

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

### Subtask: Synchrotron Radiation Characterization of Hydrogen Storage

#### Investigator

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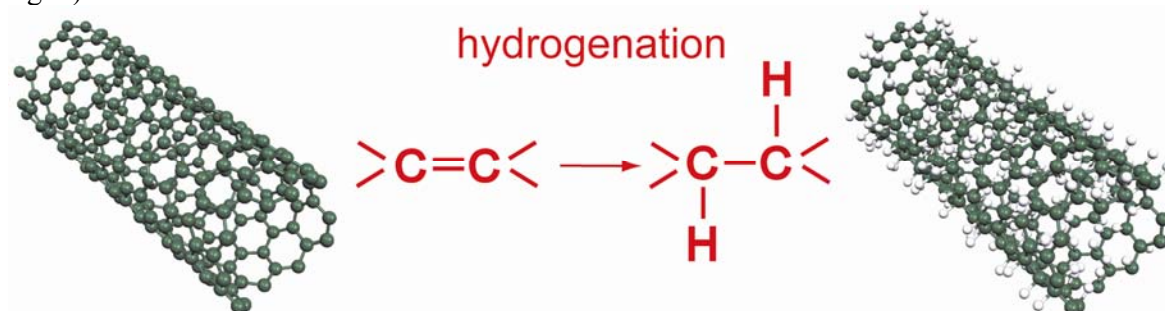
#### Motivation of subtask

There are two possible mechanisms of hydrogen interaction with single-walled carbon nanotubes (SWCN) which are considered to be important in the storage of hydrogen. These are physisorption and chemisorption.

In the case of physisorption, H<sub>2</sub> forms weak Van der Waals bonds with the surface of the nanotube. Theoretical calculations show that the bonding energy is of the order of ~0.11 eV per molecular H<sub>2</sub>. Numerous theoretical studies and experimental measurements conclude that physisorption of H<sub>2</sub> molecules in SWCN can not provide more than 1 – 2 wt % of hydrogen capacity at room temperature which is far from the requirements of the FreedomCAR program.

In the case of chemisorption, an H atom is bonded to the C atom in the nanotube wall through covalent C-H bond formation with a bonding energy ~2.5 eV per H atom. There are theoretical predictions that this mechanism can provide up to 7.7 wt % of hydrogen capacity for nanotube material. Also it was shown theoretically that the strength of the C-H bond depends on the curvature of the graphene sheet so there is a potential mechanism to tune the energetics of the C-H bonds.

Based on these previous results chemisorption of hydrogen on the nanotube surface looks more promising as a possible way to store hydrogen in SWCN material and in our study we focused our attention on this particular mechanism of hydrogen interaction with SWCN (see fig. 1).

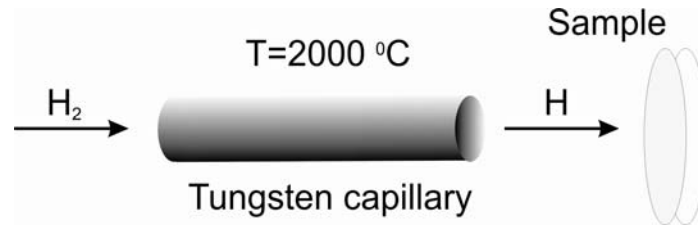


**Fig. 1** The illustration of the chemisorption of hydrogen on the surface of SWCN.

As probing tools we used synchrotron radiation based X-ray Photoelectron Spectroscopy (XPS) and X-ray Adsorption Spectroscopy (XAS). These techniques are sensitive to the formation of C-H bonds and allow to quantify the amount of hydrogen that is chemically adsorbed in terms of per carbon atom. In XPS chemical shifts of the C1s level due to hydrogen coordination can provide both chemical identification of C-H bonds and from the relative intensity the number of affected carbon atoms. XAS provides means to observe the unoccupied orbital structure using a core excitation process. The formation of C-H bonds can be observed

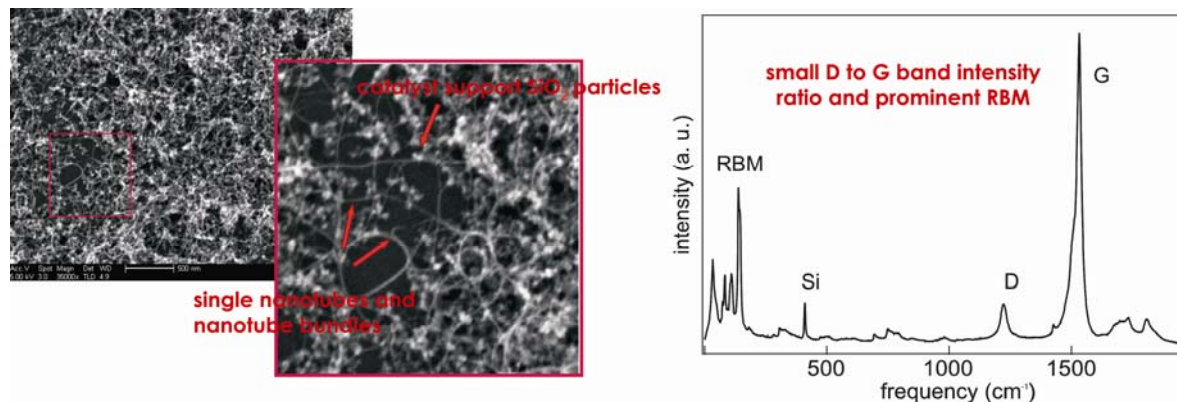
through the modification of the carbon nanotube electronic structure around specific carbon atoms.

To perform the SWCN hydrogenation we used *in situ* atomic hydrogen treatment inside the ultra-high vacuum chamber. This approach allowed us to exclude the  $H_2$  molecular dissociation step and focus on the possibility of hydrogen chemisorption on the nanotube surface. To generate atomic hydrogen beam we used the source schematically shown in fig. 2.



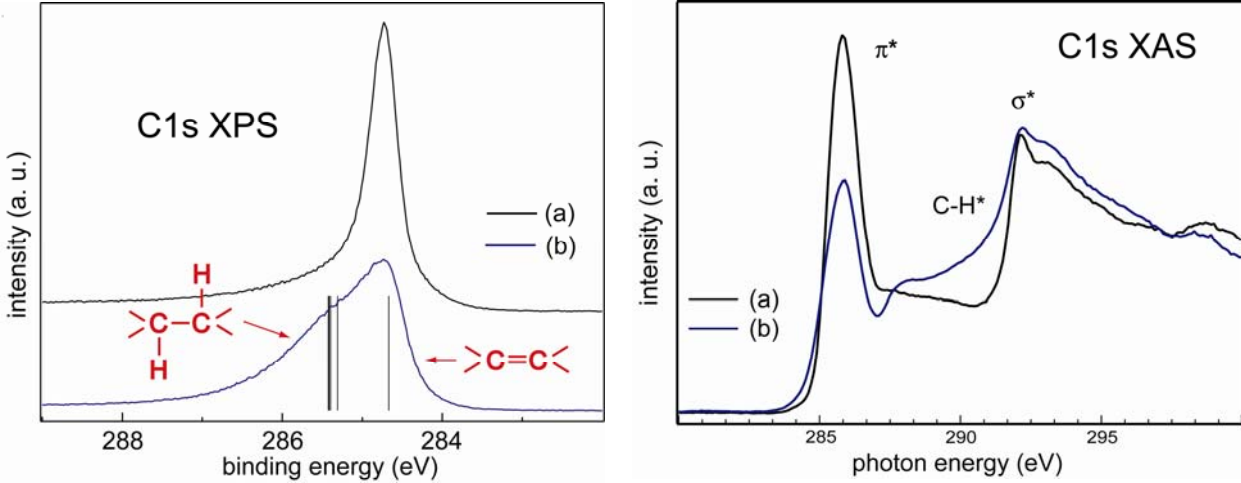
**Fig. 2** The scheme of the atomic hydrogen source.

To eliminate the influence of amorphous carbon and defects in the SWCN walls on the hydrogenation process we used ultra pure as grown SWCN films which were produced by the alcohol CVD method in the Dai group. Small D to G band ratio in the Raman spectrum (see fig. 3) confirms the low concentration of the defects and amorphous carbon in the used samples. RBM mode position in the spectrum indicates the diameter distribution of SWCN in the sample from 1.0 nm to 1.8 nm.



**Fig. 3** SEM picture and Raman spectrum of the investigated samples.

We found that H treatment of the SWCN film leads to dramatic changes both in the XPS and XAS spectra (see fig. 4).

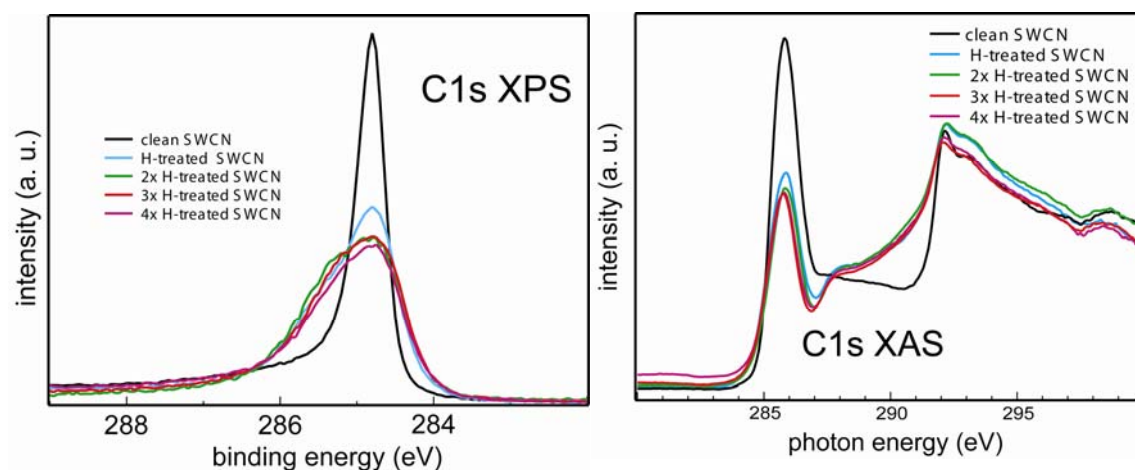


**Fig. 4** XPS (left) and XAS (right) spectra of (a) clean SWCN sample and (b) SWCN sample exposed to H treatment. As vertical lines in the left figure the theoretical values of the C1s core level chemical shifts due to C-H bond formation for different types of nanotubes are shown.

We observe that the H treatment causes the appearance of the second peak in the XPS spectrum which we can be seen as a broad shoulder. The position of this peak is in the good agreement with computed values of the C1s chemical shift due to C-H bond formation carried out by the Zhang and Cho group. In the case of XAS, H treatment leads to the decrease of the  $\pi^*$  resonance and the increase of intensity in the energy range of the C-H\* and  $\sigma^*$  resonances. These spectral changes are evidence of rehybridization of the carbon atoms in the SWCN walls from  $sp^2$  to  $sp^3$ . Also the spectral intensity increase in the C-H\* resonance energy range directly points to the formation of C-H bonds as a result of atomic hydrogen interactions with SWCN surface. By performing decomposition of the XPS C1s spectrum into two components (one corresponds to the signal from the C atoms unaffected by H treatment and another one is due to the signal from the H bonded carbon atoms) we can directly determine the amount of hydrogenation.

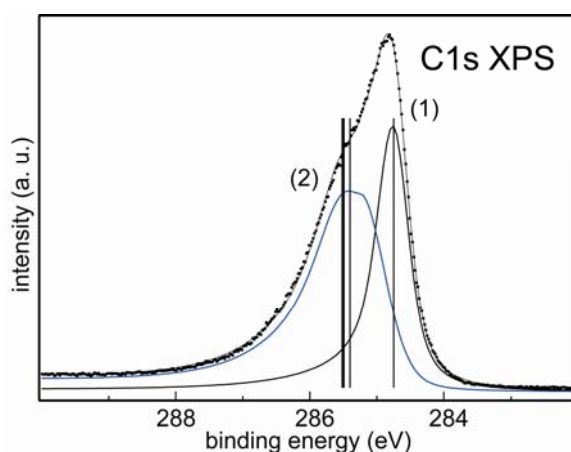
#### The stable phase of hydrogenated SWCN.

We found that there is a stable phase of hydrogenated SWCN. As we can see from fig. 5 after obtaining this stable phase ("H-treated SWCN") any additional H treatment does not cause any significant changes both in the shape of the C1s XPS and XAS spectra. The XPS spectra measured at different excitation energies providing different kinetic energies of the escaping electrons and as a result the different probing depth does not show any changes in the spectral line shape. We can conclude that hydrogenation is uniform in the SWCN film and the observed phenomenon is not due to a "surface – to – bulk" ratio problem.



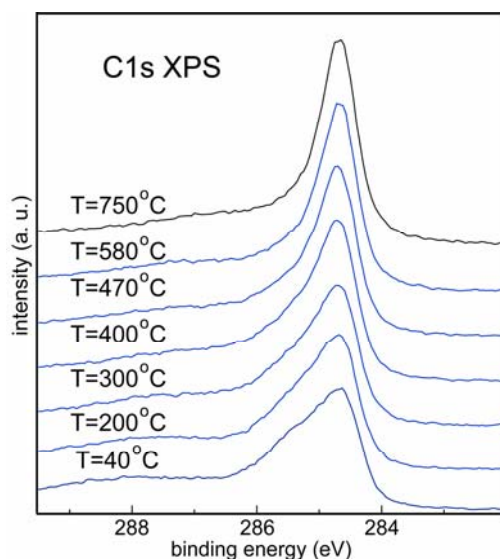
**Fig. 5** XPS (left) and XAS (right) spectra of the clean sample and sample of SWCN exposed to the different dozes of atomic hydrogen.

The decomposition of the C1s XPS spectrum of the sample possessing this phase (see fig. 6) allowed determining the degree of hydrogenation for the stable phase of hydrogenated SWCN. The ratio between intensities of the peak (1) corresponding to clean C atoms and of the peak (2) which is due to signal from H bonded carbon atoms is 4 to 6. So taking into consideration the error in the peak area determination we can conclude that the hydrogenation degree is  $60 \pm 10$  at %. This degree of hydrogenation corresponds to  $4.8 \pm 0.8$  wt % of hydrogen capacity if we suppose 1 H atom per 1 C atom with C-H bond.



**Fig. 6** The decomposition of C1s XPS spectrum of the stable phase of hydrogenated SWCN. Vertical lines correspond to the theoretical values of the C1s core level chemical shifts due to C-H bond formation for different types of nanotubes.

Using XPS as a probing tool we also defined the temperature range of hydrogen desorption for the stable phase. In fig. 7 we show the XPS spectra which were measured from the stable phase of hydrogenated SWCN during annealing to different temperatures. We see the decrease of the intensity in the energy range of the peak (2) taking place in the temperature range between  $300$  °C and  $600$  °C. It should be pointed out that the total C1s peak area is constant during annealing demonstrating no hydrocarbon desorption which otherwise could cause the loss of carbon.



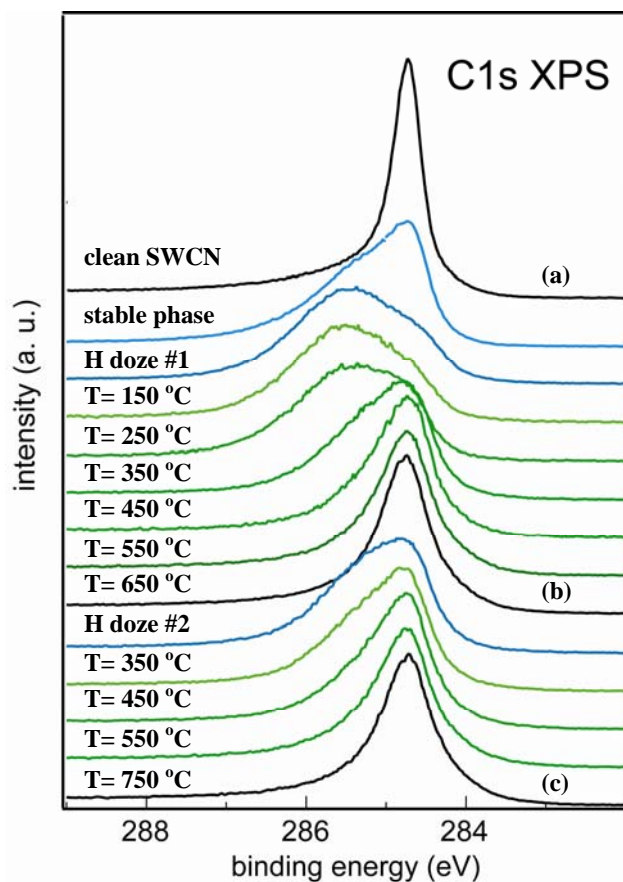
**Fig. 7** XPS spectra measured during annealing of the stable phase of hydrogenated SWCN at different temperatures.

### Potassium promoted hydrogenation of SWCN

One of the possible way to increase the reactivity of the SWCN surface and as a result to increase the degree of hydrogenation and hydrogen weight capacity of the material is to use promoters. We tested if potassium could have an effect since it is known to change the electronic structure of graphite. We deposited K through evaporation on the surface of the SWCN that already contained the stable phase of hydrogenated SWCN which was followed by further H treatment. The XPS C1s spectra measured during this procedure are shown in fig. 8. We see that after H doze #1 almost all intensity moved from peak (1) region to the peak (2) region. This means that we could get a much higher hydrogenation degree in comparison with the stable phase. The sample was also annealed at different temperatures with XPS spectra shown in fig. 8. We observe that the decrease of the intensity in the area of peak (2) takes place in the temperature range between 250 °C and 450 °C which is lower than the stable phase of hydrogenated pure SWCN.

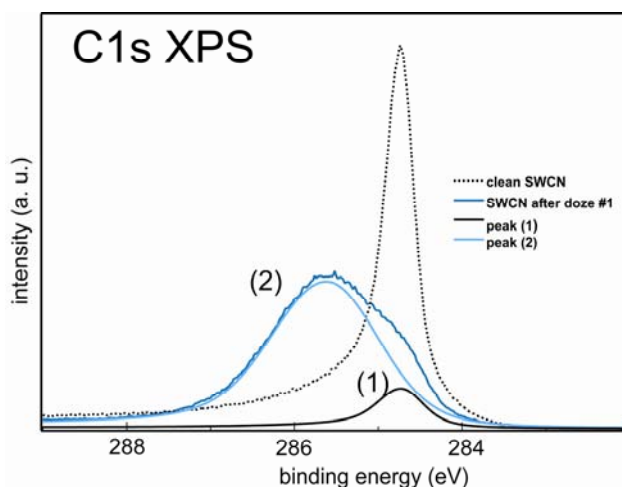
After the first hydrogenation/annealing cycle the sample was exposed to another H treatment. We could see that C1s XPS spectrum (see “H doze #2”, fig. 8) has a similar shape as the spectrum measured for the stable phase of the hydrogenated SWCN (we could not reach a similar degree of hydrogenation as we got for the “H doze #1” case due to that most K evaporated from the sample surface during the first annealing cycle). The additional annealing sequence restored the spectral shape of C1s XPS spectrum (see spectra (b) and (c), fig. 8). We can conclude that it is possible to cycle the hydrogenation/dehydrogenation process of SWCN.

It should be pointed out that the C1s peak in spectra (b) and (c) is much broader than the C1s peak in spectrum (a) which was measured for the clean SWCN sample. Such increase of the FWHM of the peak indicates that the hydrogenation/dehydrogenation cycles induce defects. This is confirmed by the Raman measurements which showed an increase of the D to G band intensity ratio. The SEM pictures showed that the morphology of the clean SWCN sample and the sample which was exposed to 2 cycles of hydrogenation/dehydrogenation is the same. In spite to the fact that the average density of defects in the nanotube walls increased seriously the nanotube framework was preserved after such a treatment.



**Fig. 8** XPS C1s spectra measured during two hydrogenation/annealing cycles of SWCN which were hydrogenated with the usage of potassium as a promoter.

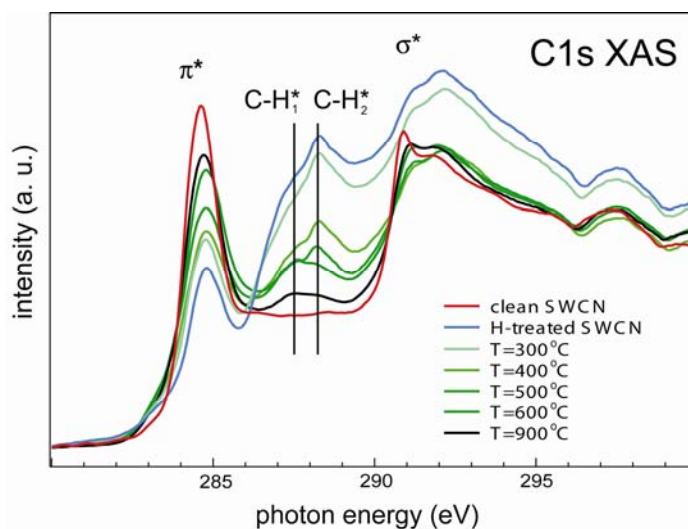
To quantify the degree of hydrogenation for the “H doze #1” case the C1s XPS spectrum was decomposed (see fig. 9). The ratio between intensities of peak (1) and peak (2) is 1 to 9 which corresponds to 90 +/- 10 at % of hydrogenation. The hydrogen capacity is 7.0+/-0.8 wt % (under the assumption that we have one H atom per one C atom with C-H bond). It should be pointed out that this value is higher than the hydrogen weight capacity of the 2010 goal of the DOE FreedomCAR roadmap.



**Fig. 9** The decomposition of XPS C1s spectrum which was obtained after H doze #1 treatment. As a reference the spectrum of clean SWCN is shown.

### The influence of the 3d metals on the hydrogenation process

One of the possible ways to increase the hydrogen storage capacity of SWCN and also to tune the energetic of the C-H bonds in the system is to use metal catalysts deposited on the SWCN surface. To check the possibility to use such 3d metals as iron and nickel as catalysts which could improve the hydrogenation of SWCN we deposited Fe and Ni on the SWCN film surface and exposed it to the H treatment. XAS spectra measured from the hydrogenated sample and during the annealing sequence are shown in fig. 10.



**Fig. 10** The XAS spectra of SWCN films with Ni and Fe on the surface which were exposed to the H treatment and annealing sequence.

From fig. 10 we see that the presence of 3d metals leads to a different type of the C-H bond formation during H treatment. Two prominent C-H\* resonances are seen while in the case of the stable phase of the hydrogenated SWCN such prominent features are absent, see fig. 4. Also the presence of Ni and Fe allowed to reach higher degree of SWCN hydrogenation which can be seen from the  $\pi^*$  resonance to  $\sigma^*$  resonance intensity ratio (see fig. 10). The energetics of C-H bonds is different in comparison with the C-H bonds in the stable phase of hydrogenated SWCN. We see that the largest decrease of the C-H\* resonances takes place in the temperature range between 300 °C and 400 °C.

### Conclusions

1. The stable phase of hydrogenated SWCN exists with 60 +/- 10 at. % hydrogenation degree. Without promoters or catalysts it is difficult to reach higher degree of hydrogenation. For the stable phase H desorbs in the temperature range from 300 °C to 600 °C.
2. The usage of K as a promoter allows 90 +/- 10 at. % hydrogenation of SWCN, that is equivalent to 7.0 +/- 0.8 wt. % of hydrogen storage capacity. The temperature range of the H release is between 250 °C and 450 °C. The hydrogenation/ dehydrogenation process can be cycled.
3. The presence of the 3d metals as catalysts allows higher degree of hydrogenation than the hydrogenation degree of the stable phase as well. Also the nature of the C-H bonds is different in comparison with C-H bonds present in the stable phase.

### Future Plans

We can point out the following major directions in the future research.

1. Using XPS and XAS as probing tools we want to study the influence of the nanotube diameter distribution on the energetic of the C-H bonds in the SWCN-H complexes. By measuring the C1s XPS spectra of the H treated SWCN samples with different diameters at different annealing temperatures we can learn if it is possible to use the diameter distribution to tune the H release temperature.

2. We are planning to study the influence of different promoters like Li on the hydrogenation process of SWCN and try to obtain reliable experimental confirmation that it is possible to obtain 100 % hydrogenation of SWCN in a reproducible manner. With the addition of Li there will not be any significant change in relative weight % of H since Li is a very light element.

3. We are also planning to study the interaction of different metals (3d metals, Ti, Pt and Pd) with nanotubes and their influence on the nanotube hydrogenation process.

4. As we showed in fig. 1, it is in principle possible that H atoms can form C-H bonds locating both on the outer and inner surface of the nanotube. To determine if there is any preference in the C-H bond direction (inside of the nanotube or outside of it) we are going to use infrared spectroscopy which is sensitive to the local C-H bond structure.

5. When we have optimized the conditions of SWCN for the formation of C-H bonds with the right energetic and 100% degree of hydrogenation we will investigate the dissociation process of molecular H<sub>2</sub> with different metal catalysts. The experiments will be performed by evaporating possible promoters and metal catalysts under clean vacuum conditions and then expose the samples in-situ to gaseous hydrogen at pressures up to 5 atm in a special high pressure cell. The amount of hydrogenation can then be followed using XPS without exposure to air after evacuation and removal of the cell.

### Publication

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)

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