Nanoengineering of Hybrid Carbon Nanotube-Metal Nanocluster Composite Materials for Hydrogen Storage

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Introduction

The objective of this project is to develop optimized nanomaterials for high-density reversible H_2 storage applications. Specifically, carbon nanotube-catalyst nanoparticle composite materials with well-controlled nanotube atomic structure will be developed. Multiscale modeling method will provide rationally designed nanomaterial structures optimized for hydrogen storage and guide the experimental steps of controlled fabrication and detailed characterization of nanomaterials. A systematic design and fabrication process will be followed by detailed analysis of the incorporated nanoparticles in the nanotube samples to catalyze H_2 adsorption and desorption processes. The fundamental understanding on the nature of interaction between H_2 molecules and nanomaterials will provide a conceptual foundation to rationally design nanomaterials such as nanostructured metal hydrides with improved H_2 storage capacity.

Background

Nanomaterials have diverse tunable physical properties as a function of their size and shape due to strong quantum confinement effects and large surface/volume ratios. A single wall carbon nanotube (SWCNT) has the same structure as a roll of a single graphene sheet and has nanometer sized diameters ranging from 4 to over 100 Å. Due to their large surface areas with relatively small mass, SWCNTs have been considered as potential materials for high capacity hydrogen storage. Theoretically, they can chemically store hydrogen up to 7.7 wt% if every carbon atom in SWCNTs chemisorbs one hydrogen atom. In addition, the subsequent physisorption of hydrogen molecules on the surfaces of hydrogenated SWCNTs can increase the capacity of hydrogen storage even further. In spite of this potential of SWCNTs in hydrogen storage applications, there are substantial challenges in developing optimized materials for hydrogen storage due to the lack of fundamental understanding on the nature of H interaction with nanotubes. A systematic and thorough study of the ultimate hydrogen storage capacity of carbon nanotubes will elucidate basic mechanisms of hydrogen storage in nanomaterials and the role of carbon nanomaterials in future hydrogen storage material development.

Results During 2006

(1) Ultra-High Yield Growth of Vertical Single-Walled Carbon Nanotubes: Hidden Roles of Hydrogen and Oxygen.
(Dai Group, 2005 published in PNAS. Patent disclosed to GCEP and OTL)

In this work, an oxygen assisted hydrocarbon chemical vapor deposition (CVD) method is developed to afford large-scale highly reproducible ultra high-yield growth of vertical single-walled carbon nanotubes (SWNT). It is revealed that reactive hydrogen (H)-species, inevitable in hydrocarbon-based growth, are damaging to the formation of sp^2-like SWNTs. The addition of oxygen scavenges H-species and provides a powerful control over the C/H ratio to favor SWNT growth. The revelation of the roles played by hydrogen and oxygen leads to a unified and universal optimum growth condition for SWNTs. Further, a versatile method is developed to form vertical SWNT films on any substrate, lifting a major substrate-type limitation for aligned SWNTs. This work enables PECVD synthesis of high quality SWNTs useful for various energy and hydrogen storage related applications, and is being patented by GCEP.

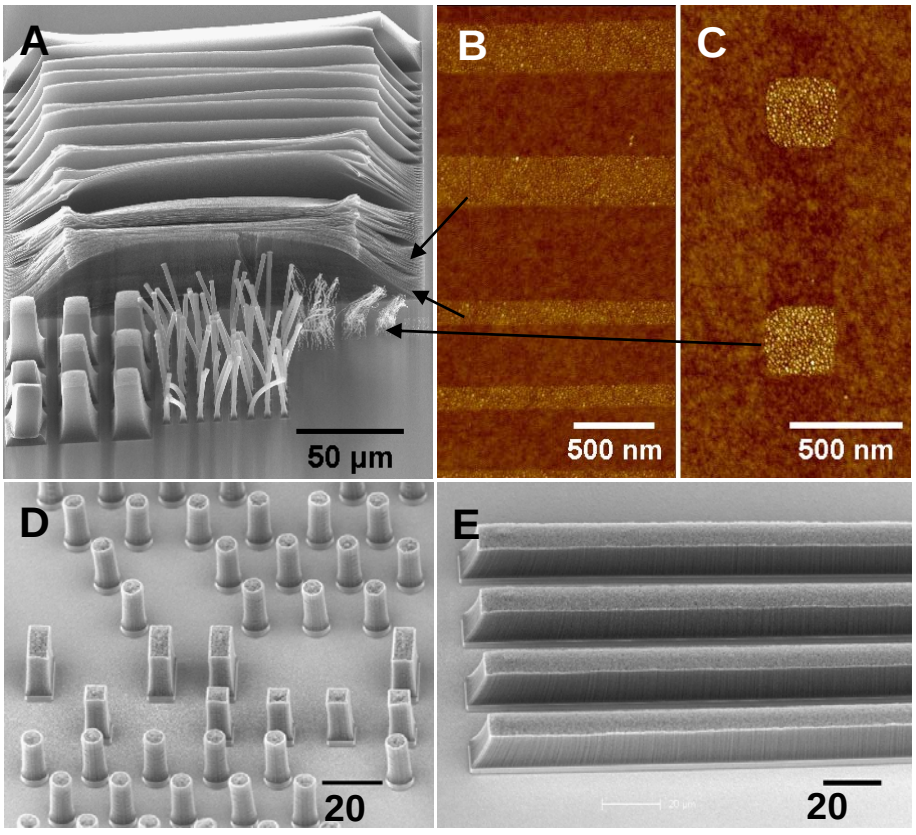

Figure 1. Molecular O_2 assisted growth of vertical SWNT towers and sheets with down to sub-micron dimensions. (a) A SEM image showing SWNT towers with various widths (20 μm, 5μm, 1μm, 500 nm, 300 nm from left to right of the front region of the image) and vertical SWNT sheets (20 μm, 5 μm, 1 μm, 500 nm, 300 nm, 100 nm thick from top to bottom of the upper part of the image) after 30 min growth. (b) An AFM image of the patterned catalyst strips (bright 300nm and 100nm wide regions respectively) comprised of densely packed Fe nanoparticles used for the

growth of the 300 nm and 100 nm thick vertical SWNT sheets (pointed by arrows) in (a). (c) An AFM image of two of the patterned catalyst squares (300 nm in width) used for the growth of the smallest towers (pointed by an arrow, tilted due to high aspect ratio) in (a). (d)&(e) Two SEM images of square, circular towers and lines of V-SWNTs record on sample independent of (a) to show the reproducibility of the synthesis.

(2) Hydrogenation and Hydro-Carbonation and Etching of Single-Walled Carbon Nanotubes (Dai Group, 2006 published in J. Am. Chem. Soc.)

Understanding the interactions between molecules and single-walled carbon nanotubes (SWNTs) is of fundamental and practical importance. While weak adsorption of molecular hydrogen on SWNTs has been widely investigated and debated, covalent reactions between hydrogen and SWNTs are less explored. In this work, we present a systematic experimental investigation of the reactions between hydrogen plasma and single-walled carbon nanotubes (SWNTs) at various temperatures. Microscopy, infrared (IR) and Raman spectroscopy and electrical transport measurements are carried out to investigate the properties of SWNTs after hydrogenation. Structural deformations, drastically reduced electrical conductance and increased semiconducting nature of SWNTs upon sidewall hydrogenation are observed. These changes are reversible upon thermal annealing at 500ºC via dehydrogenation. Harsh plasma or high temperature reactions lead to etching of nanotube likely via hydro-carbonation. Smaller SWNTs are markedly less stable against hydro-carbonation than larger tubes. The results are fundamental and may have implications to basic and practical applications including hydrogen storage, sensing, band-gap engineering for novel electronics and new methods of manipulation, functionalization and etching of nanotubes.

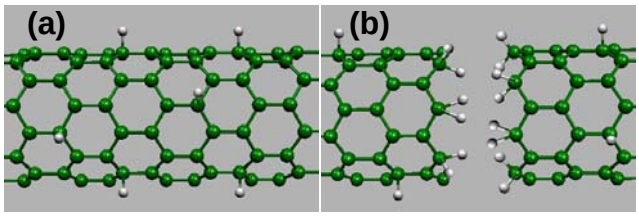

Figure 2. Schematic drawing of **a**) hydrogenation and **b**) hydrogenation plus etching of SWNT by H plasma at elevated temperatures (200-400ºC) or harsh plasma conditions at room temperature.

(3) Hydrogenation of Single-Walled Carbon Nanotubes.
(Nissan and Dai groups, 2005 published in Phys. Rev. Lett.)

Safe, efficient, and compact hydrogen storage is a major challenge for realizing hydrogen powered transport. Thus, a media that absorbs and releases a large quantity of hydrogen easily and reliably is being actively sought. Since Dillon *et al.* showed that carbon nanotubes can store hydrogen, this material has been considered as a candidate for hydrogen storage media. Previous studies have reported hydrogen capacities for carbon nanotubes ranging from 0.25 to 20 wt%. The reasons for such large variation in experimental results can be interpreted in the following ways. Nanotube samples often contain impurities that can influence the hydrogen adsorption (amorphous carbon, water, hydrocarbons), and the amount of impurities can change considerably between different

studies in an uncontrollable manner, leading to large systematic errors. Also, different samples have varying diameter distributions, which can strongly affect hydrogen uptake performance. Consequently, it is essential to determine the hydrogen uptake on well defined samples.

Towards the development of a useful mechanism for hydrogen storage, we have studied the hydrogenation of single-walled carbon nanotubes with atomic hydrogen using core-level photoelectron spectroscopy and x-ray absorption spectroscopy. We find that atomic hydrogen creates C-H bonds with the carbon atoms in the nanotube walls, and such C-H bonds can be completely broken by heating to 600 _C. We demonstrate approximately 65 _ 15 at% hydrogenation of carbon atoms in the single-walled carbon nanotubes, which is equivalent to 5*:*1 _ 1*:*2 wt% hydrogen capacity. We also show that the hydrogenation is a reversible process.

Publications

1. A. Nikitin, H. Ogasawara, D. Mann, R. Denecke, Z. Zhang, H. Dai, K. Cho, and A. Nilsson, "Hydrogenation of Single-Walled Carbon Nanotubes" Phys. Rev. Lett. 95, 225507, 2005.
2. Guangyu Zhang, David Mann, Li Zhang, Ali Javey, Yiming Li, Erhan Yenilmez, Qian Wang, James P. McVittie, Yoshio Nishi,, James Gibbons, and Hongjie Dai, "Ultra-high-yield growth of vertical single-walled carbon nanotubes: Hidden roles of hydrogen and oxygen", PNAS 102 no. 45 16141–16145, 2005
3. Guangyu Zhang, Pengfei Qi, Xinran Wang, Yuerui Lu, David Mann, Xiaolin Li, and Hongjie Dai, "Hydrogenation and Hydrocarbonation and Etching of Single-Walled Carbon Nanotubes" J. AM. CHEM. SOC. 2006, 128, 6026-6027

Future Plans

My group will continue our planned research in carbon nanotube synthesis and characterization for hydrogen storage. More specifically, we will be investigating covalent hydrogenation of nanotubes as a way to store hydrogen. We will measure the hydrogenation and reversible dehydrogenation of nanotubes as a function of nanotube diameter. We will identify a diameter that can release hydrogen at low temperatures for realistic hydrogen storage applications. We will also explore hydrogenation as a way to manipulate nanotubes. Further, nanotube synthesis with diameter control will be continued for the hydrogen storage project.

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