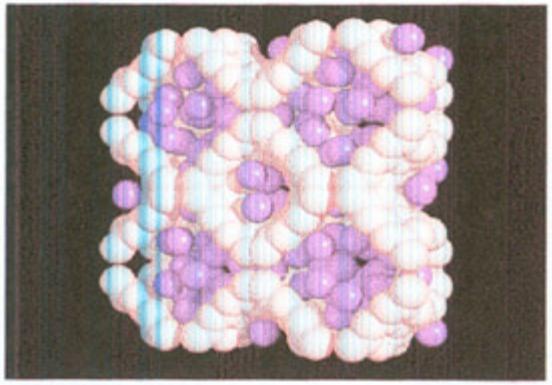
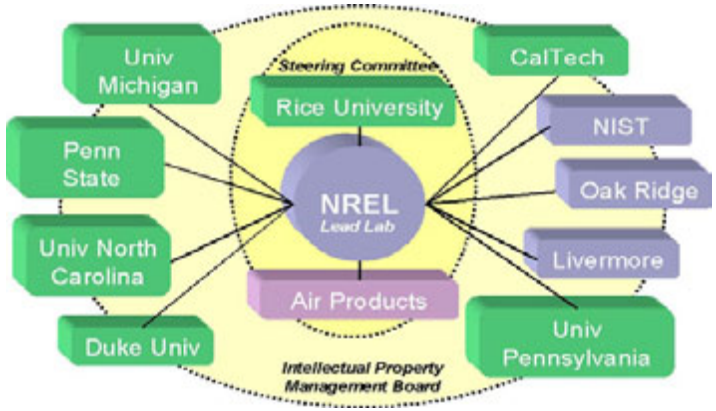





## 2006 DOE Hydrogen Program

# Advanced Boron and Metal Loaded High Porosity Carbons

**M. Chung, V. Crespi, P. Eklund and H. Foley**

*Pennsylvania State University*

May, 2006

This presentation does not contain any proprietary or confidential information

Project ID: **ST # 27**

# Overview

## Timeline

- Project start: 2/1/05
- Project end: 1/31/10
- % complete: 20%

## Budget

- Total project funding
  - DOE share: $1.2M
  - Contractor share: $0.3M
- FY05 $ 150,000
- FY06 $ 225,000

## Barriers addressed

A: *System Wt & Vol:* Hydrogen volumetric (1.5 kWh/L) and gravimetric (6wt%) storage density goals for 2010

B: *System Cost:* High-volume low-cost synthesis routes (via pyrolysis, arc)

C: *Energy Efficiency:* Low pressure, moderate temperature operation (via enhanced binding energy through chemical modification)

E: *Charge/discharge rate:* via Mixed micro/mesopore structures through precursor design

J: *Thermal management:* via designed moderate binding energies of mixed physi/chemi-sorption

P: *Improved understanding:* via calculations in close coupling with fundamental measurements on well-characterized, well-ordered systems

R: *Reproducibility:* PC-based differential volumetric apparatus

## Partners

- Dispersed throughout CbHS:NIST (neutron), NREL (TPD), Air Products (vol. ads.)
- S. Bandow & S. Iijima (Nagoya U)
- M Dresselhaus (MIT)
- Carbolex, Inc

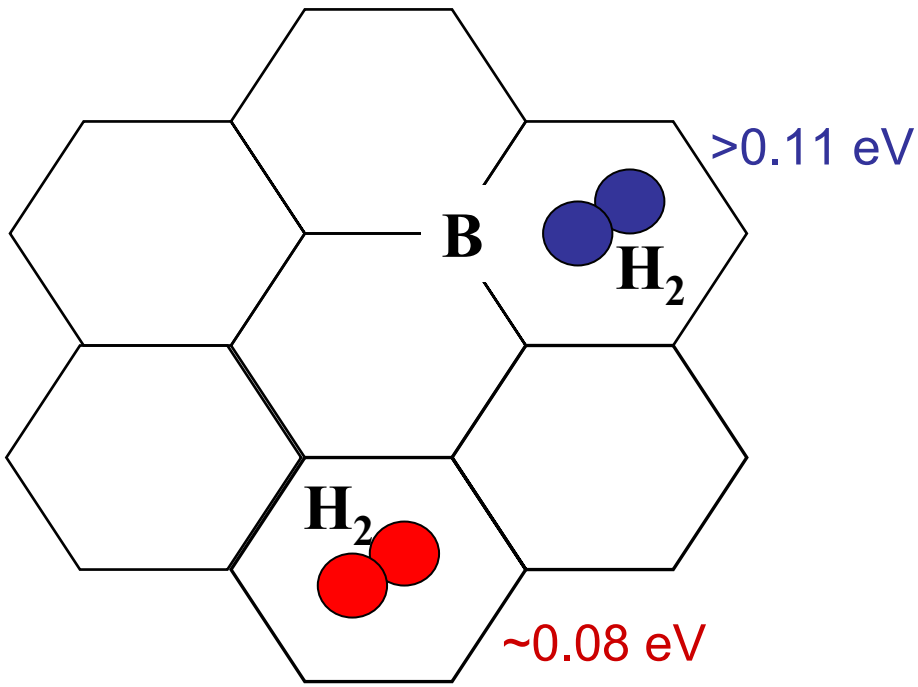
# Objectives / Approach (I)

- **Advanced Hydrogen Phys/Chem-isorption Materials**
  - *Reversible, low mass density, low volume, good thermodynamics*
  - *Materials Goal: Reversible storage of ~6wt% at 200K, 100 atm by 2008.*
- **High SSA Carbons as the Launching Platform**
  - *Many precedents for high surface area $sp^2$ bonded carbons*
  - *Chemically modify carbon framework for* ***enhanced*** *$H_2$ binding energy*
  - *Use this platform to atomically disperse H-active metals*
- **Boron-substitution to enhance binding energy of hydrogen**
  - *Boron is the only element known to substitute in the $sp^2$ framework without serious structural distortions.. Must maintain high Specific Surface Area (SSA)*
  - *Boron is a light element.. We need large gravimetric storage*
  - *Shake up the Chemistry of the Carbon Framework with Boron*
    - *Load Boron as high as $BC_3$ to create an electron-deficient framework*
- **Atomically dispersed metal atoms to further enhance binding**
  - *We predict boron stabilizes atomic dispersion of metal atoms*
  - *Metal atoms supported on top of high SSA framework*
  - *Bi-functional H-storage: Metal atoms available for multi-center $H_2$ coupling& chemisorption via M-H bonds*

# Objectives / Approach (II)

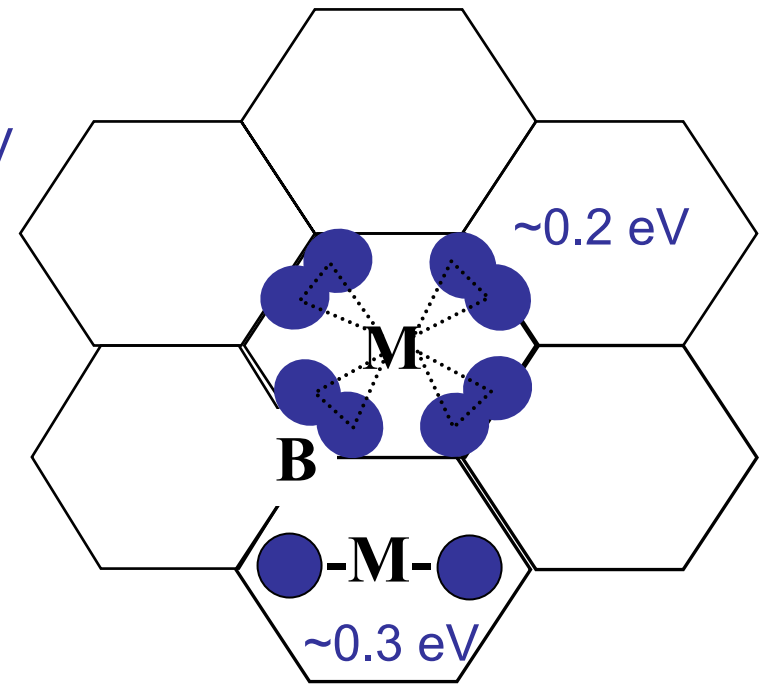
**Schematic of $sp^2$ carbon network and sites for binding atomic and molecular hydrogen**

**Substituted Boron Enhances $H_2$ Binding**



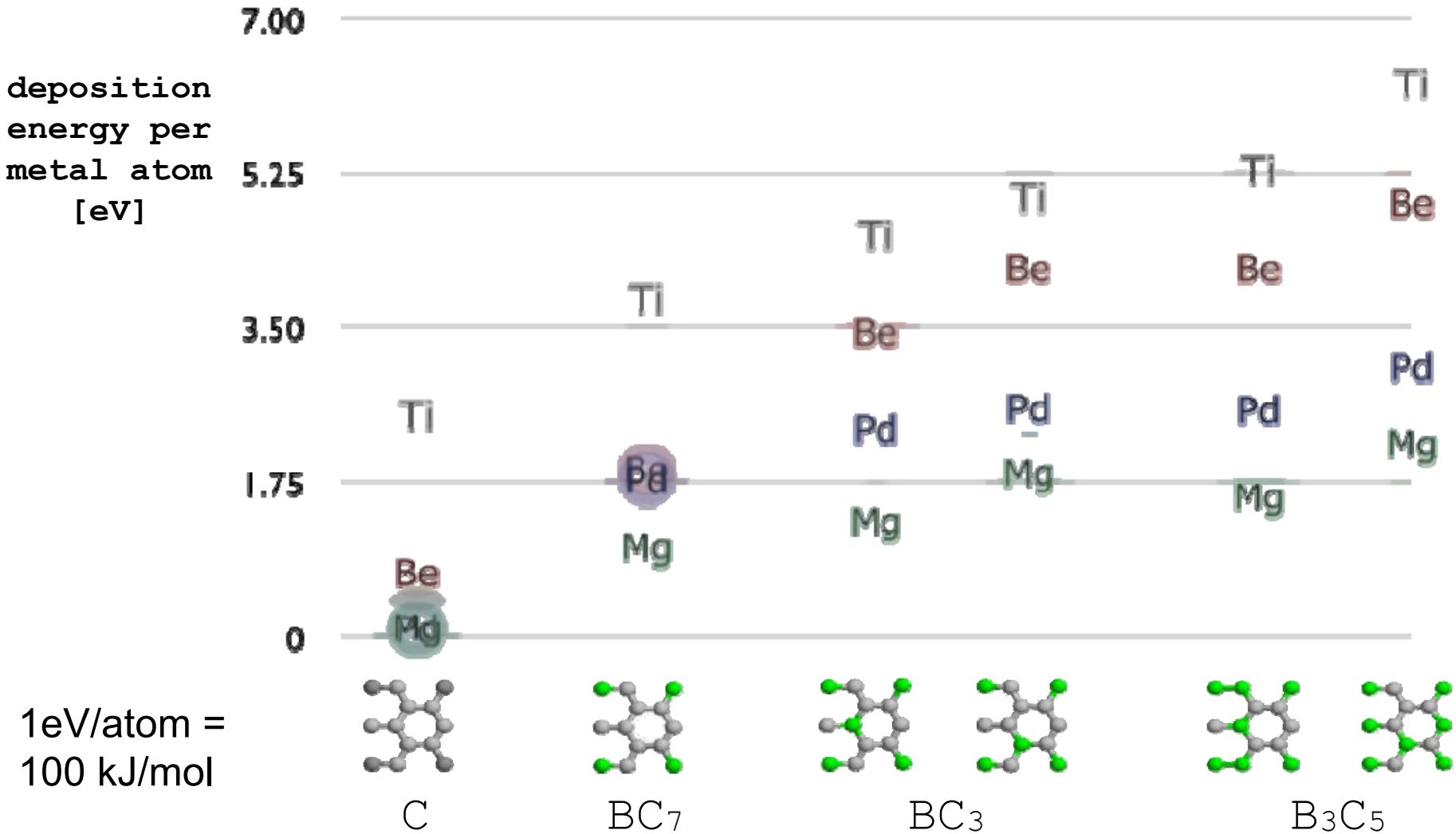

B=Boron

**Substituted Boron stabilizes Atomic Metal**




M=Metal

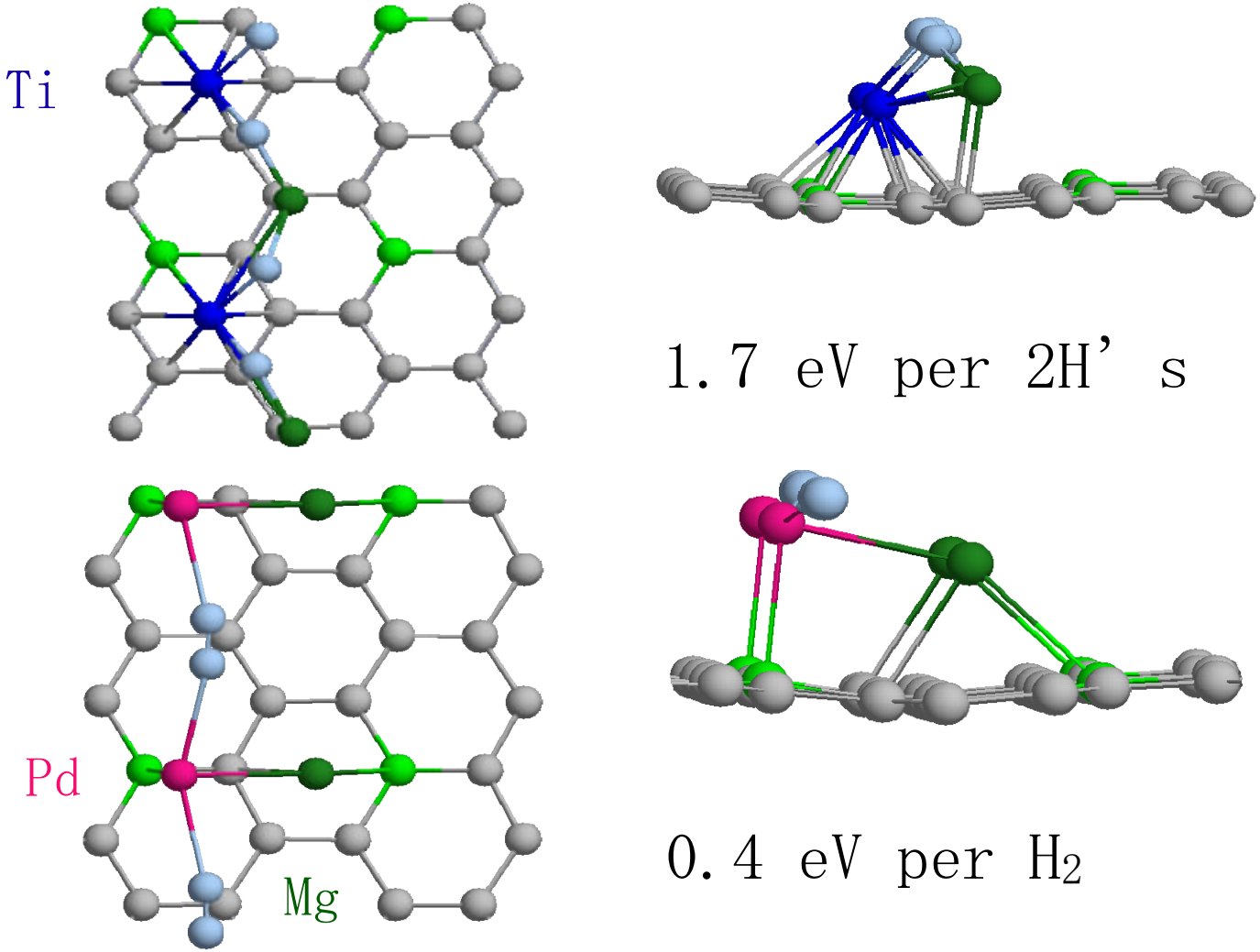
**Boron and metal modifications of the carbon framework show promise to raise the binding energy of H2 into the range necessary to meet DOE wt%, volumetric, pressure and cost targets for 2010 and beyond.**




1eV/atom = 100 kJ/mol

Accomplishment: Calculations demonstrate that boron incorporation stabilizes many metals atomically dispersed, and so defines a highly promising synthetic target for physical/chemical binding of hydrogen

# Calculated Hydrogen Interaction with Dispersed Metals

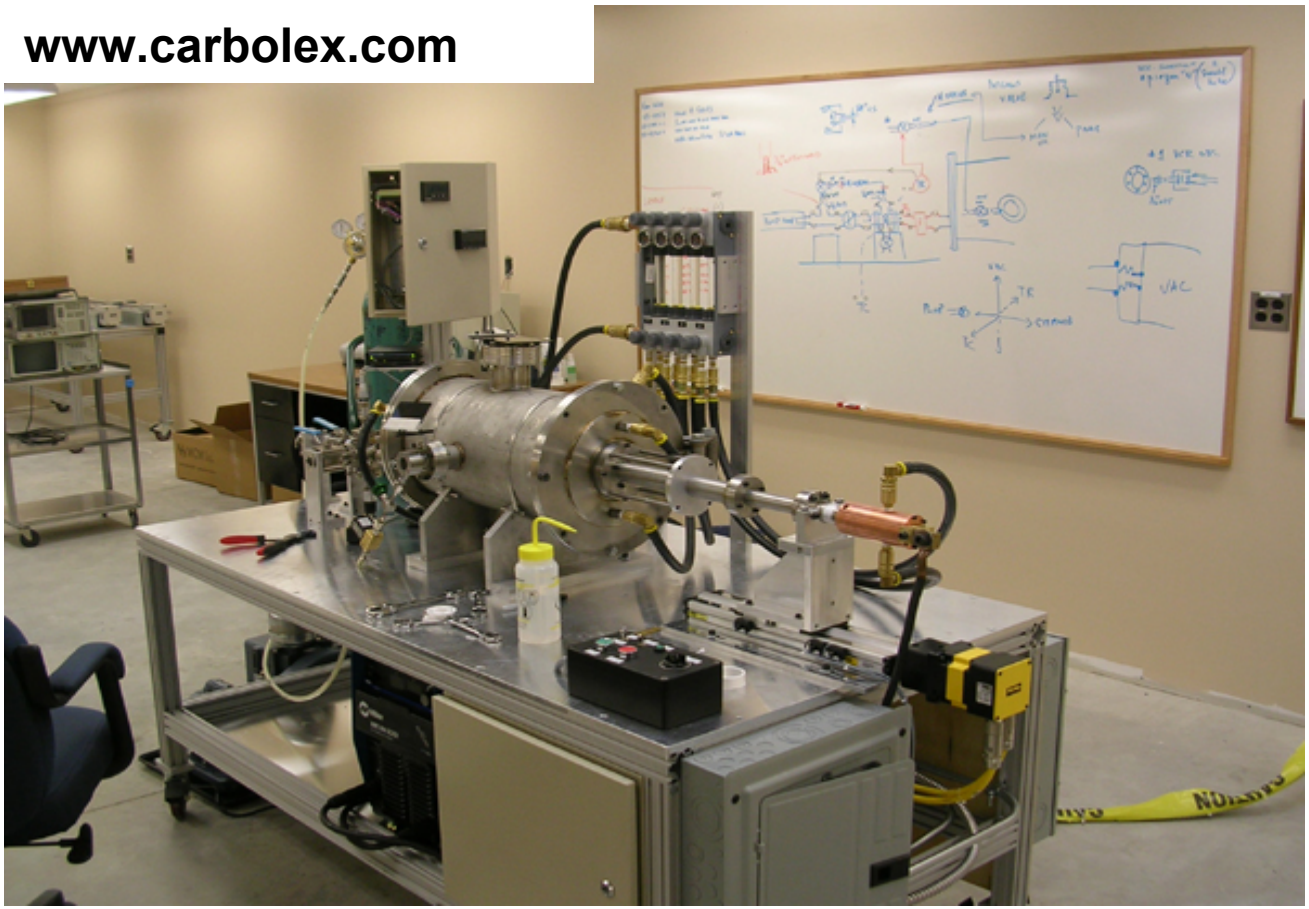



**Accomplishment:** Calculations demonstrate that metal-boron-carbon systems can bind hydrogen at intermediate energies between physical and chemical adsorption, the "sweet spot" to obtain reversible storage at >5wt%[6] and >45 g/L

# Three complementary approaches to materials synthesis of metal dispersed B-substituted carbons

- Electric arc vaporization from M-B-C Electrodes *(Eklund)*
  - *Non-equilibrium high-energy conditions*
  - ***Accomplishment:*** *Production of highly ordered uniform high SSA B-doped carbon nanotubes with boron doping up to 3%. Neutron scattering reveals higher-binding energy sites for* $H_2$ *near boron*
- B-Containing Molecules / Pyrolysis *(Chung)*
  - *Ability to design precursors with exceptionally high boron concentrations*
  - ***Accomplishment:*** *5-10 atomic% boron incorporation into* $sp^2$ *carbon frameworks. Preliminary data show the first substantial (0.6-1wt%) binding of hydrogen to a boron-carbon material at room temperature and low pressure in the initial unoptimized batches of material.*
- Molecular Reaction / Pyrolysis *(Foley)*
  - *Combinations of precursors to control complex pyrolitic decomposition*
  - ***Accomplishment:*** *Synthesis of highly porous materials with a controlled mixture of micropores (for large storage) and mesopores (for rapid transport)*

**Accomplishment:** Arc synthesis of kg quantities of high-quality, porous nanotubes as a framework for chemical modification to enhance hydrogen binding in a well-controlled system

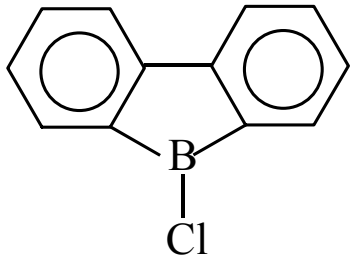



SWNT Research Chamber at CarboLex-Broomall(PA) facility

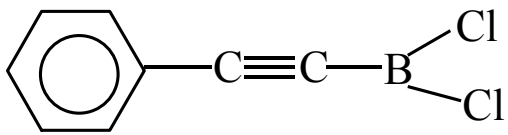
- Fully automatic Arc; no operator necessary
- 100 grams SWNT soot in ~2 hours
- Post synthesis purification by selective oxidation and acid reflux for high-quality materials

**Accomplishment:** B-C molecular precursors have been implemented which pyrolyze into $sp^2$ carbons with **high** (5-10at%) boron.

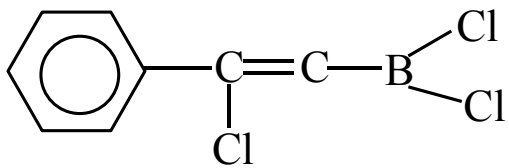
**CBF**




**DCBPA**

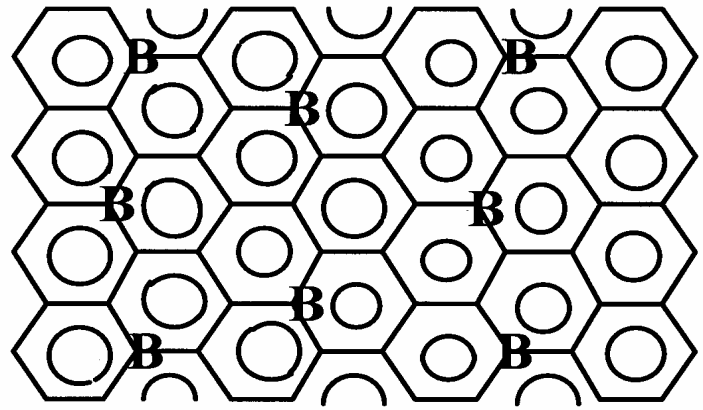



**DCBCS**




pyrolysis

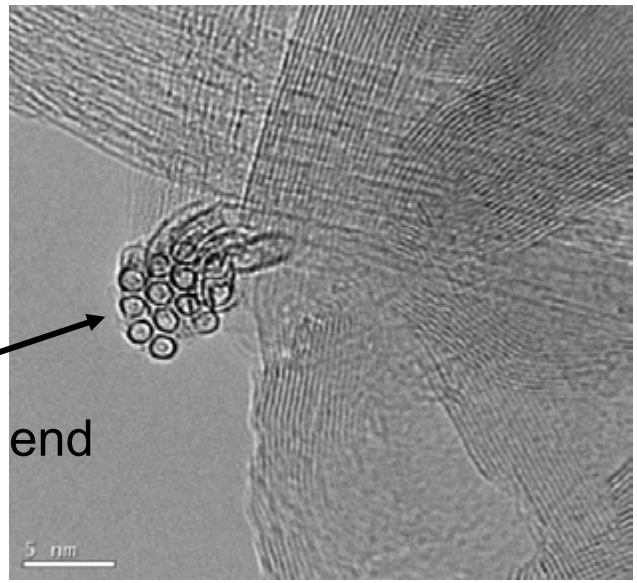
> 800 °C




**Built-in reactive B-Cl bonds reactive are designed reactions that retain boron in the final structure. A simple scalable process that can produce *large amounts* of material at *low cost*.**

**Mixtures of precursors, some B-containing, some designed to generate mesopores that *improve transport* of gas into and out of system.**

## HRTEM Image of Purified, Bundled B-SWNTs



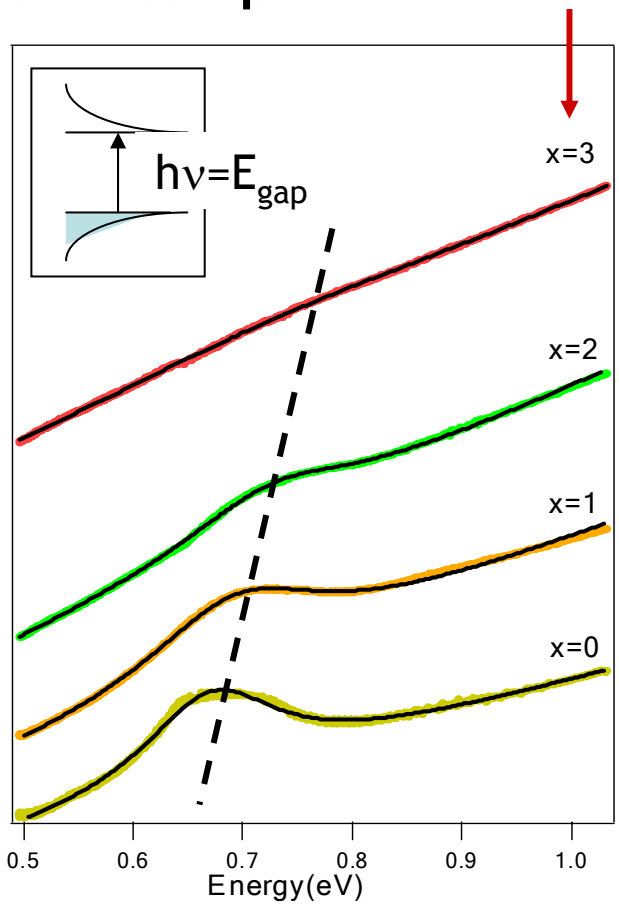

Bundle end view

Pure carbon tubes with roughened surfaces store 6wt% hydrogen at 77K and low pressure (JMR ’04). These new boron-doped tubes show enhanced binding energy as compared to pure carbon tubes: they point toward a pathway for reversible room-temperature storage at moderate pressures to meet the 2010 goals, if sufficient boron can be incorporated.

**Accomplishment:** HRTEM of purified B-doped SWNTs reveals high structural quality and high porosity. Raman, optical absorption and neutron demonstrate that *boron substitutes into the carbon framework*, as desired.

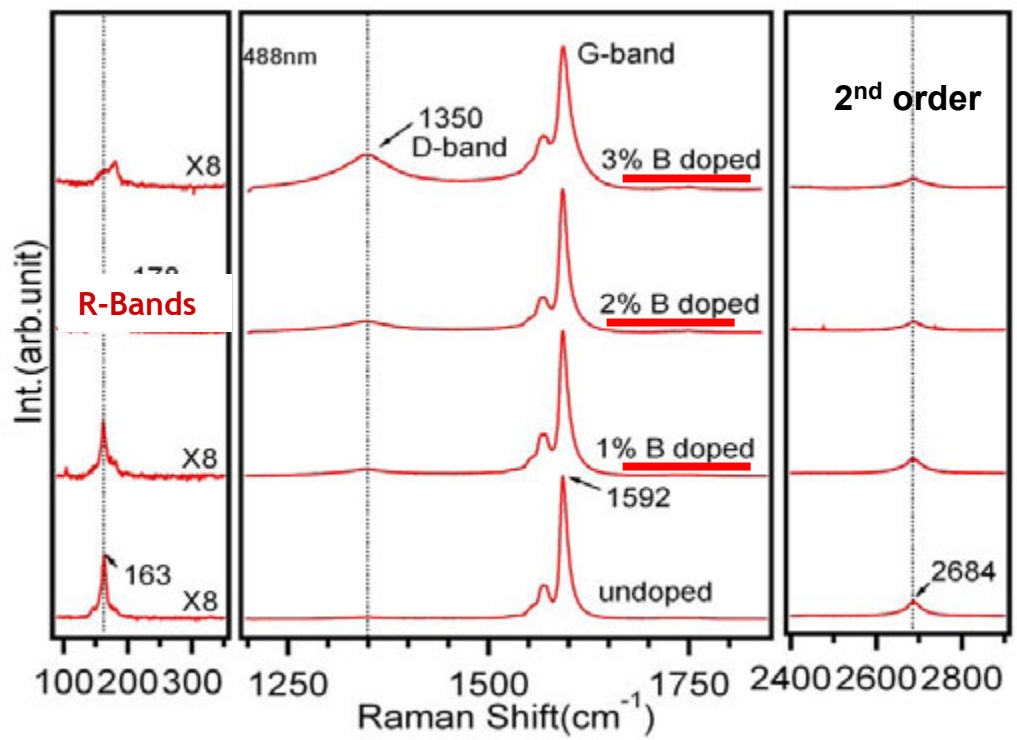
# Boron is in the tube wall: Evidence

**Optical Absorption** **% Boron**




The absorption band above is due to transitions across the semi-conducting bandgap of the SWNTs. Note that the peak up-shifts with boron at%. The width is a measure of the diameter distribution.

**Raman Scattering (488 nm excitation)**

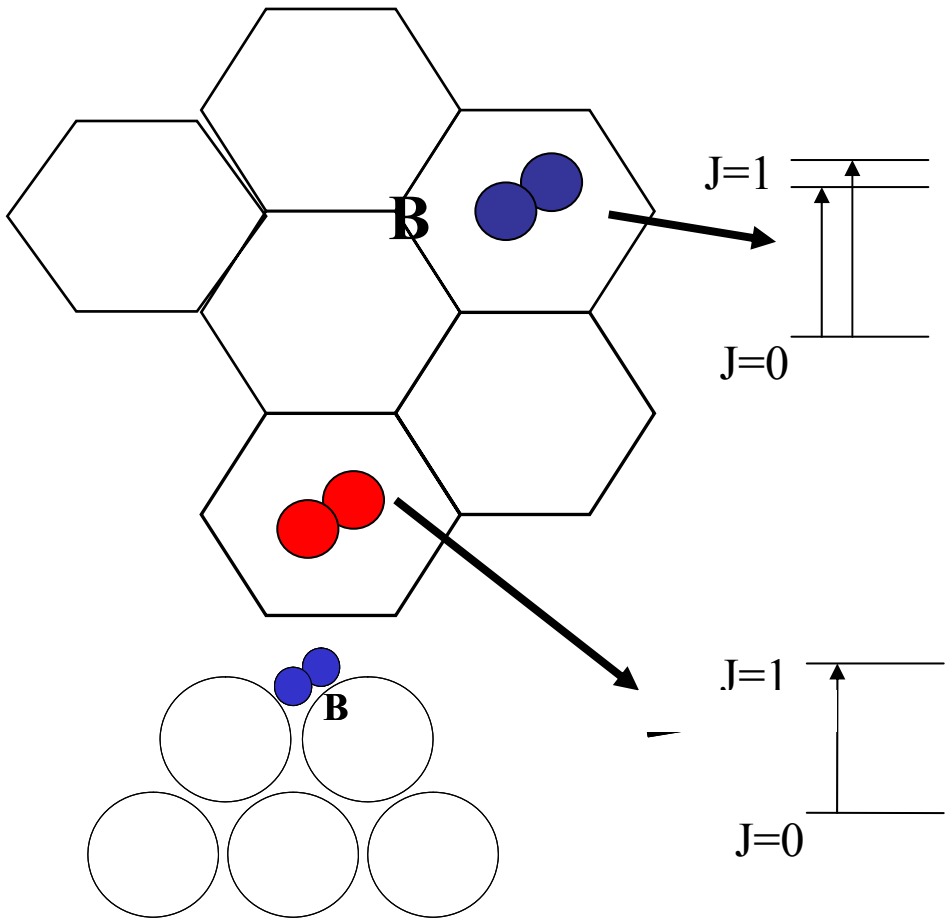


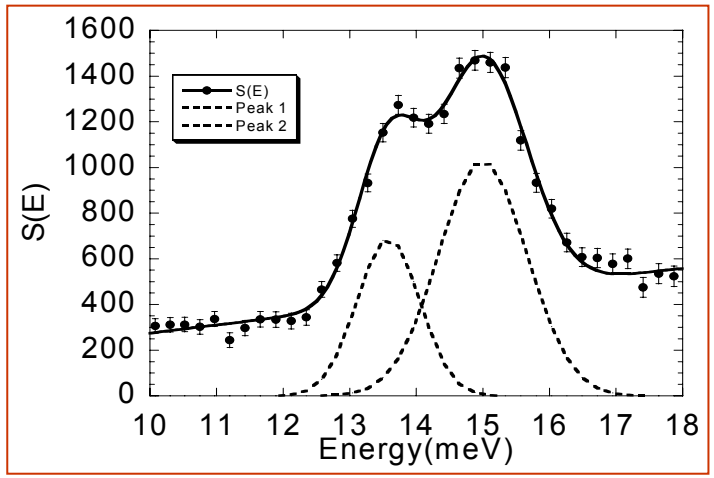

The Boron disrupts the translational symmetry of the SWNT…this leads to disorder-induced (D-band) scattering. Annealing at 1000 C does not remove the D-bands => scattering is NOT from wall defects

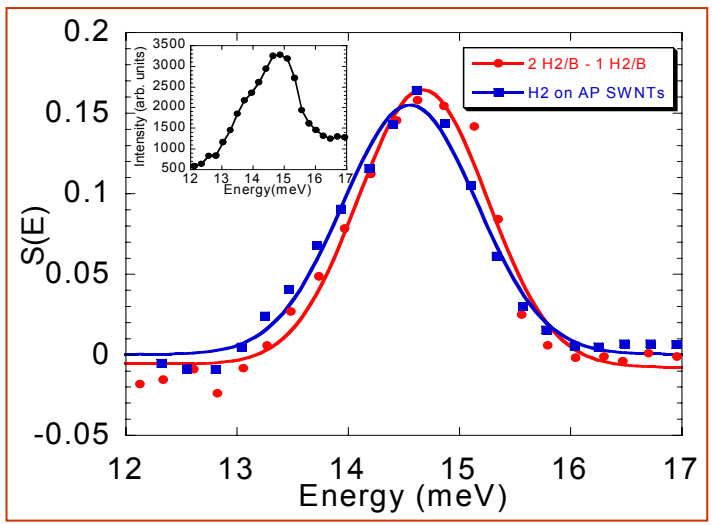


**X.M. Liu,…, P.Eklund, in prep.**

# **Accomplishment:** Inelastic neutron scattering* of $H_2$ rotational transitions reveals *15% higher $H_2$ binding* to the boron site



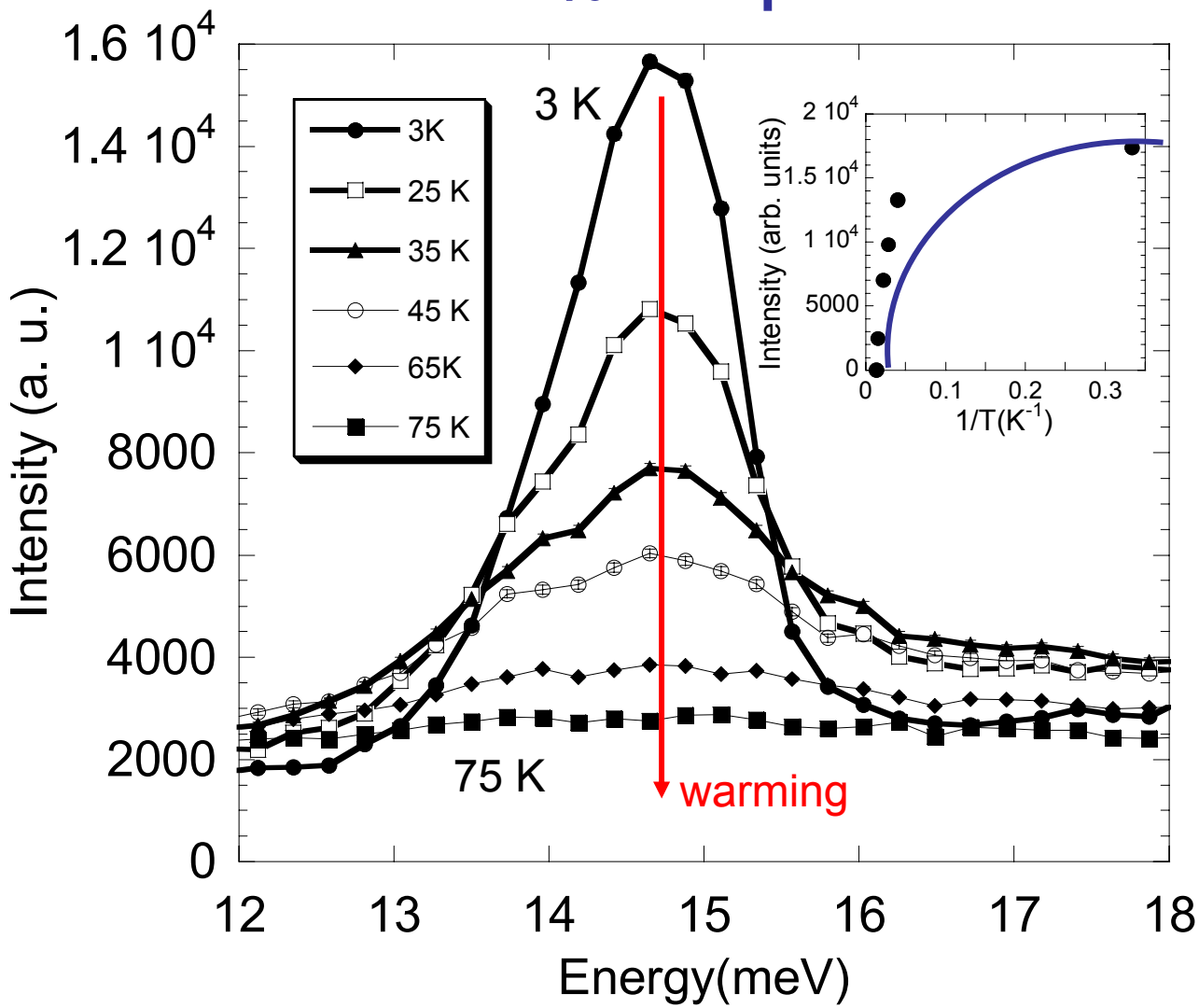






*****Craig Brown***, ***Dan Neumann*** and ***Yun Liu*** at the NCNR.

# Rotational $H_2$ Spectra vs Temperature

**~ 1% B-doped SWNTs**




At high temperatures, only the hydrogen bound to boron sites survives, demonstrating *higher binding through boron substitution*.

# Summary: Effect of B-Substitution

- **Inelastic neutron scattering shows clear increase in temperature which the hydrogen becomes mobile on the carbon framework and an increase binding energy while maintaining high surface area.**

- **Calculations show that higher boron at% in higher-curvature bonding geometries have intermediate physical-chemical adsorption (~0.3 eV/atom). The binding of $H_2$ to boron sites increases a further 40% when the host $sp^2$ sheet is deformed, substantially raising the uptake/release temperature.**

# Future Work FY06

- **Remaining FY06**
  - **Begin in-depth volumetric studies of H-storage capacity of B-substituted carbons. Verify and extend observed enhancements in wt% storage capacity and binding energy towards 2010 targets of 6wt% and 45 g/L. We have already observed 6wt% at 77K and 20 atm in surface-roughened nanotube systems (without boron).**
    - **Use PC-controlled differential volumetric apparatus designed and built at PSU by P. Eklund/A. Lueking**
    - **Companion measurements made at AirProducts (A. Cooper)**
  - **Continue development of potential high-impact Boron-Carbons that maintain High SSA with high B-loading**
  - **Determine the effectiveness of stored electrochemical charge as a simple screening technique for H-storage materials: tracks same physical properties of accessible surface area and also depends upon electronic characteristics of the surface which may correlate to enhanced hydrogen binding**

# Future Work FY07

- **Develop synthesis protocols for metal dispersion onto Boro-Carbon platforms to further increase binding energy and raise the operating temperature.**
  - **Investigate bi-functional (atomic & molecular) H-storage and determine (T,P) needed for 6 wt% reversible H and $H_2$ storage**
- **Push B/C ratio to 5-20% to increase wt% and volumetric storage capacity at high temperatures**
  - **Via B-containing Monomers and Polymers (c.f., FY06) and through C-defect formation and B-replacement**
- **Synthesis, H-storage, and design/modeling in continual developmental feedback loop**

# Summary Table

1eV/atom = 100 kJ/mol

| | Wt% H | Binding energy | Temperature | Pressure |
|---|---|---|---|---|
| Roughened carbon nanotubes (JMR, '04) | 6%<br>0.3% | ~0.13 eV | 77K<br>300K | 5 atm<br>20 atm |
| Boron-doped nanotubes | TBD | ~0.15 eV | TBD | TBD |
| Boron-doped pyrolytic carbon | 0.6-1.0% | TBD | 300K | 20 atm |
| Boron in highly curved carbon sheets & dispersed metal sites (calculation) | >5% | 0.3 to 0.8 eV | 300K | 1-10 atm |

This **new class of boro-carbon materials** is being optimized to meet the 2010 goals with higher boron concentrations, greater surface areas, and metal dispersion for bi-functional (physical/chemical) adsorption & storage. Our intent is to "change the game".

# Summary: Penn State Effort

- **Relevance:** Increase reversible hydrogen BE by developing new storage materials through chemical modification of carbon frameworks.
- **Approach:** Three complementary synthesis techniques closely coupled to adsorbtion measurements and first-principles materials theory.
- **Technical accomplishments:**
  - All three Penn State synthesis routes are producing boron-substituted $sp^2$ carbons.
  - B-SWNTs produce enhanced $H_2$ binding ($\Delta BE$ ~ 15% ).
  - Porous materials derived from pyrolysis of B-containing polymers show substantial physisorption *at room temperature*.
  - Theoretical calculations have demonstrated that Boron stabilizes atomically dispersed metals on the $sp^2$ carbon framework and that curvature of the framework improves $H_2$ binding to B substitutional sites, to the levels required by 2010 goals.
- **Collaborations: NIST, AirProducts, NREL, Carbolex**
- **Next six months:**
  - Drive up B-content and SSA; begin in-depth $H_2$ adsorption-desorption studies
  - Measure BE enhancement vs sample morphology
  - Begin preliminary light metal element dispersion in B-substituted Carbons
  - Continue theoretical modeling in metal-dispersed B-substituted Carbons, emphasizing light element metals to meet gravimetric goals

# ADDITIONAL SLIDES

# Publications and Presentations

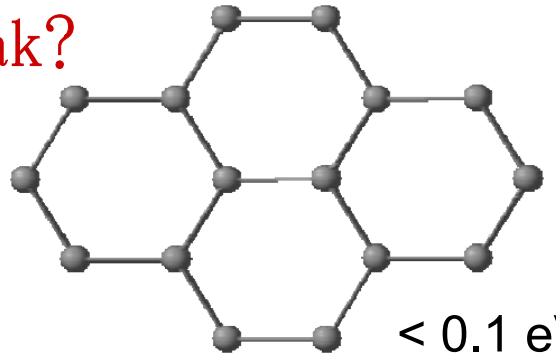
- *Molecular hydrogen adsorption on the boron-doped graphene sheet in presence of magnesium and transition metal,* Z. Huang and V Crespi, Bull. Am. Phys. Soc. (Baltimore, 2006).
- *Inelastic Neutron Scattering from $H_2$ in B-doped SWNTs, D. Narehood, D. Neumann, C. Brown, Y. Liu, P. Eklund;* Bull. Am. Phys. Soc. (Baltimore, 2006).
- *Carbon Nanotube Technology*, P. C. Eklund; NSF-sponsored US-China Nanotechnology Workshop, Arlington, VA (Mar 22-5, '06).
- *Enhanced Binding Energy Sites for $H_2$ associated with Substituted Boron in Single-Walled Carbon Nanotubes,* Y. Liu, C. Brown, D. Neumann, D. Narehood and P.C. Eklund; NanoLetters (submitted).
- *Electric Arc Production of Boron-Substituted Single-Walled Carbon Nanotubes,* X.M. Liu, D. Narehood, Y. Liu, C. Brown, D. Neumann and P.C. Eklund, J. Matter. Res. (submitted).

# Critical Assumptions and Issues

- **Challenges:** How high of a substitutional B concentration can be obtained while maintaining a high surface area? Can metals be stably dispersed at an atomic or near-atomic level through the creation of an electron deficient $sp^2$ carbon framework?
- **Responses:** Introduce metals in elemental or chemical form as precursors during synthesis or post-synthesis via vapor or electrochemical deposition. Exploit synergistic metal/boron-in-carbon interactions to increase concentrations of both within the carbon framework. Exploit kinetics-driven synthesis conditions to widen compositional palette.

# Observations that inform the design and search strategy

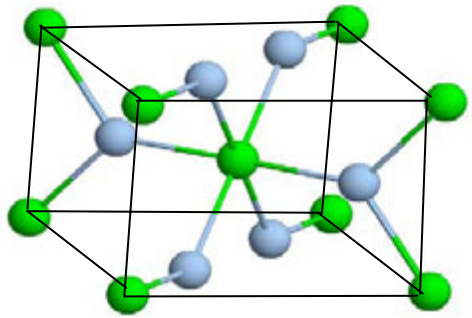
too weak?



< 0.1 eV

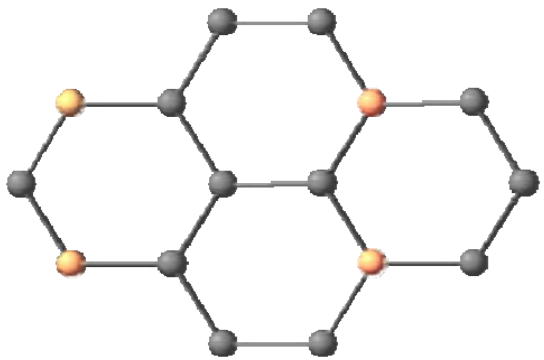
Graphene

too strong?

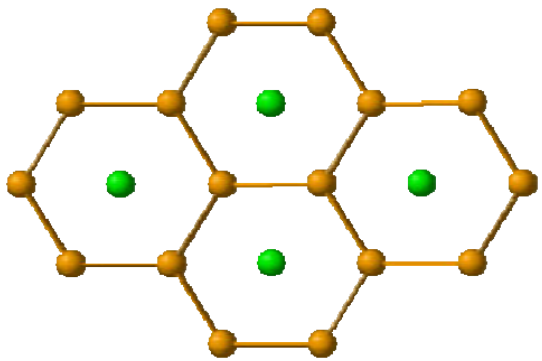


$MgH_2$

1eV/atom = 100 kJ/mol



~0.2 - 0.7 eV

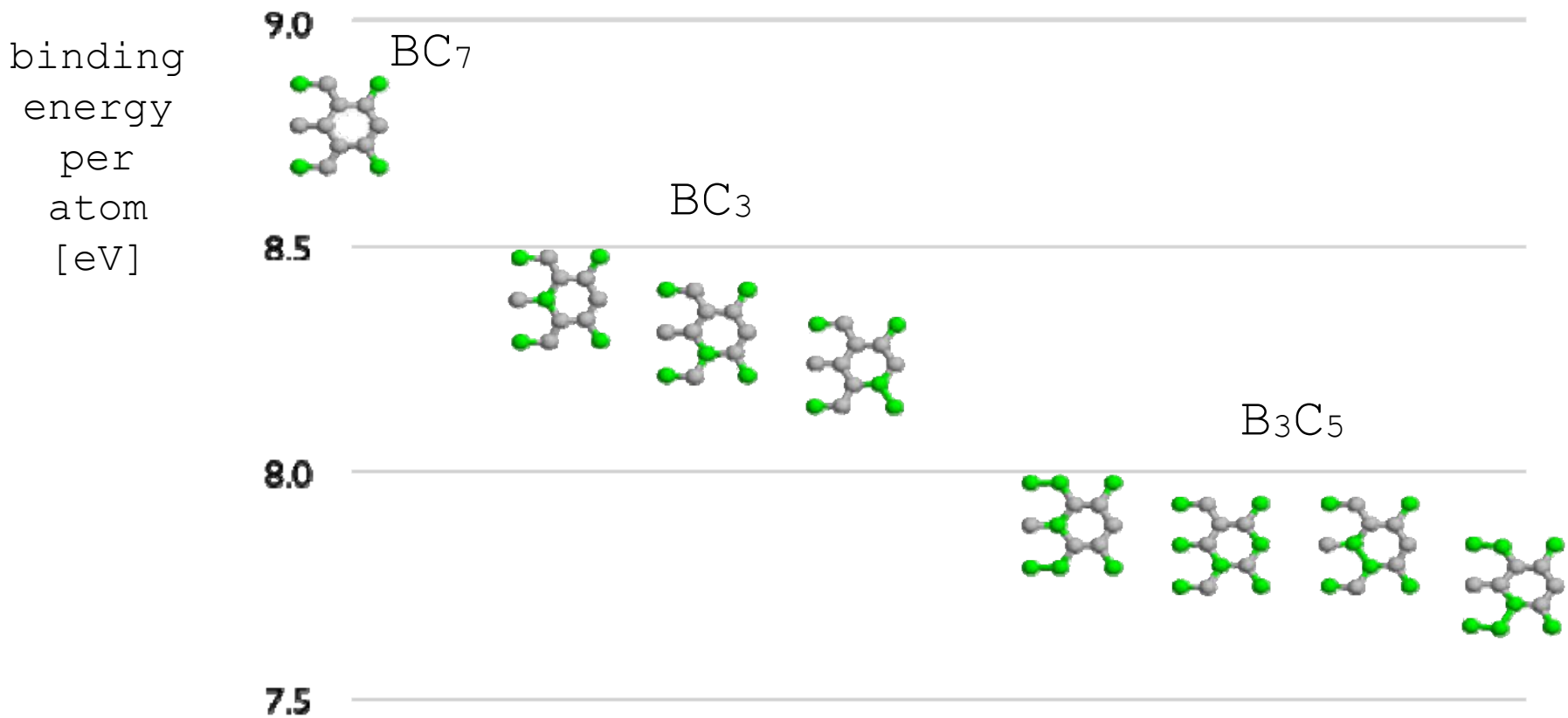


$BC_3$

$MgB_2$

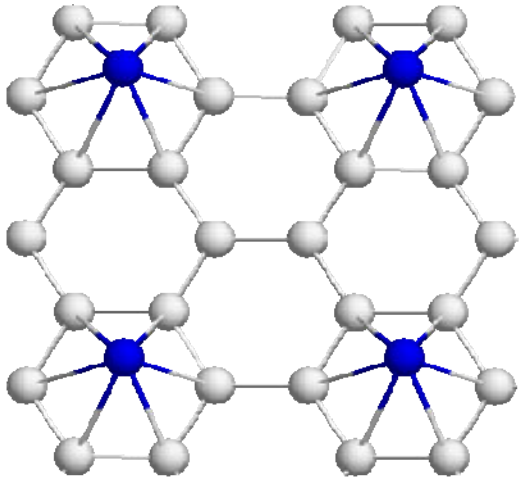
Boron/metal materials can hit the sweet spot

# Calculation demonstrates that boron disperses in a carbon host



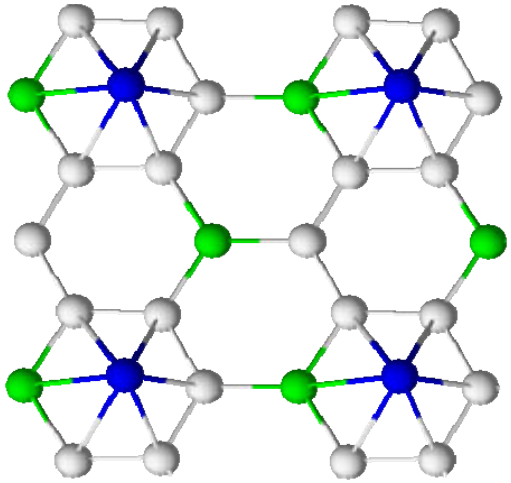

Density functional calculations demonstrate that boron disperses atomically in a carbon framework, a requirement for improving wt% and volumetric hydrogen storage.

Ti on pure graphene

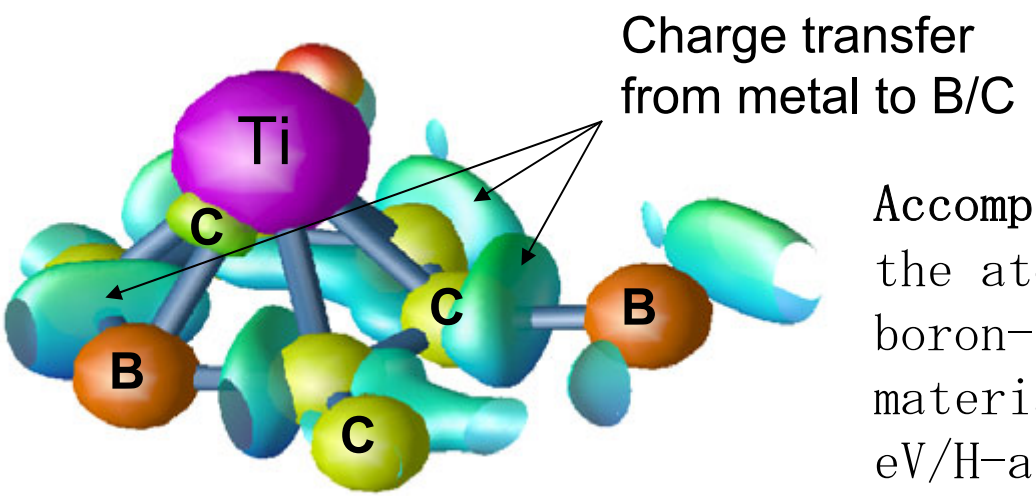


2.5 eV per Ti binding

Ti on $BC_3$

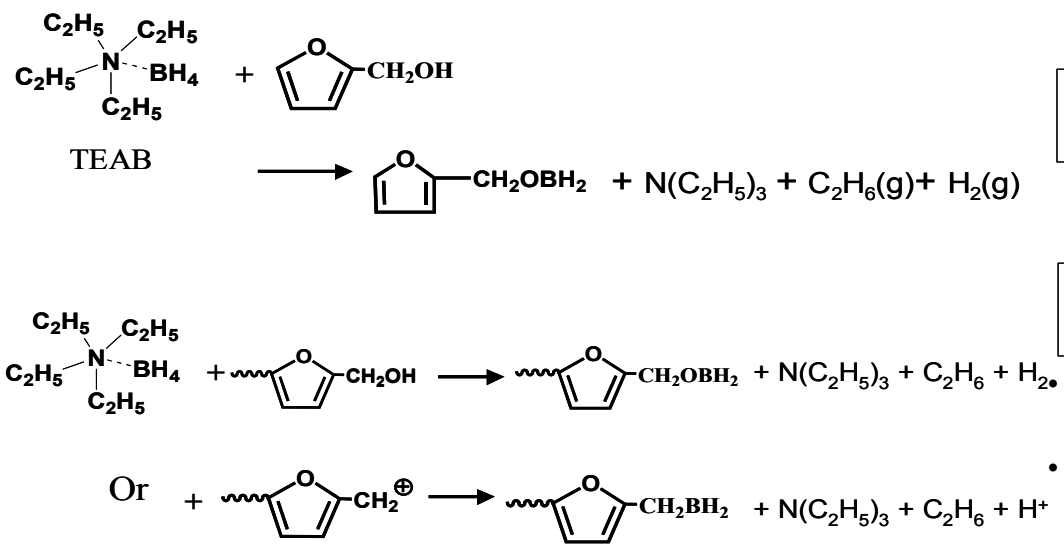


4.6 eV per Ti binding




**Accomplishment:** Boron greatly stabilizes the atomic dispersion of metals on boron-carbon sheets; this is a new material which can bind H at 0.2-0.8 eV/H-atom, sufficient to meet 2010 targets at moderate pressures

# Molecular Reaction / Pyrolysis route to high SSA boro-carbons




**Scheme 1**

TEAB add in FA/PFA mixture

Stir well

Pyrolyze at 800ºC

**Scheme 2**

FA add in p-TSA/THF solution

Polymerize for 1 day

Add TEAB

Polymerize for another day

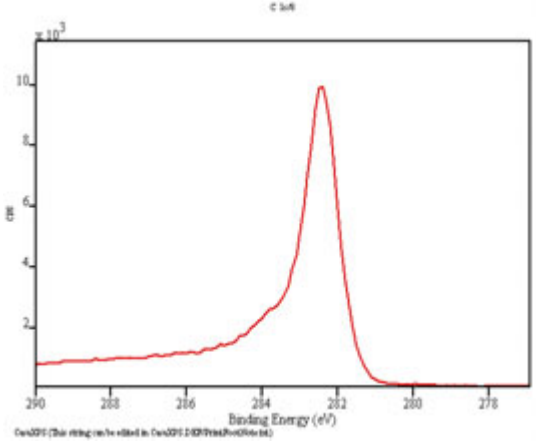
Add PEG600 diacid

Stir overnight

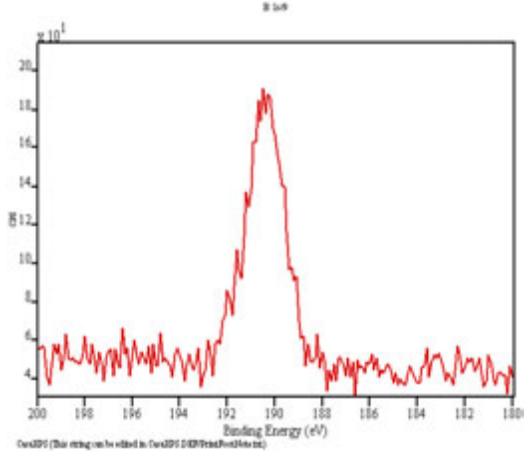
Pyrolyze at 800ºC

Activate with $CO_2$

- BET surface area ⏲0.5m²/g.
- B:C⏲1:50 (by XPS))




**C1s spectrum**




**B1s spectrum**

- Accomplishments:
  - BET surface area > 1000m²/g.
  - B:C~1:200 (by XPS)
  - **Mixture of micropores for storage and a small subpopulation of mesopores for rapid uptake and release.**

XPS spectra demonstrate boron incorporation