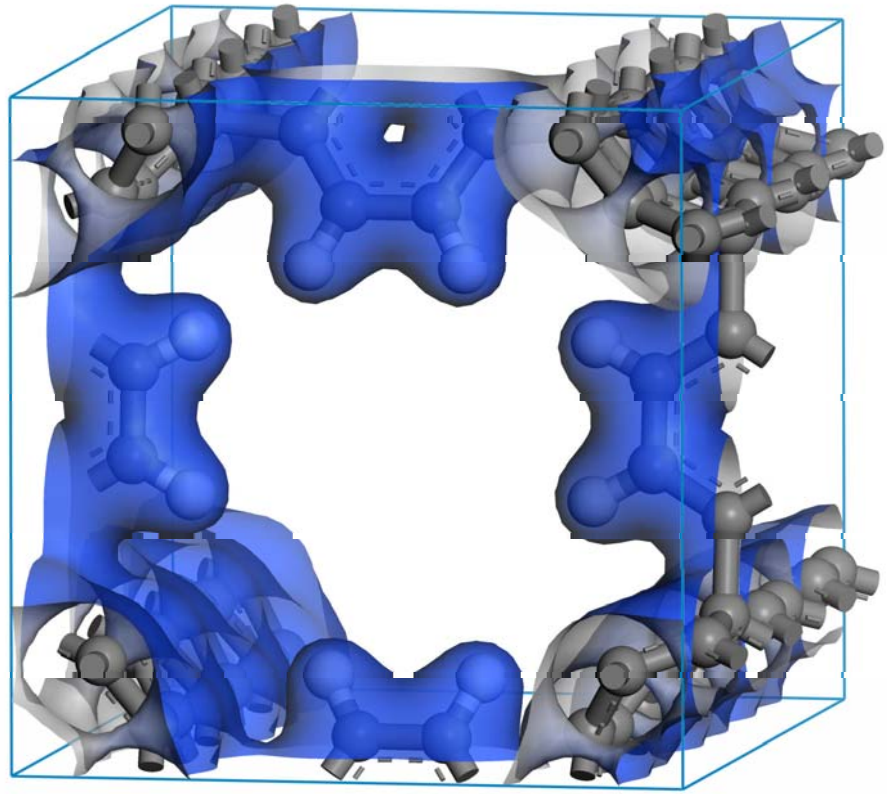
Optimized nanoframework structure consisting of (5,0) SWCNTs constrained by phenyl spacers. The unit cell is shown in blue.



HOMO (left) and LUMO (right) of pristine (5,0) SWCNTs (top) and the framework (bottom) consisting of (5,0) SWCNTs and phenyl ligands.

Properties of the nanoframeworks are being calculated (Task 1)

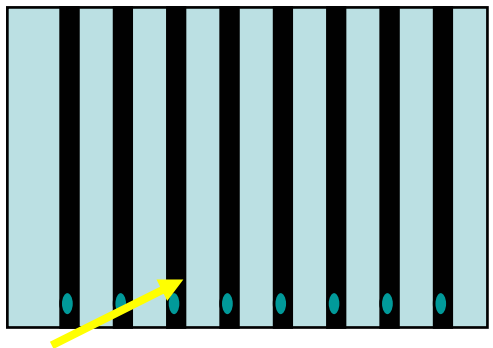
- The calculated frequencies of the radial-breathing modes (RBM) of pristine (5,0) and (3,3) SWCNTs are 534 cm^{-1} and 553 cm^{-1}, in good agreement with the Raman experimental values of 538 cm^{-1} and 576 cm^{-1}, respectively, for freestanding SWCNTs.
- Functionalization redshifts RBM frequencies to 511 cm^{-1} and 528 cm^{-1} for (5,0) and (3,3) frameworks.
- **Car-Parrinello molecular dynamics simulations indicate that the proposed frameworks are thermodynamically stable up to 600 K for at least up to 2 ps.**
- The role of metal doping (Li, Mg, …) and hydrogen uptake capacity of these nanoframeworks are being explored.



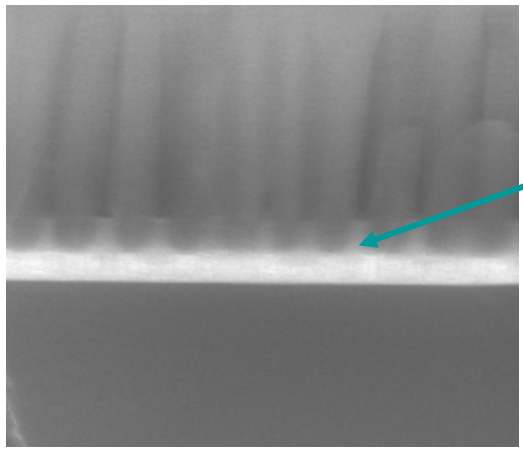
Electronic charge density of a framework consisting of (5,0) SWCNTs constrained by phenyl spacers. The value of the isosurface corresponds to 0.2 electrons/$Å^3$.

Carbon Nanotube Growth (Task 1)

Approach: Synthesize CNT inside an anodized alumina matrix

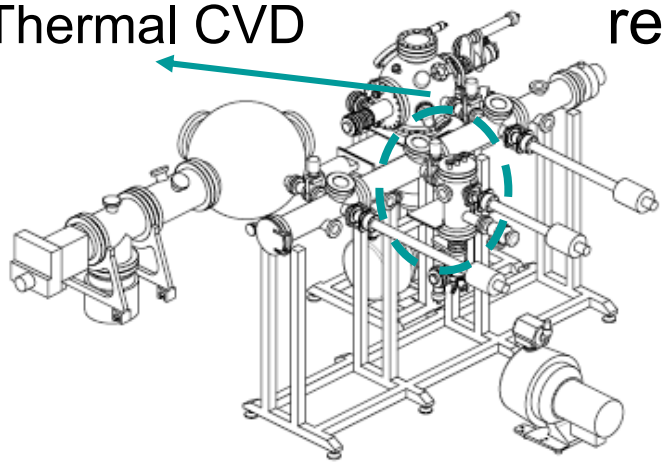


Catalyst

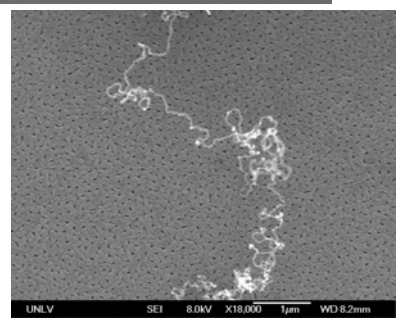


Ni nanowire array inside alumina matrix as catalysts for CNT array growth

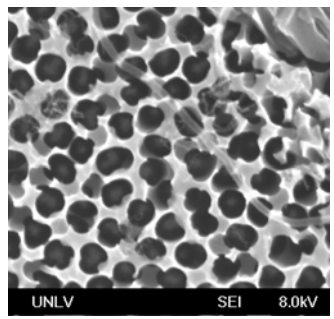
PECVD and Thermal CVD



First results



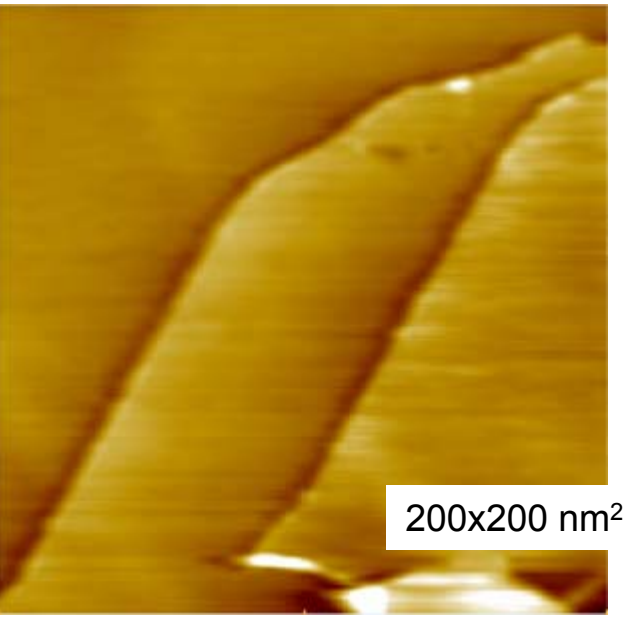
A long carbon nanotube anchored at different points inside the nanomatrix containing Ni seeds

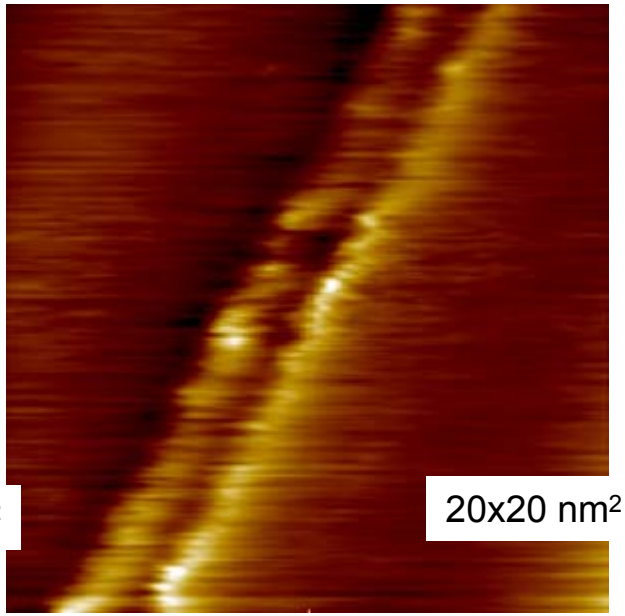


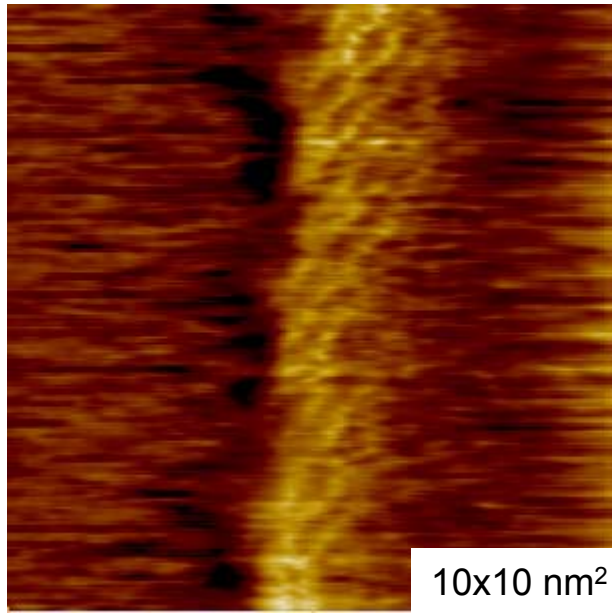
Carbon nanotubes inside the nanoporous matrix

New STM at UNLV allows atomic resolution imaging of SWCNT (Task 1)

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

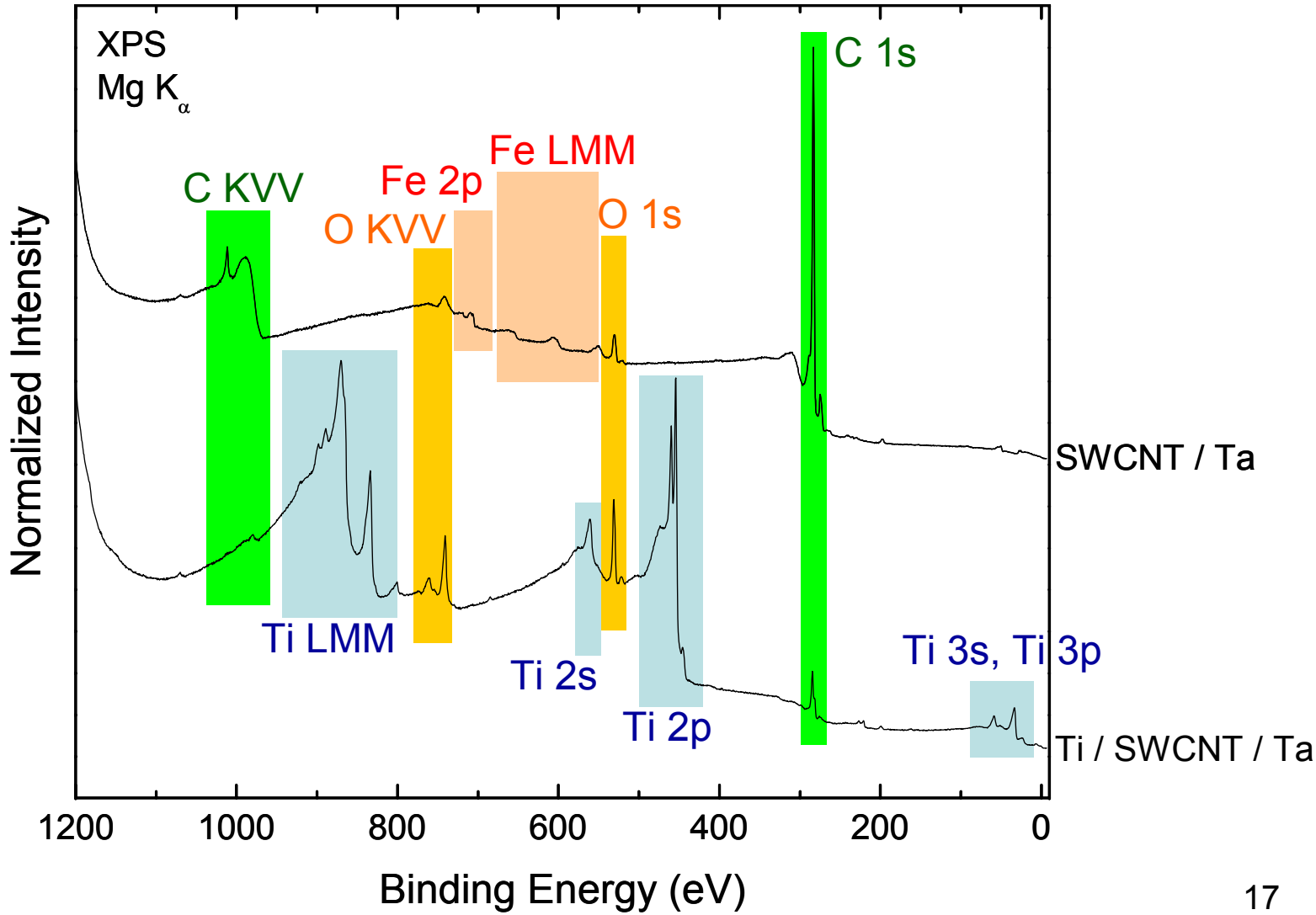




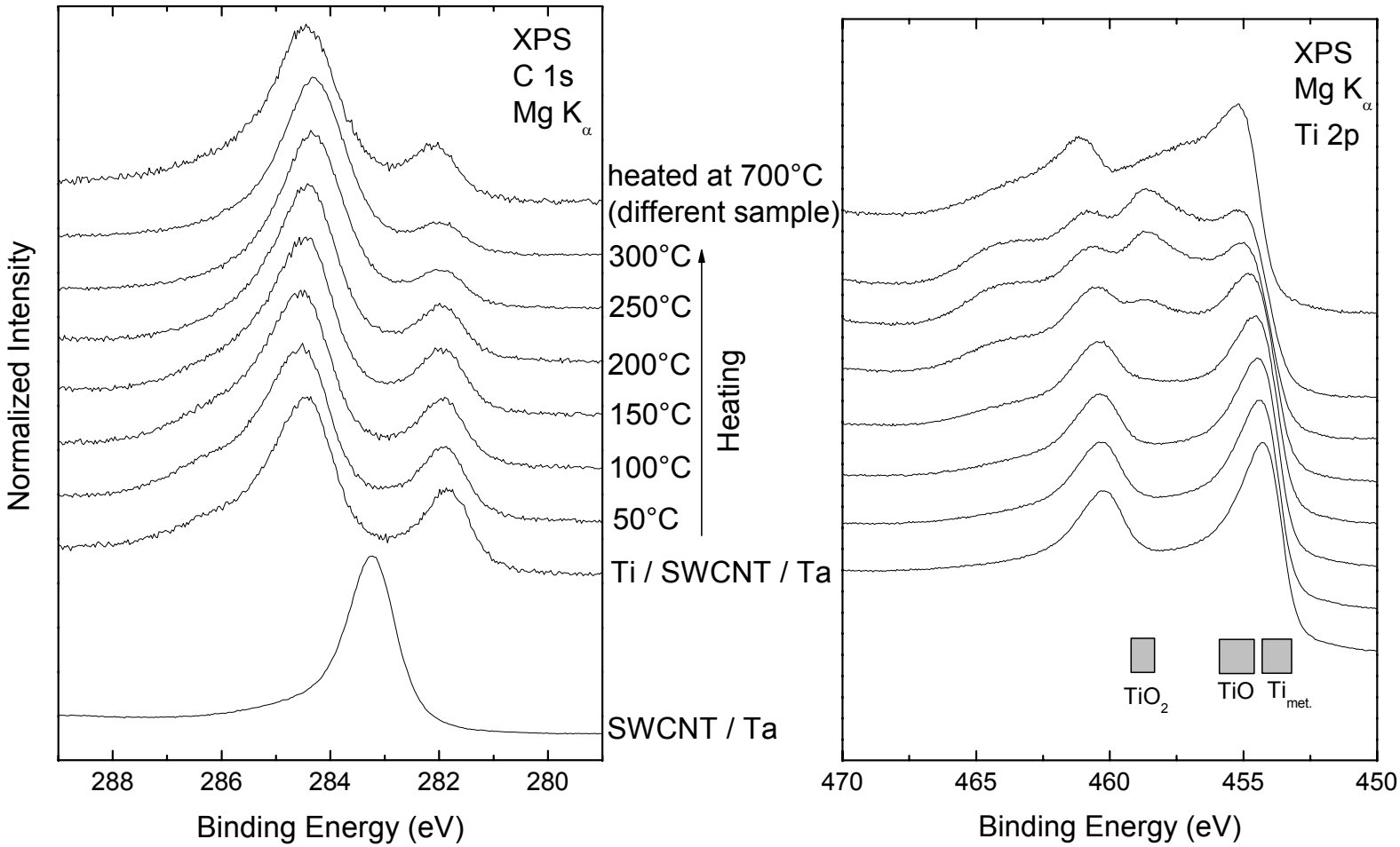


- Electro deposition worked
- Low coverage with long SWCNT
- “Small” bundles (e.g. two bundled tubes) and individual tubes are observed
- Atomic resolution can be achieved

XPS measurements show electronic structure changes in C with Ti doping (Task 1)

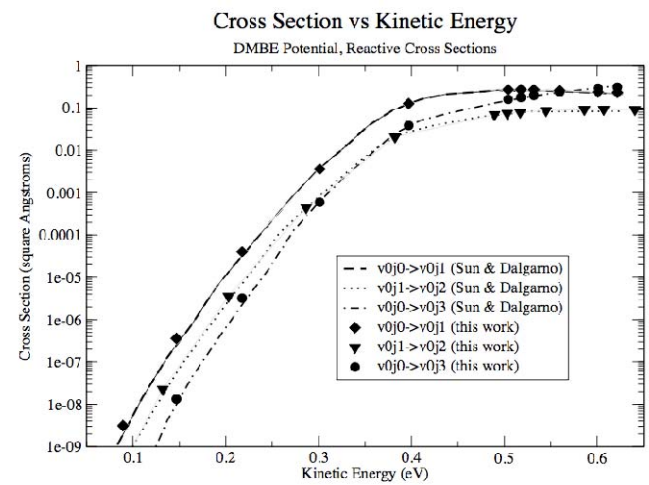


Heat-treatment of Ti-decorated SWCNT induces oxidation! (Task 1)

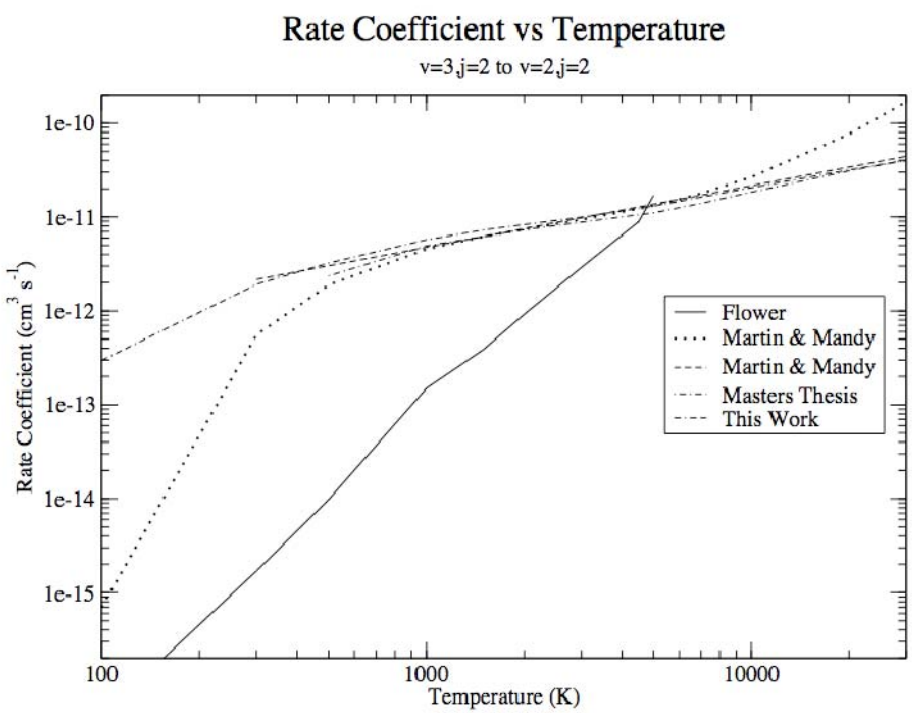


- C 1s shifted, new C 1s component visible
- Low binding energy component decreases after heating
- New Ti 2p component (TiO_2) emerges after heating

H-H_2 Cross Sections up to 3.5 eV have been completed; further work on this topic will be done under other funding sources



- The rotational cross sections agree well with previous calculations of Sun and Dalgarno (right panel).
- The improved set of cross sections will be valuable in modeling hydrogen combustion processes (e.g., hydrogen ICEs).



- The present study provides improved rates that are valid at low and high temperatures and smoothly connect to previous high temperature results derived from classical trajectory calculations.
- The previous quantum calculations (Flower - see left panel) underestimate the rates by several orders of magnitude at low energies.

Task 1: Summary of Technical Accomplishments

- Coordinated Experimental and theoretical studies of hydrogen sorption on pristine and functionalized carbon nanoclusters in progress. Newly installed spectrometer allows complete RIXS mapping in much reduced time.
- Graphitic BC_2N as potential high capacity hydrogen storage media being explored. Stable structures of g-BC_2N identified. Band structure calculations with DFT-GW method predict band gap in excellent agreement with experiment. Further experimental probe is planned.
- Systematic study of hydrogen storage capacity of transition metal (Sc, Ti, V) bonded organic C_mH_m (m=4-6) systems performed. ScC_4H_4 is predicted to have a H_2 -uptake capacity of 9.3 wt% with an average binding energy of 0.33 eV/H_2.
- Novel 3D-carbon nanoframework consisting of small diameter SWCNTs functionalized by phenyl spacers is proposed as potential hydrogen storage media. MD simulations indicate that the structures are stable up to 600 K.
- UNLV nanomatric system installed and first results of carbon nanotube growth in anodalized alumina obtained using chemical vapor deposition.
- XPS studies of Ti-decorated SWCNTs show substantial oxidation upon heat-treatment leading to TiO_2 formation.
- Peer-reviewed publications (4 published, 1 in print, several in preparation)

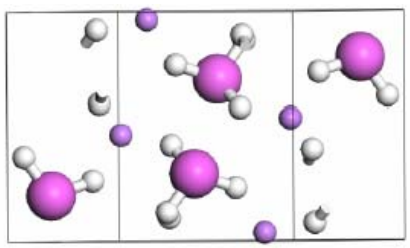
Hydrogen storage in complex solid hydrides (Task 2)

- ***Goal***: examine the thermodynamic phase stability of various existing and proposed solid hydrides and predict reaction path, reversibility and barrier; explore new materials and the effect of doping and pressure

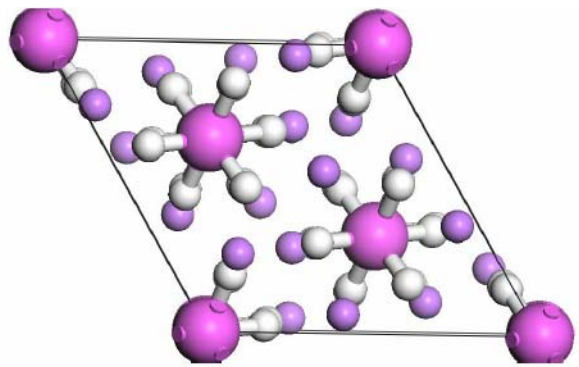
- ***Approach***: first-principles electronic structure and lattice dynamics calculations within and beyond the harmonic phonon approximation

- ***Current Status:***

- Extensive calculations on $LiAlH_4$ and Li_3AlH_6 clarify the reaction pathway and phase diagram
- Study of other hydrides in progress



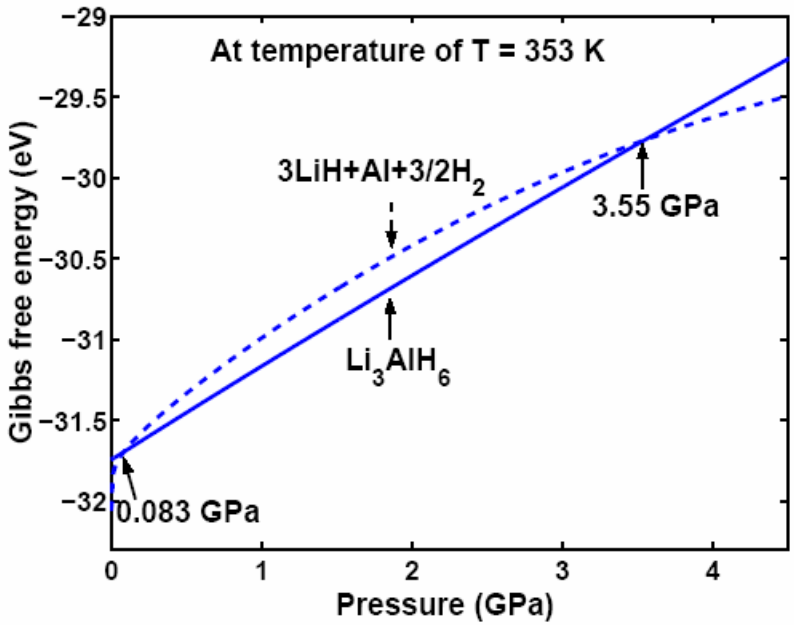
$LiAlH_4$

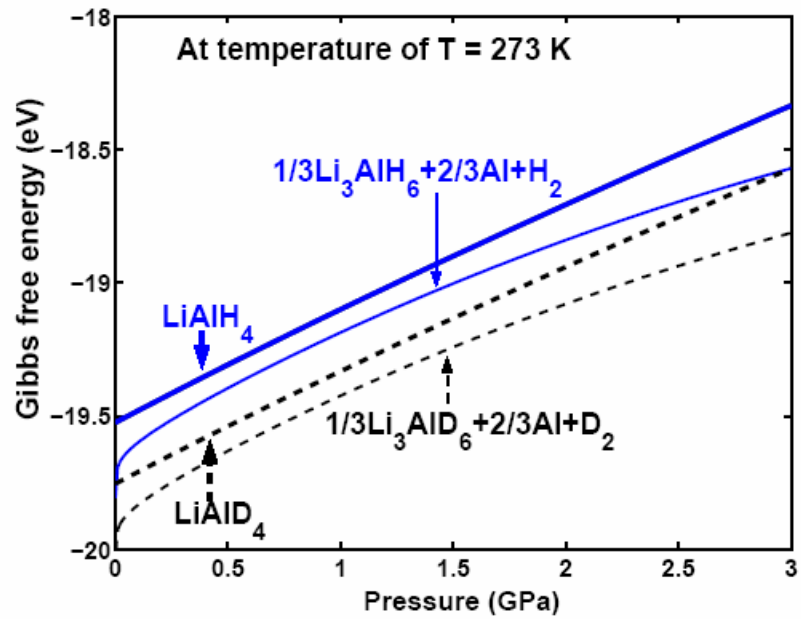


Li_3AlH_6

$LiAlH_4$ and Li_3AlH_6: reaction reversibility and phase diagrams calculated

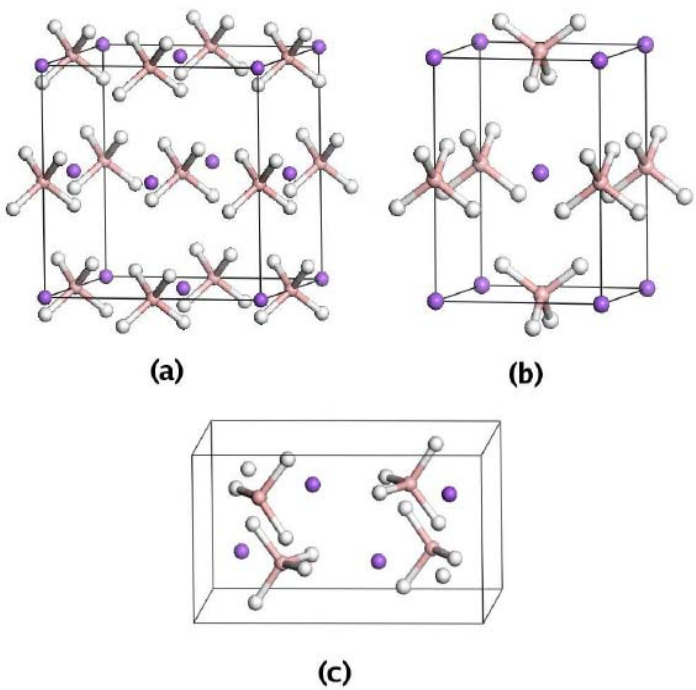
- The calculated Gibbs free energies clarify the issue of reaction reversibility and help establish the phase diagram
- $LiAlH_4 \rightarrow 1/3Li_3AlH_6+2/3Al+H_2$ is irreversible
- $Li_3AlH_6 \rightarrow 3LiH+Al+3/2H_2$ is reversible; phase diagram proposed

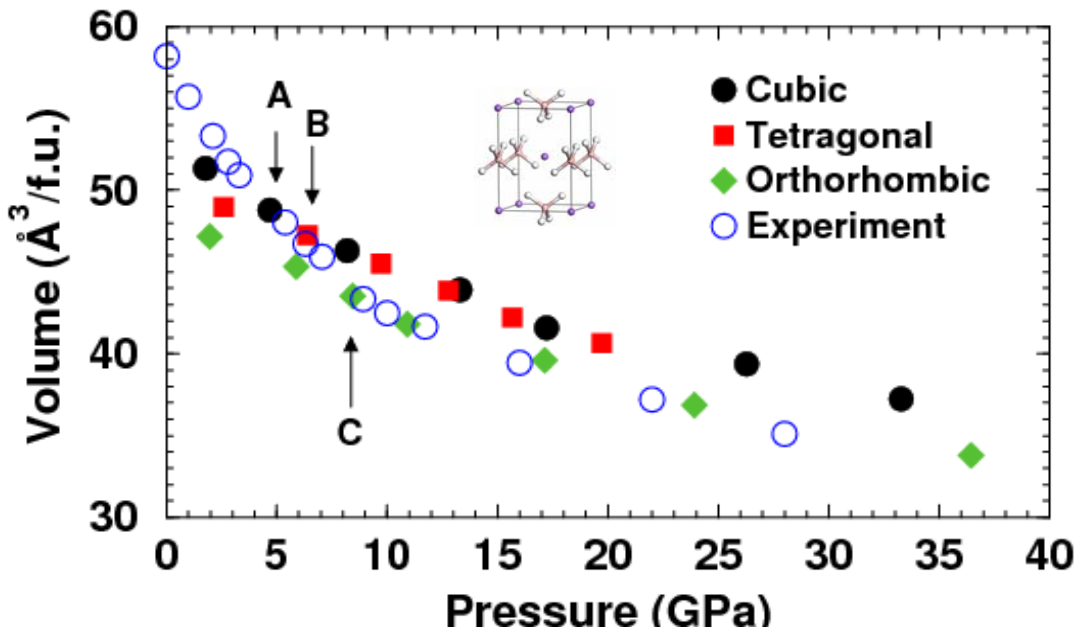




Structural characterization of $NaBH_4$ (Task 2)

Structural transitions in $NaBH_4$ and $NaAlH_4$ have been investigated theoretically and compared to x-ray diffraction and neutron scattering experiments. We identify the high pressure phases which might identify methods to improve the hydrogenation process.

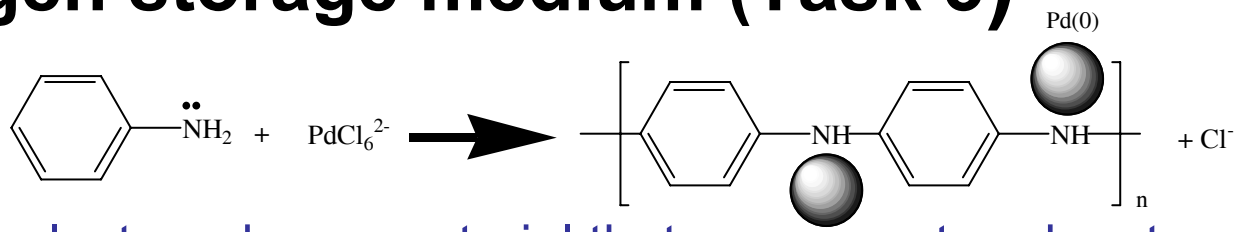




Task 2: Summary of Technical Accomplishments

- First principles electronic structure and lattice dynamics calculations are performed to predict reaction path, reversibility and the effects of doping and pressure on hydrogen storage in complex solid hydrides.
- Reaction path and phase diagram of $LiAlH_4$ and Li_3AlH_6 established.
- Structural transitions in $NaBH_4$ and $NaAlH_4$ have been investigated theoretically and results compared to x-ray diffraction and neutron scattering experiments.
- High pressure phases of $NaBH_4$ and $NaAlH_4$ identified which may provide clues to enhance hydrogenation process.
- Joint theory-experiment peer-reviewed publications (1 published, 2 in print, 1 submitted).

Mesoporous Polyaniline/Pd synthesized as a hydrogen storage medium (Task 3)



- PANI is electron dense material that can accept or donate electrons to a given chemical species
- Nitrogen head groups provide sites for chemical and electronic interactions
- PANI provides 3-D matrix for the dispersions of metal species and increased surface area of the metal
- Potential-dependent reduction of metal anions and cations allows the controlled uptake and dispersion of metals into the polymer
- Polymer/metal composites show unique properties relative to bulk metal electrodes
- The metals can be used as chemical platforms within the polymer to develop specific chemical interactions for hydrogen storage (and sensing, catalysis, …)

This approach does not duplicate earlier work

- First one-pot synthesis of PANI/Pd composite using $PdCl_6^{2-}$ anion as the only chemical oxidant

  Bulk quantities of material produced

  Optimum electronic properties (equal oxidized/reduced units)

- Controlled electrochemical uptake and reduction of $PdCl_6^{2-}$ and $PdCl_4^{2-}$

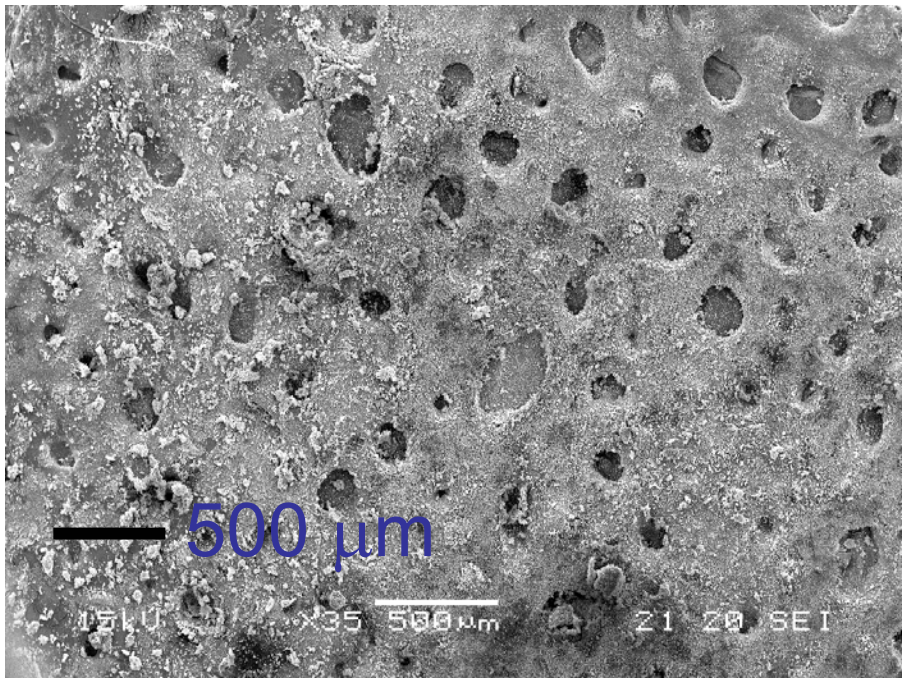
  Electronic connection between electron-dense polymer and Pd metal

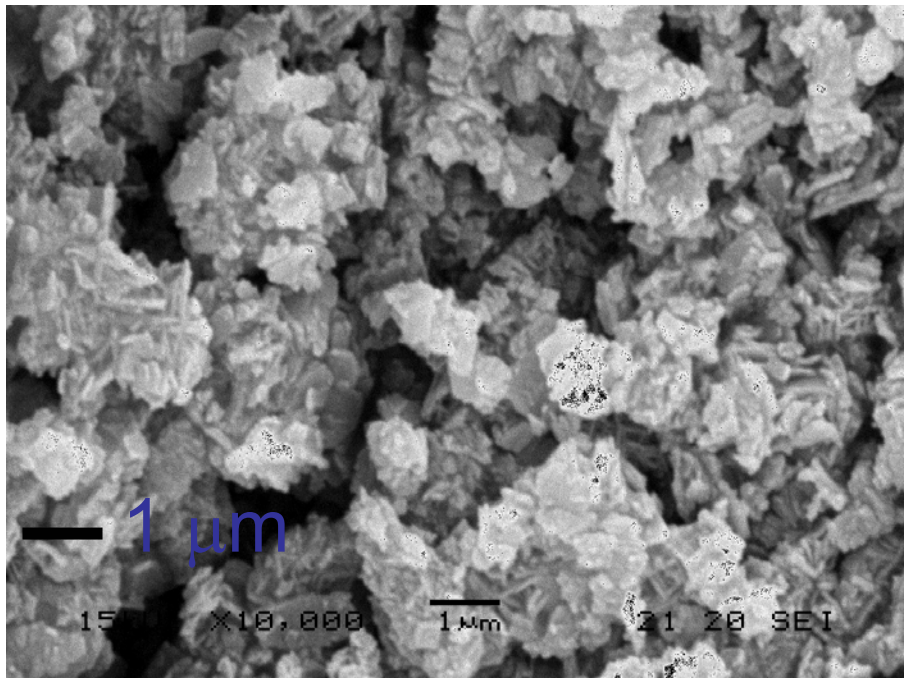
  Oxidation state not optimum (not equal oxidized/reduced units), but conductivity of polymer is not significantly reduced

  $\Rightarrow$ Symbiosis between polymer and metal?

  Morphology difference due to difference in nucleation and growth energies of the two Pd-anions (as in the case of Pt)?

SEM of chemical PANI/Pd shows porous structure (Task 3)





High surface area/fast diffusion

Task 3: Summary of Technical Accomplishments

- First one-pot chemical synthesis of PANI/Pd composite using $PdCl_6^{2-}$ anion as the only chemical oxidant accomplished.
- Bulk quantities of the material with optimum electronic properties synthesized.
- SEM shows that PANI/Pd composites have porous structure with high surface area for fast hydrogen diffusion.
- PANI/Pd composites provide chemical platforms for hydrogen storage, sensing and catalysis.
- Two peer-reviewed publications in 2006.

Hydrogen storage future work

Task 1

- Continue combined theoretical and spectroscopic investigations of hydrogen interaction with Ti-decorated SWCNTs. Further explore the effect of oxidation of doped Ti upon heat-treatment.
- Continue experimental and theoretical studies of hydrogen uptake on pristine and functionalized B-C-N nanostructures.
- Investigate hydrogen storage capacity and the effect of metal doping on the proposed carbon nanoframeworks.

Task 2

- Understand the role of Ti as a catalyst in reversible hydrogen storage in complex metal hydrides. In particular, the formation and bonding of the Ti-Al phase and the interaction of H_2 with nanoclusters of Ti-Al systems is being investigated.

Task 3

- Further synthesis and measurement of hydrogen uptake on PANI/Pd composites already synthesized.

Summary

- 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
- Synthesized bulk quantities of mesoporous PANI/Pd composites for hydrogen storage
- UNLV nanomatrix system installed. First results of carbon nanotube growth in anodized alumina using chemical vapor deposition have been obtained
- All experimental and computational capabilities are in place