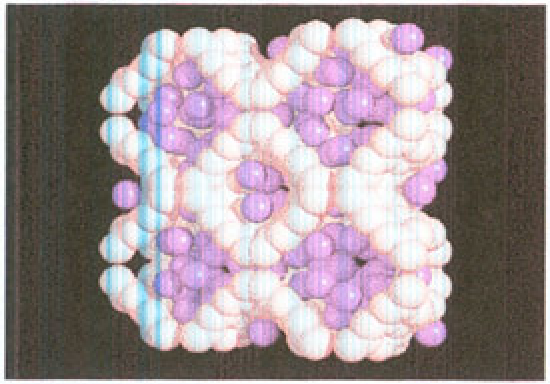
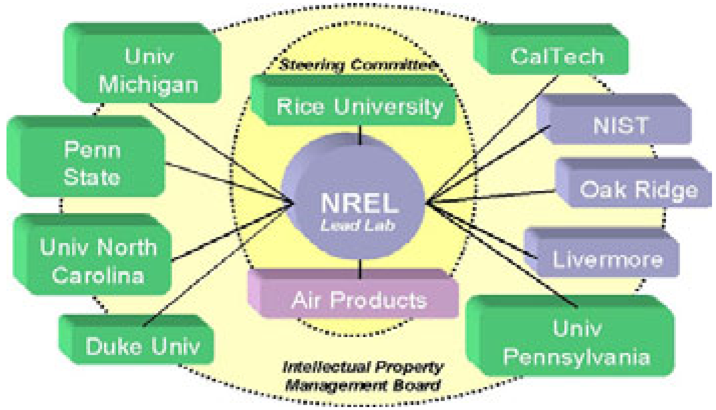




2006 DOE Hydrogen Program

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

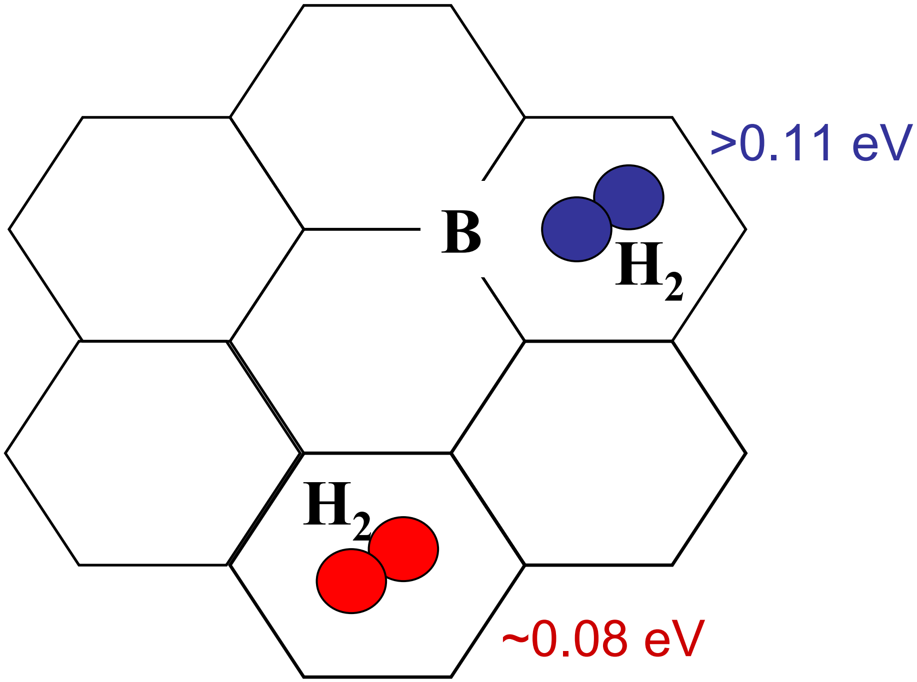
Objectives / Approach (I)

- **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)

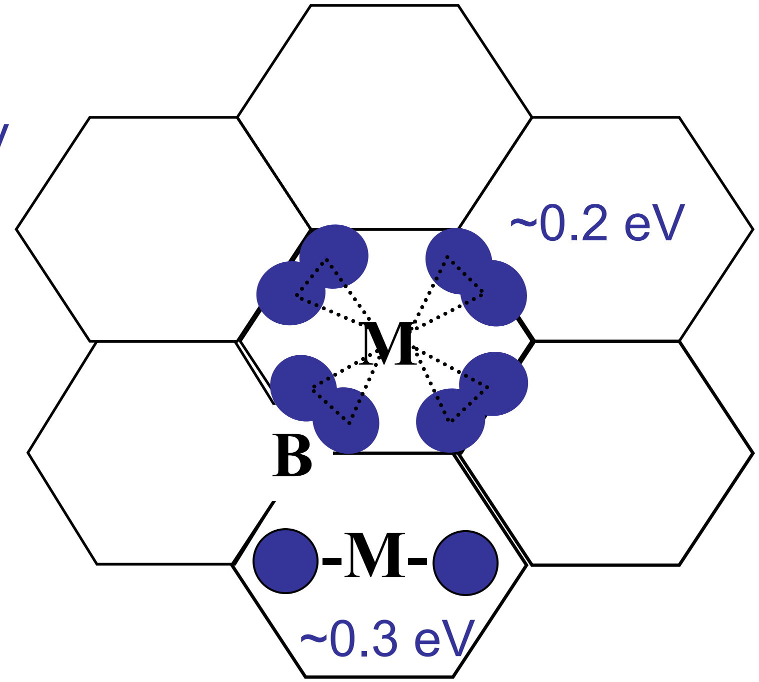
Schematic of sp[2] carbon network and sites for binding atomic and molecular hydrogen

Substituted Boron Enhances H_2 Binding



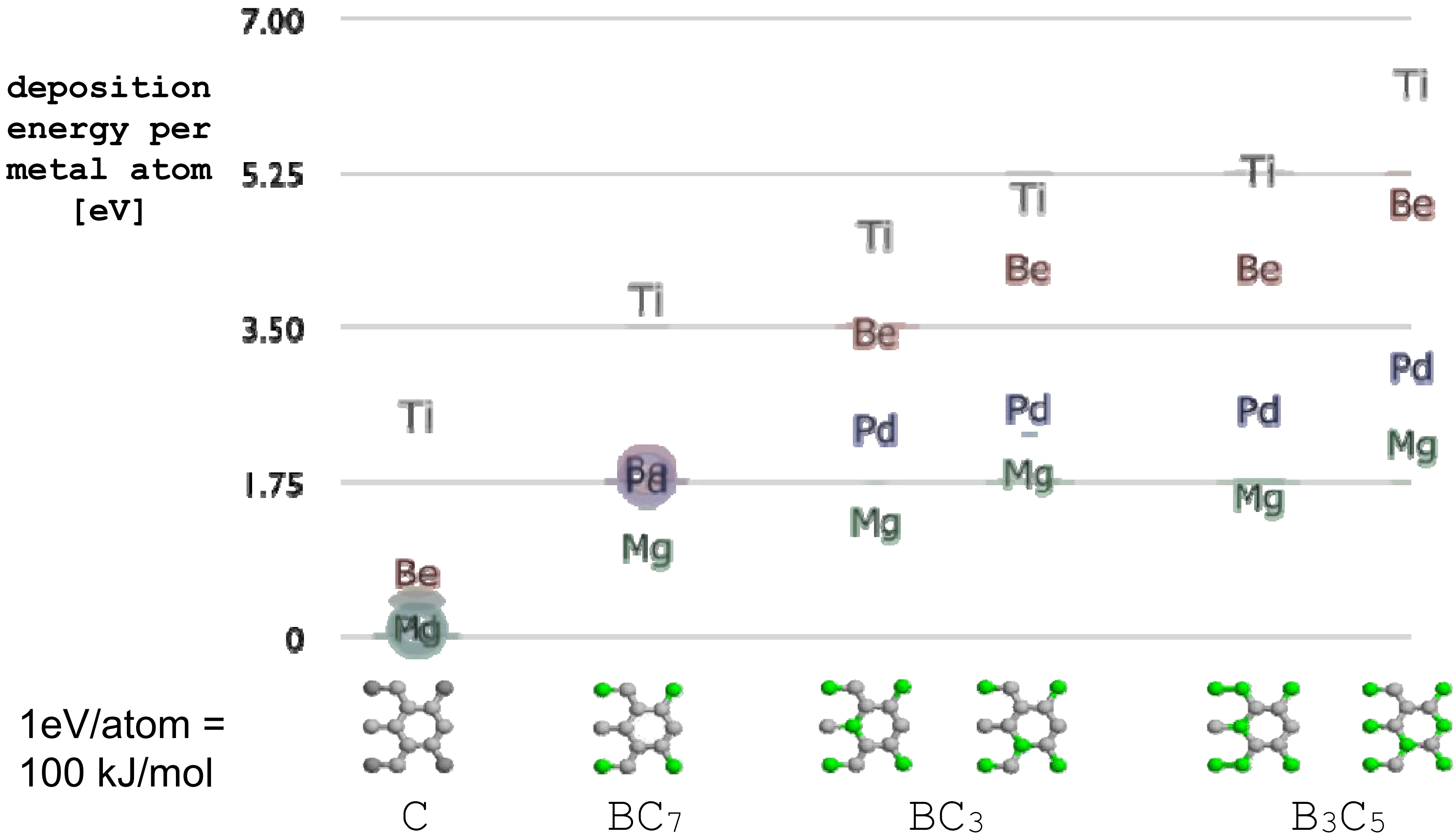
B=Boron

Substituted Boron stabilizes Atomic Metal



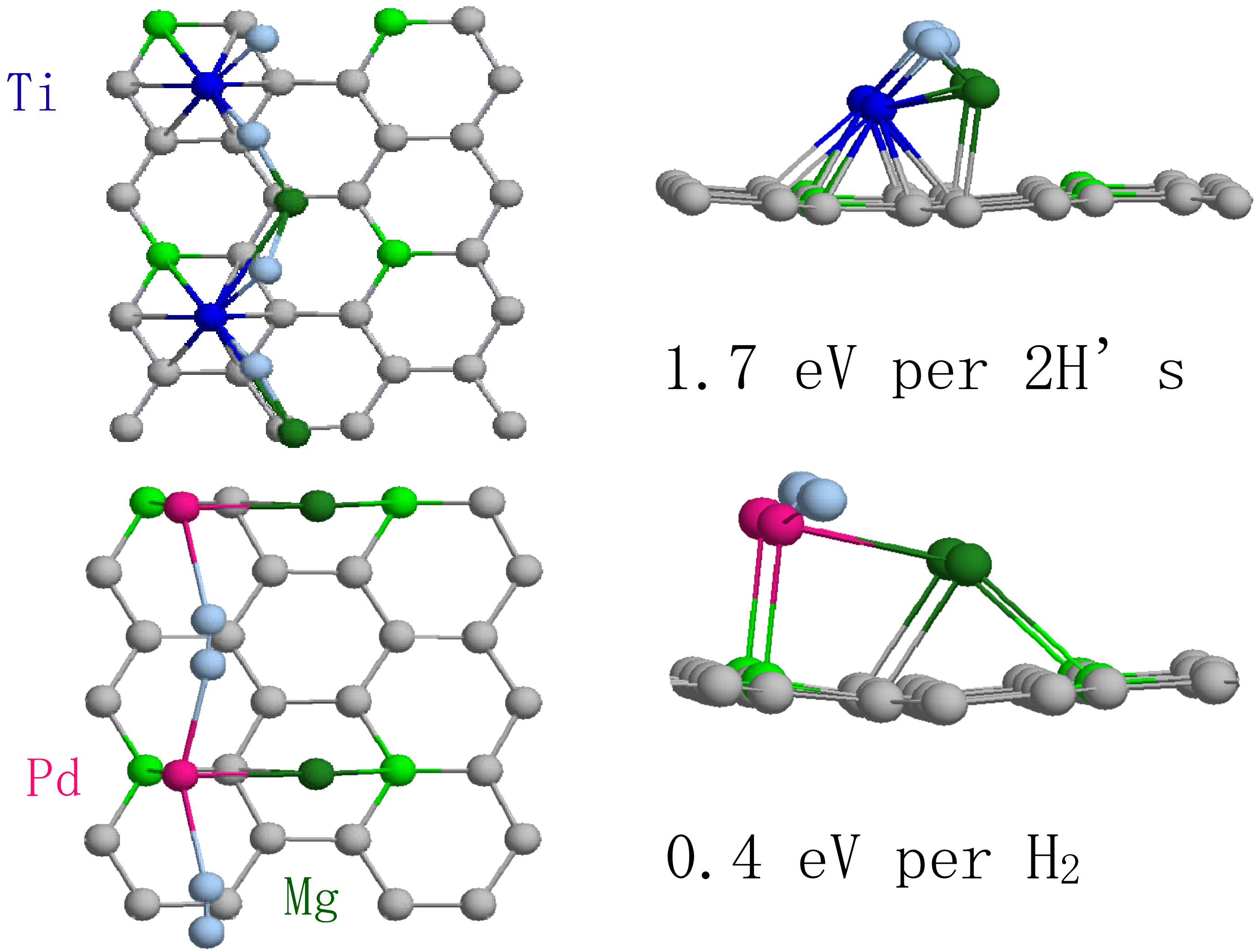
M=Metal

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.



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



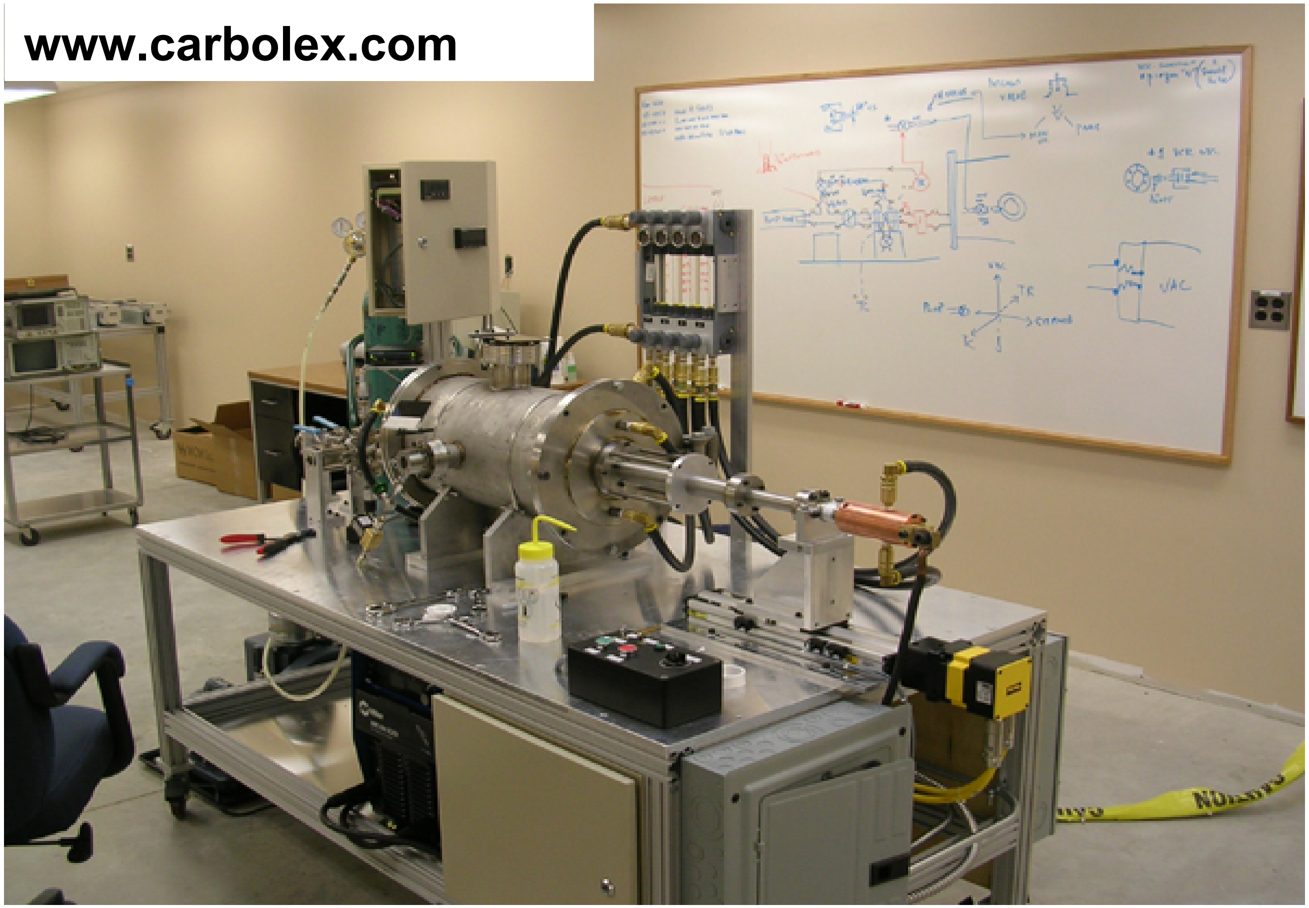
1eV/atom =
100 kJ/mol

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

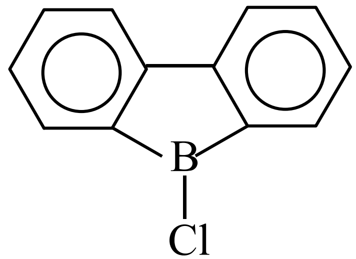


SWNT Research Chamber at CarboLex-Broomall(PA) facility

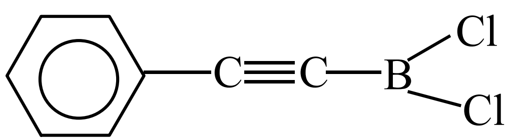
- Fully automatic Arc; no operator necessary
- 100 grams SWNT soot in ~2 hours
- Post synthesis purification by selective oxidation and acid reflux for high-quality materials

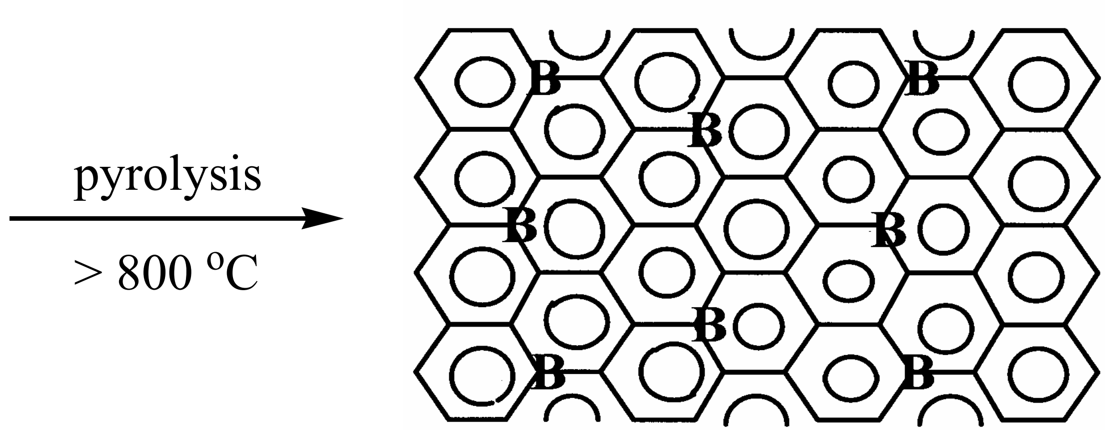
Accomplishment: B-C molecular precursors have been implemented which pyrolyze into sp^2 carbons with **high** (5-10at%) boron.

CBF

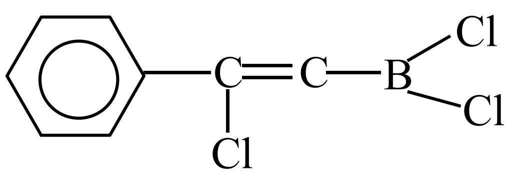


DCBPA





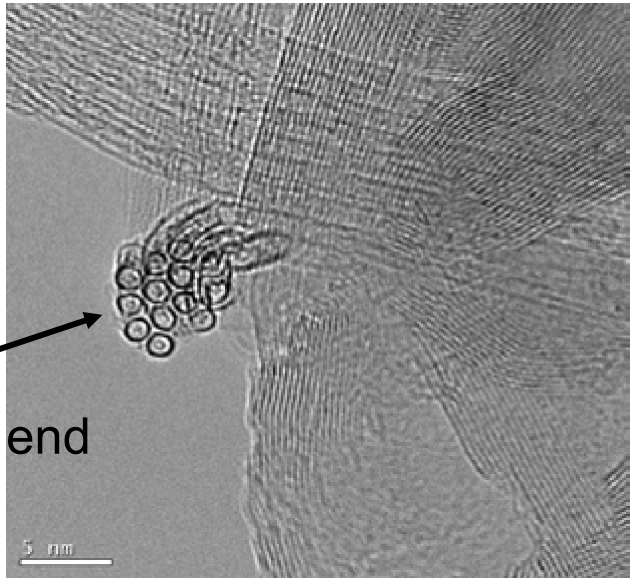
DCBCS



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



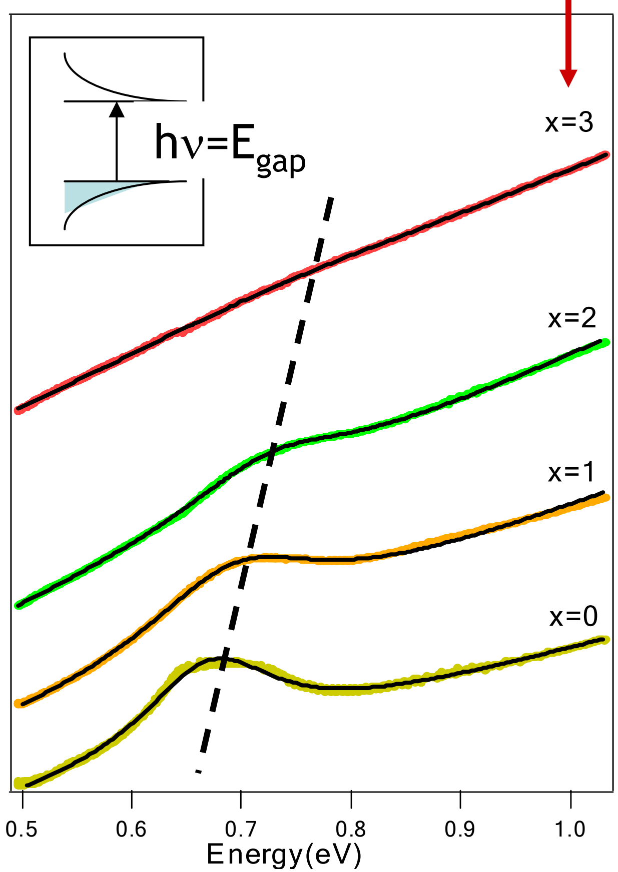
Bundle end view

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.

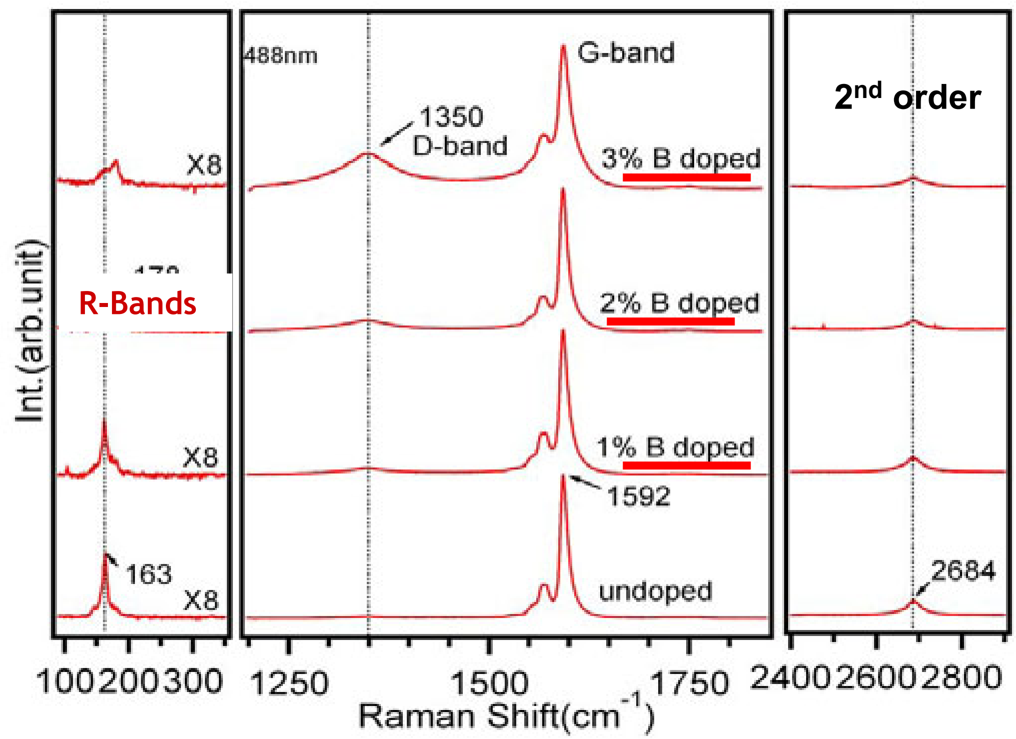
Boron is in the tube wall: Evidence

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.

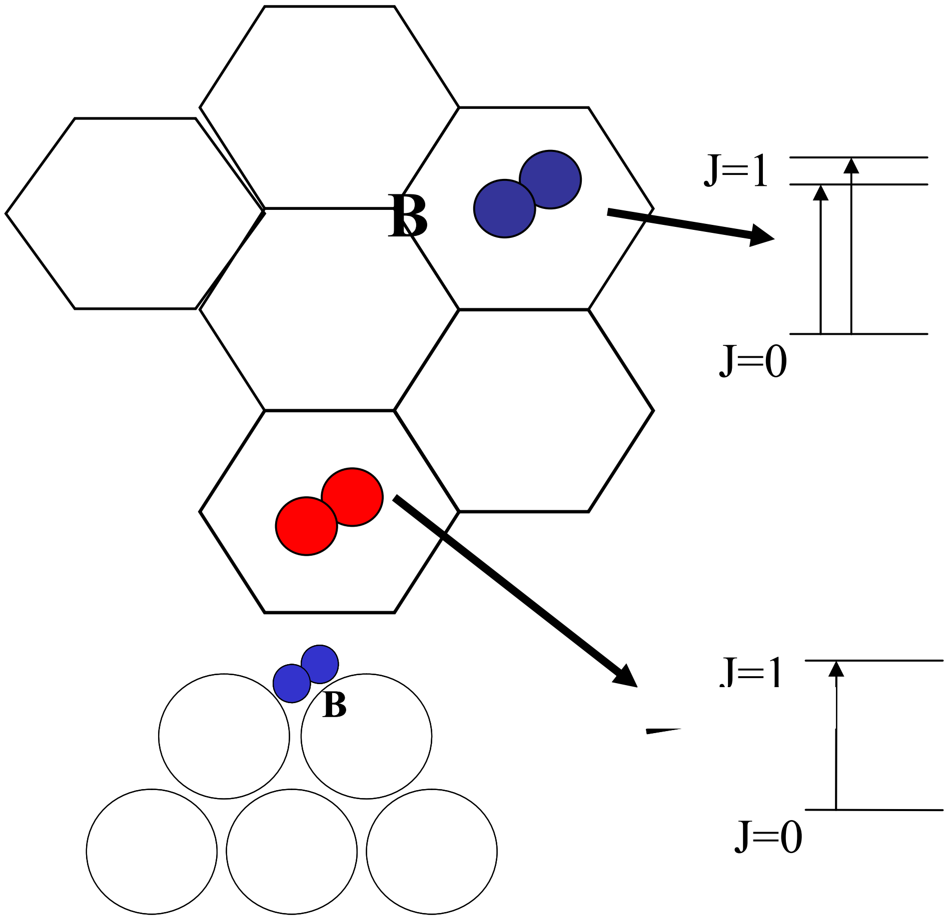
Raman Scattering (488 nm excitation)

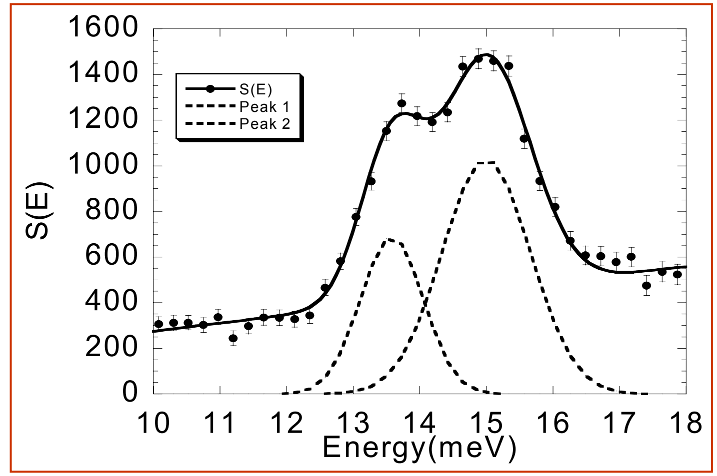


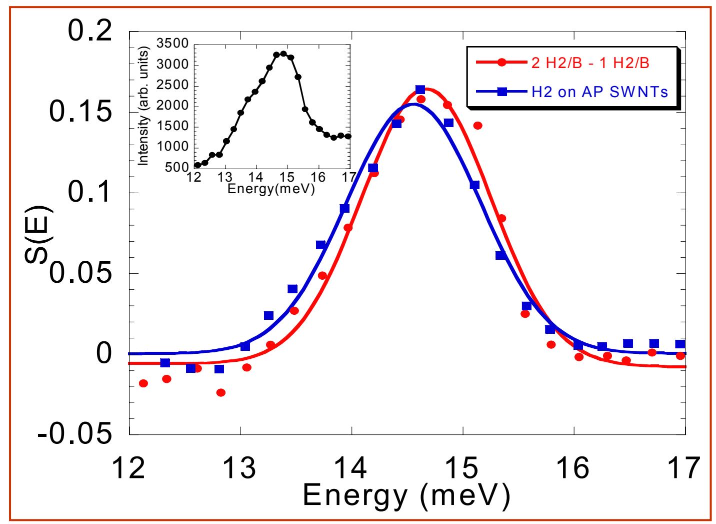
The Boron disrupts the translational symmetry of the SWNT…this leads to disorder-induced (D-band) scattering. Annealing at 1000 C does not remove the D-bands => scattering is NOT from wall defects

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

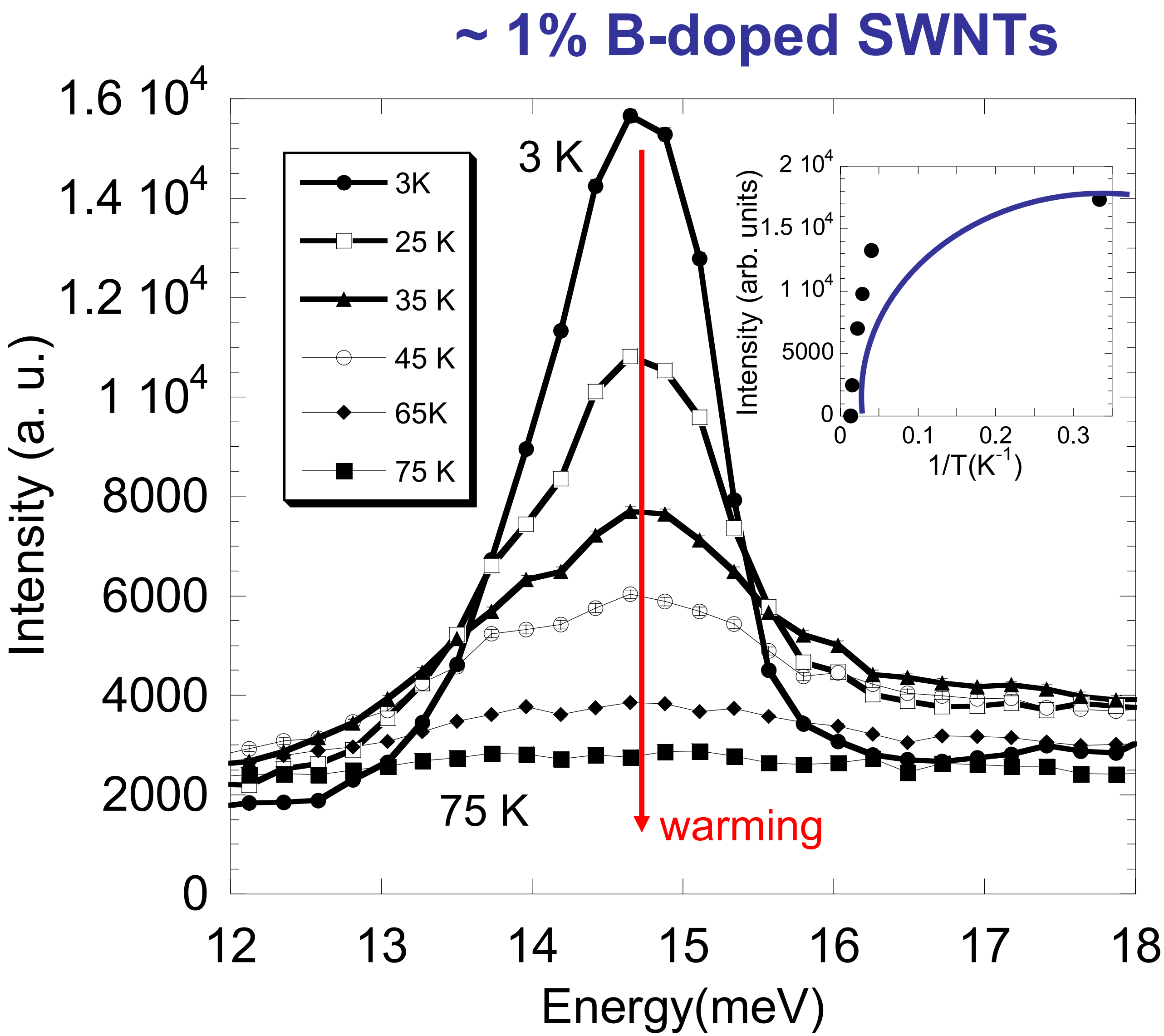






*__Craig Brown__, __Dan Neumann__ and __Yun Liu__ at the NCNR.

Rotational H_2 Spectra vs Temperature



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% 0.3%	~0.13 eV	77K 300K	5 atm 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 (ΔBE ~ 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

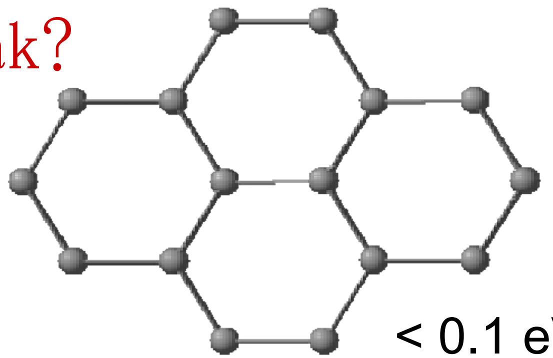
- *Molecular hydrogen adsorption on the boron-doped graphene sheet in presence of magnesium and transition metal,* Z. Huang and V Crespi, Bull. Am. Phys. Soc. (Baltimore, 2006).
- *Inelastic Neutron Scattering from H_2 in B-doped SWNTs, D. Narehood, D. Neumann, C. Brown, Y. Liu, P. Eklund;* Bull. Am. 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.

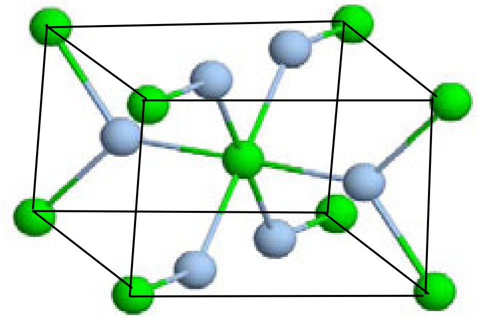
Observations that inform the design and search strategy

too weak?



< 0.1 eV

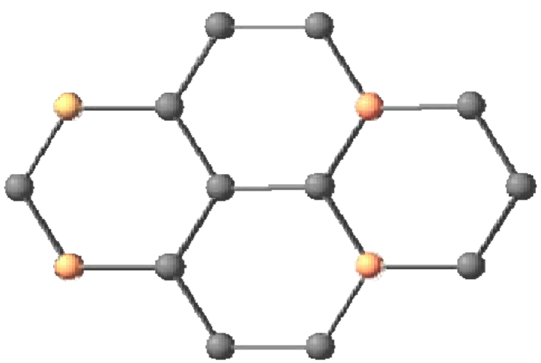
Graphene



too strong?

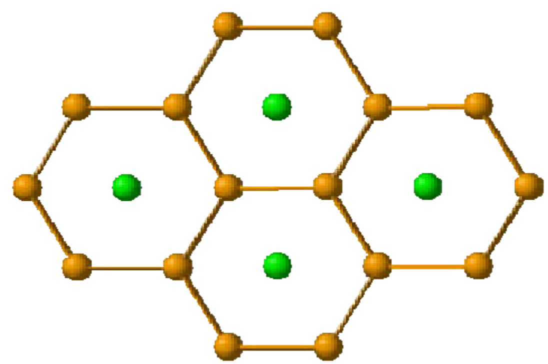
MgH_2

1eV/atom = 100 kJ/mol



BC_3

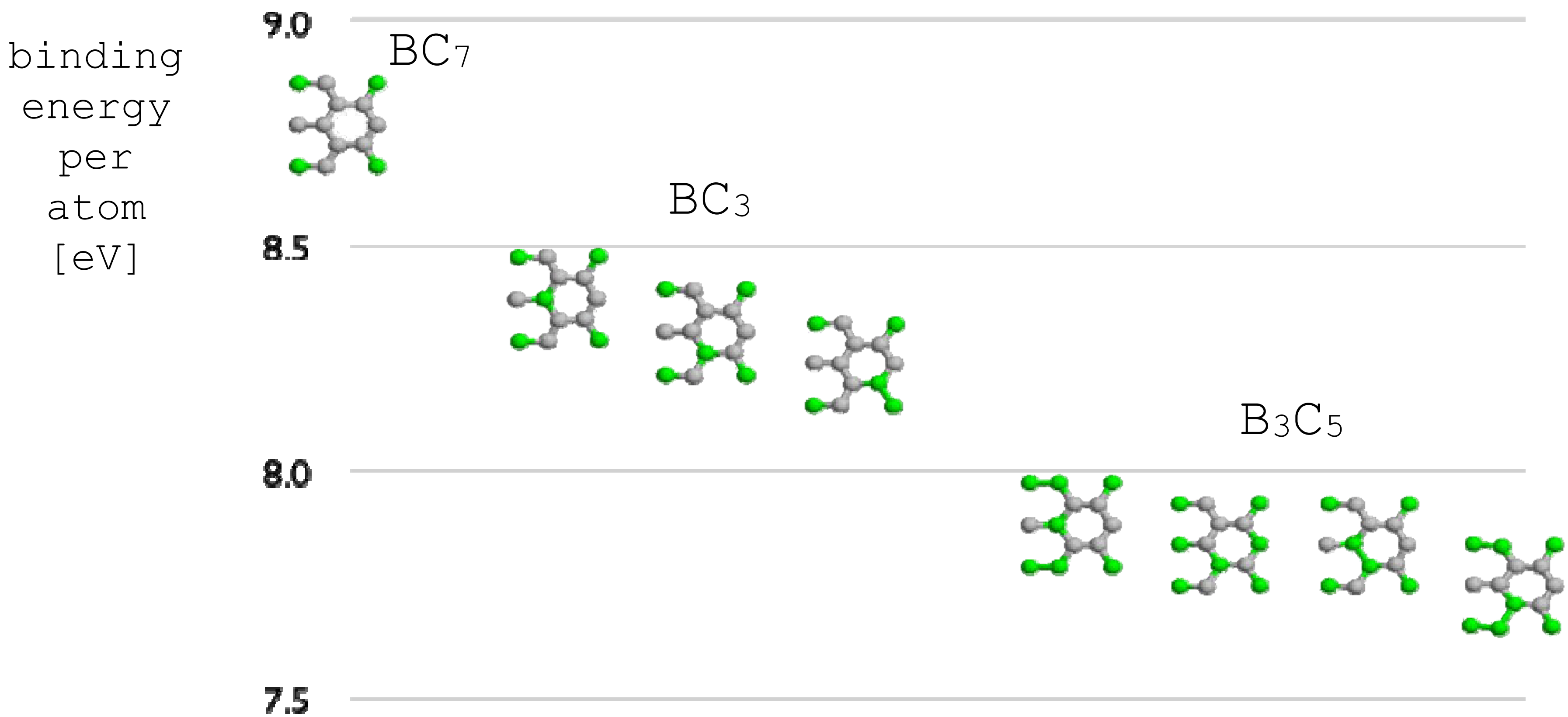
~0.2 - 0.7 eV



MgB_2

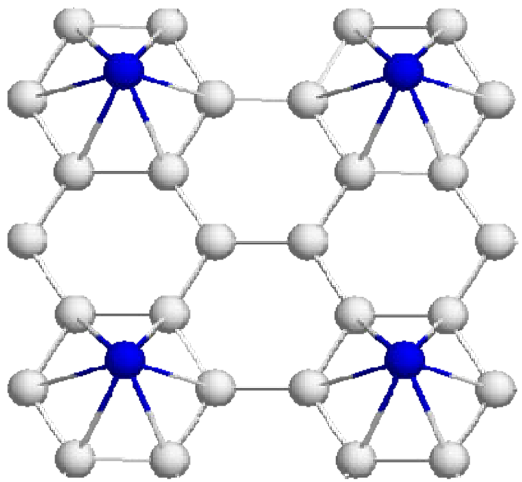
Boron/metal materials can hit the sweet spot

Calculation demonstrates that boron disperses in a carbon host



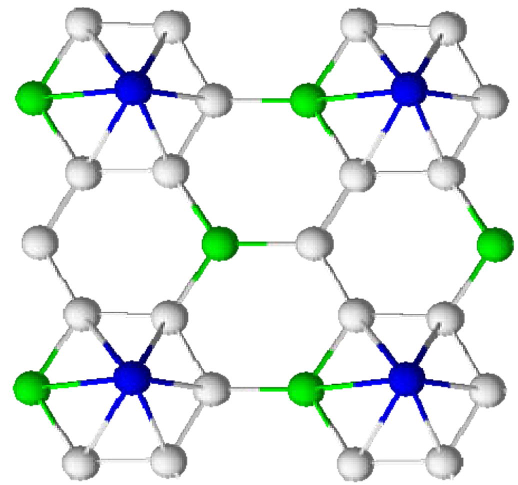
Density functional calculations demonstrate that boron disperses atomically in a carbon framework, a requirement for improving wt% and volumetric hydrogen storage.

Ti on pure graphene

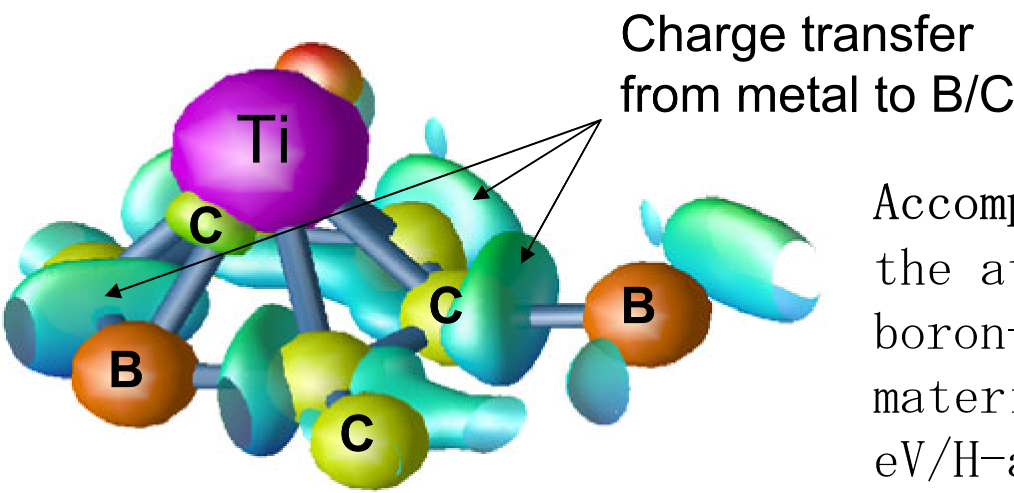


2.5 eV per Ti binding

Ti on BC_3

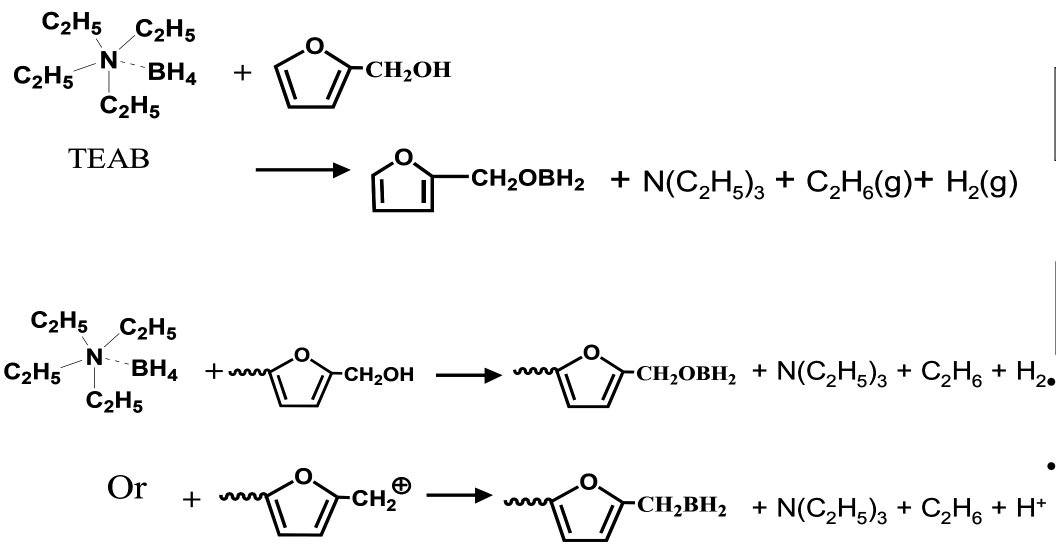


4.6 eV per Ti binding

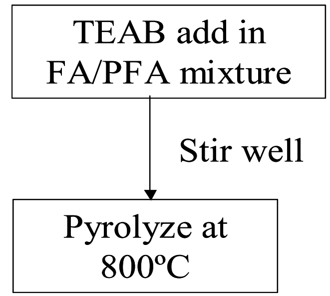


Accomplishment: Boron greatly stabilizes the atomic dispersion of metals on boron-carbon sheets; this is a new material which can bind H at 0.2-0.8 eV/H-atom, sufficient to meet 2010 targets at moderate pressures

Molecular Reaction / Pyrolysis route to high SSA boro-carbons

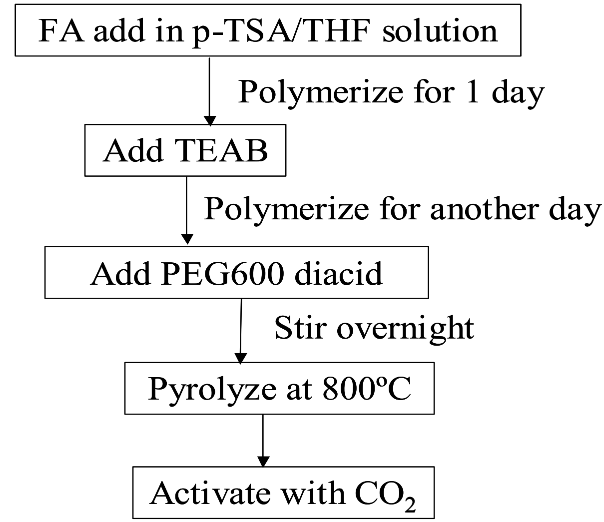


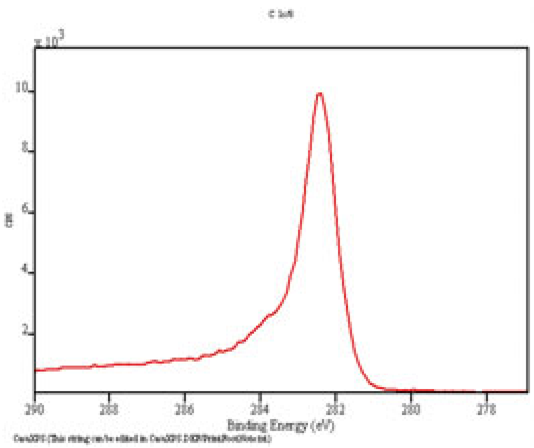
Scheme 1



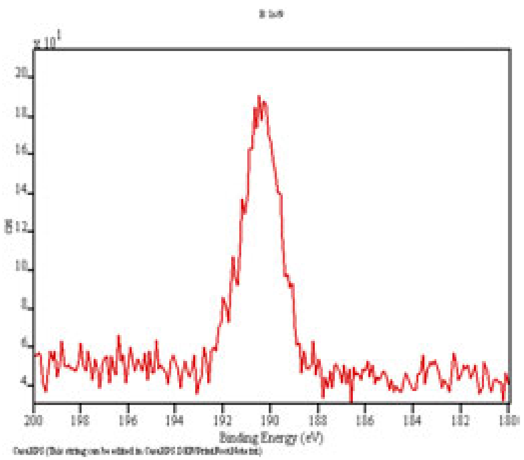
- BET surface area ~0.5m^2/g.
- B:C~1:50 (by XPS))

Scheme 2





C1s spectrum



B1s spectrum

- Accomplishments:
  - BET surface area > 1000m^2/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