

# C-H bonds in Carbon Nanotubes as an Energy Carrier

A. Nilsson, B. Clemens, H. Dai (Stanford University)

## Investigators

Anders Nilsson, Professor, SSRL; Bruce Clemens, Professor, Materials Science and Engineering; Hongjie Dai, Professor, Chemistry; Hirohito Ogasawara, staff scientist, SSRL; Daniel Friebel, post-doctoral researcher, SSRL; Xiaolin Li, post-doctoral researcher, Chemistry; Srivats Rajasekaran, Ranadeep Bhowmick, Cara Beasley, Graduate Researchers, Stanford University.

## Abstract

We investigate the capability of single-walled carbon nanotubes (SWNT) as a possible material for hydrogen storage through the reversible formation of stable C-H bonds by electrochemical means. We have previously shown that the exposure of SWNTs to a source of atomic hydrogen leads to successful hydrogenation without degradation of the nanotube material. We are now investigating alternative hydrogenation reaction pathways that require significantly lower activation energy. We found that SWNTs can be hydrogenated by exposure to molecular hydrogen if they are modified with a Pd or Pt nanoparticle catalyst. Hydrogen molecules dissociatively adsorb on the catalyst surface, and the chemisorbed H atoms can diffuse to the adjacent SWNT surface where they form C-H bonds. Using x-ray photoelectron spectroscopy we found direct evidence for this “spillover” mechanism. We started investigating an alternative hydrogenation pathway that uses the same catalyst. Here, H atoms are formed electrochemically by the reduction of protons from water and can then spill over to the SWNTs. The reversible electrochemical hydrogenation could completely avoid the use of molecular hydrogen in the energy storage/transport/release cycle.

## Introduction

The current vision of hydrogen as a green-house-gas-free fuel for the transportation sector is based on using a renewable energy source to make molecular hydrogen for use in a fuel cell vehicle. In this project we instead propose a completely different concept of hydrogen where we will use C-H covalent bonds in carbon nanotubes as an energy carrier instead of molecular hydrogen. This should allow the use of one material for (i) generation and storage of hydrogen in carbon-hydride packages serving as fuel supply for fuel cells (carbon hydride fed fuel cells) or (ii) generation, storage and conversion of hydrogen (carbon hydride battery concept). In this transformative technology, molecular hydrogen will not be involved, so that the formation and dissociation processes can be avoided making the system more energy efficient and safe.

We have already demonstrated in our previous GCEP project that the exposure of carbon nanotubes to a source of atomic hydrogen leads to the hydrogenation of the nanotubes. Up to 7 wt.-% hydrogen uptake could be achieved without degradation of the nanotubes. In our current project, we are now looking for a more feasible hydrogenation technique without the need of thermal dissociation of molecular hydrogen. By bringing

the carbon nanotubes in close contact with a noble-metal catalyst such as Pt or Pd, the hydrogenation could occur at low to moderate temperatures using molecular hydrogen, which readily dissociates at these metal surfaces and is adsorbed in the atomic form. H atoms would then diffuse over the metal/nanotube composite surface and could eventually be chemisorbed onto the nanotubes by the formation of covalent C-H bonds (spillover mechanism). First evidence for an enhanced hydrogen uptake of SWNTs in contact with Pt nanoparticles has been found by the Clemens group. With our current project we are using synchrotron-based x-ray spectroscopy as a direct probe for C-H bond formation, we are optimizing the fabrication of SWNT/metal composites in order to maximize the hydrogen storage capacity, and we are investigating the electrochemical hydrogenation of SWNTs which could completely avoid the formation of molecular hydrogen and instead directly attach hydrogen atoms from water electrolysis to the carbon nanotubes.

## **Background**

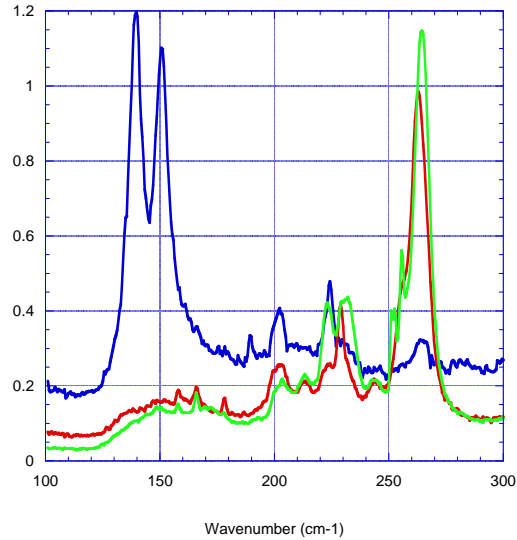
Several groups have reported about hydrogen storage enhancement with the doping of carbon nanotubes with metal catalysts, mainly Pd, Pt, Ni and Co [1-4]. The increase in storage capacity has been attributed to the “spillover effect”. A similar enhancement was reported for other graphitic materials, e.g. carbon nanofibers, metal-organic frameworks, carbon nanospheres [3,5-6]. Thus there is a wealth of experimental evidence supporting the spillover effect. However, details of interaction between hydrogen and the carbon surface have not been adequately studied and hence there is much speculation about the formation of C-H bonds on the nanotube surface. Recent DFT calculations predict that it is thermodynamically viable for H to migrate from the metal nanoparticle to the nanotube substrate. However, migration on the nanotube surface itself is facile only if the H atom is physisorbed and becomes difficult upon C-H bond formation [7].

It has been attempted to increase the surface area of the nanotubes by introducing defects into the structure [8-9], but this leads to stability issues for the defective nanotube matrix.

## **Results**

### **Single Wall Carbon Nanotube growth (Clemens group)**

The CVD growth of single-walled carbon nanotubes has been studied with ethanol as the carbon source under different conditions, e.g. temperature and carbon concentration. These studies are providing insight into the mechanism of growth of single-walled carbon nanotubes via CVD and allow for tailoring the distribution of SWNTs by changing the growth parameters to obtain a higher concentration of the desired SWNTs (Figure 1). Complete chirality control and monodisperse growth have not yet been achieved, but distinct distribution shifts have been seen and reproduced.



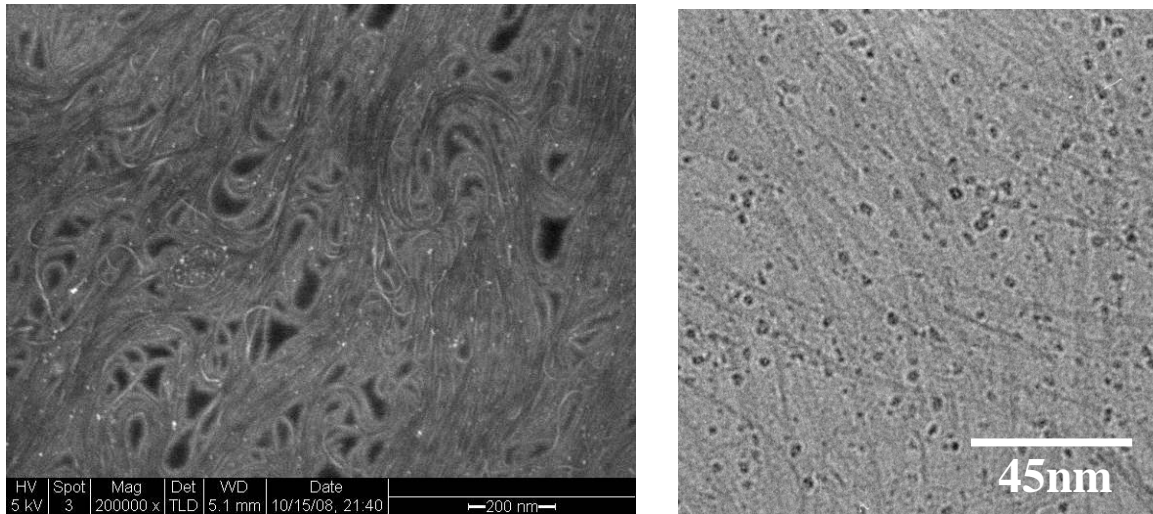
**Fig. 1:** RBM region of Raman spectra of growth samples using a 785 nm laser showing distinct chirality and diameter distributions.

In addition to silicon dioxide and single crystal quartz, silicon nitride, titanium nitride, ITO, FTO, thick cobalt films, and thin cobalt films over platinum films have been tested as substrates for the nanotube growth. To date vertical forest growths have only been produced on silicon dioxide and single crystal quartz. Horizontal mat growths have been produced on silicon dioxide, single crystal quartz, silicon nitride, and thick cobalt films.

### **Sample preparation for electrochemical and XPS studies**

We developed a technique to make SWNT films for the electrochemical studies. HiPCO SWNT sputtered with predetermined Pt thickness were dispersed in a surfactant and then filtered through mixed cellulose ester filtration membranes. The dispersion is filtered under vacuum, till the film is almost dry. Once the film has set the surfactant is removed by repeated washing with distilled water. Next the filtration membrane with the attached nanotube film is placed in an acetone bath, where the membrane dissolves. The nanotube film, left drifting in the bath, can be transferred onto any desired substrate.

For the XPS studies to determine the extent of hydrogen storage, Pt was sputter deposited on LB films. Sputtering thickness was varied from 2nm to 8nm. Fig 2(a) and 2(b) are the SEM and TEM images of 5nm Pt doped LB films.



**Fig. 2:** Electron microscope images of the LB films doped with sputtered Pt (5 nm nominal thickness)

### **Carbon Nanotube Synthesis, Langmuir-Blodgett Film Fabrication and Characterization with Raman Spectroscopy and AFM (Dai group)**

Dai group has been contributing to the GCEP project in several aspects, like providing carbon nanotubes samples for hydrogen storage based on the collaborators' request and carrying out Raman and AFM characterization on the samples.

Dai group developed two kinds of carbon nanotube samples, which have different diameter distribution, for the hydrogen storage using atomic hydrogen: small diameter carbon nanotubes grown with FeCoMo catalyst and ethanol vapor, and big diameter carbon nanotubes grown with FeCo catalyst and methane gas.

Dai group provided these two kinds of tubes in two different types of growth patterns and tube densities: One type is thick carbon nanotube film for XPS measurement; the other type is low-density carbon nanotube that is grown from patterned catalyst islands for AFM imaging.

Dai group carried out Raman and AFM characterization that demonstrate the diameter distribution of these two kinds of tubes. Dai group also developed a method to do AFM on the same nanotube before and after hydrogenation showing that the nanotube diameter increased after the hydrogenation. Some cutting effect on small diameter tubes after hydrogenation was also found.

In 2008, Dai group and Nilsson group published a paper "Hydrogen storage in carbon nanotubes through the formation of stable C-H bonds" in Nano Letter based on the XPS, Raman and AFM data.

Dai group provided carbon nanotube Langmuir-Blodgett film samples for the hydrogen storage of using molecular hydrogen and spillover process.

These carbon nanotube Langmuir-Blodgett films were made using the method that Dai group developed in their previous work “Langmuir-Blodgett assembly of densely aligned single-walled carbon nanotubes from bulk materials” published in Journal of the American Chemical Society.

The Hipco tubes were suspended in DCE with conjugate polymer PmPV. And then the tubes were centrifuged and filtered several times to get clean, individual tubes suspended in DCE without excess PmPV. Then the tubes were deposited onto a substrate by using the Langmuir-Blodgett (LB) assembly method. The LB film of the tubes is mostly single layer. The tubes in the film are mostly single tubes with small amount of bundles. These films were calcined to remove the surfactant residue and provided for hydrogenation.

In addition to these sample preparation and characterization, Dai group also actively involved in the GCEP meetings and contributed many valuable ideas on the projects.

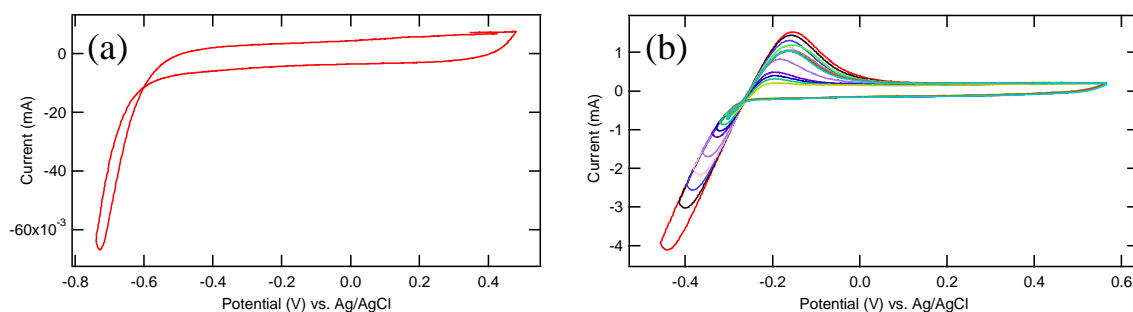
### **Electrochemical characterization of pure and Pt-modified carbon nanotubes (Nilsson group)**

We have established a setup for the electrochemical testing of different carbon nanotube samples. We used cyclic voltammetry (CV) for the detection of current peaks which could be characteristic for an electrochemical hydrogenation/dehydrogenation of the nanotubes.

We assume that the mechanism for electrochemical hydrogen reduction at *pure* carbon nanotube surfaces involves electron tunneling between the nanotube surface and the outer Helmholtz plane, and thus a significant overpotential. Hydrogen atoms would thus be generated at a greater distance from the nanotube, and would likely recombine to form molecular hydrogen before they could reach the nanotube surface. Once the molecular hydrogen has been formed, too high activation energy would be required to break the H-H bond and form C-H bonds instead. Therefore, we expect that electrochemical hydrogen reduction at *pure* nanotube electrodes will merely lead to the production of hydrogen gas. The CV for pure carbon nanotubes supports this assumption (Fig. 3 a). It shows only capacitive currents over a broad potential range and, at very low potentials, an exponential negative current increase that originates from the reduction of water to molecular hydrogen. If C-H bonds were formed during the hydrogen reduction, we would expect a positive current peak to appear in the anodic sweep.

A different hydrogen reduction mechanism occurs at carbon nanotubes coated with Pt nanoparticles (Fig. 3 b). The electrochemical formation of hydrogen at Pt surfaces requires only a very low overpotential, and a chemisorbed layer of H atoms on the Pt surface forms already at potentials above the onset of molecular hydrogen formation. These H atoms could be available for a reaction with the carbon nanotubes to form C-H

bonds (spillover effect). In fact, CVs for a Pt-modified carbon nanotube sample show the onset of hydrogen reduction already at much higher potentials than for pure nanotubes, due to the presence of the Pt catalyst. In addition, a positive current peak appears in the anodic potential sweep. This indicates the oxidative formation of water from adsorbed hydrogen, which could originate from C-H bonds. This hydrogen oxidation current peak increases with decreasing cathodic potential limits until saturation is reached. A corresponding reduction peak cannot be distinguished from the overall hydrogen reduction ( $H_{\text{ads}}$  and  $H_2$  formation) current. This indicates the concurrence of two competitive reaction pathways, (irreversible) formation of molecular hydrogen and (desired) formation of C-H bonds. However, because the hydrogen oxidation current peak appears in a potential region where we would also expect the oxidation of H adsorbed at the Pt surface, the interpretation of the current-voltage curves alone will not be unambiguous.



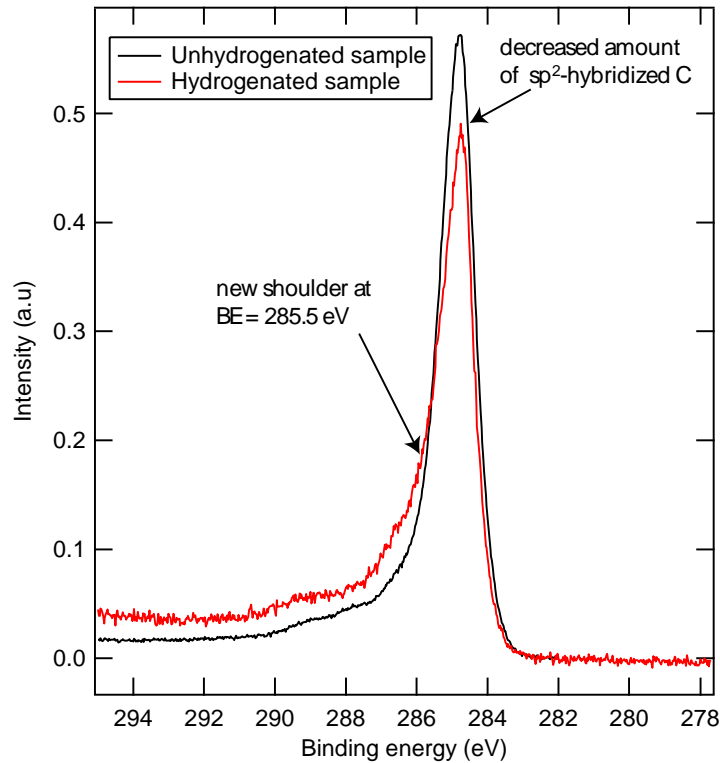
**Fig. 3:** Cyclic voltammograms of (a) Pt-free and (b) Pt-modified HiPCO nanotubes in 0.05 M  $H_2SO_4$ ,  $dE/dt = 10$  mV/s. Curves in (b) in different colors indicate different lower potential limits.

We will further investigate the electrochemistry of carbon nanotubes, using x-ray photoelectron spectroscopy at SSRL beamline 13-2. We will electrochemically treat carbon nanotube samples and then quickly transfer the samples into the ultrahigh vacuum chamber. The C 1s XP spectra will then reveal to which extent C-H bonds have been formed. We will also study the effect of different temperatures and overpotentials on the electrochemical hydrogenation of carbon nanotubes.

### **XPS studies of carbon nanotubes after high pressure hydrogen treatment (Nilsson, Clemens, Dai)**

We used x-ray photoelectron spectroscopy (XPS) at SSRL beamline 13-2 to study the effect of high pressure treatment of Pt-modified carbon nanotubes with molecular hydrogen. Thin Langmuir-Blodgett (LB) films of nanotubes on a native oxide covered Si substrate were provided by the Dai group. Pt was then sputtered onto the samples. We

measured the C 1s XPS for these samples both with and without hydrogen treatment. A Pt-free control sample was also studied. The C 1s XPS of the sample without hydrogen treatment can be deconvoluted into 4 peaks. The strongest component at 284.75 eV binding energy is assigned to  $sp^2$ -hybridized C atoms in the nanotubes. Three additional weak components at higher binding energies originate from residual surfactant (PmPV) used for the LB film deposition. Using the same sample after exposure to hydrogen at a pressure of 120 psi, we observe a significant shoulder at 285.5 eV binding energy (Fig. 4). This can be attributed to  $sp^3$ -hybridization due to the formation of C-H bonds. Concomitantly, the peak corresponding to  $sp^2$ -hybridized C has decreased in intensity. Using the weights of the deconvoluted peaks, we can estimate the amount of carbon nanotube hydrogenation to ca. 13% per carbon atom, or 1% per weight of the nanotubes. This experiment clearly demonstrates a spillover of hydrogen from the Pt catalyst to the carbon nanotubes. Moreover, the effect of the Pt as catalyst for the hydrogenation/dehydrogenation becomes obvious as we can observe the C-H signal only when any contact of the hydrogenated sample with air is avoided. For samples transferred through air, the XP spectra with and without hydrogen treatment are identical. This can be explained with the catalytic oxidation of hydrogen to water at the Pt surface which leads to a reversal of the spillover process.



**Fig. 4:** XPS spectra of a HiPCO nanotube LB film deposited on oxide-covered Si and sputtered with 5 Å Pt, before (black curve) and after (red curve) exposure to hydrogen gas at 120 psi.

## Progress

We have established a variety of techniques for the fabrication of well defined carbon nanotube-metal nanoparticles composite materials which are candidates for hydrogen storage using the spillover mechanism. Carbon nanotubes can be provided with different diameters and with different metal catalyst loadings in a variety of film thicknesses and morphologies. We have carried out a first electrochemical characterization of these samples. By characterizing nanotube samples with XPS after treatment with pressurized molecular hydrogen, we were able to detect a small amount of C-H bond formation. We have thus achieved a proof of principle for the proposed spillover mechanism which could be used for hydrogen storage. Provided that the amount of C-H bond formation can be increased by finding the most suitable combination of catalyst/nanotube materials, the spillover effect could be used in future applications for the reversible storage of chemical energy in the form of C-H bonds. The release of this energy by the oxidative splitting of the C-H bonds would leave the carbon backbone of the nanotubes unchanged and thus avoid any carbon dioxide formation.

## Future Plans

Concurrently, we will also characterize electrochemically hydrogenated samples. Electrochemical experiments to assess the feasibility of “feeding” a fuel cell anode with hydrogenated SWNTs – to release the stored chemical energy as electrical energy – will also be carried out. We will characterize electrochemically hydrogenated samples using XPS for the spillover process. Using the characterization with XPS, we plan to also improve the amount of nanotube hydrogenation by exposure to higher H<sub>2</sub> pressures up to 100 bar, by optimizing the morphology of the Pt-nanotube composite to facilitate the spillover process, and by varying the nanotube diameter to increase the C-H bond strength.

We are currently developing an in situ x-ray electrochemical cell which allows for C 1s x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) of the nanotubes under electrochemical conditions. In addition to the above described “ex-situ” XPS characterization of “as-prepared” samples, this experiment allows us to follow the electrochemical hydrogenation process “in situ”, i.e. under working conditions. We also plan to use x-ray inelastic scattering to measure x-ray absorption spectra using hard x-rays under operating conditions.

We have developed an interferometer with a HeNe laser for film thickness measurements which will be used to study the growth kinetics of carbon nanotubes in situ. Very recently we have found a growth enhancement to occur under the influence of an electric field. We will study this effect in detail because it will enable us to grow nanotubes at lower substrate temperatures. This could make a variety of new substrates available which so far could not be used at the required high growth temperatures.

## Publications

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## Contacts

Anders Nilsson: nilsson@slac.stanford.edu  
Bruce Clemens: bmc@stanford.edu  
Hongjie Dai: hdai1@stanford.edu  
Hirohito Ogasawara: hirohito@slac.stanford.edu  
Daniel Friebe: dfriebe@slac.stanford.edu  
Xiaolin Li: xiaolinl@stanford.edu  
Srivats Rajasekaran: vatsr@stanford.edu  
Ranadeep Bhowmick: ranadeep@stanford.edu  
Cara Beasley: cbeasley@stanford.edu