Theoretical Models of H$_2$-SWNT Systems for Hydrogen Storage and Optimization of SWNT

Boris I. Yakobson$^{1,2}$, Rober Hauge$^2$
$^1$Department of Mechanical Engineering & Materials Science, and $^2$Department Chemistry
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 to be addressed

• Flexible representation of H₂-carbon binding, to identify carbon-based architectures for the best sorption
• Enhance the binding of H₂ 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)
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 H₂-trapping on generic carbon structures, for achieving 7-9% storage.
• Transition-metal enhanced adsorption via the various ways of doping carbon backbone Me@Cₙ + m*H₂, Me = Sc, Ti, ... or Li, K, with the emphasis on metal aggregation.

2007:
• continue the above and
• Synthesis of metal- and electronegative-group- (F, BF₃) enhanced VANTA (vertically aligned nanotube arrays, contrast to fibers) for H₂ adsorption.
• Theory of hydrogen spillover, its thermodynamics and kinetics: energy states, cooperative effects, mobility.

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

U

30 kJ/mole

~8 kJ/mole

catalyst

~8 kJ/mole

U
**APPROACH**

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

\[ \text{Example: graphene double-layer} \]
Superposition of the potentials can enhance adsorption at the optimum spacing

\[ \text{H}_2----\text{carbon potential optimization [up to 7\% storage, per PNAS (2005)]} \]

- 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
[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.
The foam has nanometer pores and channels, all its surface (~2600 m²/g) is accessible, it’s lighter than water (~0.9 g/cm³), excellent thermal conductor, and it is metallic!
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
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.

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

(Becke98/6-31G, Gaussian 03)

...However we observe transition from Kubas interaction to catalytic function of a larger metal cluster (as side effect of its possible aggregation): H₂ dissociates completely as needed for spillover!
Vertically Aligned NanoTube Arrays = VANTA scaffolds, best growth parameters defined for an atomic hydrogen activated rapid insertion reactor, growth rate ~2 mm/min, VANTA as thick as 1 mm.

NT non-fiber scaffolds now available for 3-D engineering, adds of metals or electronegative- (F, BF₃) enhancer for H₂ adsorption [to NREL and AirP]
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.

Technical accomplishments 4

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 H₂ 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 \( \text{H}_2 \) 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 \( \text{H}_2 \).
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):

<table>
<thead>
<tr>
<th>Method/Basis</th>
<th>E(H₂) /eV/H</th>
<th>E(H@)/eV/H</th>
<th>E(2H@)/eV/H</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/631g</td>
<td>2.380</td>
<td>0.547</td>
<td>1.496</td>
</tr>
<tr>
<td>B3LYP/631g**</td>
<td>2.422</td>
<td>0.657</td>
<td>1.595</td>
</tr>
<tr>
<td>B3LYP/6311+g**</td>
<td>2.384</td>
<td>0.678</td>
<td>1.595</td>
</tr>
<tr>
<td>B3LYP/6311++g**</td>
<td>2.382</td>
<td>0.676</td>
<td>1.593</td>
</tr>
<tr>
<td>PBEPBE/631g</td>
<td>2.363</td>
<td>0.584</td>
<td>1.528</td>
</tr>
<tr>
<td>PBEPBE/631g**</td>
<td>2.310</td>
<td>0.685</td>
<td>1.610</td>
</tr>
<tr>
<td>PBEPBE/6311+g**</td>
<td>2.267</td>
<td>0.703</td>
<td>1.606</td>
</tr>
<tr>
<td>PBEPBE/6311++g**</td>
<td>2.262</td>
<td>0.699</td>
<td>1.601</td>
</tr>
<tr>
<td>LSDA/631g</td>
<td>2.369</td>
<td>0.887</td>
<td>1.895</td>
</tr>
<tr>
<td>LSDA/631g**</td>
<td>2.495</td>
<td>0.991</td>
<td>1.979</td>
</tr>
<tr>
<td>LSDA/6311+g**</td>
<td>2.451</td>
<td>1.032</td>
<td>1.991</td>
</tr>
<tr>
<td>LSDA/6311++g**</td>
<td>2.447</td>
<td>1.028</td>
<td>1.989</td>
</tr>
<tr>
<td>MP2/cc-pvtz</td>
<td>2.245</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PW91/pw[Hornekær 06]</td>
<td>2.27</td>
<td>0.85</td>
<td>1.25</td>
</tr>
</tbody>
</table>

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)

- **H in front**
  - 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
  - H₂: 2.31 eV/H
- **H behind the carbon plane**
  - 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).
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 $<r^2> \sim D \times t$ diffusion.
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.


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).

Boris I Yakobson
713-348-3572
biy@rice.edu