

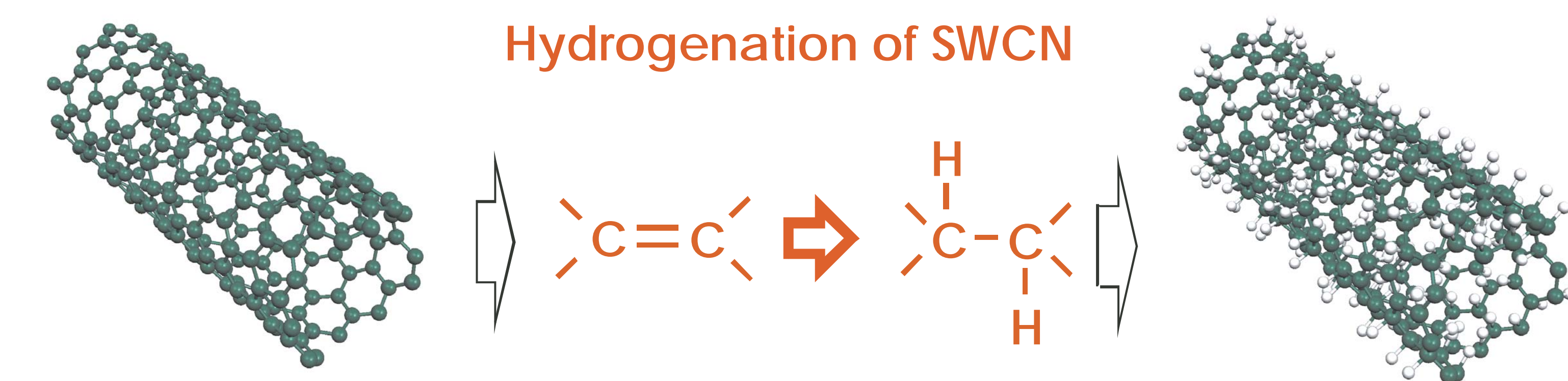
# Hydrogen storage in single-walled carbon nanotubes through the stable C-H bond

## formation: mechanism details and possible technological application

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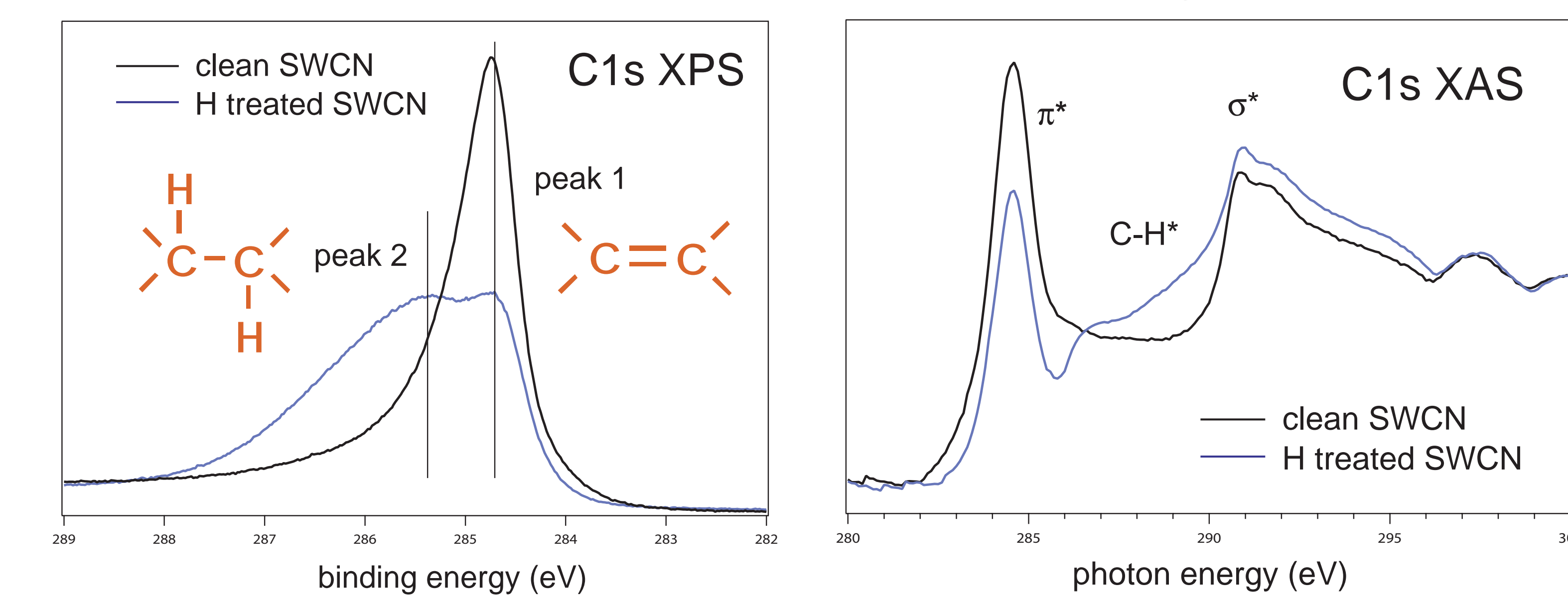
**Idea:** storing hydrogen in the chemisorbed form on the surface of carbon nanotubes nanotubes



### Investigation strategy

- **Probing tools:** X-ray Photoelectron Spectroscopy (XPS), X-ray Adsorption Spectroscopy (XAS), Atomic Force Microscopy (AFM)
- **Hydrogenation:** *in situ* atomic hydrogen treatment
- **Samples:** ultra clean "as grown" SWCN films
- **Modeling:** *ab initio* DFT calculations of the C-H bond energy

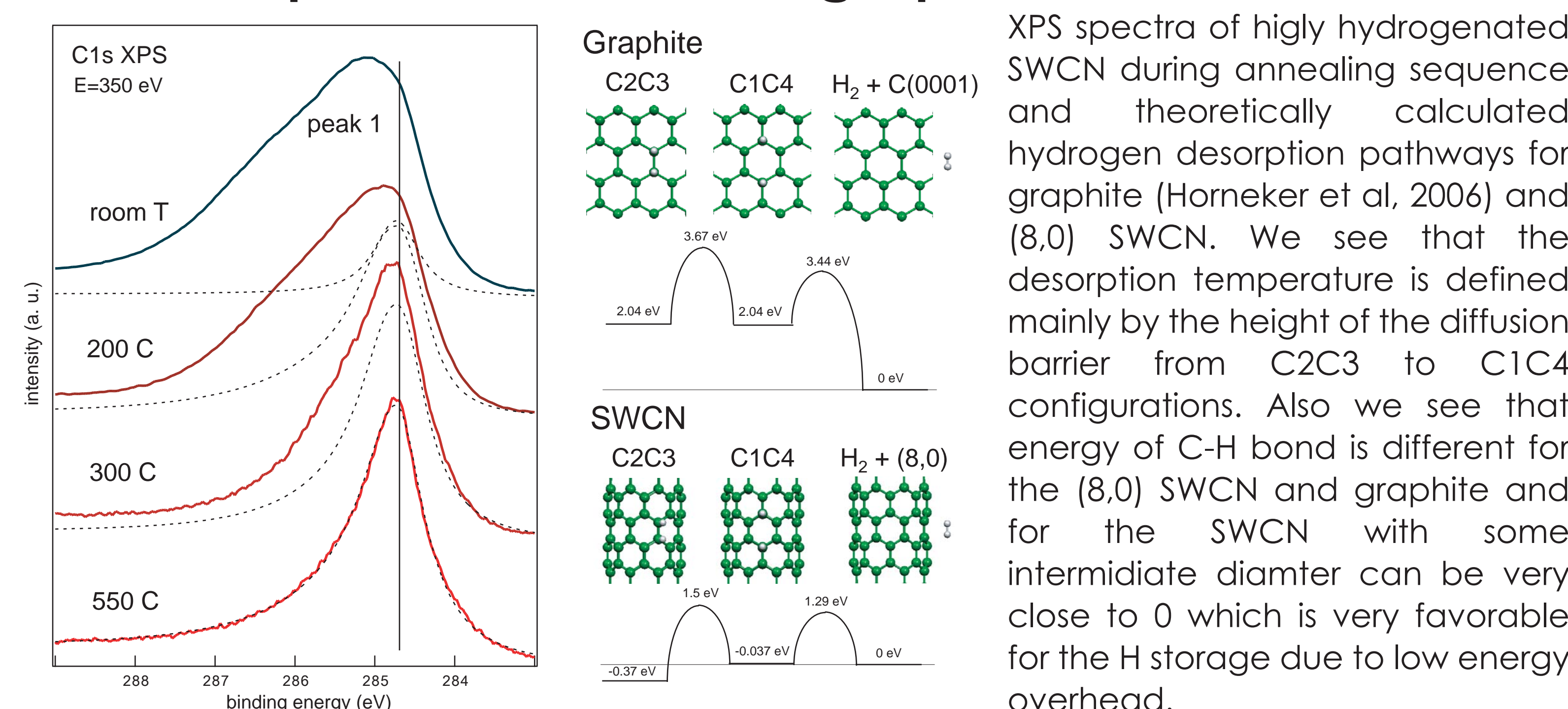
### XAS and XPS spectra of clean and hydrogenated SWCN



The increase of the intensity in the XAS spectrum around C-H\* resonance after H treatment directly indicates the formation of C-H bonds at the SWCN surface.

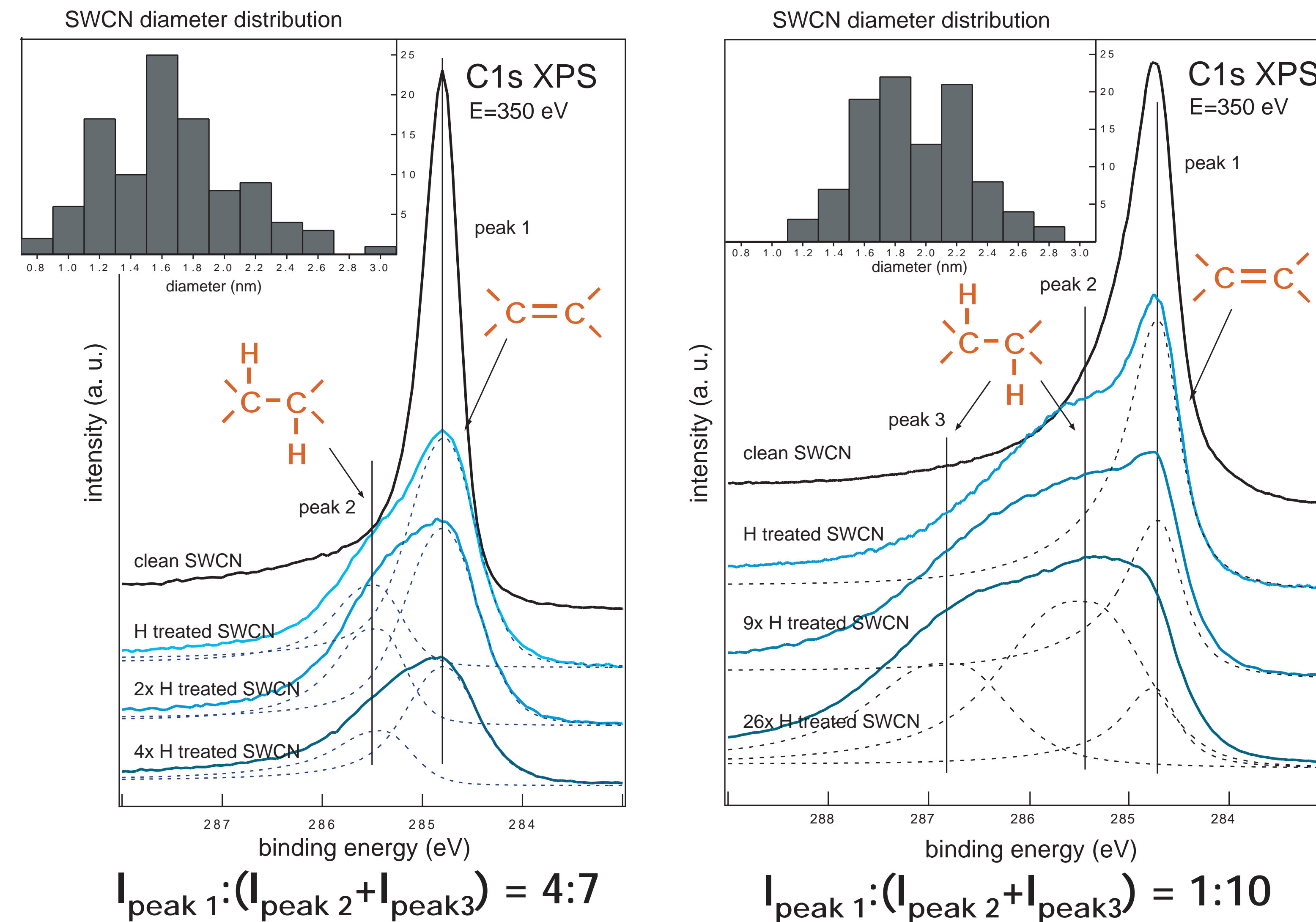
A. Nikitin et al, PRL 95, 225507 (2005)

### H desorption mechanism: graphite and (8,0) SWCN



XPS spectra of highly hydrogenated SWCN during annealing sequence and theoretically calculated hydrogen desorption pathways for graphite (Horneker et al, 2006) and (8,0) SWCN. We see that the desorption temperature is defined mainly by the height of the diffusion barrier from C2C3 to C1C4 configurations. Also we see that energy of C-H bond is different for the (8,0) SWCN and graphite and for the SWCN with some intermediate diameter can be very close to 0 which is very favorable for the H storage due to low energy overhead.

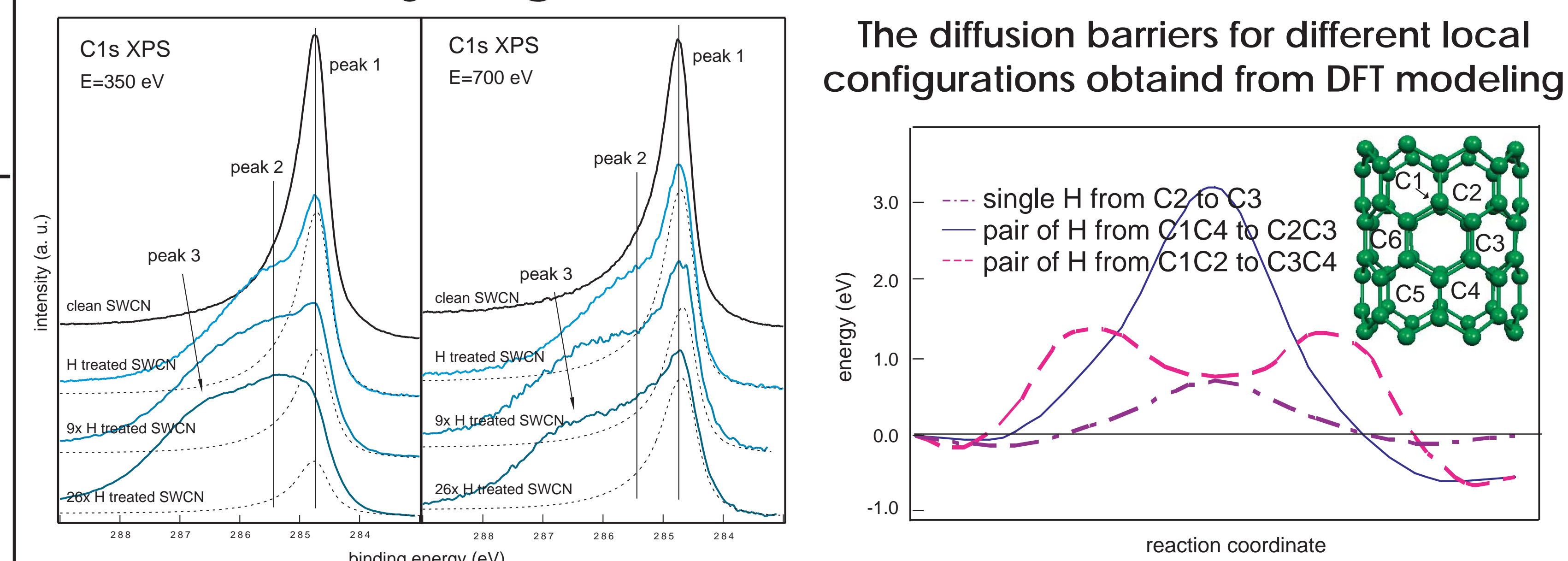
### The influence of SWCN diameter distribution on hydrogenation process



From XPS spectra measured during H treatment sequence we see that the absolute intensity of C1s peak of SWCN with diameter around 1.6 nm (left) decreases with the H doze increase without peak profile change. This means that for this type of SWCN under the H treatment the etching of the material starts before reaching the high degree of hydrogenation. For SWCN with diameter around 2.0 nm (right) H treatment allows hydrogenating almost 100 % of carbon atoms. So specific SWCN can have up to ~7 wt % of hydrogen storage capacity through the formation of the stable C-H bonds.

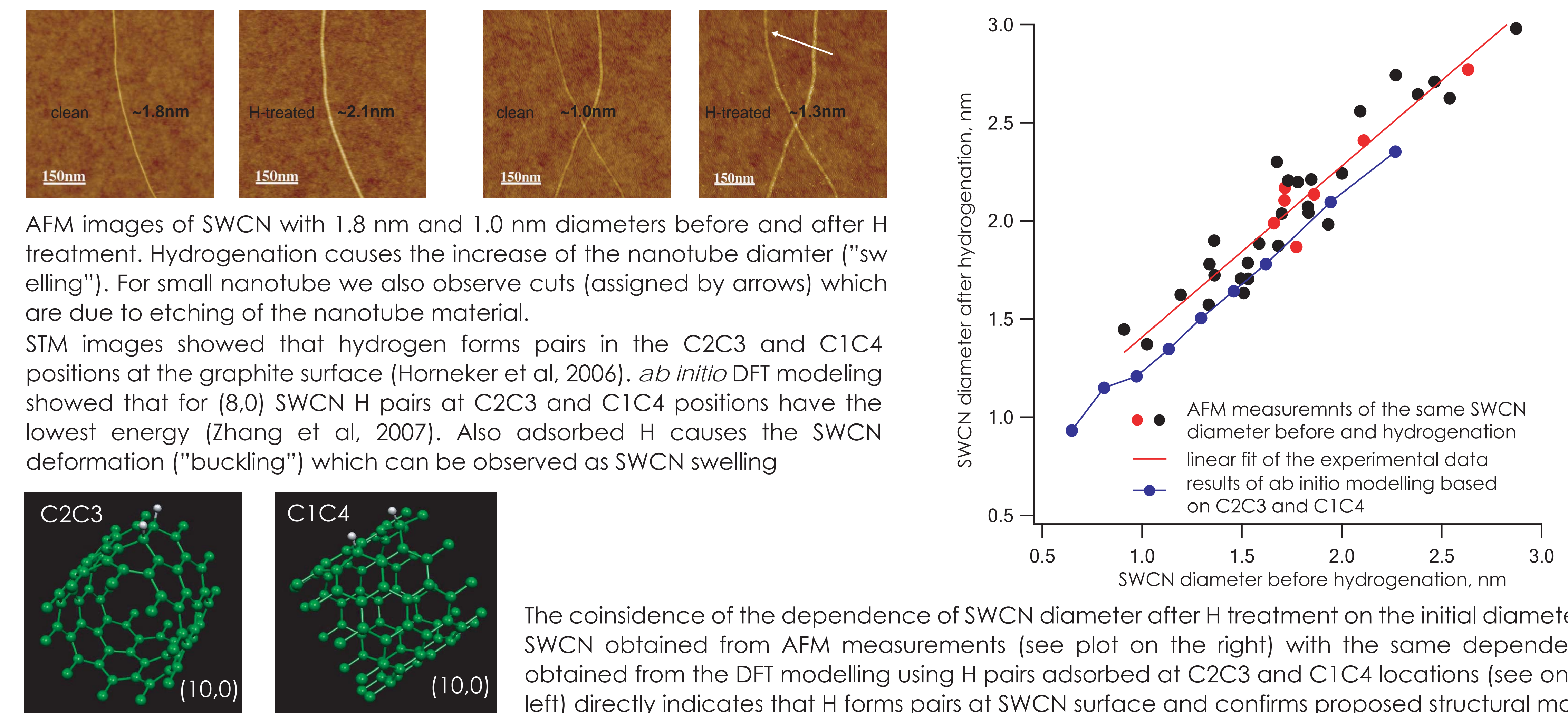
A. Nikitin et al, NanoLetters, submitted DOE budget narratives 2007

### Hydrogen diffusion on SWCN surface



From XPS spectra measured during H treatment sequence at two different excitation energies providing different probing depths (left) we see that C1s spectra measured at 700 eV (bulk sensitive) have the similar shape as surface sensitive spectra (measured at 350 eV) up to 40 % hydrogenation rate. The additional H treatment causes only the increase of the hydrogenation at the sample surface. The results of the diffusion barrier modeling (right) shows that single H atom can diffuse much easier than the H pair what is the most energetically favorable local configuration. So as soon as SWCN surface H coverage reaches ~40 % each new H atom is adsorbed in pair configuration and diffusion of H is stopped. In this case H treatment can hydrogenate only part of SWCN which can see H beam directly.

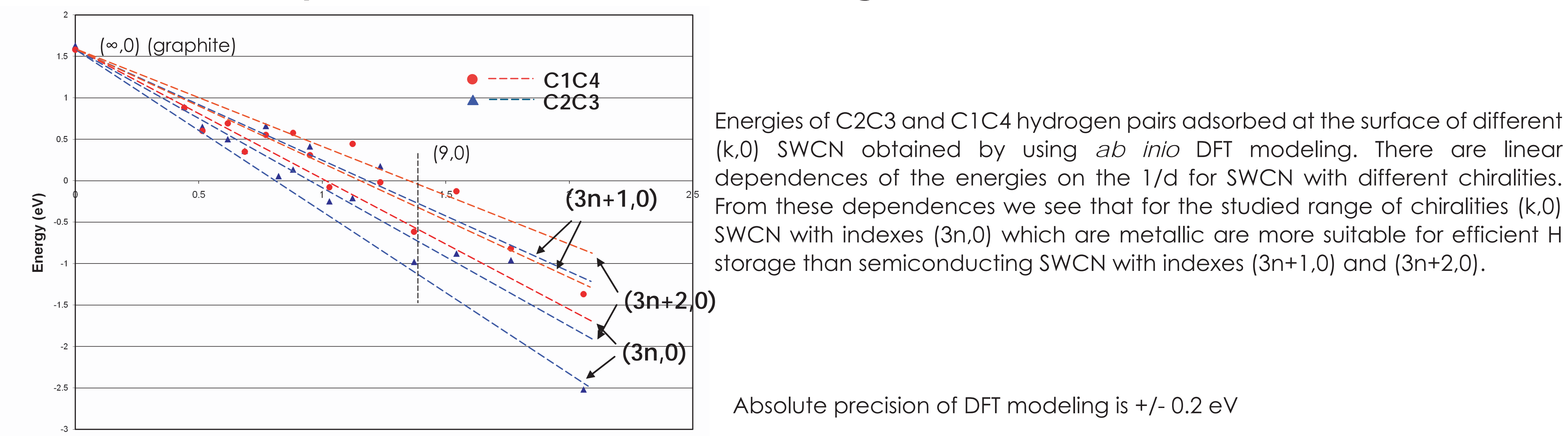
### The local structure of hydrogenated SWCN



AFM images of SWCN with 1.8 nm and 1.0 nm diameters before and after H treatment. Hydrogenation causes the increase of the nanotube diameter ("swelling"). For small nanotube we also observe cuts (assigned by arrows) which are due to etching of the nanotube material. STM images showed that hydrogen forms pairs in the C2C3 and C1C4 positions at the graphite surface (Horneker et al, 2006). *ab initio* DFT modeling showed that for (8,0) SWCN H pairs at C2C3 and C1C4 positions have the lowest energy (Zhang et al, 2007). Also adsorbed H causes the SWCN deformation ("buckling") which can be observed as SWCN swelling

The coincidence of the dependence of SWCN diameter after H treatment on the initial diameter of SWCN obtained from AFM measurements (see plot on the right) with the same dependence obtained from the DFT modelling using H pairs adsorbed at C2C3 and C1C4 locations (see on the left) directly indicates that H forms pairs at SWCN surface and confirms proposed structural model

### The dependence of C-H bond energetics on the SWCN structure

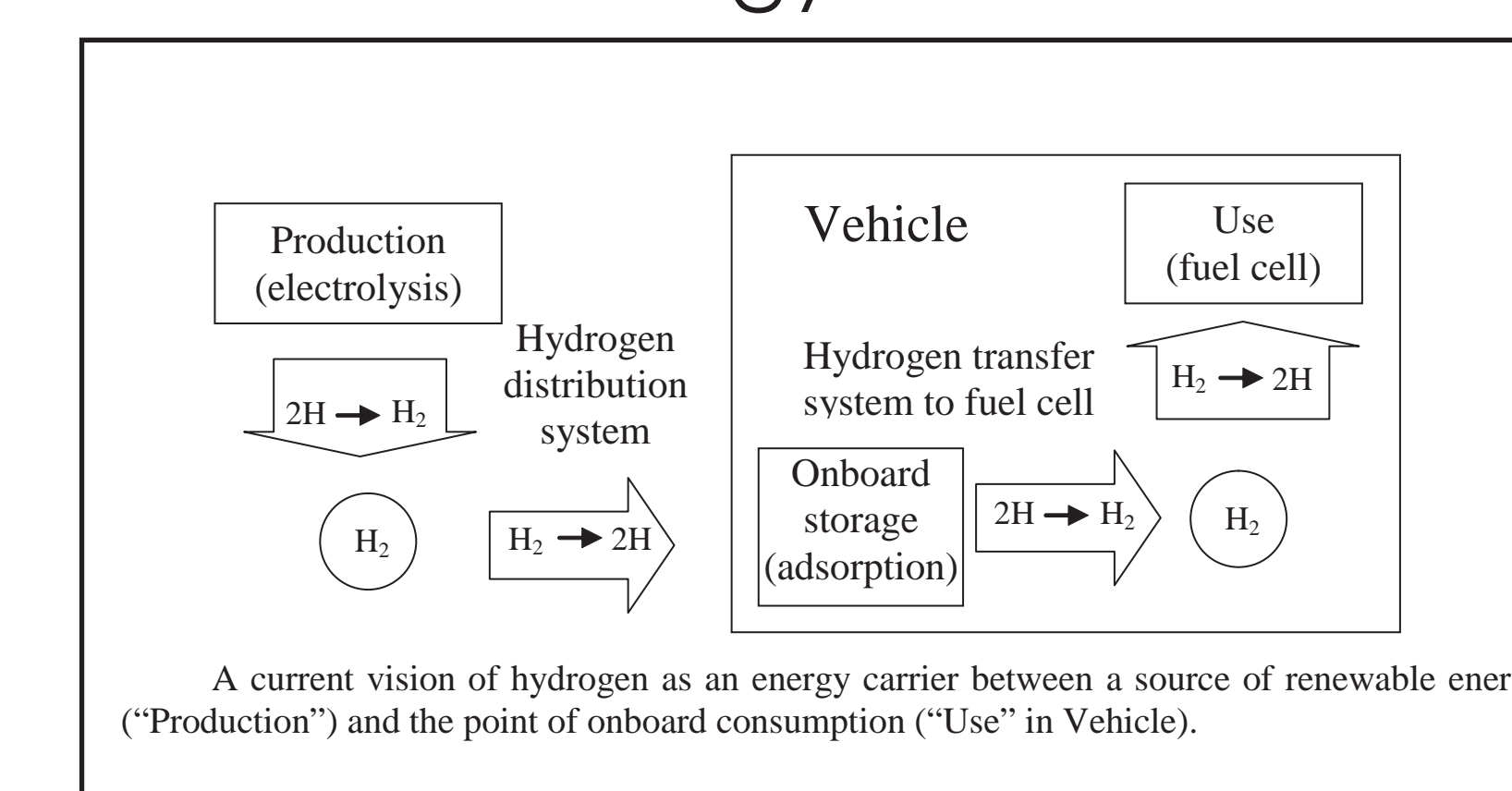


Energies of C2C3 and C1C4 hydrogen pairs adsorbed at the surface of different (k,0) SWCN obtained by using *ab initio* DFT modeling. There are linear dependences of the energies on the 1/d for SWCN with different chiralities. From these dependences we see that for the studied range of chiralities (k,0) SWCN with indexes (3n,0) which are metallic are more suitable for efficient H storage than semiconducting SWCN with indexes (3n+1,0) and (3n+2,0).

Absolute precision of DFT modeling is +/- 0.2 eV

### Possible technological application

Current renewable paradigm: H2 as an energy carrier



We envision the following technological application of C-H bond formation in SWCN: to use this mechanism as a basis for the new electrochemical device which could eliminate the necessity of H2 and could work at all stages of energy transfer. In this case SWCN - metal composite works as carrying media for the energy in the form of C-H bonds.

Alternative paradigm: reversible C-H bonds as an energy carrier

