



C-H Bonds in Carbon Nanotubes as Energy Carrier



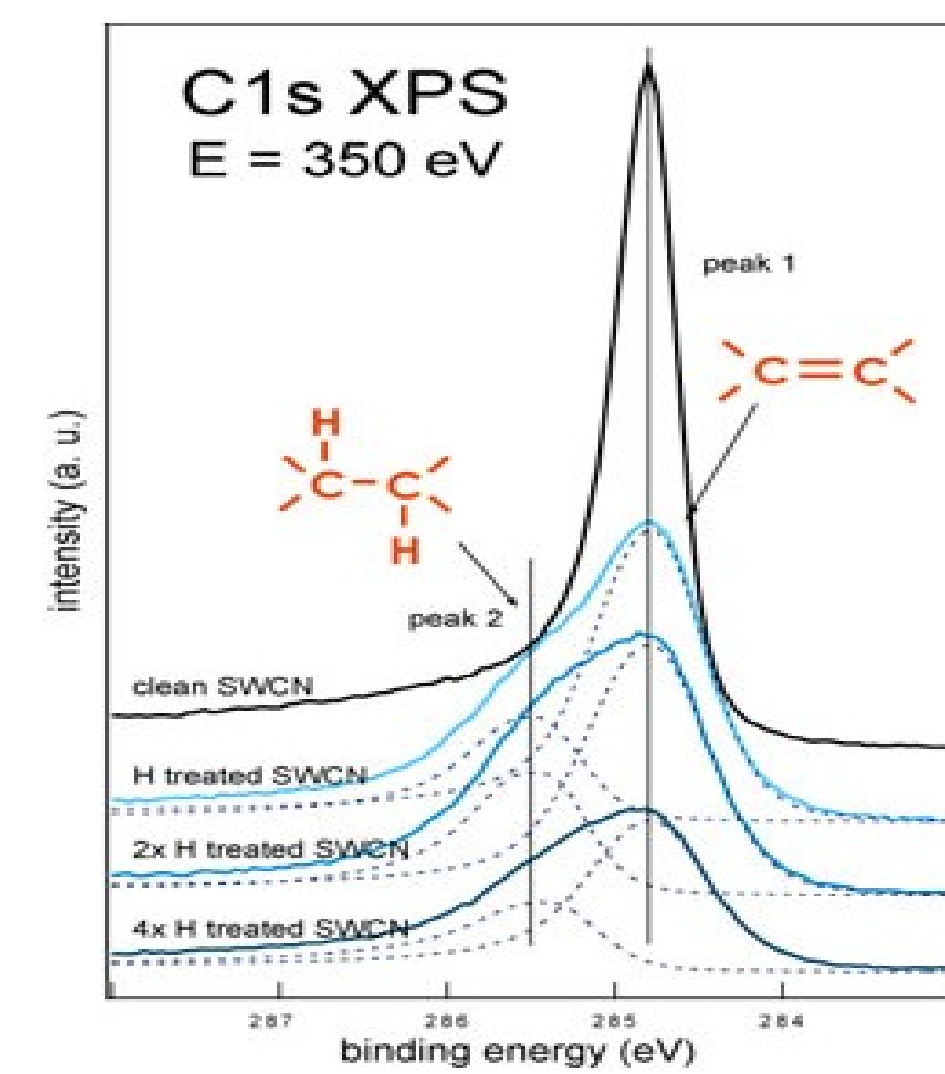
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Introduction

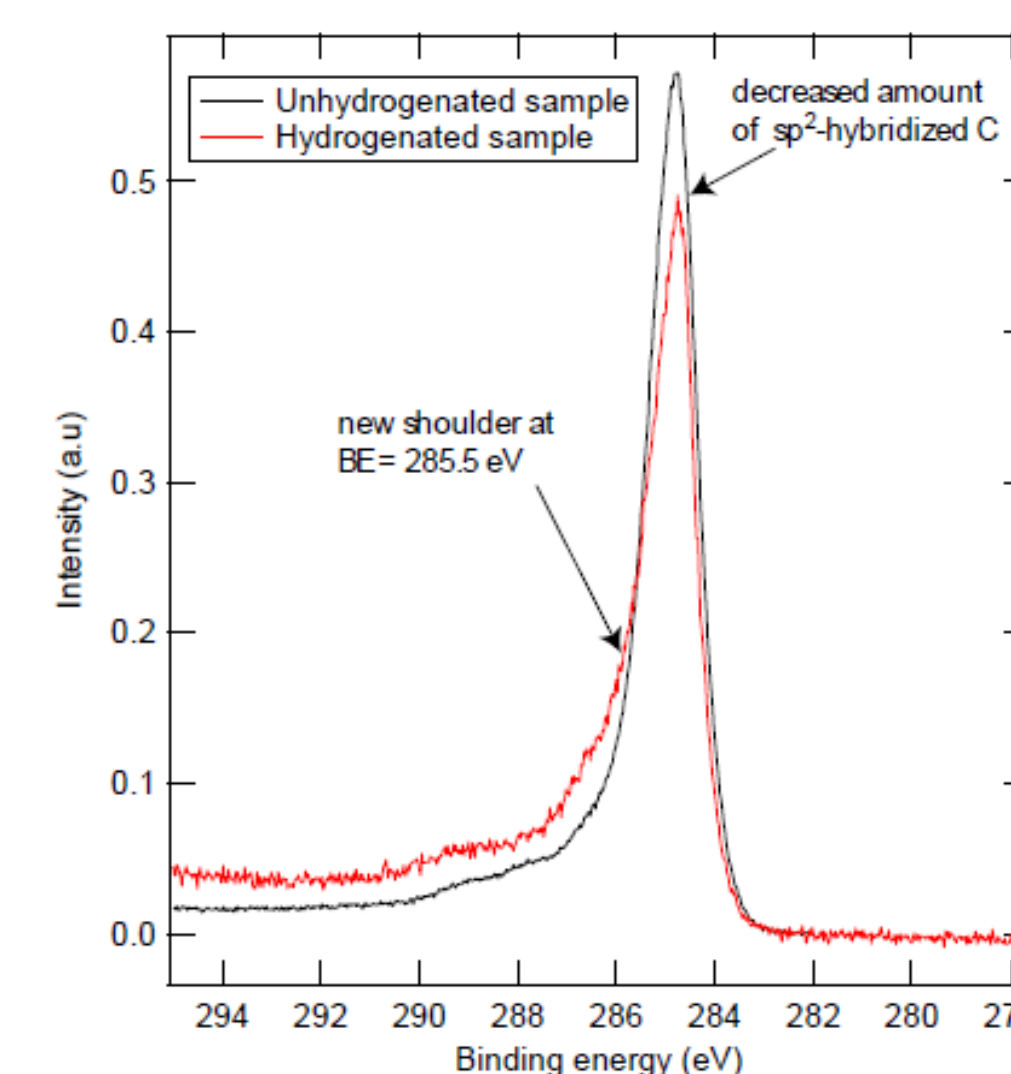
- Carbon nanotubes because of its high surface area and low weight could be used to store hydrogen.
- It was found by our group (previous GCEP project) that Carbon nanotubes react with atomic hydrogen and up to 7 wt% hydrogen uptake could be achieved [1].
- Molecular hydrogenation of carbon nanotubes at high pressure and electrochemical possibility of hydrogenation of nanotubes with catalyst (platinum) deposit are investigated in this project.



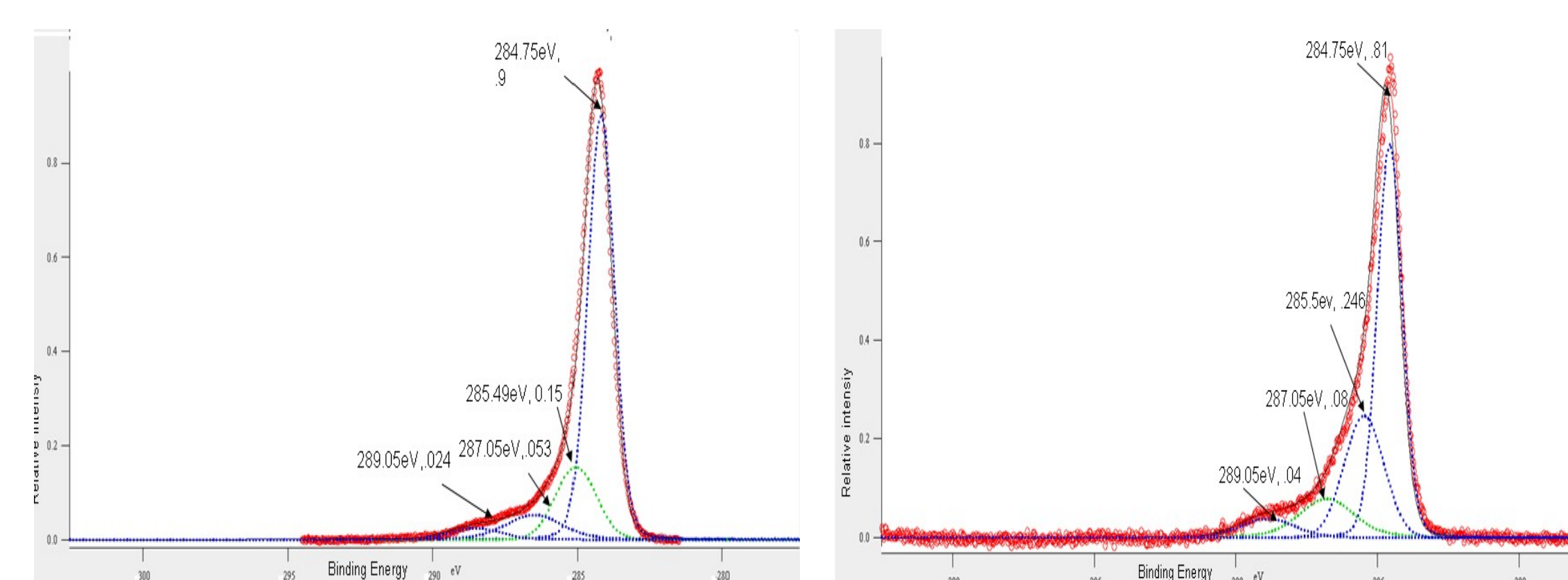
C1s XPS spectra measured during the hydrogenation sequence of SWCNT[1]

C-H bond formation through molecular hydrogen

- Thin LB films (sputtered with 5Angstrom Pt) were applied to 120psi pressure of molecular hydrogen.
- Carbon 1s X-ray Photoelectron Spectroscopy was studied at beamline 13-2 in SSRL.
- C sp² peak occurs at 284.75eV and sp³ peak at 285.5eV.
- A shoulder is seen when XPS of sample exposed to hydrogen is compared with the XPS taken before exposure. (peak fitting of this peak indicated the shoulder is because of another peak at 285.5eV), which could be attributed to hydrogenation of the sample.

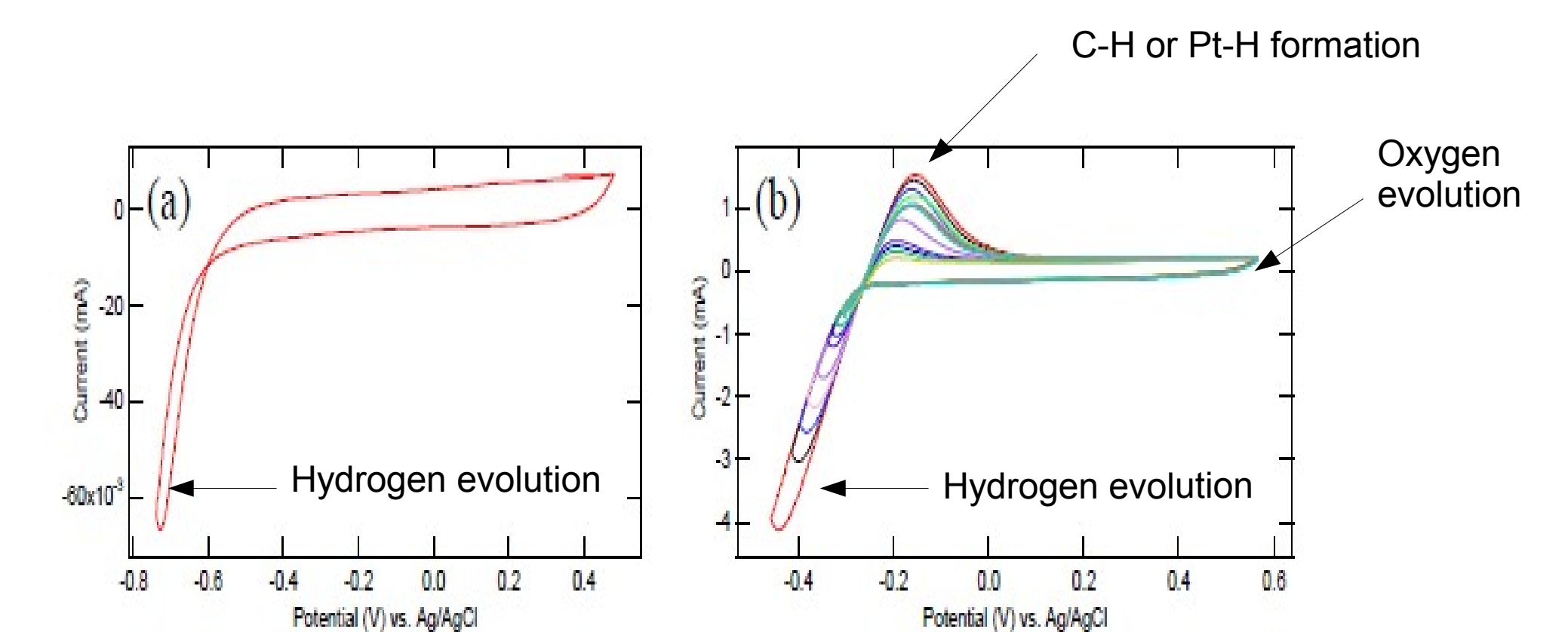


C1s XPS peak of hydrogen exposed sample compared with unexposed sample (above). Peak deconvolution of C1s peak of sample (below left) and that exposed to hydrogen (below right)



- 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.

Electrochemical Hydrogenation

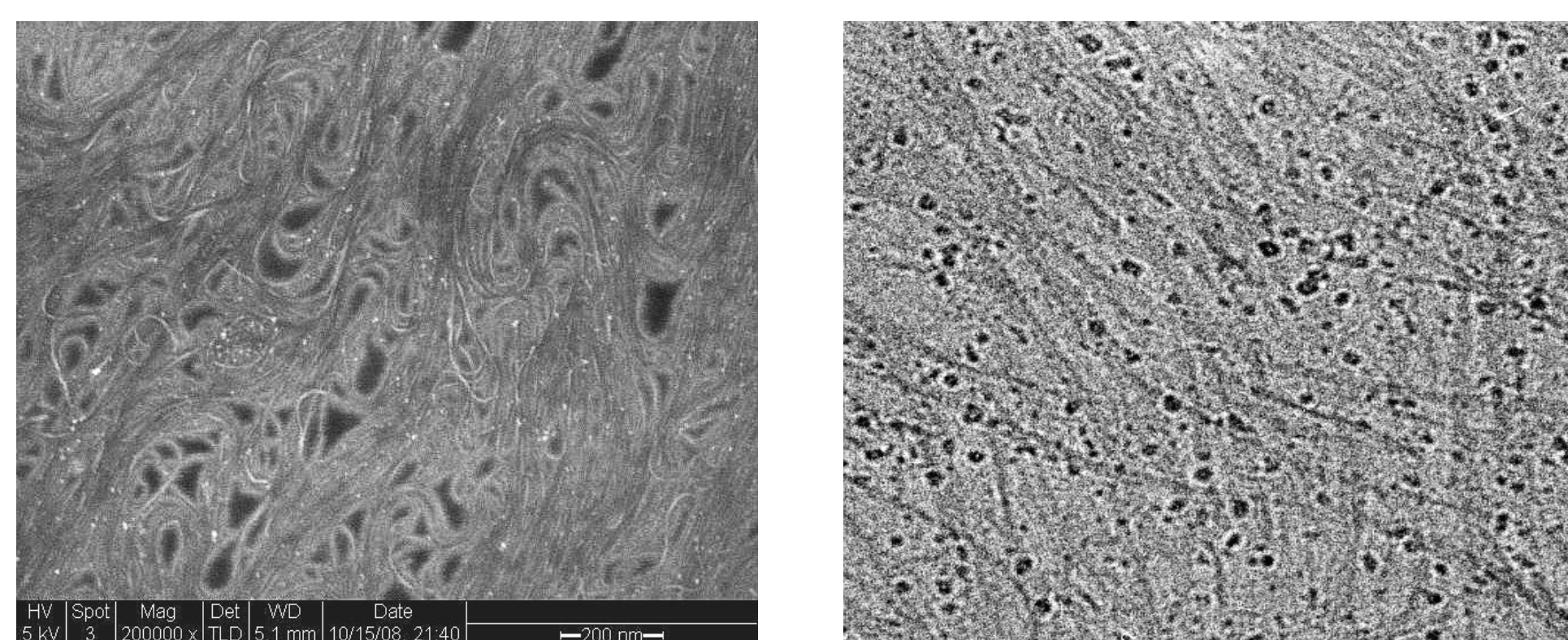


Cyclic voltammograms of (a) Pt-free and (b) Pt-modified HiPCO nanotubes in 0.05M sulphuric acid, dE/dT=10mV/s, (b) Different colors indicate different lower potential limits.

- Hydrogen reduction happens at -0.8V for Pt-free sample while it happens at -0.4V for sample with Pt.
- A positive current peak (hydrogen oxidation) is seen only in sample with Pt and this peak increases with the decreasing cathodic potential limits. Could possibly mean formation of C-H bonds.
- 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

Sample Preparation

- HiPCO tubes were suspended in DCE with conjugate polymer PmPV and then centrifuged and filtered.
- Langmuir Blodgett (LB) Films were prepared using the method described in reference [2].
- LB films were then sputter deposited with different thickness of Platinum (2Angstrom to 8Angstrom).



SEM (left) and TEM (right) images of LB films sputter deposited with 5Angstrom of Pt

Conclusions

- We have thus achieved a proof of principle for the proposed spillover mechanism which could be used for hydrogen storage

Future work

- We will characterize electrochemically hydrogenated samples using XPS for the spill over process.
- We are currently developing an in-situ x-ray electrochemical cell for C1s x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) in electrochemical conditions.
- We plan to also improve the amount of nanotube hydrogenation by exposure to higher H₂ pressures up to 100bar.

References

- A.Nikitin et.al Hydrogenation of Single-Walled Carbon Nanotubes, PRL 95, 225507 (2005)
- X.Li et.al "Langmuir-Blodgett assembly of densely aligned single-walled carbon nanotubes from bulk materials , JACS, 129 (16) (2009)

Acknowledgements

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