

## IV.C.1n Advanced Boron and Metal-Loaded High Porosity Carbons

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- (A) System Weight and volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharge Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

### Technical Targets

This project conducts fundamental studies of the hydrogen-substrate interaction to develop novel classes of electron-deficient framework materials based on carbon and boro-carbon aromatic networks, including a subclass wherein light metal atoms are dispersed on the framework to both facilitate spillover effects and to directly adsorb hydrogen. We have recently demonstrated substantial enhancement in the interaction of hydrogen with such a modified surface, increasing the adsorption energy from the 4–6 kJ/mol typical of standard carbons and silica aerogels to 12.5–15 kJ/mol, near the target adsorption energy of 15–30 kJ/mol. In the previous year, we have built upon our demonstration that boron incorporation facilitates uptake of nano-dispersed metals, obtaining detailed information on the local bonding geometry (a requirement for further optimization) and extending this result to the Ti system (with a large number of empty d orbitals potentially suitable for interaction with H<sub>2</sub>). We have further developed a testbed for investigating spillover effects by in situ measurement of transport and optical signatures of stored hydrogen in a well-characterized nanoscale geometry, developing suspended membrane devices with integrated transport leads and characterizing these devices' response to adsorbed species. A novel boron-nitrogen (BN) framework system that is resistant to formation of bulk BN upon hydrogen removal (and hence may afford improved reversibility) has been simulated. We are continuing towards the goal of developing sorbents which can meet the DOE 2015 hydrogen storage targets for gravimetric and volumetric storage densities at reasonable cost in a reversible system, although further breakthroughs in synthesis will be necessary to simultaneously increase boron content, tune local geometries, increase porosity, exploit spillover, control chemical frustration, and obtain optimal local hydrogen binding properties throughout the macroscopic sample.

### Objectives

- Identify new materials system with high surface area in boro-carbons and metal-boro-carbons with surface chemistry tuned for a stronger hydrogen binding interaction that will enable 2015 DOE-target volumetric and gravimetric reversible hydrogen storage capacity, through a combination of materials synthesis, characterization and first-principles computation.
- Synthesize highly porous boro-carbons and metal boro-carbons with simultaneous ultra-high boron content, high surface area, tuned and optimized pore distributions, controlled spillover effects, metal loading, and tunable curvature.
- Enhance the stability of highly dispersed metals on boro-carbon frameworks, including atomic-level dispersion that is stable against aggregation, by tuning electron deficiency.
- Maintain these properties in a system with moderate economic cost of raw materials and stability over many cycles.

### Technical Barriers

This project addresses the following technical barriers from the x section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

## Accomplishments

- The binding energy for H<sub>2</sub> as measured by isosteric heats of adsorption has been increased to ~15 kJ/mol, much higher than in conventional activated carbons (4–6 kJ/mol), due to the presence of boron. These values approach those necessary for high-capacity reversible room-temperature hydrogen storage (15–30 kJ/mol). The next task is to maintain these high values through a greater surface area. Deposition of BC<sub>3</sub> onto aerogel frameworks and optimization of B-containing precursors and LiCl pore-formers are being pursued towards this goal.
- Demonstrated that incorporation of boron into nanoporous carbon framework improves the uptake of nanodispersed metals Pt, Zr and now also Ti, in accord with goals in atomic dispersion of metals for enhanced wt% and volumetric hydrogen storage, following computational predictions for hydrogen binding energies of 30 kJ/mol in light-weight frameworks designed to be resistant to aggregation. These systems also demonstrate spillover.
- A BC<sub>12</sub> material with specific surface area (SSA) = 780 m<sup>2</sup>/g shows H<sub>2</sub> binding energy 20–10 kJ/mol and more than doubles H<sub>2</sub> absorption capacity per surface area compared to prior materials. A BC<sub>8</sub> material with SSA = 330 m<sup>2</sup>/g shows even higher H<sub>2</sub> adsorption capacity per surface area (3.8 wt% at 77 K). A BC<sub>6</sub> material with 15% B has been prepared, but with very low SSA. Transition metal doped BC<sub>x</sub> materials exhibit well-dispersed Pt, Ti, Zr nano-particles (size <2 nm).
- Novel adsorptive strategies involving framework stabilization of BN systems are being pursued computationally in exploratory work aimed at opening up a novel materials strategy for enhanced hydrogen storage.



## Introduction

Before our investigations, only a few reports discussed the activated carbon with acidic boron groups, in dense morphologies with crystalline structure and limited compositions: either very low boron content (<2.35 mol%) from B doping of graphitic C at high temperature or very high boron content (25 mol%) in BC<sub>3</sub> from chemical vapor deposition reaction of BCl<sub>3</sub> and benzene. A new class of hydrogen sorbents with enhanced hydrogen binding energies in a low-mass framework shows potential to meet DOE gravimetric targets, with further optimization. The introduction of boron into a curved high-surface-area carbon framework induces electron deficiency and so increases the propensity to bind H<sub>2</sub> reversibly at energies intermediate between traditional physical and chemical adsorption.

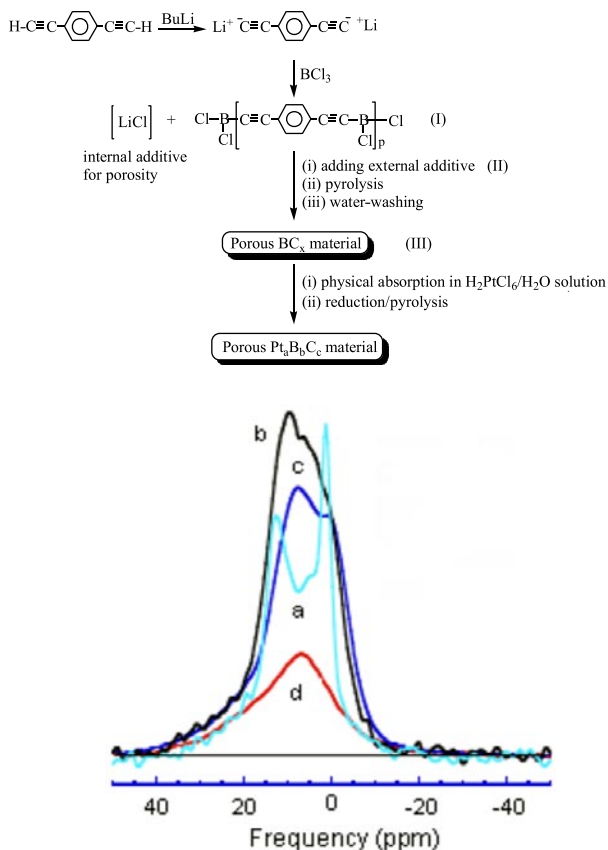
Additionally, we have demonstrated through first-principles calculations that this same electron deficiency can help stabilize the atomic dispersion of light metal atoms. The exposed orbitals of these atoms then provide another venue for new binding chemistry in a geometry that is naturally resistant to aggregation due to the rigidity of the porous framework. We also continue to develop improved means to control porosity and activate surface area in heavily boron-doped carbons, expanding the number of dispersed metals, and new candidate materials with novel nanometer-scale chemistry to be exploited for hydrogen storage.

## Approach

Our approach intimately couples the synthetic, computational and characterization efforts locally at Penn State with the world-leading characterization tools (and also synthetic and computational efforts) available throughout the Center to break new ground in the discovery of new materials systems that modify the binding chemistry towards hydrogen at a fundamental level by controlling electron content, local bonding geometry and spillover geometry in a rigid framework. The starting point, a boro-carbon-based nanoporous framework, provides a robust, lightweight, high surface area, mechanically rigid, low-cost system with the structural cohesiveness to withstand the substantial variations in local chemistry that are necessary to induce enhanced hydrogen adsorption. These modifications include withdrawing substantial numbers of electrons from the structure, dispersing exposed metal atoms onto the structure, and forcing topologically or topographically frustrated geometries that have the potential to generate large local electric fields, resistance against aggregation, and open-shell electronic configurations. Pyrolysis of carefully designed boron-containing polymeric precursors, which are the polyaddition adducts of phenylene diacetylene (with and without lithiation, see Figure 1) and BCl<sub>3</sub> has shown significantly higher hydrogen binding energy and physisorption capacity, compared with the corresponding carbonaceous materials. Each of these final states: electron deficiency, exposed uncompensated orbitals, and uncompensated local fields, provides a distinct fundamental means to generate new classes of adsorptive interaction that is intermediate between traditional chemical and physical adsorption and in the optimal range for reversible room-temperature hydrogen storage. In all stages of this process careful attention is paid to DOE goals in materials cost, volumetric and gravimetric density, and stability over multiple cycles.

## Results

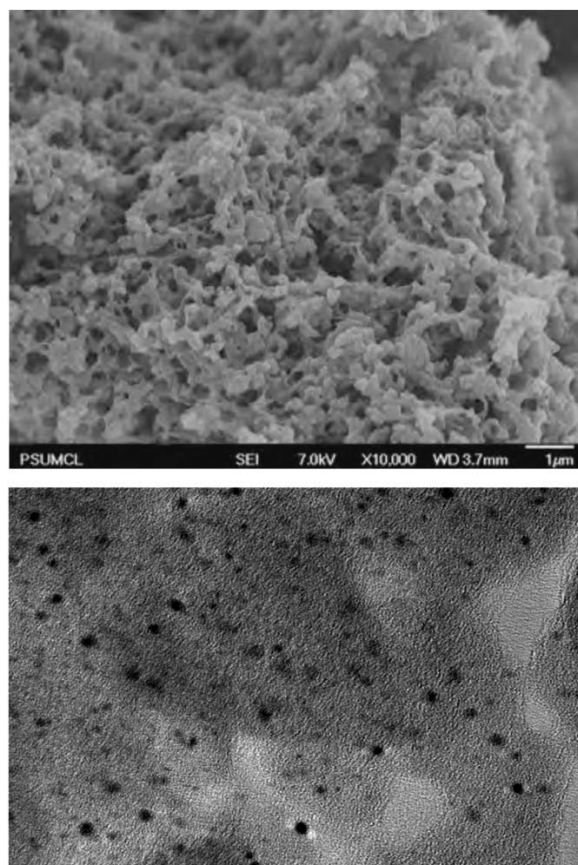
The research team has extended studies to include an additional synthetic method (BC<sub>3</sub> deposition onto highly porous aerogels), additional metals (e.g. Ti),



**FIGURE 1.** Top: Synthesis route for preparing porous BC<sub>x</sub> and Pt<sub>a</sub>B<sub>b</sub>C<sub>c</sub> materials. Bottom: <sup>11</sup>B magic angle spinning nuclear magnetic resonance (NMR) spectra of BC<sub>x</sub> samples prepared from pyrolysis of precursor (I) at 150: a, 600: b, 800: c, and 1,100: d °C. The lower of two peaks corresponds to the desired aromatic boron – its upshift after heat treatment indicates a desirable greater electron deficiency. Excessive heat treatment leads to a crystalline non-porous material. LiCl pore formers ameliorate this effect.

spillover testbeds, and simulations of new framework materials. For enhanced H<sub>2</sub> physisorption it is important to simultaneously optimize several materials properties: micro-porous B/C material (Figure 2) with both a high surface area and a substantial electron deficiency, stabilizing dispersed metals whose open orbitals then provide sites for enhanced hydrogen binding and spillover.

X-ray investigations of the structure of LiCl in the previous year provide greater control over these important pore-forming agents. At pyrolysis below 400°C, LiCl shows no diffraction peak. Above 400°C, sharp diffraction peaks reflect the presence of hydrated and anhydrous LiCl crystals. These in situ formed LiCl molecules in the boron precursor are conveniently used as pore-forming additives removable by water-washing. A shift from micropores when treating at 600°C to predominately mesopores at 800°C is consistent with LiCl agglomeration above its melting temperature. The combination of additives and pyrolysis temperature

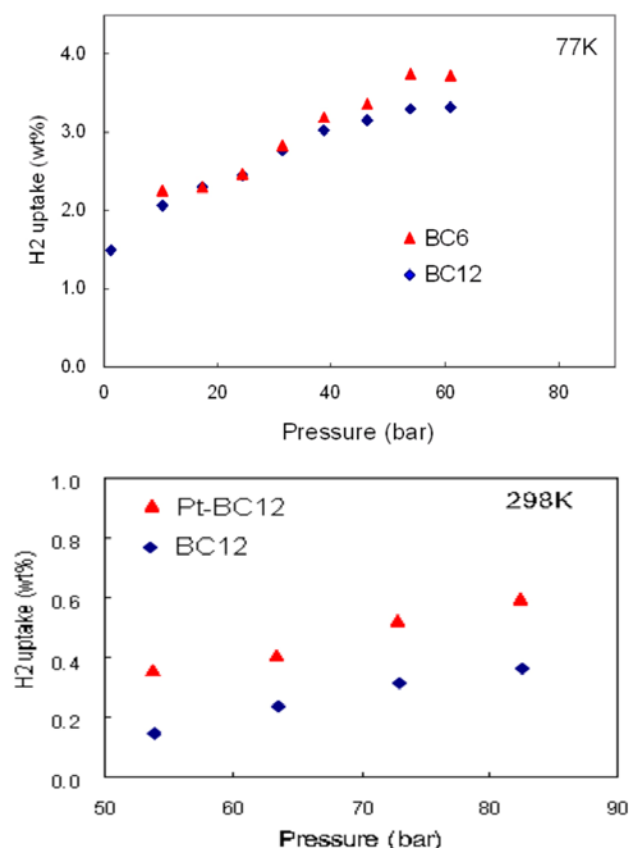


**FIGURE 2.** Top: Scanning electron micrograph of BC<sub>x</sub> obtained after pyrolysis at 600°C, maintaining porous structure in a highly boron-doped carbon. Bottom: Transmission electron micrograph of a Ti<sub>a</sub>B<sub>b</sub>C<sub>c</sub> with dispersed Ti particles (actually TiO<sub>2</sub>, due to oxygen exposure) containing 12 wt% Ti and 6.9 wt% B.

offers a tool to control B<sub>b</sub>C<sub>c</sub> morphology. External additives such as NaBH<sub>4</sub> enhance boron content and porosity in the final products. Other porosity-enhancing additives with higher melting temperatures and good solubility for removal from BC<sub>x</sub> matrix have also been developed in the past year. Several porous BC<sub>x</sub> materials show consistent B content up to 15%. Results for samples 5 and 7 are given in Figure 3. These samples maintain high adsorption energy to high surface coverage, significantly higher than those observed in undoped carbons (4 kJ/mole) and some metal-doped C materials. The increase of B content increases the hydrogen binding energy, as shown in the figure.

Introduction of metal nanoparticles plays an important role in hydrogen adsorption and binding energy. H<sub>2</sub>PtCl<sub>6</sub> was deposited from aqueous solution and platinum acetylacetonate was reduced to platinum nanoparticles using ethanol and ultraviolet radiation on the surface of high surface area nanoporous carbon derived from perfluoroalkoxy with a mean pore size of ~0.8 nm. These investigations were





**FIGURE 3.** Top: Comparison of hydrogen adsorption for BC<sub>6</sub> (sample 7) and BC<sub>12</sub> (sample 5) at 77 K. Although sample 5 has a lower specific surface area, it has a larger uptake due to a stronger H<sub>2</sub> binding from the higher B content. Bottom: Comparison of hydrogen adsorption for BC<sub>12</sub> containing 1 wt% Pt and the corresponding pure BC<sub>12</sub> at 293 K. Pt increases the hydrogen uptake, possibly from spillover. The hydrogen binding energy is at the edge of the range needed to hit DOE 2010 targets, but the specific surface area, boron content, and metal loading must be optimized to obtain this binding energy over more sites.

extended to Ti metal. Figure 2 shows a transmission electron micrograph of a Ti<sub>a</sub>B<sub>b</sub>C<sub>c</sub> material containing 12 wt% Ti and 6.9 wt% B, which was prepared by bis(cyclopentadienyl)titanium dichloride in toluene solution, then following the same thermal reduction. Due to the air-sensitivity of Ti, the observed nanoparticles are TiO<sub>2</sub>. The resulting M<sub>a</sub>B<sub>b</sub>C<sub>c</sub> material maintains a porous structure with slightly reduced surface area. Figure 3 compares hydrogen adsorption at 273 K for a pair of BC<sub>x</sub> and Pt<sub>a</sub>B<sub>b</sub>C<sub>c</sub> materials, in which Pt<sub>a</sub>B<sub>b</sub>C<sub>c</sub> was prepared from BC<sub>12</sub> containing only 1 wt% Pt nanoparticles. The remarked increase of hydrogen adsorption, from 0.38 wt% to 0.6 wt%, is associated with Pt nanoparticles (1–2 nm) in intimate contact with BC<sub>x</sub>, possibly as H<sub>2</sub> spill-over. Pt<sub>a</sub>B<sub>b</sub>C<sub>c</sub> reversibly physisorbs hydrogen at ambient temperature under moderate H<sub>2</sub> pressure (<90 bar). Absorption isotherms indicate an H<sub>2</sub> binding energy of greater than 15 kJ/mol.

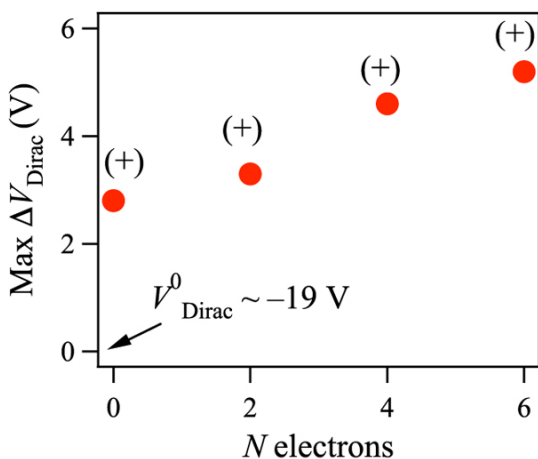
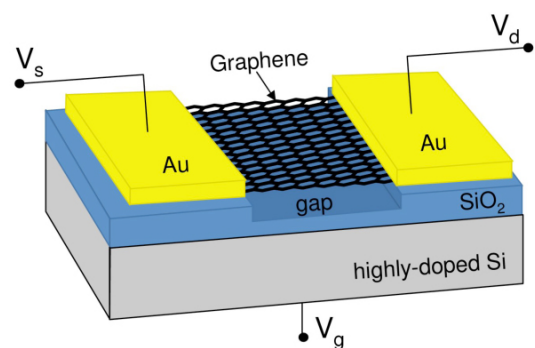
In an alternative synthetic technique, boron trichloride and benzene (2:1 by volume) were mixed in a He carrier gas and deposited on a high surface area mesoporous silica aerogel in a 900°C tube furnace. The deposited BC<sub>3</sub> was then analyzed using X-ray photoelectron spectroscopy and <sup>11</sup>B NMR spectroscopy. After BC<sub>3</sub> deposition, the surface area reduced slightly from 730 m<sup>2</sup>/g (heat-treated aerogel alone) to 670 m<sup>2</sup>/g. Heat of adsorption using adsorption isotherms at 77 and 87 K indicates that the BC<sub>3</sub> coating dramatically increases the initial heat of adsorption, from ~4 kJ/mol to ~9 kJ/mol, with a nearly double heat of adsorption maintained at higher hydrogen loadings onto heterogeneous sites (Figure 5). The H<sub>2</sub> uptake at 77 K increased from 50 cc/g to 80 cc/g, even though the surface area decreased. This new method of creating highly porous boro-carbons enables further independent tuning of porosity and boron content, up to 25% boron.

A testbed to elucidate the critical mechanism of spillover, a single-graphene-layer device with simultaneous transport and Raman probes, has been further developed. We have previously dispersed uniform Pt nanoparticles onto the graphene sheet, and we have recently produced the requisite graphene-based field effect transistors and characterized them under controlled gas environments, including suspended graphene field effect transistors that use buffer-oxide etching to remove the substrate, as shown schematically in Figure 4. The position of the Dirac peak (resistivity maximum) with respect to the gate voltage reveals the charge transfer from the adsorbate to the high surface area substrate – this transfer is a critical mechanism in enhancing hydrogen adsorption. Characterization with aromatic adsorbates, depicted in the figure, demonstrate the feasibility of the approach. An additional device containing Pt nanoparticles was also prepared and is currently under study, with electric measurements under controlled pressure and gas flow.

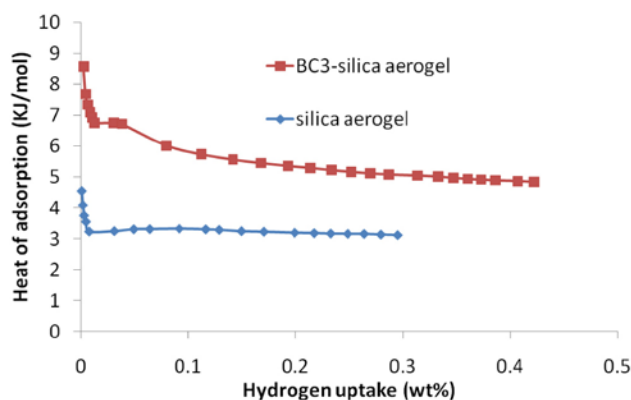
Calculations of the relative stability of various ordered and disordered high surface area boro-carbon and metal boro-carbon systems continue to support the experimental efforts. In addition, possible new materials systems continue to be investigated. For example, stabilization of atomically dispersed metals through topological frustration with halogen electron acceptors appears fruitful, and a new framework system that exploits weak hydrogen binding to boron-nitrogen motifs in a geometry that suppresses the formation of BN is also showing preliminary promise as a new strategy towards the challenge of hydrogen storage, as depicted in Figure 6.

## Conclusions and Future Directions

Our synthesis approaches to produce high surface area materials with high boron content demonstrated

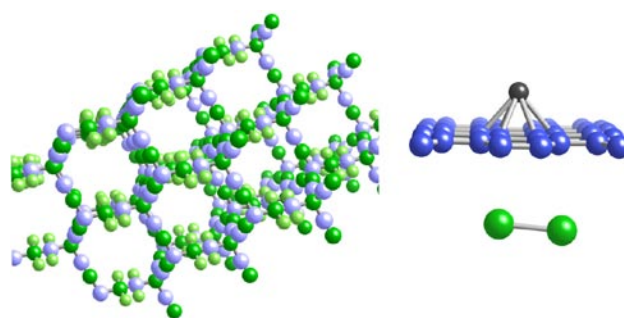


**FIGURE 4.** Top: Schematic of a suspended graphene field effect transistor testbed for spillover investigation. Bottom: Charge transfer to the substrate reflects shifts in the gate response in terms of the number of adsorbate  $\alpha$  electrons: the device is sensitive to electron deficiency.



**FIGURE 5.** Heat of adsorption vs.  $H_2$  loading for silica aerogel and  $BC_3$  coated aerogel. Although the coated material has a slightly lower specific surface area, it demonstrates improved hydrogen adsorption due to a near-doubling of the binding energy for  $H_2$ .

that boron substitution into the  $sp^2$  lattice produces an increased binding energy for  $H_2$ , one that is further enhanced by highly dispersed metals. We continue



**FIGURE 6.** Left: A new material system being assessed via first-principles simulation: an open covalent BN framework adsorbs H in a manner that suppresses formation of solid BN, hence improving reversibility. Right: A halogen dimer constraints to the underside of the boron-carbon sheet enhances the stability of an isolated Ti atom on the other side, thereby solving the primary challenge of dispersed exposed metallic atoms: suppressing aggregation.

to increase the boron content, porosity, and hydrogen binding, with computational guidance on optimizing surface chemistry via induction of high curvature, electron deficiency, large local fields, and exposed metal orbitals that are resistant to aggregation. The choices of metals to disperse is guided computationally via modeling of the interaction with B. These efforts are focused on obtaining very large densities of homogeneously distributed binding sites of 15–30 kJ/mol binding in a lightweight framework, which will provide a possible pathway to DOE 2015 targets for gravimetric and volumetric storage. Work to date has led to ~150% improvement in binding energy (nearly to the goal), validating the underlying design concept for these new advanced sorbents. The team will focus these efforts on further reducing the particle sizes of an expanding range of metals by optimizing loading conditions and thermal budgets, and pursuing multiple parallel strategies to optimize porosity while maintaining optimal local bonding geometries and boron contents. The effect of increased binding energy on high surface area nanoporous borocarbons on processes such as hydrogen spillover from noble metals like Pt will be examined in detail with new testbed geometries.

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6. *Development of nanoporous carbon based shape selective catalyst and potential hydrogen adsorbent materials* Energy Innovation Forum, Penn State University, October 23, 2008.
7. *A new energetic regime for carbon nanostructures: the bi-ribbon and graphene as a bi-continuum*, V. Crespi et al, Invited talk at IMRC Cancun, 2008.
8. *A simple approach to synthesize nanoporous carbons with high heats of adsorption of hydrogen*, R. Rajagopalan and H. Foley, submitted to JACS.