NanoEngineering of Hybrid Carbon Nanotube Metal Composite Materials for Hydrogen Storage
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Coworkers and Acknowledgement

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4) Department of Mechanical Engineering, Stanford University

GCEP
Global Climate & Energy Project
STANFORD UNIVERSITY
Hydrogen Dream

Solar $\text{H}_2$ Production

Photobiological $\text{H}_2$ Production

Gas-Water Shift

Biomass

PV/PEC

Photoelectrochemical $\text{H}_2$ Production

$\text{H}_2$ Conversion

Fuel Cells

Storage and Transport

Carbon nanotubes

Metal Hydrides
Current View of Hydrogen

Current vision of the H as an energy carrier

- numerous problems and engineering challenges to handle gaseous or liquid hydrogen at production, distribution and utilization steps;
- serious energy overhead to convert molecular to atomic hydrogen and back
Chemisorption of H atoms on Carbon Nanotubes

Idea: to store hydrogen in the chemisorbed form on the nanotube surface

H-H bond energy 4.5 eV

Adsorption Energy Decreases with diameter

Pack et al, 2003
Investigation strategy

**Hydrogenation**: in situ atomic hydrogen treatment

- elimination of H\textsubscript{2} dissociation step from hydrogenation process
- well controlled environment (base pressure < 1 \times 10^{-9} \text{Torr})

**Samples**: "as grown" CVD SWCN films

- low defect / amorphous carbon concentration (small D to G band intensity ratio)
- low concentration of contamination (in situ annealing up to 900 \text{C})

**Probing tools**: X-ray photoelectron spectroscopy (XPS) and X-ray adsorption spectroscopy (XAS)

- XPS and XAS allow to observe the formation of C-H bonds through the modification of the carbon nanotube electronic structure around specific carbon atoms
Probing tools

**X-ray photoelectron spectroscopy (XPS)**

C1s XPS spectra of n-octane and graphite (Weiss et al., 2003, Bennich et al., 1999)

**X-ray absorption spectroscopy (XAS)**

Carbon K-edge XAS spectra of graphite and diamond (Garo et al., 2001)
Hydrogenation induced changes in Graphite and SWCN XPS spectra

Graphite

C1s XPS
E=350 eV

chemical shift of C1s peak due to C-H bond formation

(a)

binding energy (eV)

intensity (a. u.)

Clean

H-treated

peak 1

peak 2

~ 0.65 eV

Single wall Carbon Nanotube

C1s XPS

0.65 eV

binding energy (eV)

Clean SWCN

H treated SWCN


Nikitin et.al Phys. Rev. Lett. 95, 225507 (2005)
The hydrogenation degree determination from XPS spectra

Calculated C1s chemical shift values (MD and DFT)

<table>
<thead>
<tr>
<th>(n,m)</th>
<th>D, nm</th>
<th>Shift, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (10,0)</td>
<td>0.78</td>
<td>0.65</td>
</tr>
<tr>
<td>(b) (12,0)</td>
<td>0.94</td>
<td>0.77</td>
</tr>
<tr>
<td>(c) (15,0)</td>
<td>1.16</td>
<td>0.74</td>
</tr>
<tr>
<td>(d) (22,0)</td>
<td>1.72</td>
<td>0.76</td>
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Decomposition of C1s XPS for hydrogenated SWCN film

Nikitin et.al Phys. Rev. Lett. 95, 225507 (2005)

Hydrogenation = \( \frac{I_{\text{peak 2}}}{(I_{\text{peak 1}} + I_{\text{peak 2}})} \times 100 \) at %
The influence of SWCN diameter on hydrogenation process

Hydrogenation sequence of SWCN, type 1
- constant C1s peak intensity with the H doze increase
- EtOH based growth

Hydrogenation sequence of SWCN, type 2
- the decrease of C1s peak intensity with the H doze increase
- CH₄ based growth

Size distribution around 2.0nm

Size distribution around 1.5nm

Nikitin et.al Nano lett. 8, 162 (2008)
Structure of XPS C1s spectrum for highly hydrogenated SWCN

Peak 1
Clean C atoms in SWCN walls

Peak 2
$\Delta E_{1-2} \approx 0.7$ eV
C-H bonded C atoms in SWCN walls

Peak 3
$\Delta E_{1-3} \approx 1.5$ eV
C-H bonded C atoms in SWCN walls with different electron screening mechanism in photoionization process

Hydrogenation sequence of SWCN, type 1

C1s XPS

binding energy (eV)

- Peak 1
- Peak 2
- Peak 3
The hydrogenation degree of SWCN

\[ \frac{I_{\text{peak 1}}}{(I_{\text{peak 2}} + I_{\text{peak 3}})} = 1:10 \]

which corresponds to \(~7\) wt % of SWCN hydrogen capacity.

Nikitin et al. Nano lett. 8, 162 (2008)
Hydrogen desorption temperature

C1s XPS spectra measured during annealing of H treated SWCN, type 1

Hydrogen desorption is observed in the range from 300 °C to 600 °C

Nikitin et al. Nano lett. 8, 162 (2008)
C1s XPS spectra of SWCN, type 1 exposed to two cycles of hydrogenation / dehydrogenation

Hydrogenation of SWCN film can be cycled

Nikitin et al. Nano lett. 8, 162 (2008)
Activated Desorption

\[ \text{C2C3} \quad \text{C1C4} \quad \text{H}_2 + \text{C}(0001) \]

\[ \begin{align*}
2.04 \text{ eV} & \quad 3.67 \text{ eV} & \quad 3.44 \text{ eV} \\
2.04 \text{ eV} & \quad & \quad 0 \text{ eV}
\end{align*} \]

Graphite

\[ \begin{align*}
\text{C2C3} \quad & \quad \text{C1C4} \quad \text{H}_2 + (8,0) \\
1.5 \text{ eV} & \quad 1.28 \text{ eV} & \quad -0.037 \text{ eV} \\
-0.37 \text{ eV} & \quad & \quad 0 \text{ eV}
\end{align*} \]

1nm SWCN

Nikitin et.al Nano lett. 8, 162 (2008)
Energetics of C-H bond

Interesting region
Energy neutral?

With Free Energy
Around 1nm

Niktin et. Al submitted Nano lett.
Catalyst Metals as Atomic Hydrogen Source

- Hydrogen molecules → Metal catalyst → Atomic hydrogen “pump” (spontaneous dissociation, subsequent spillover and diffusion)
- Catalyst metals: Ni, Pd, Pt, etc.

Potential energy of hydrogen with separation distance

- Reversible hydrogen storage in SWNT, 5.1±1.2 wt% (65±12 at%) using an atomic hydrogen source

A. Nikitin et al. *PRL* 95, 225507 (2005)

C1s XPS

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I. Accurate measurement of hydrogen uptake of CNTs

Sieverts’ type apparatus for volumetric analysis
Specially-designed setup for small size samples

II. Increase hydrogen storage capacity

Modest hydrogen uptake by molecular hydrogen $\rightarrow$ hydrogen dissociation to atomic hydrogen facilitated by metal catalysts

Synthesis of (CNT-Metal catalyst) composites for larger storage capacity

Catalyst Metal-Doped Carbon Nanotubes

HiPco SWNT (Ref)

- + Pd
  - Pd-doped SWNT
    - Electrochemical deposition (EC Pd)
    - UHV sputter deposition (Sp Pd)
    - E-beam evaporation (EE Pd)

- + Pt
  - Pt-doped SWNT
    - Electrochemical deposition (EC Pt)
    - UHV sputter deposition (Sp Pt)
Uptake Enhancement in Pt-Doped SWNT

- Hydrogen uptake in CNT corrected by using $H_{pt}=0$
- Larger enhancement for Sp Pt composite

\[ H_{total} = f_{Pt} \times H_{Pt} + (1 - f_{Pt}) \times H_{CNT} \]

\[ \therefore H_{CNT} = \frac{H_{total}}{1 - f_{Pt}} \]

No hydrogen stored in Pt

<table>
<thead>
<tr>
<th>Sample</th>
<th>$H_{total}$ [wt%]</th>
<th>$f_{Pt}$</th>
<th>$H_{CNT}$ [wt%]</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>0.17</td>
<td>-</td>
<td>0.17</td>
<td>1.0</td>
</tr>
<tr>
<td>EC Pt</td>
<td>0.40</td>
<td>0.08</td>
<td><strong>0.44</strong> (5.23 at%)</td>
<td><strong>2.59</strong></td>
</tr>
<tr>
<td>Sp Pt</td>
<td>0.51</td>
<td>0.13</td>
<td><strong>0.59</strong> (7.02 at%)</td>
<td><strong>3.47</strong></td>
</tr>
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</table>

W. Lee et.al. to be published
Sp Pt Composites w/ Different Pt Thickness

Pt particle agglomeration

Increasing Pt particle density

Nanoparticle

H-saturated region

R ~ 1 nm

0.2 nm

0.5 nm

1.0 nm

3.0 nm
Hydrogen Uptake of CNT-Pd Composites

- Significant increase in uptake for both composites
- Increase by a factor of three (EC Pd), or four (Sp Pd)
- Hydrogen stored in both SWNT (H_{CNT}) and Pd NP’s (H_{Pd})

\[ H_{total} = f_{Pd} \times H_{Pd} + (1 - f_{Pd}) \times H_{CNT} \]

Sample size [mg]

<table>
<thead>
<tr>
<th></th>
<th>SW</th>
<th>EC</th>
<th>Sp</th>
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<tbody>
<tr>
<td>NT</td>
<td>29</td>
<td>23</td>
<td>17</td>
</tr>
</tbody>
</table>

\[ P_{H_{1/2}} \] [Bar]

<table>
<thead>
<tr>
<th></th>
<th>SW</th>
<th>EC</th>
<th>Sp</th>
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</thead>
<tbody>
<tr>
<td>30 bar</td>
<td>6.8</td>
<td>3.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Hydrogen uptake at 30 bar [wt%]

<table>
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<th>EC</th>
<th>Sp</th>
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</thead>
<tbody>
<tr>
<td>0.17</td>
<td>0.53</td>
<td>0.72</td>
<td></td>
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</table>

Uptake kinetics during isotherm measurements

30.0 Bar  29.61 atm  3.0 MPa  435.0 psi
• hydrogenation of SWCN with molecular hydrogen

Conclusions

- SWCN with different diameters can reach different hydrogenation degree before "unzipping" and etching

- For specific SWCN it is possible to hydrogenate almost 100 at % of the carbon atoms in the walls to form C-H bonds which corresponds to 7.7 weight % of hydrogen capacity

- We can generate spillover processes using Catalyst for gas phase hydrogenation

- Maybe spillover process for electrochemical storage