Theoretical Models of H_2-SWNT Systems for Hydrogen Storage and Optimization of SWNT

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Rice University

Hydrogen Sorption Center of Excellence

May 15, 2007, Washington DC Project ID#: ST4

The presentation contains no proprietary, confidential, or otherwise restricted information

Overview

Timeline

- **Start: 01 February 2005**
- **End: 31 January 2010**
- **38% complete**

Budget

- **Total project funding**
  - **DOE: $1,065,209 (1.75M request)**
  - **Contractor: $269,181**
- **Funding in FY06 $205,000**
- **Funding for FY07 $235,000**

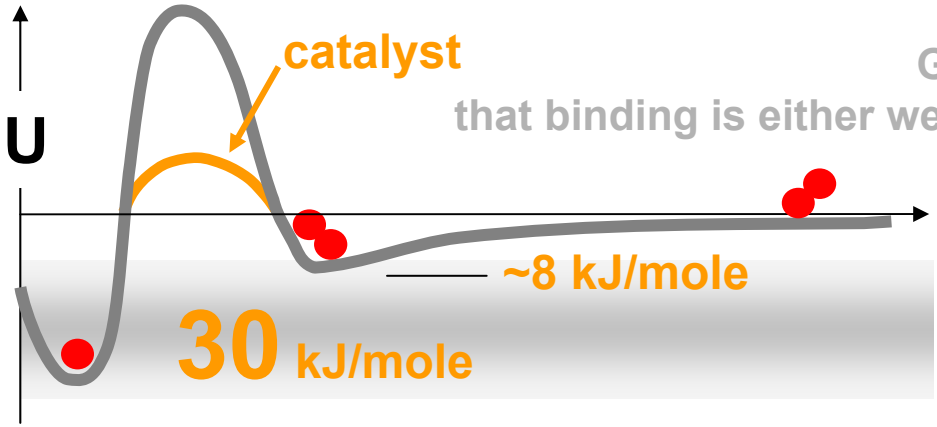
Barriers

Barriers to be addressed

- **Flexible representation of H_2-carbon binding, to identify carbon-based architectures for the best sorption**
- **Enhance the binding of H_2 by introducing charge into the synthesized carbon arrays (VANTA)**
- **Identify role of metal atoms in hydrogen retention, and how to prevent Me-aggregation**
- **Understand thermodynamics and kinetic mechanisms of spillover**

Partners

- **NREL, Air Products Corp,** regular teleconferences, face-to-face meetings (Houston, Golden, CO, Washington, Gaithersburg, MRS San Francisco, MRS Boston).



Generic potential curve illustrates
that binding is either weak or separated by large barriers

OBJECTIVES

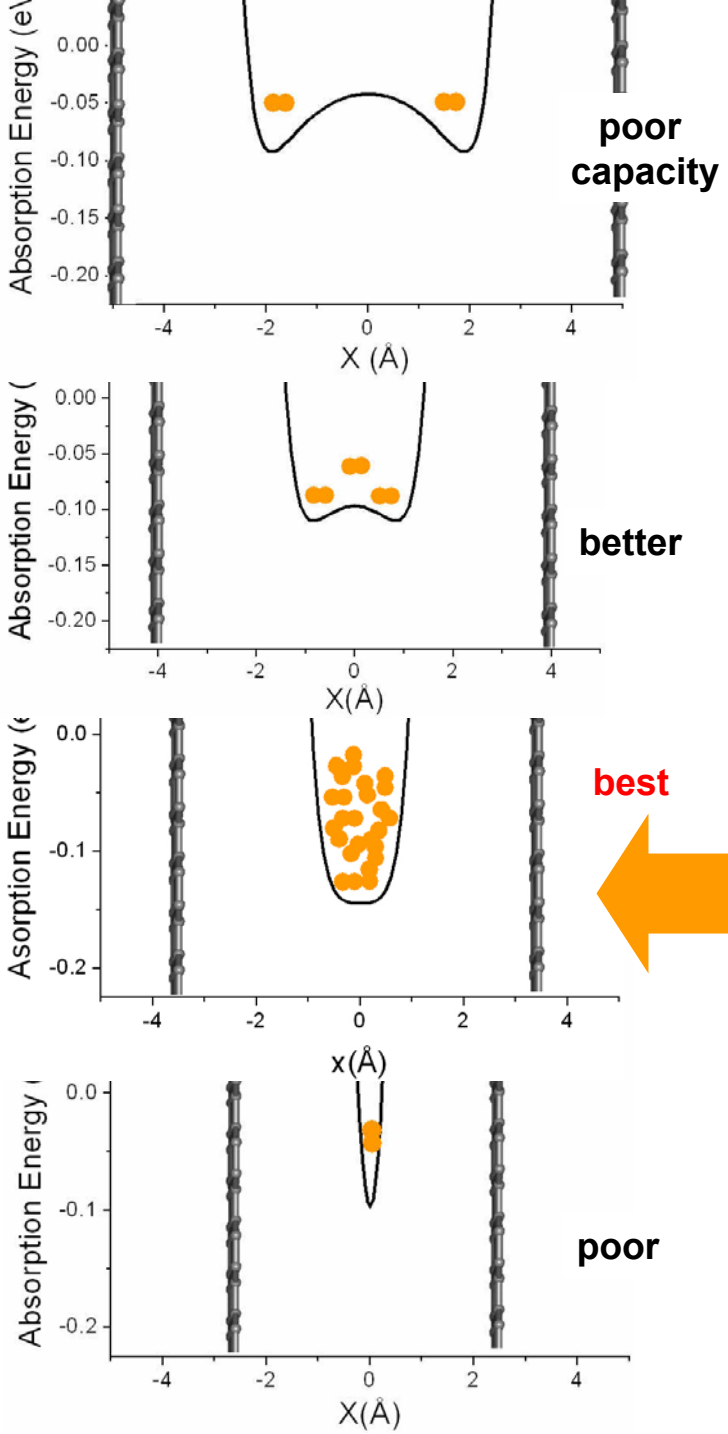
OVERALL: Model materials structures' interaction with hydrogen, optimize their makeup for storage and assess the gravimetric and volumetric capacity. Provide recommendations for the synthetic goals (e.g. pore/channel size, metal enhancement routes).

2006:

- **Explore full utilization of physisorption by van der Waals forces through carrier geometries–3D-foams–for best surface, accessibility, and retention capacity--binding energy. Compute van der Waals wells for H_2-trapping on generic carbon structures, for achieving 7-9% storage.**
- **Transition-metal enhanced adsorption via the various ways of doping carbon backbone Me@C_n + m*H_2, Me = Sc, Ti, … or Li, K, with the emphasis on metal aggregation.**

2007:

- **continue the above and**
- **Synthesis of metal- and electronegative-group- (*F, BF_3*) enhanced VANTA (vertically aligned nanotube arrays, *contrast to fibers*) for H_2 adsorption.**
- **Theory of hydrogen spillover, its thermodynamics and kinetics: energy states, cooperative effects, mobility.**



APPROACH

- **Utilize superposition of weak vdW attraction in the nanopore-3D-foam materials**

← Example: graphene double-layer
Superposition of the potentials can enhance adsorption at the optimum spacing

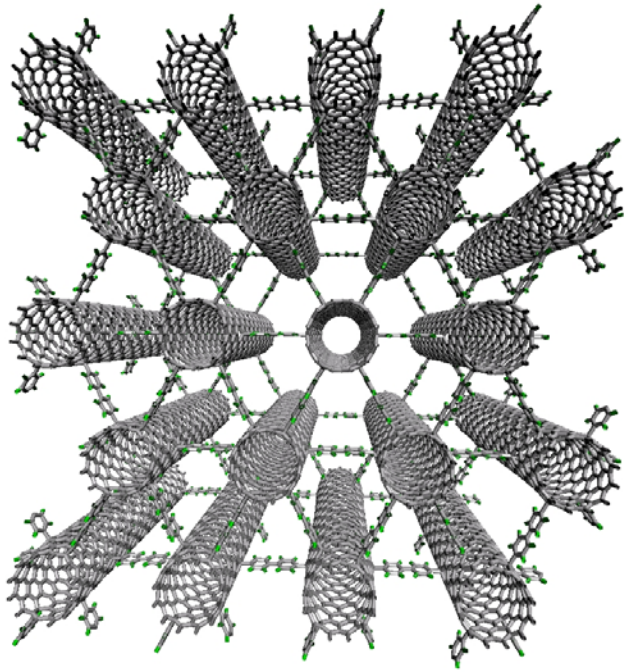
H_2----carbon potential optimization [up to 7% storage, per PNAS (2005)]

- **Enhance binding by strategically placing Me-atoms, yet avoiding their aggregation**

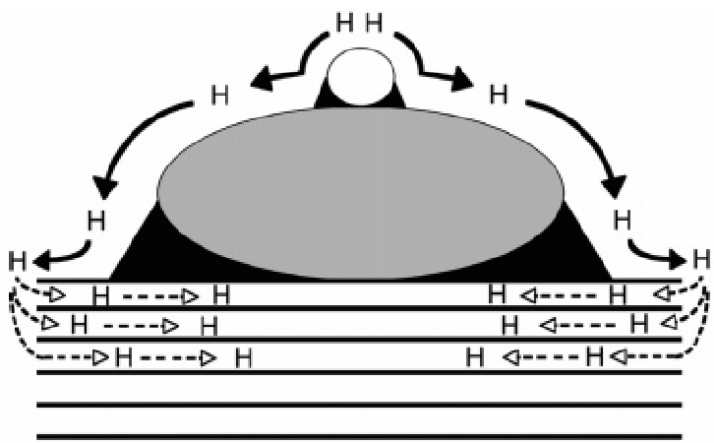
APPROACH

- **Synthesized VANTAs' architecture offers good gas transport, thermal conduction, openness for insertion of molecular spacers and metal- and electronegative- (*F, BF_3*) enhanced centers for H_2 storage. Good *precursor* for 3D-nanopore engineering**

- **For spillover, perform accurate energy calculation with the emphasis on configurational and cooperative effects, and compute the barriers for the H-diffusion, to provide fundamental understanding of the observations [at the U of Michigan]**

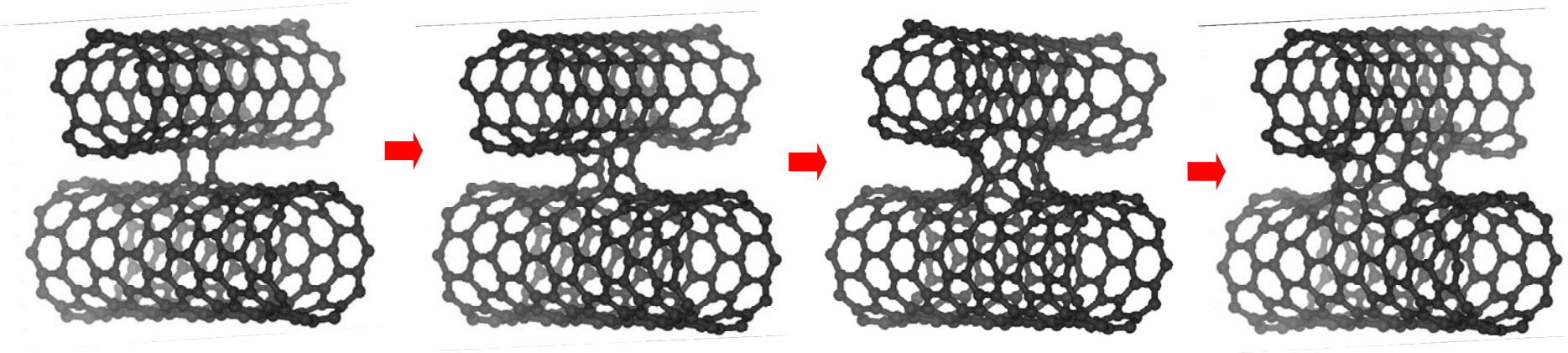


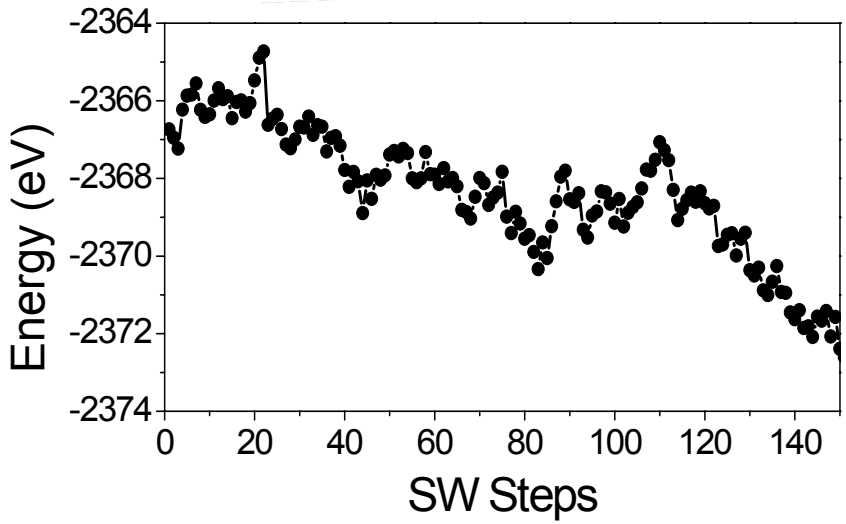
Biphenyl cross-linked SWNT 3D-structure, Y. Lin, F. Ding, B.I. Yakobson

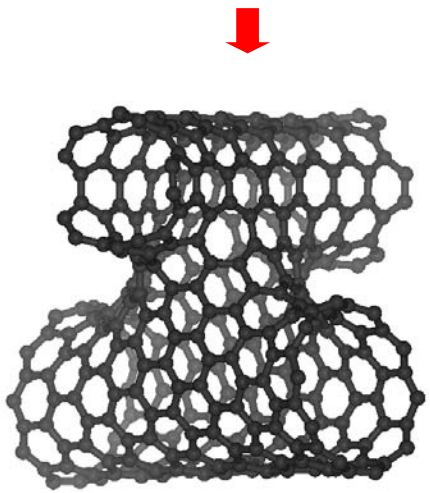


phenomenological spillover schematics
R. T. Yang et al, *Langmuir* 2005, 21, 11418
[Center's project at U of Michigan]

Based on previous experience (PRL, 2002) show thermo-radiation welding of tubes to form cross-junction and open interior channel

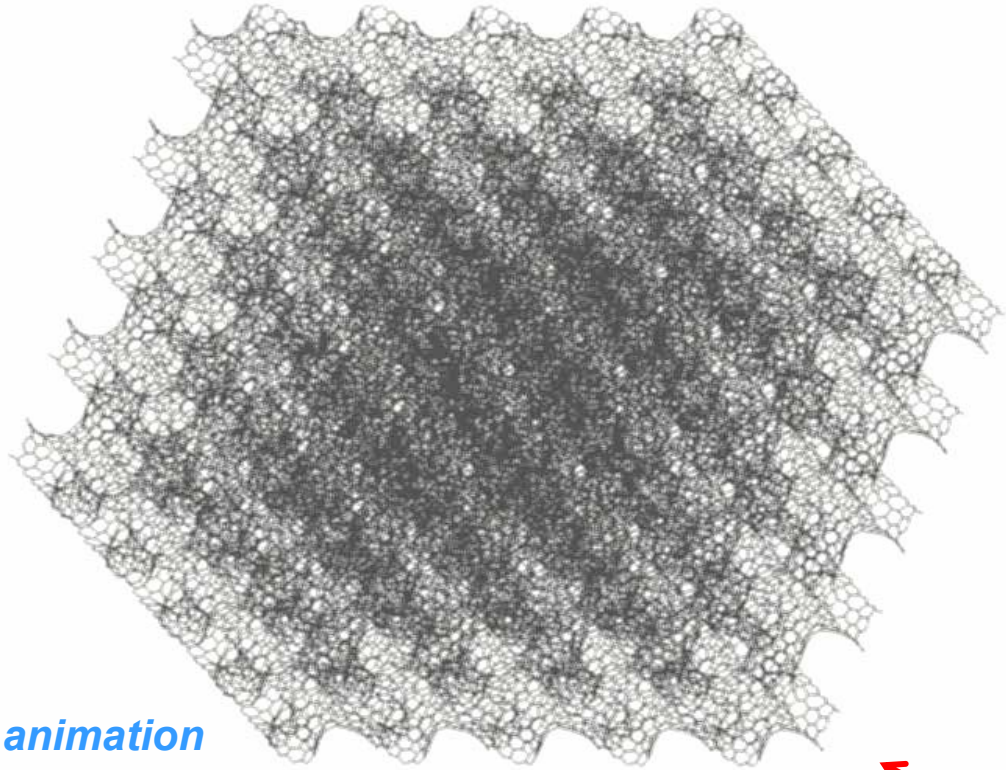




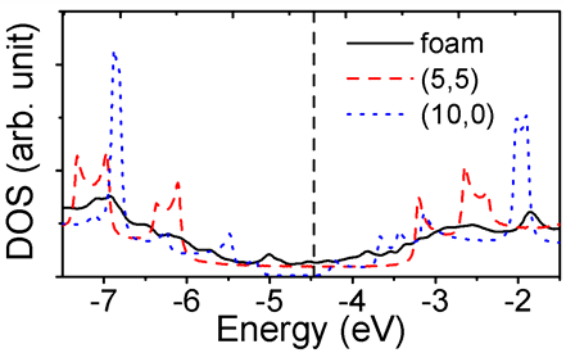


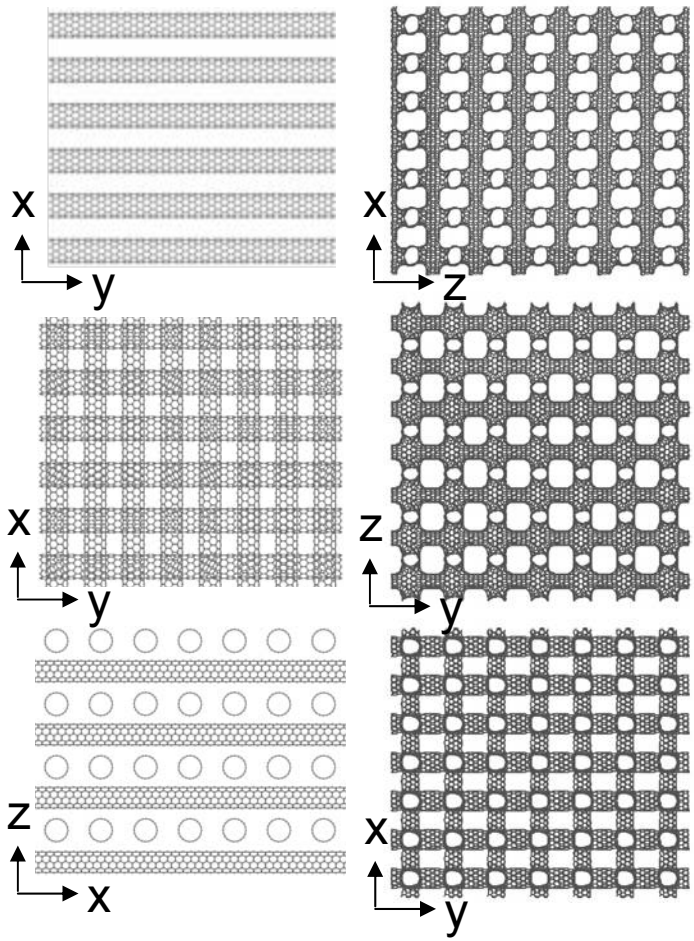
Identified energetically favorable kinetic path to the cross-welding of nanotubes (or VANTA material), which shows how the nano-foams can be engineered via physical processing

Engineering one SWNT-based foam



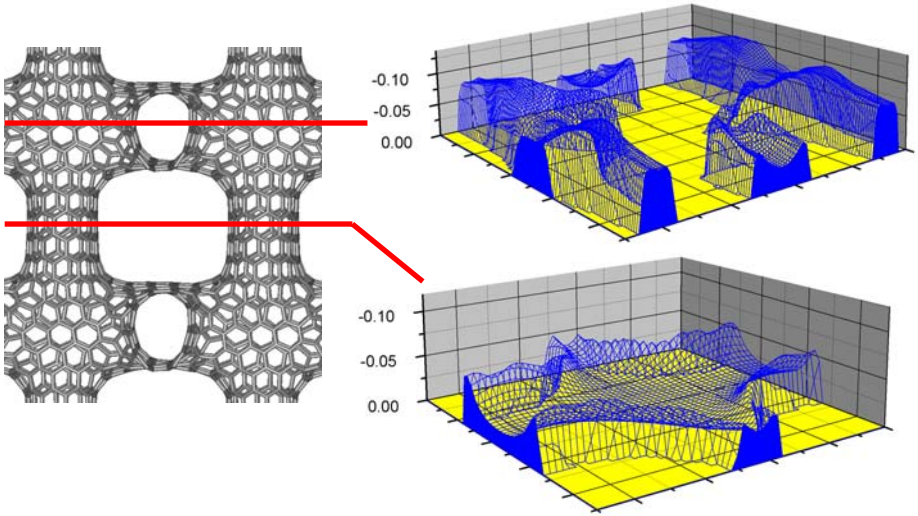
animation

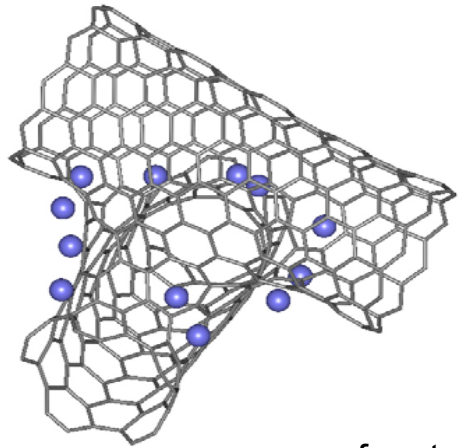




The foam has nanometer pores and channels, all it's surface (~2600 m^2/g) is accessible, it's lighter than water (~0.9 g/cm^3), excellent thermal conductor, and it is metallic!

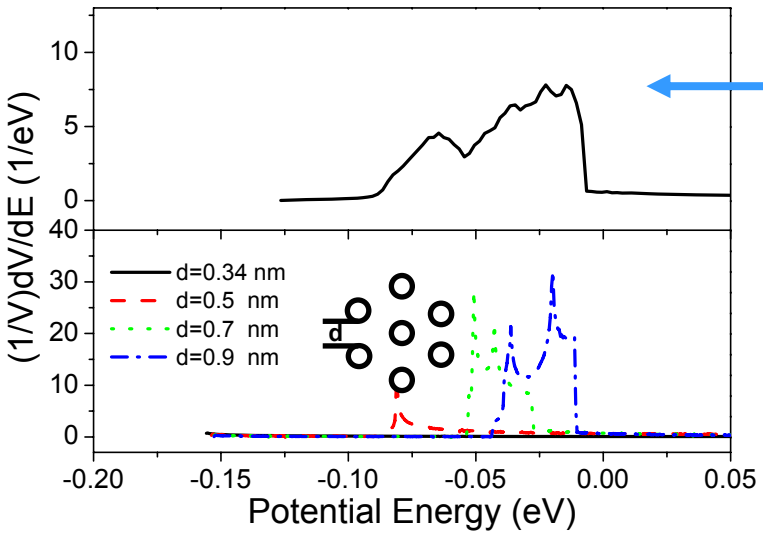
Adsorption energy landscape in a foam





presence of metal-enhanced anchors-heptagons

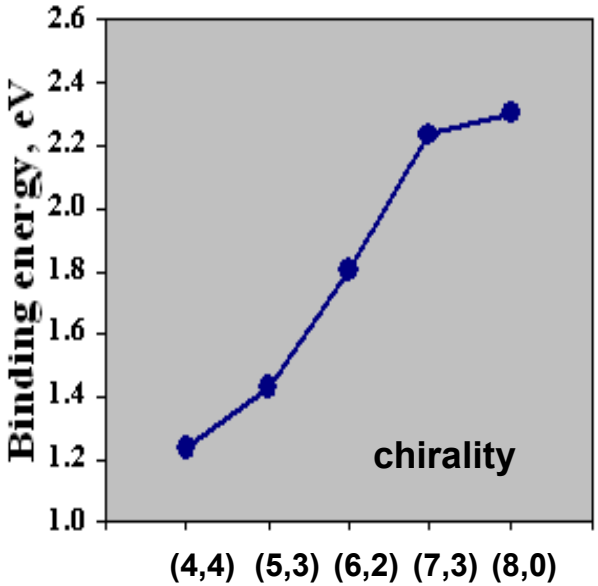
Distribution density of adsorption energy inside the foam

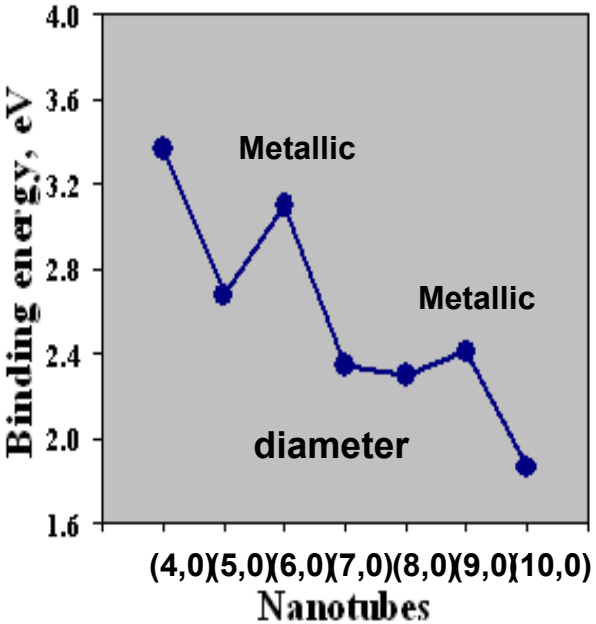


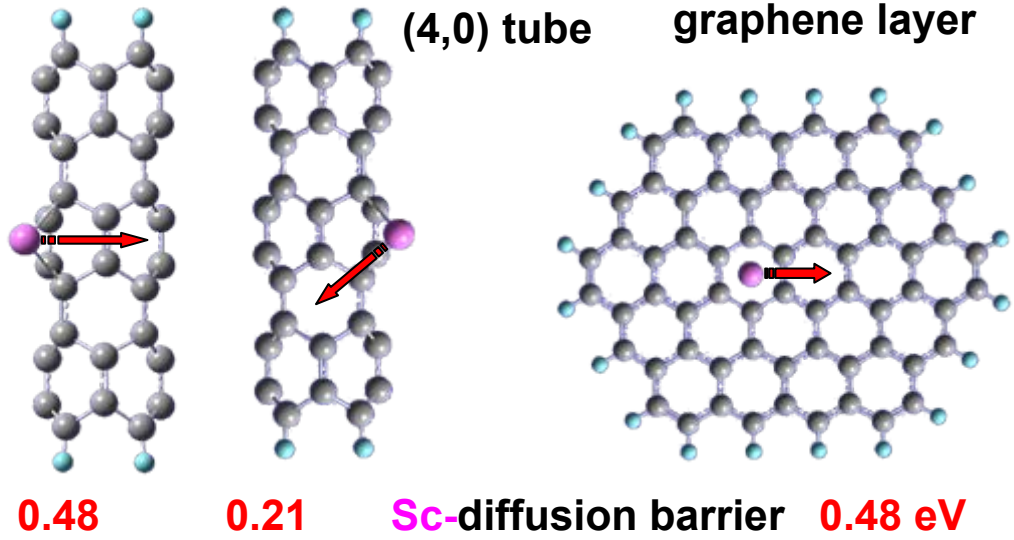
The statistics of absorption energy in this foam exceeds even the best-spaced SWNT bundles (s = 0.7 nm). It promises better hydrogen storage capacity than SWNT bundles.

Recommended: d = 0.9-1.1 nm

technical accomplishments 2





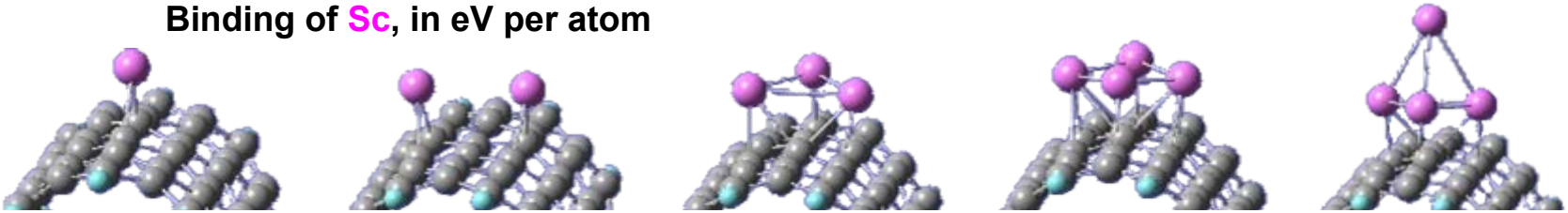


Computed stability of the Me, e.g. binding energies of Sc with SWNT, energy barriers for its diffusion

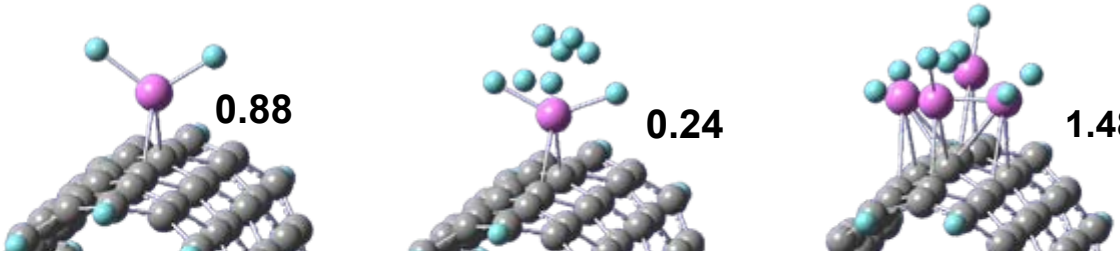
Established: metal-tube binding is sensitive to diameter and chirality, stronger to zigzag thin tubes [in support of synthetic work at *Duke U* and at *Rice U*]. Low barriers indicate possibility of metal aggregation, detrimental for storage! Recommend: anchoring Me in "5" or "7" sites.

technical accomplishments 2

Binding of Sc, in eV per atom

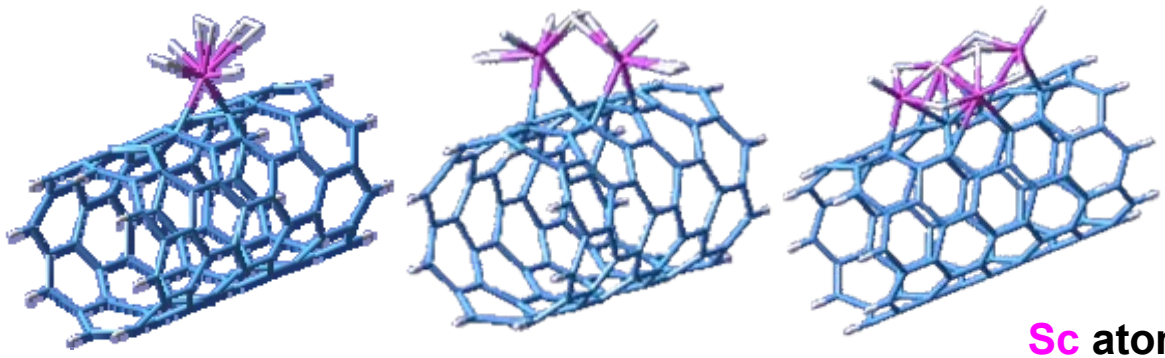


2.303 **2.439** **2.522** **2.453** **2.353 eV**



1.48 eV per H_2, adsorption on Sc-clusters

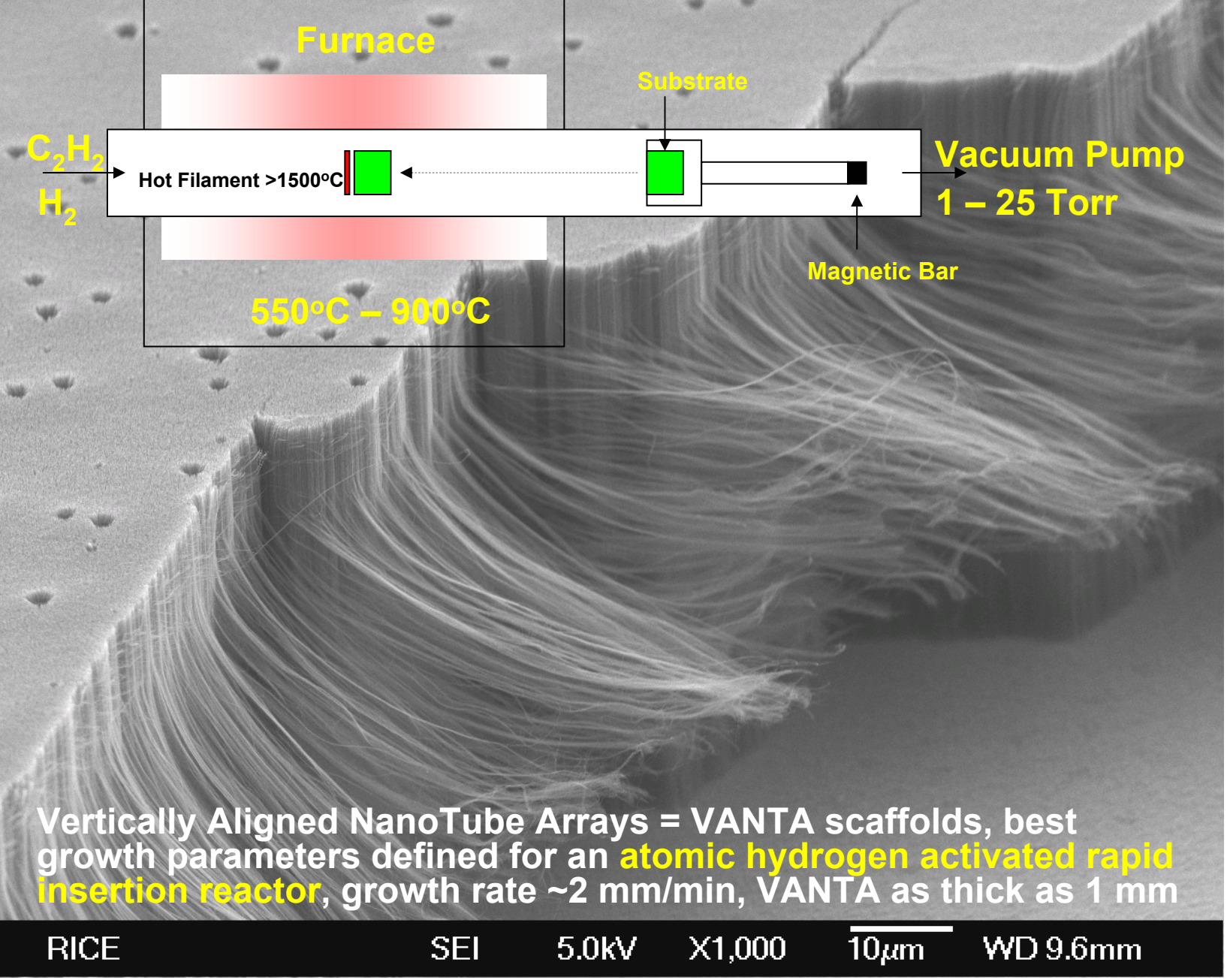
Aggregation of Sc atoms on the SWNT surface is shown to reduce the hydrogen storage capacity...



(Becke98/6-31G, Gaussian 03)

Sc atoms→clusters on nanotube surface

…However we observe transition from Kubas interaction to catalytic function of a larger metal cluster (as side effect of its possible aggregation): H_2 dissociates completely as needed for spillover!



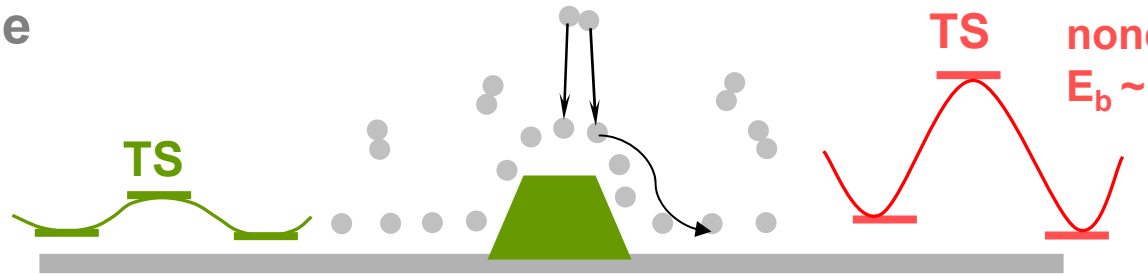
NT non-fiber scaffolds now available for 3-D engineering, adds of metals or electronegative- (*F, BF_3*) enhancer for H_2 adsorption [to NREL and AirP]

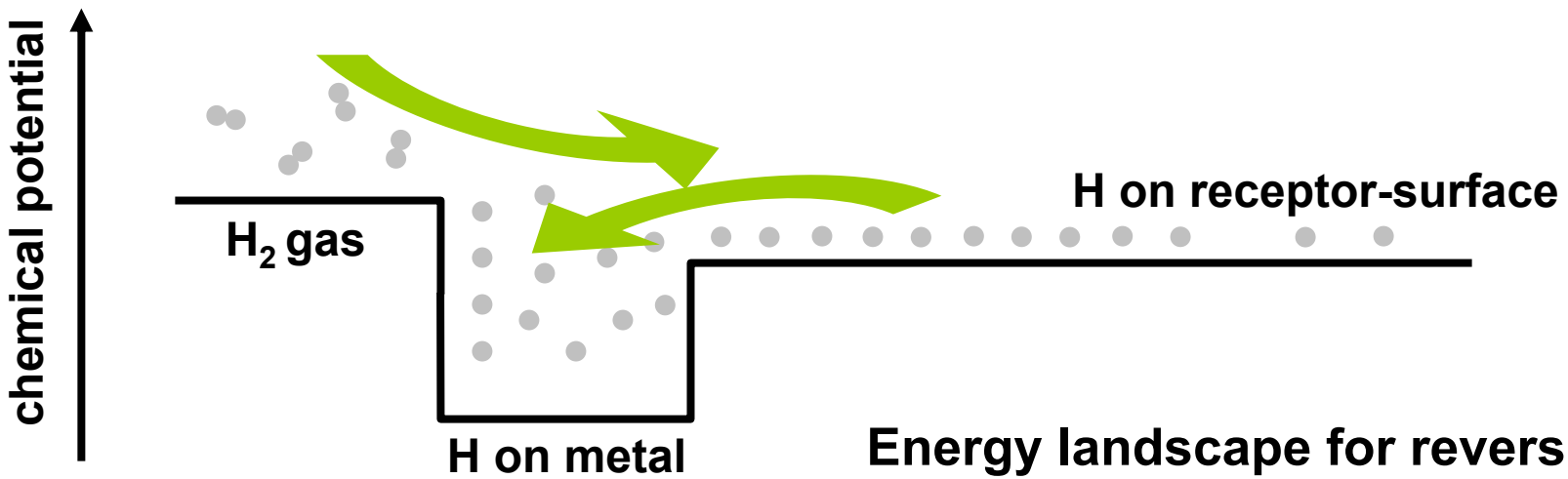
technical accomplishments 4

Global view of the spillover path in the energy scale: downhill, with reasonably small kinetic barriers

H_2O spillover in the field of gravity…

…and H spillover in the chemical force-field

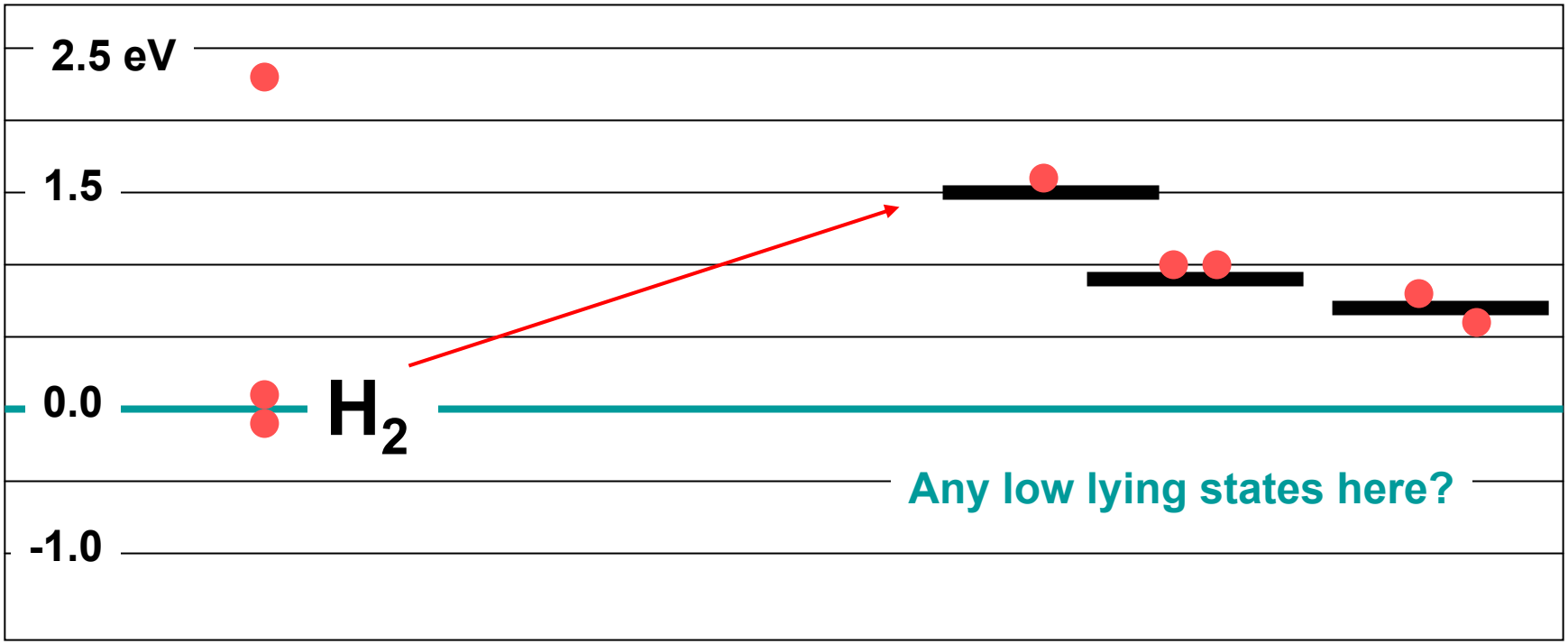




Energy landscape for reversible spillover should be reasonably flat

Why theory had problem with this?

1. Is chemisorption of H on carbon receptor thermodynamically suitable?

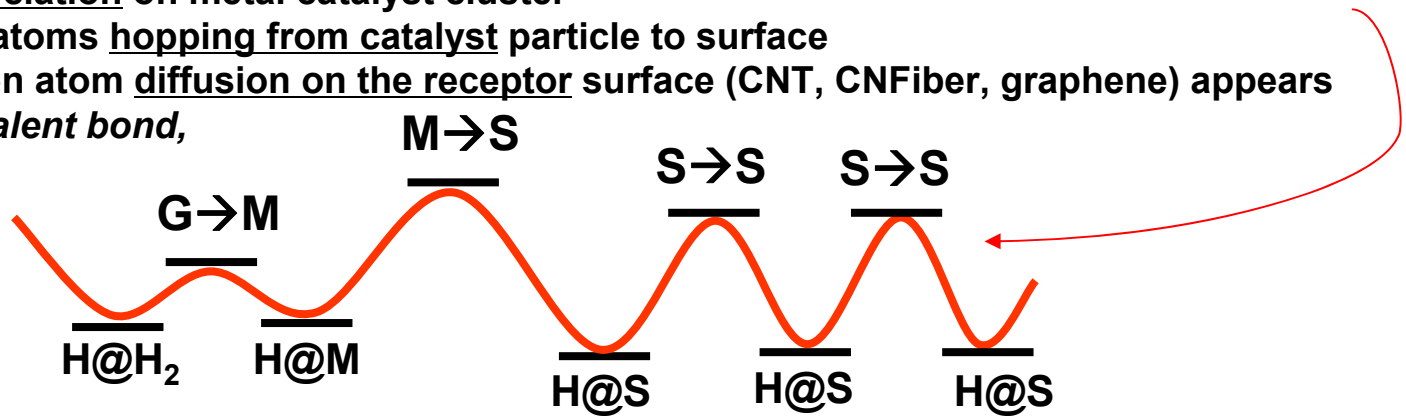


- What's the binding energy compared to H_2 gas? ~0.3 eV is the best for storage at room temperature and not very high pressure
- Too strong binding (>1 eV) is not good because hydrogen release is impossible or highly endothermic

2. Analysis of kinetics, how is this feasible?

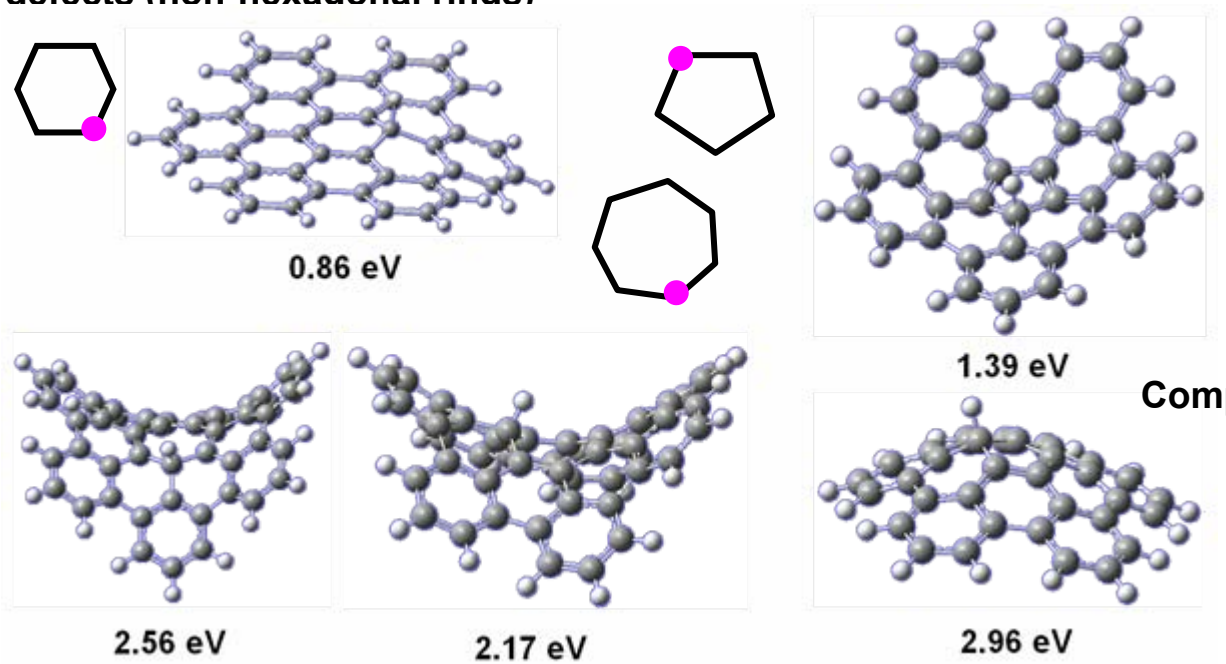
If low energy states are reached then the transport barriers must be high

* The barrier of H_2 dissociation on metal catalyst cluster
* The barrier of carbon atoms hopping from catalyst particle to surface
* The barrier of hydrogen atom diffusion on the receptor surface (CNT, CNFiber, graphene) appears as rate controlling: *covalent bond, large distances*



Search for proper energy states, 0.3 eV below the H_2.

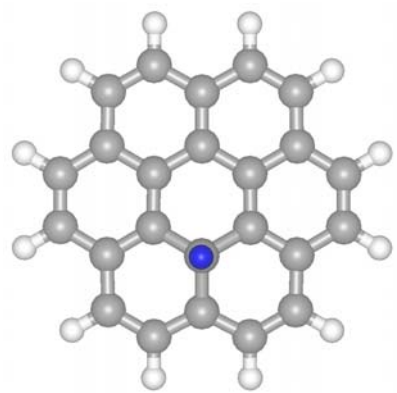
Single atom absorption on flat graphene is too weak, but appears more suitable on topological defects (non-hexagonal rings)



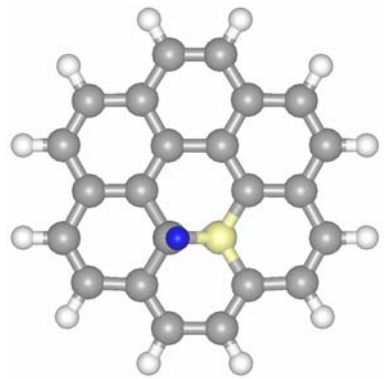
Computational method: B3LYP/6-31g*

Various and often contradicting predictions are partially due to different computational methods used. We must perform necessary comparative testing of methods and orbital-bases choices. Two representative (odd- and even differ!) test samples (yes, in theory we do use samples too):

E(H@)



E(2H@)

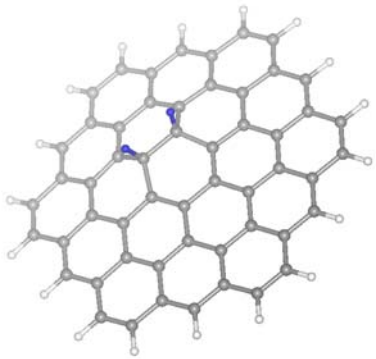


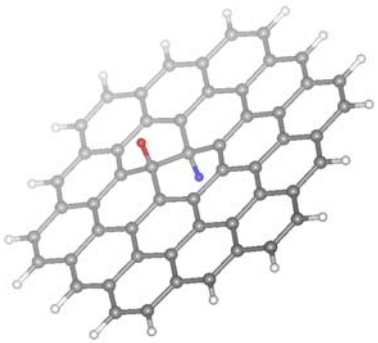
Method/Basis	E(H_2) /eV/H	E(H@)/eV/H	E(2H@)eV/H
B3LYP/631g	2.380	0.547	1.496
B3LYP/631g**	2.422	0.657	1.595
B3LYP/6311+g**	2.384	0.678	1.595
B3LYP/6311++g**	2.382	0.676	1.593
PBEPBE/631g	2.363	0.584	1.528
PBEPBE/631g**	2.310	0.685	1.610
PBEPBE/6311+g**	2.267	0.703	1.606
PBEPBE/6311++g**	2.262	0.699	1.601
LSDA/631g	2.369	0.887	1.895
LSDA/631g**	2.495	0.991	1.979
LSDA/6311+g**	2.451	1.032	1.991
LSDA/6311++g**	2.447	1.028	1.989
MP2/cc-pvtz	2.245		
PW91/pw[Hornekær 06]	2.27	0.85	1.25

Each computation is precise, but “error-bar” can be assessed from comparison of different methods and samples

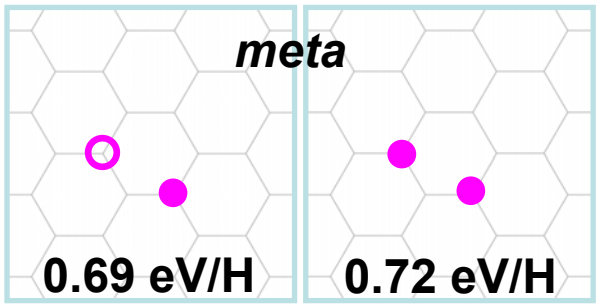
So, we launched a systematic quest for the low energy configurations.

(PBEPBE/6-31G**, Gaussian03)

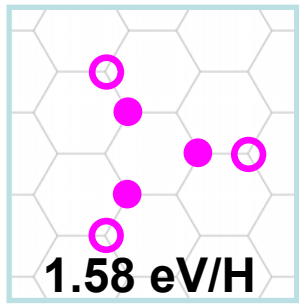




meta

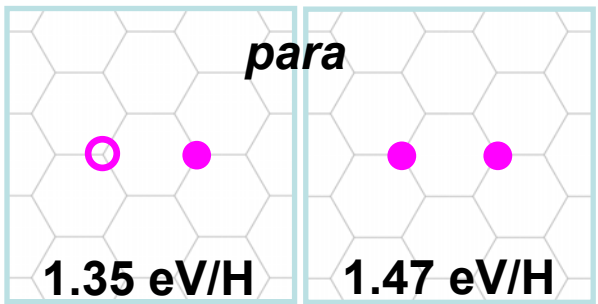


0.69 eV/H 0.72 eV/H

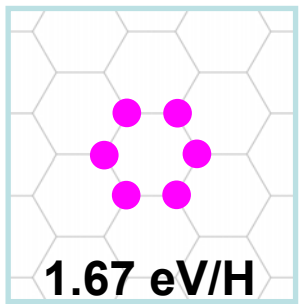


1.58 eV/H

para

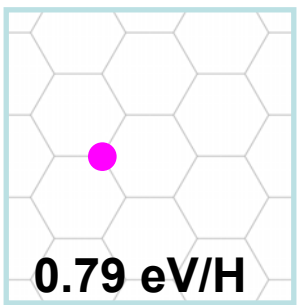


1.35 eV/H 1.47 eV/H

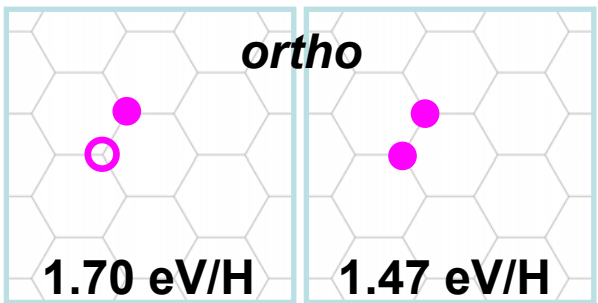


1.67 eV/H

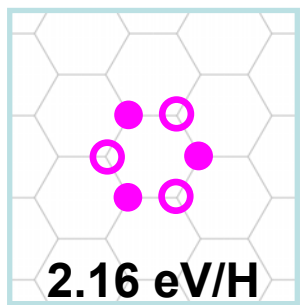
ortho



0.79 eV/H



1.70 eV/H 1.47 eV/H

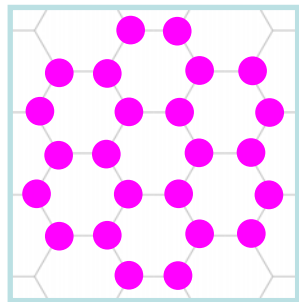


2.16 eV/H

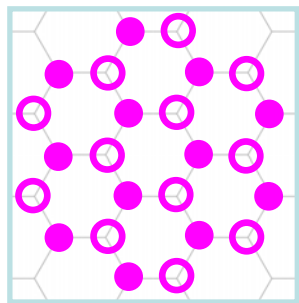
● H in front

○ H behind the carbon plane

H_2: 2.31 eV/H

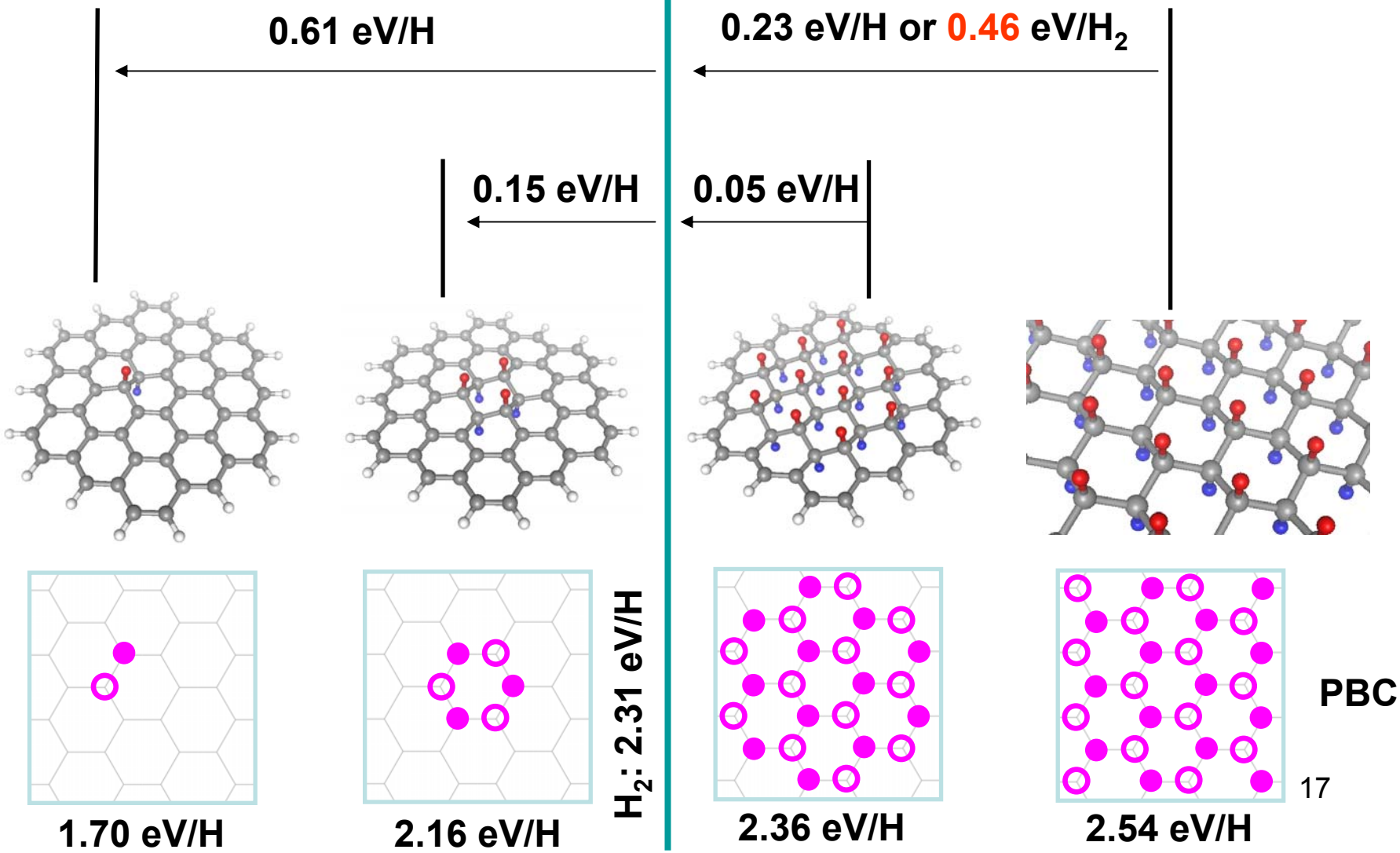


1.91 eV/H

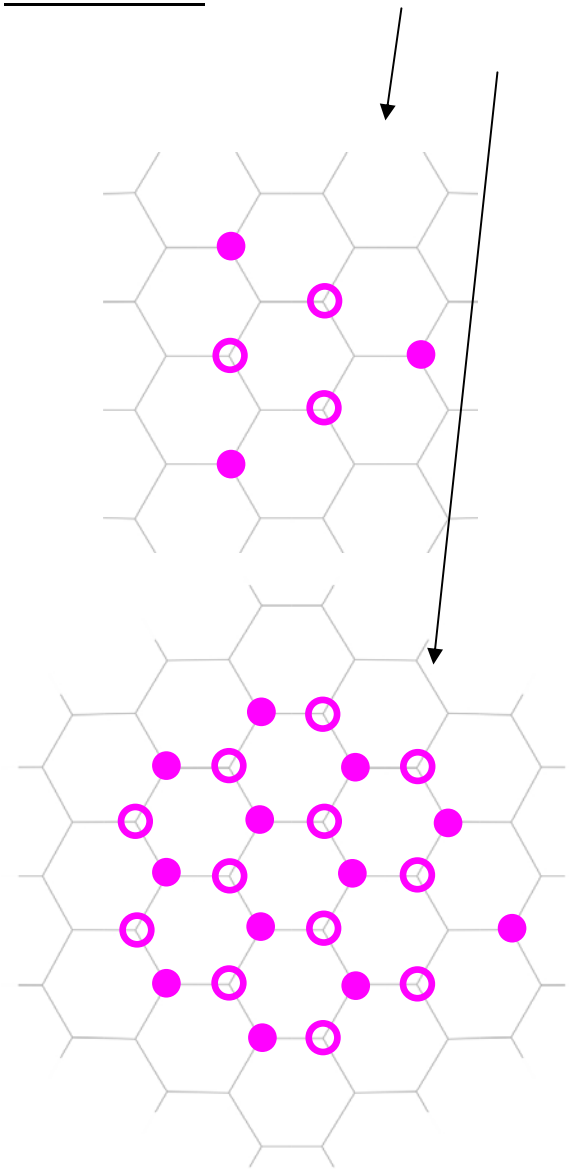


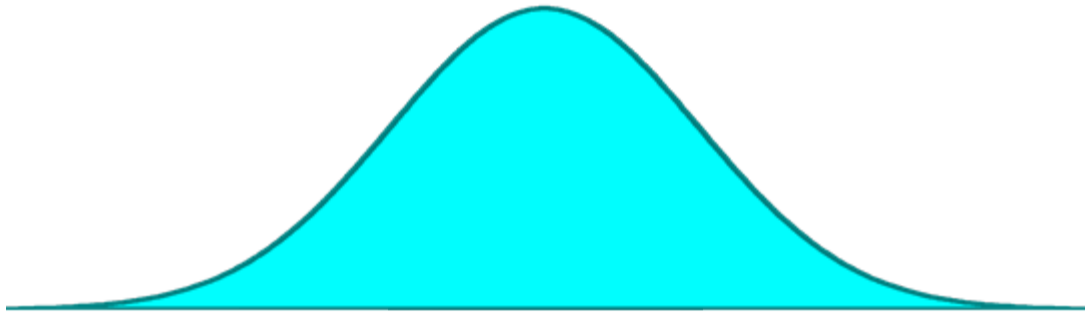
2.36 eV/H

The low energy configurations found – Bingo!?
Provides much needed ground for experimental evidence at U of Michigan.



Clusters proven favorable, stable, and diffusion must display localized front behavior





Diffusion of normal lattice gas

Front propagation of hydrogen cluster requires detailed study. May collaborate with Center's Penn State team (Crespi).

future work FY07-FY08

3D-foams

- 1. Evaluate SWNT-based 3D-foam capacity by direct Monte-Carlo simulations. Further refinement of van der Waals force-field, with an eye on topological and elastic curvature effects. Develop statistical-thermodynamics model for H_2 "pumping" into potential wells provided by carbon-based carrier material.

Me-centers stability

- 2. Compute detailed binding strength and mobility barrier for metal-centers, determine stable sites which prevent aggregation of Me! Determine size of Me-cluster where *Kubas'* interactions transition into the dissociative (and spillover commences)

VANTAs synthesis

- 3. Densify VANTA for H_2 adsorption testing. Perform Li-decoration, functionalization with fluorine and BF_3 in order to create highly charged nanotube salts, and test for H_2 adsorption

spillover dynamics

4.

- Further precise energy calculations of H@receptor configurations (along with v-signatures for experimental detection). Other receptor geometry/materials, e.g., MOF, Met-Car.
- Dynamics of the chemically bound/absorbed hydrogen atoms: barriers and sigmatropic selection rules for H-hopping. Diffusion of H atom from catalyst to graphene and the rate of spread, quantitative front propagation model in contrast to conventional $\langle r^2 \rangle \sim D \times t$ diffusion.

summary

Relevance: Path-finding to reach DOE goals by modeling of major options: sorption on *3D-foams*, *metal-enhancement*, *spillover*.

Approach: Quantum ab initio and empirical representations of H-carriers interaction, to assess their retaining ability. Selectively test synthetic options.

Technical Accomplishments and Progress:

- Concept of "engineerable" 3D-foams developed.
- For H-binding metal-atoms on C-carriers (5-7% gravimetric) addressed aggregation at elevated temperatures, detrimental for storage.
- Synthesis of vertically aligned nanotube arrays (VANTA) as raw-material for further densification and chemical decoration for hydrogen sorption.
- Spillover kinetics: Identified energetically feasible chemisorption states on carbon receptor at high H content. Dynamics of H-clustering and front-propagating fashion.

Tech Transfer/Collaborations: Partnership with NREL, Air Products, NIST (spectroscopy). Emerging partnership with U Michigan and U Nevada Las Vegas.

Future Research: ● 3D-foam storage capacity by Monde-Carlo simulations and screening of Me-centers for stability against aggregation. ● Synthesis of chemically-decorated VANTA for enhanced storage. ● Emphasis on theory spillover dynamics, including other material-receptors (in collaboration with Yang's project).

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