Carbon Nanotubes: Development of Nanomaterials for Hydrogen Storage

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Outline

• Can carbon nanotubes (CNTs) be used for efficient hydrogen storage?
  - Physisorption (non-covalent)?
  - Chemisorption (covalent)?

• Synthesis of CNTs for hydrogen storage

• Interaction of CNTs with reactive H-species

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Single-Walled Carbon Nanotubes (SWNT)

- Diameter ~1-2 nm, ‘molecular wire’
- Length: 10 nm to 10 mm
- Sp2 C-C bonding: one of the strongest bond in nature
- Multi-walled CNTs: ~ 10-20 nm in diameter
- Radius of curvature is important to physical/chemical properties
Synthesis by Chemical Vapor Deposition

CVD

\[ \text{C}_x\text{H}_y \rightarrow \text{C} + \text{H}_2 \]

PECVD

Yuegang Zhang, Yiming Li, J. Phys. Chem, 1999;
Previous:
Patterned Growth of SWNTs by CVD

Jing Kong, Hyongsok Soh, Calvin Quate, H. Dai
SWNTs Synthesis From Individual Nanoparticles

pattern individual “seeds”

grow 1 tube per “seed”

CVD Growth of Vertically Aligned Multi-Walled CNTs

Synthesis of Single-Walled Nanotubes by PECVD

CH₄ → C + H₂

600-800 °C
1% O₂

2 nm Fe particle as growth seed

A quasi-remote plasma enhanced CVD approach
High Yield Vertical-SWNTs by PECVD

Grown by oxygen Assisted PECVD

Exclusively single-walled, no multi-walled; Highly repeatable

Guangyu Zhang, et al., *PNAS*, 2005; GCEP patent
Patterned Growth of Vertical SWNTs

Reproducible growth of vertical SWNTs
Vertical SWNTs (V-SWNT) Patterns
O$_2$ Addition (~1\%) Drastically Enhances PECVD of SWNTs From CH$_4$ Plasma

- Same catalyst, drastically different yield with and without oxygen!
- In plasma CVD, H species are detrimental to SWNT formation
- Oxygen scavenging of H: O + H → OH favors SWNT formation
O Scavenging of H: \( O + H \rightarrow OH \) Favors SWNT Growth

- Plasma of \( C_xH_y \): \( C_xH_y \rightarrow C + H \) (H is inevitable)
- C is needed for growth of SWNT.
- H does not favor SWNT formation, especially for small tubes

- Solution to the dilemma of PECVD: add oxygen (\(<4\%\))
Vertical SWNTs Transferred onto Various Substrates (Cu, polymer...)

A: V-SWNT film floating on H2O

B: V-SWNT on Cu substrate

Si substrate

H2O bath

Cu substrate

Polymer binding layer
Vertical SWNTs on Various Substrates (Cu, polymer...)

Cu

Plastic

Glass
An Artistic Presentation of V-SWNT Films
Hydrogenation @300K of SWNTs

(Guangyu Zhang, et al., JACS, 2006)

- SWNTs ‘swell’ upon hydrogenation
- Swelling uniform along tube length
Theoretical Prediction

• Atomic structure change due to hydrogenation

Raman Spectroscopy of Hydrogenation/dehydrogenation of SWNTs

- Hydrogenation decreases ‘G’/‘D’ band ratio.
- Complete reversal upon 500 ºC annealing (starts at ~200ºC).
Infrared Spectroscopy of Hydrogenated/dehydrogenated SWNTs

- CH_x species observed on SWNTs, x=1, 2
- 2920 cm⁻¹: sp3 CH stretch/asymmetric stretch of sp3 CH_2 groups.
- 2850 cm⁻¹: symmetric stretch of sp3 CH_2
Electrical Transport in a SWNT Through Hydrogenated/Dehydrogenation

- Hydrogenation decreases conductance by orders of magnitude
- Reversible upon 500°C annealing.
Hydrogenation/Hydro-carbonation (Etching) Under ‘Harsh’ Plasma

@300K, ‘high’ Plasma power, 3min 10 min
Smaller diameter SWNTs are more easily etched

Diameter dependent chemical reactivity!
Conclusions Based on Microscopy, Spectroscopy & Electrical Data

• Reversible hydrogenation can be achieved with SWNTs under specific hydrogenation conditions
• SWNTs can retain structural integrity through hydrogenation/dehydrogenation processes
• A viable hydrogen storage approach

• Optimum diameter of may SWNTs exists for repeated reversible hydrogenation/dehydrogenation at low temperatures
Summary

• Role of hydrogen in PECVD growth identified.
• Highly efficient growth of SWNTs achieved.

• Reversible hydrogenation of SWNTs can be achieved with retained structures and properties.

• Hydrocarbonation/etching can occur.
• Diameter dependent reactivity elucidated.

• Next: Identify optimum diameter of SWNTs that allow for hydrogenation and reversal at low temperatures.
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