Ab Initio Study of Hydrogen Storage on CNT

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Rational Design of Hydrogen Storage Material

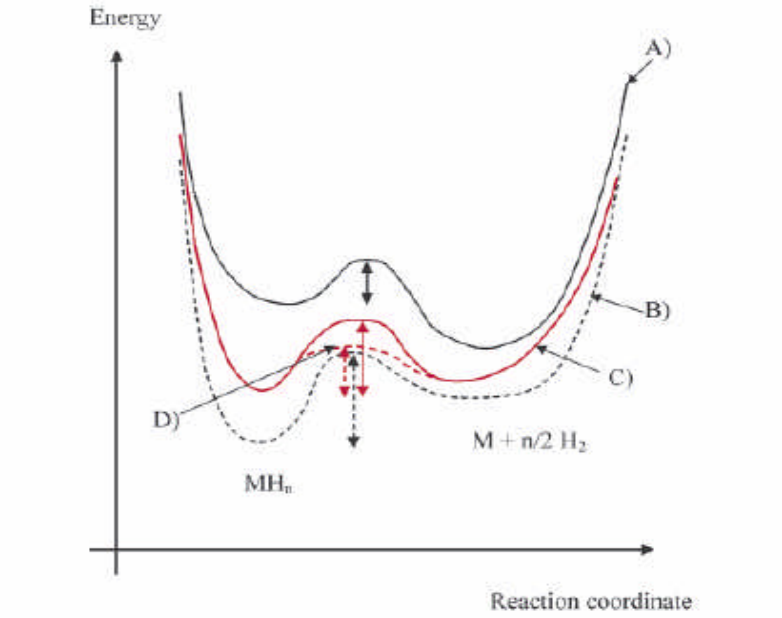


Figure 12. Reaction path for hydrogen evolving from different HSMs. (A) Thermodynamically very unstable HSM with low activation barrier and low T_{dec}, which stores hydrogen irreversibly. (B) Thermodynamically very stable HSM with high activation barrier and high T_{dec}, which stores hydrogen reversibly. (C) Thermodynamically slightly stable HSM with intermediate T_{dec}, which stores hydrogen irreversibly. (D) Target situation: catalytically enhanced thermodynamically slightly stable HSM with low T_{dec}, which stores hydrogen reversibly. Vertical arrows symbolize the activation barrier for the decomposition process.

- High Storage Capacity: 6.5 wt%, 65 g/L
- Desorption Temperature: 60~120 °C
- Thermodynamically slightly stable hydrogen storage systems are desired and can be achieved through material engineering.
- Reversibility dilemma: Reversibility is usually associated with high-energy barrier for dissociation and adsorption.
- Solution: Engineered catalyst can tune the energy barrier.

Multiscale *Design* of Nanomaterials for Hydrogen Storage

Chemisorption: H_2 + NM → NM-2H

- H-H bond breaking = 4.5 eV
  → poor reversibility (too strong bonding)
+ high surface coverage
? stability of NM-2H states

Physisorption: H_2 + NM → NM-H_2

+ weak adsorption
  → good reversibility
- small surface coverage (much less than a few wt. %)

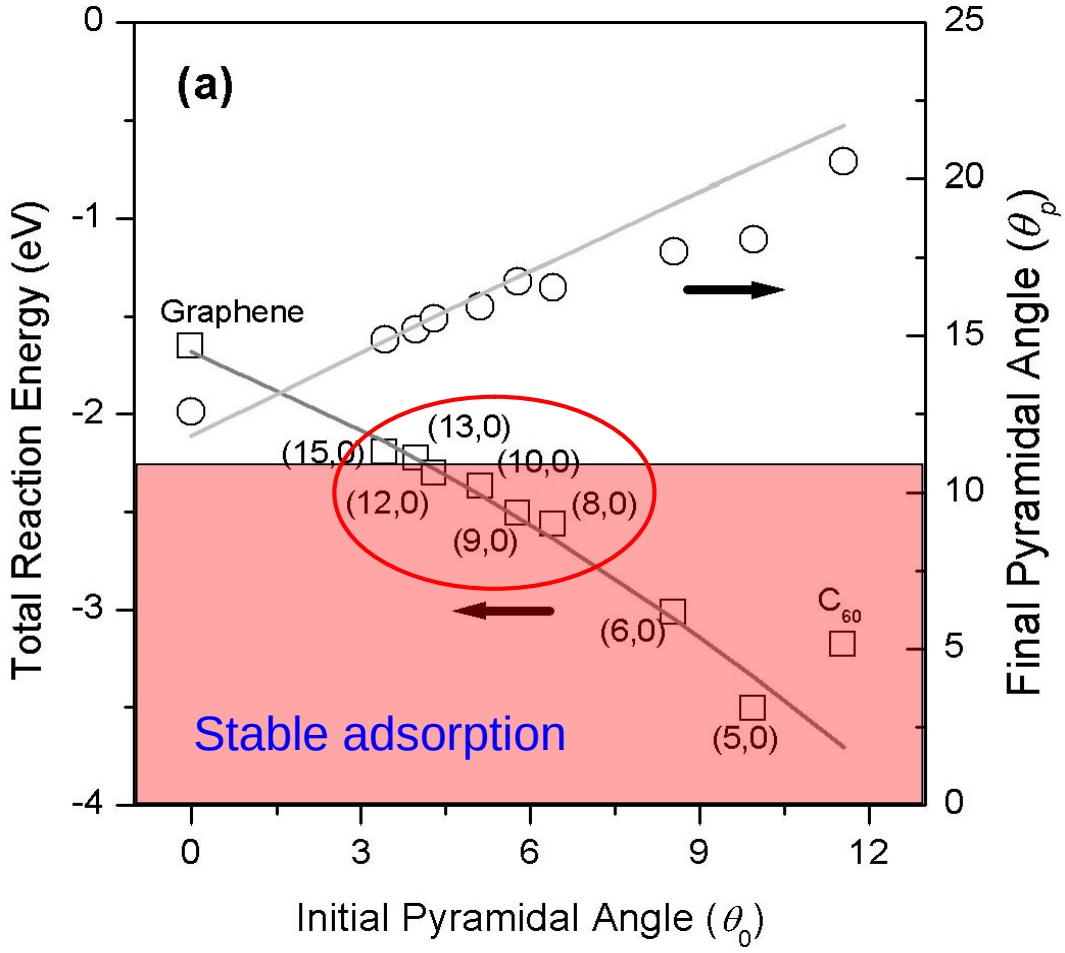
Controlled Catalytic Chemisorption

+ high surface coverage & good reversibility

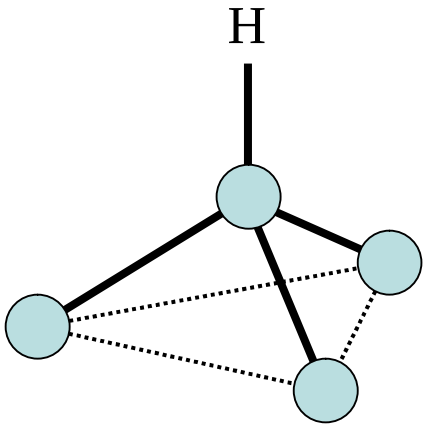
Experimental results

- Dillon et al., Nature, **386**, 377 (1997)
  - Room temperature, 300 torr, **soot with 0.1 wt% SWNT**
  - 0.01 wt% hydrogen adsorption, equivalent to 5~10 wt% on pure SWNT.
- Ye et al., Appl. Phys. Lett. **74**, 2307 (1997)
  - 80K, 100 bars, **pure sample**.
  - 8.25 wt% hydrogen adsorption.
- Liu et al., Science **286**, 1127 (1999)
  - Room temperature, 100 MPa, **pure sample.**
  - 4.2 wt% hydrogen adsorption.
- Chen et al., Science **285**, 91 (1999)
  - Ambient pressure, **Li or K doped carbon nanotubes**.
  - 14 ~ 20 wt% hydrogen adsorption. ***FTIR show that H_2 is dissociative.*** Other experiment suggests it is due to water adsorption.
  - Only 0.4 wt% hydrogen adsorption without doping.
- Nu¨tzenadel et al., Electrochem. Solid-State Lett. **2**, 30 (1999)
  - 0.39 wt%, **electrochemical hydrogen storage.**

Controlled Hydrogen Bonding on Carbon Nanotubes



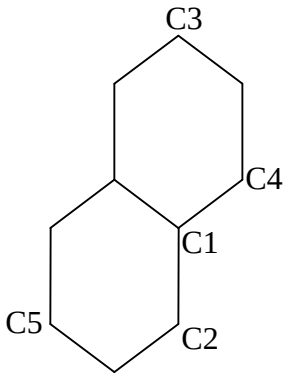
Prediction (solid curves)
***Ab-initio* results (□ and ○)**



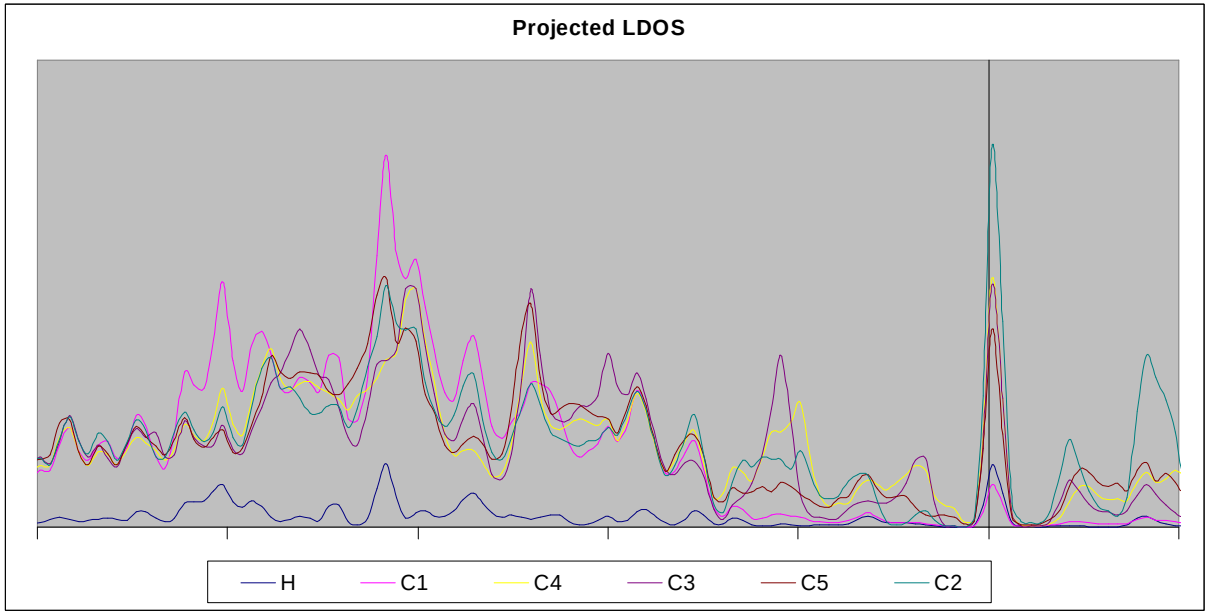
stability of chemisorbed hydrogen (NM-2H) states relative to H_2 gas can be tuned by nanotube size: (8,0) - (12,0) CNTs would have enough binding energy (up to 0.5 eV) per H_2 molecule

S. Park, D. Srivastava, and K. Cho, "Local reactivity of fullerenes and nano-device applications," Nanotechnology 12, 245 (2001).

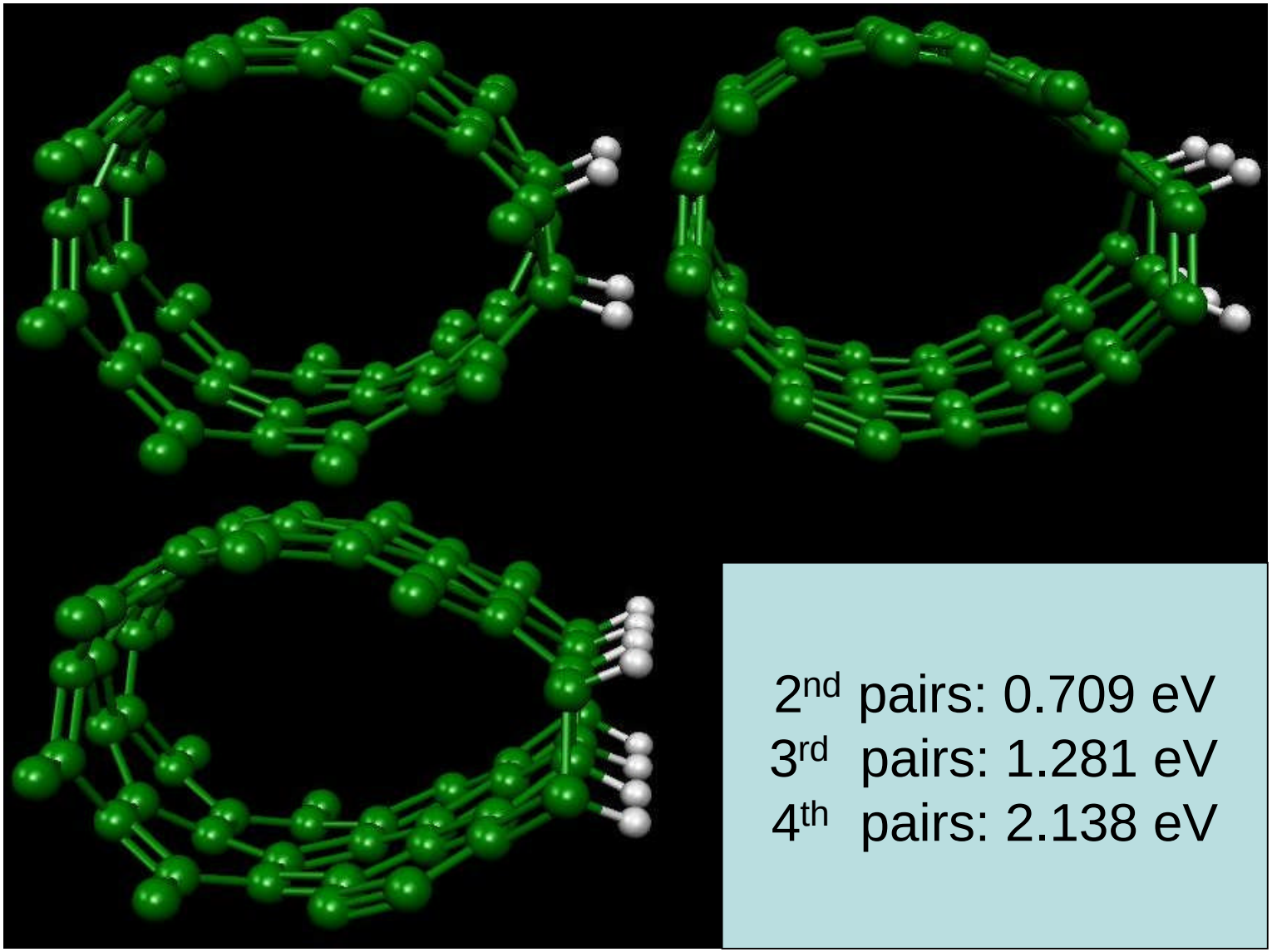
Optimal Configurations of Adsorbed Hydrogen Pairs



	LDA, US	*LDA*, PAW	*GGA*, US	*GGA*, PAW
C1C2:	0.263 eV	0.291 eV	0.142 eV	0.222 eV
C1C3:	0.018 eV	0.046 eV	-0.374 eV	-0.264 eV
C1C4:	-0.045 eV	-0.017 eV	-0.403 eV	-0.306 eV
C1C5:	-0.317 eV	-0.289 eV	-0.483 eV	-0.402 eV

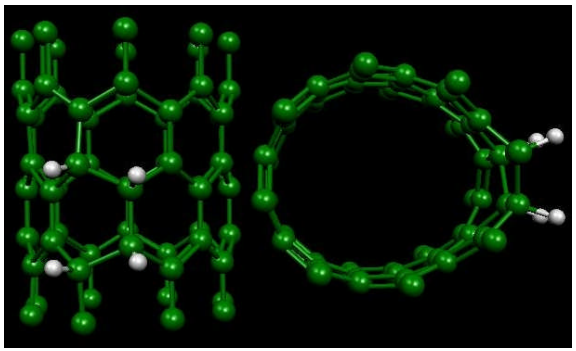


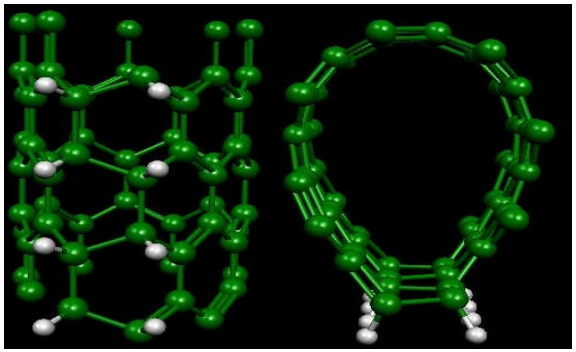
Optimal Configurations of Adsorbed Hydrogen Pairs

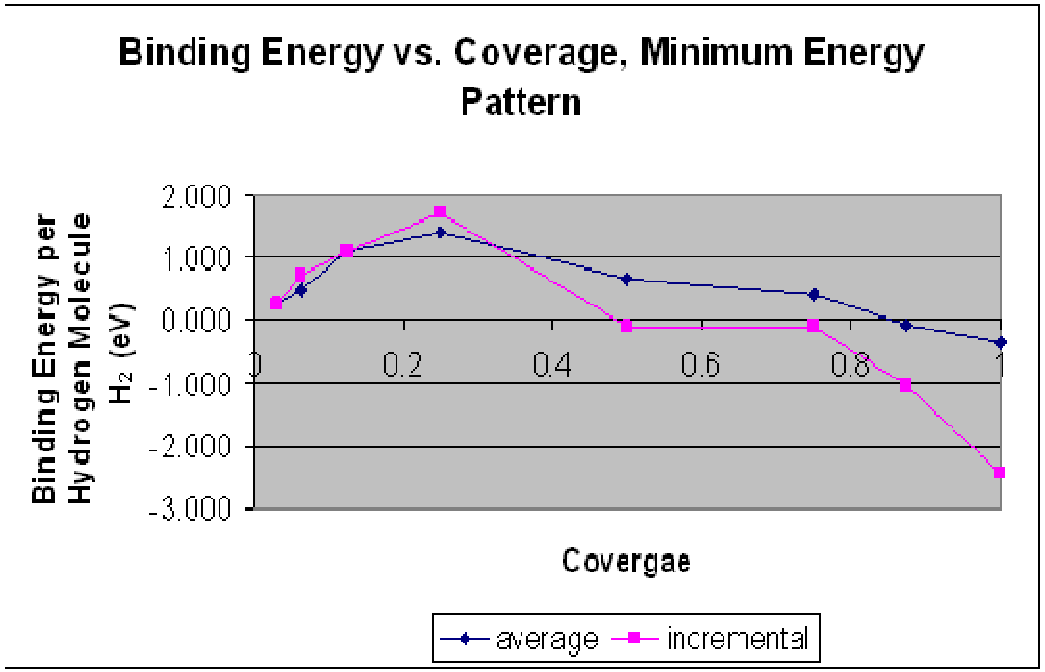


2^{nd} pairs: 0.709 eV
3^{rd} pairs: 1.281 eV
4^{th} pairs: 2.138 eV

Coverage Dependence of Binding Energy

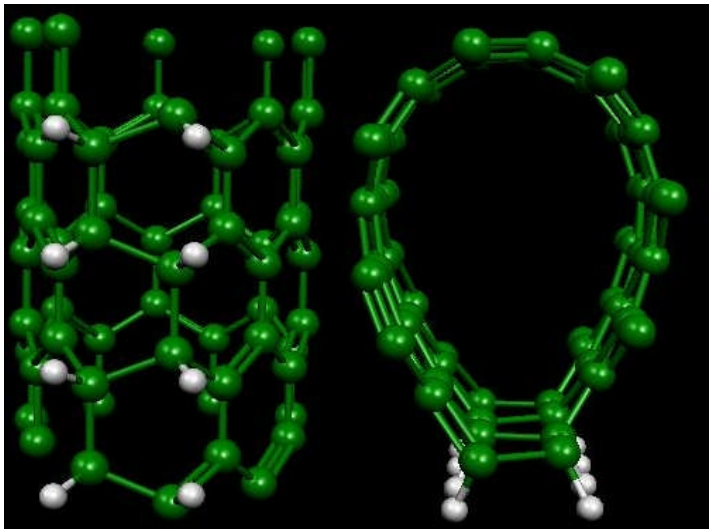


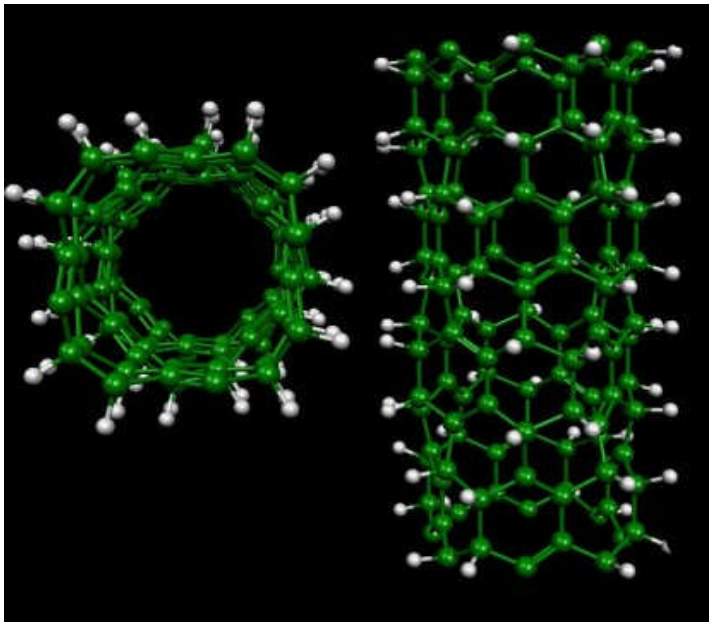


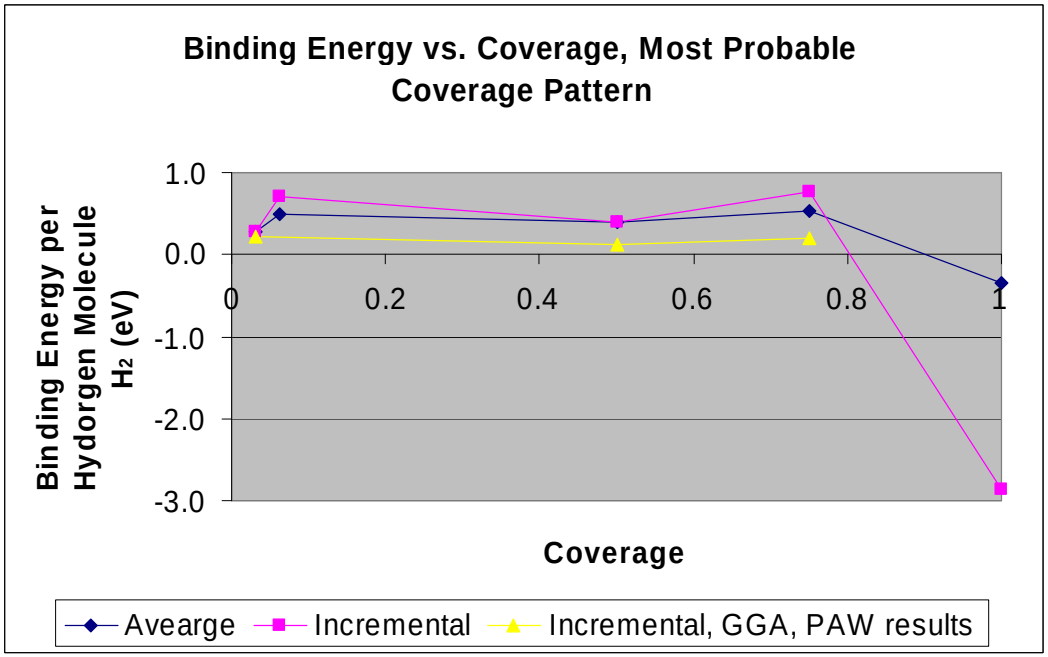


- The maximum chemi-sorption capacity is around 50% or less
- Binding is very strong at low coverage.

Coverage Dependence of Binding Energy

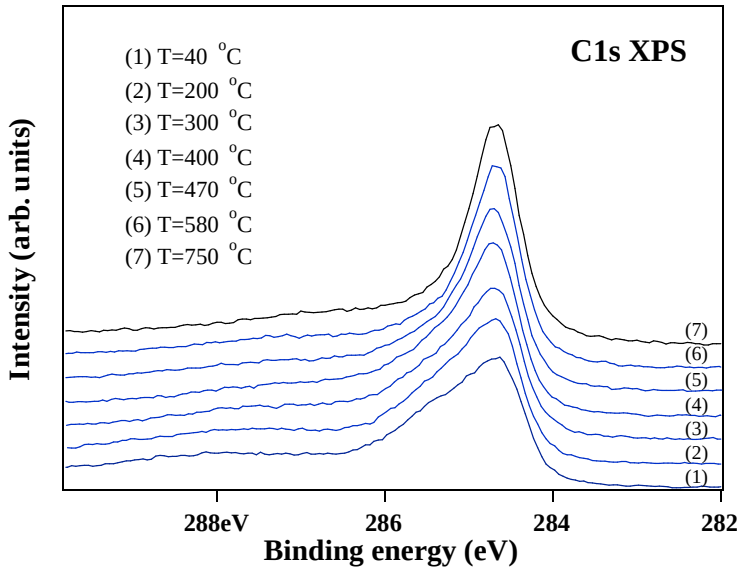


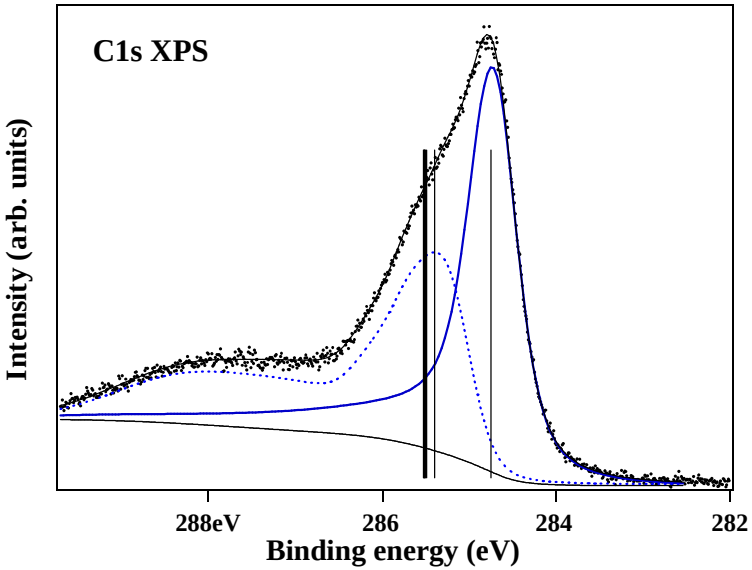




- The maximum coverage is around 75% with external binding.
- The binding energies are in a narrow range of 0.4 eV ~ 0.6 eV (0.12 ~ 0.22 for GGA and PAW)

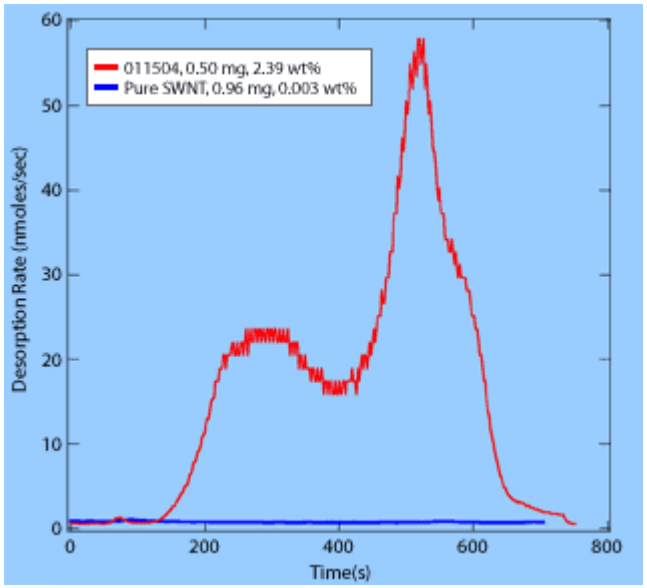
Absorption of Atomic Hydrogen on SWCNT

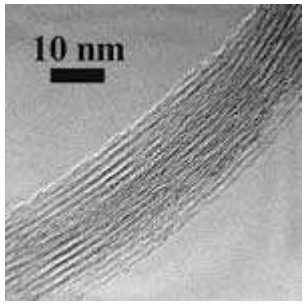




- Atomic source of H for hydrogenation.
- Diameter of SWCNT in the range of 1nm to 1,8 nm.
- 65±15% (5.1±1.2wt%) of hydrogenation.
- Stable in the temperature range of 300~600°C.

Experimental results, Dissociative H_2 Adsorption

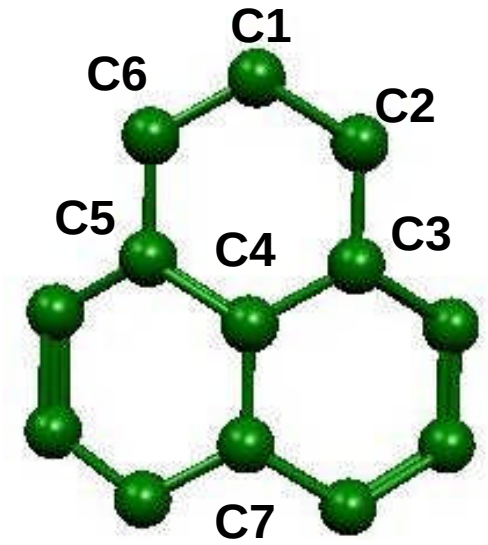


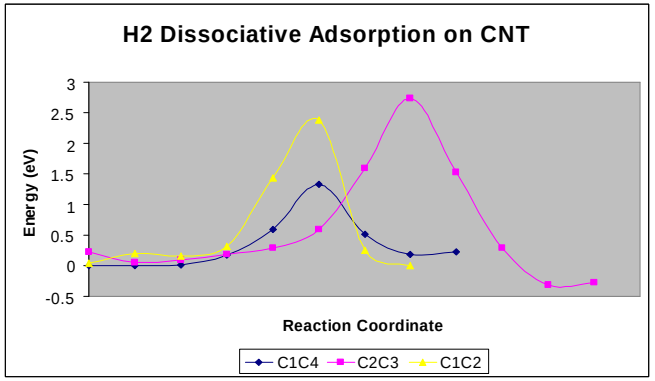


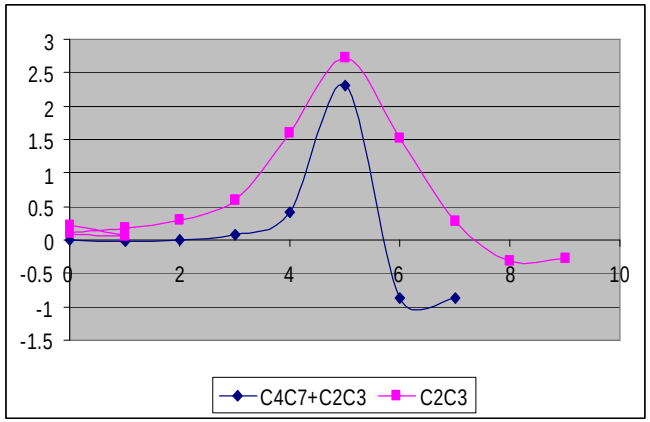
Carbon Nanotube Sorption Science External Peer Review of NREL Activities, January 19-23, 2004

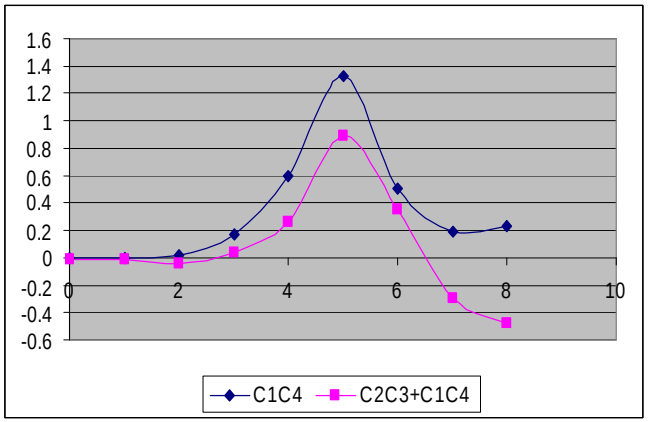
- No hydrogen storage was observed in pure single-walled carbon nanotubes.
- Roughly 3 wt.% was measured in metal-doped nanotubes at room temperature.

H2 Dissociation on CNT

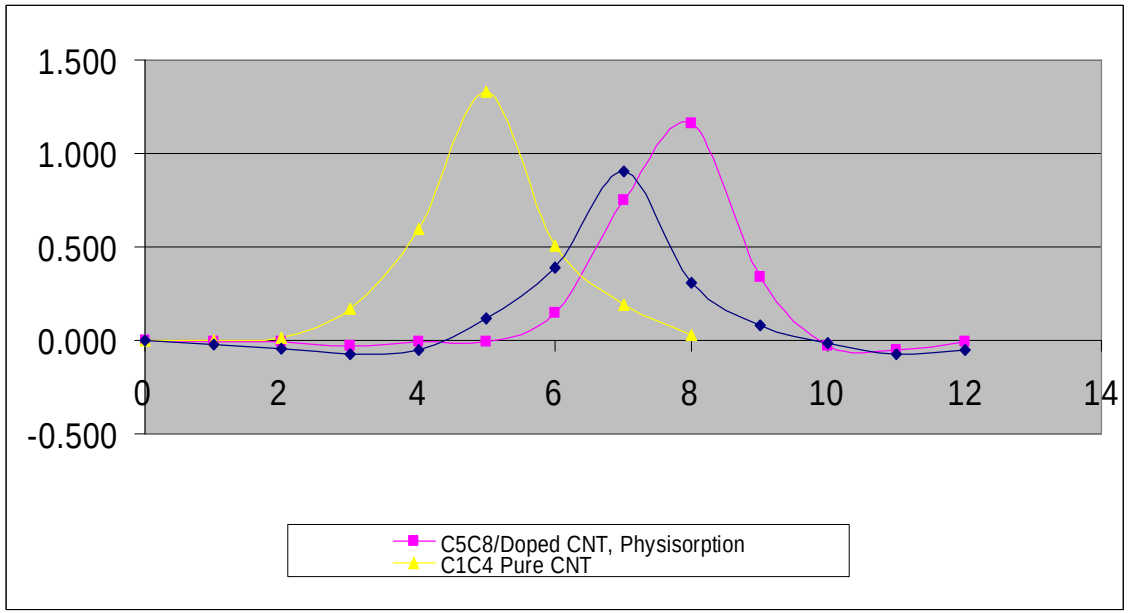




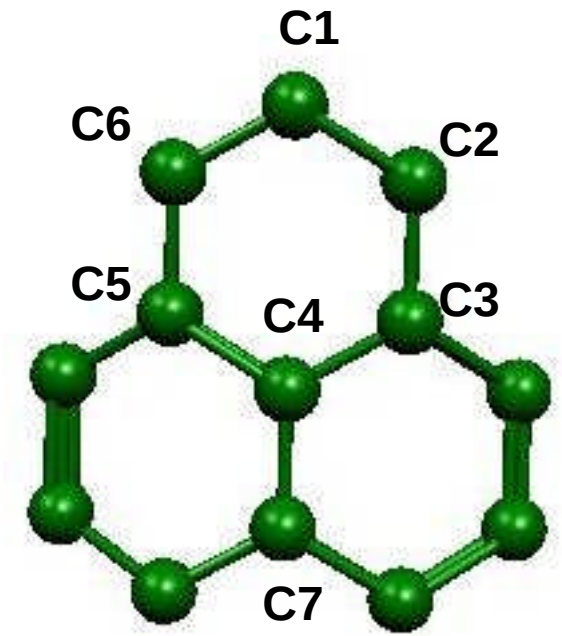


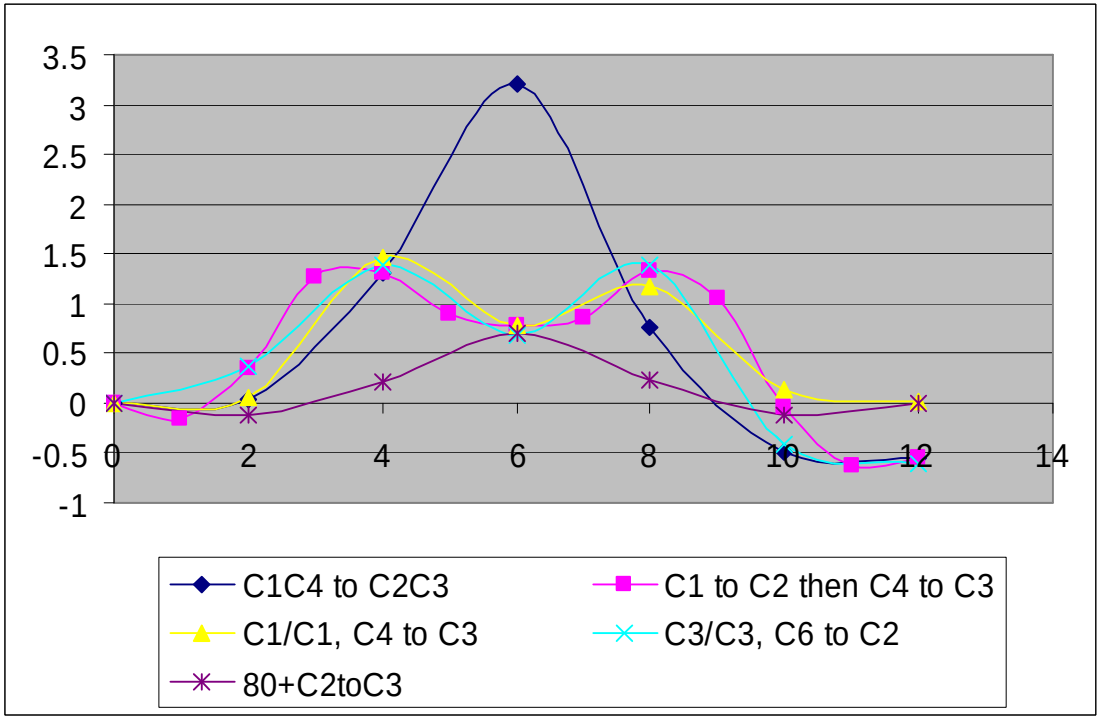


H2 Dissociation on N-Doped CNT



H Diffusion CNT





Conclusion

- The hydrogen biding energy strongly depends on the coverage on the CNT. Computational results indicate that the binding energies fall within a narrow range of energy in the most likely coverage pattern.
- We have identified the most likely dissociative adsorption pathway and studied the diffusion pathway of hydrogen on CNT.
- Computational results indicate that doping the CNT can substantially lower the dissociative adsorption pathway and thus improve the hydrogen storage kinetics.