Robert Schlögl Fritz-Haber-Institut der MPG

NANOSTRUCTURED CARBON AS HETEROGENEOUS CATALYSTS

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FUNDAMENTALS

Some Facts about "Carbon"

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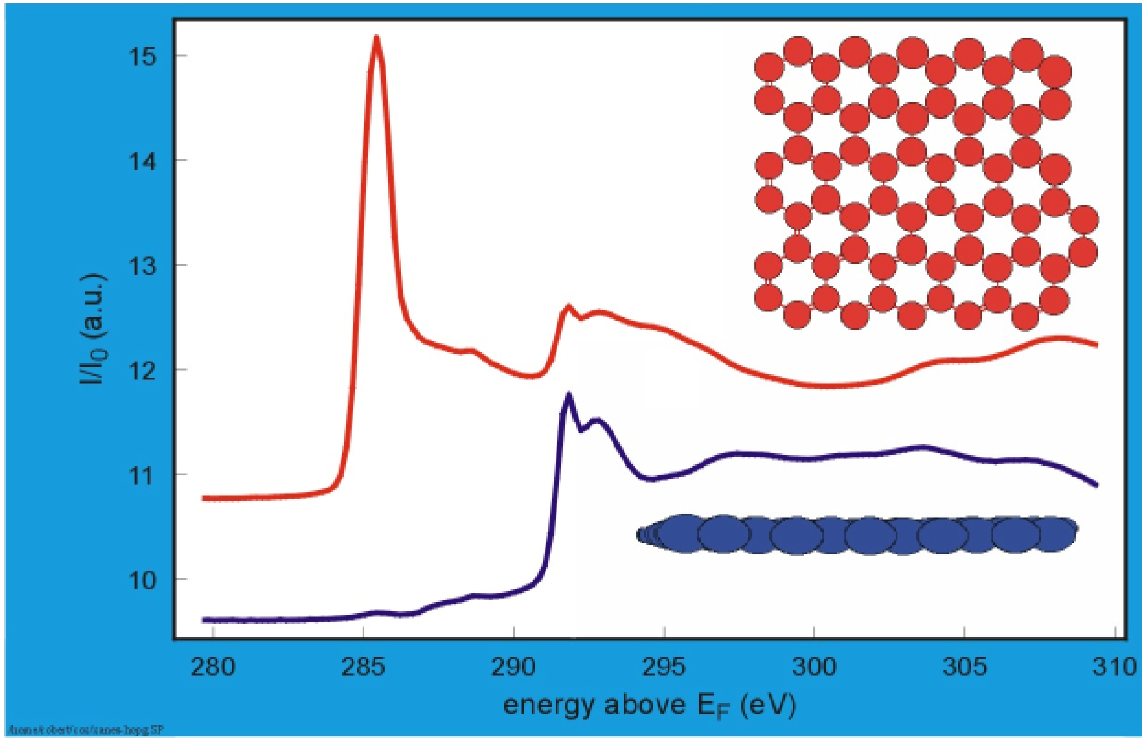
Anisotropy



There is no other material than graphitic carbon showing such pronounced electronic structural anisotropy resulting from the anisotropy of the sp^2 bonding: only the (blue) prism face is reactive, the (red) basal plane is inert

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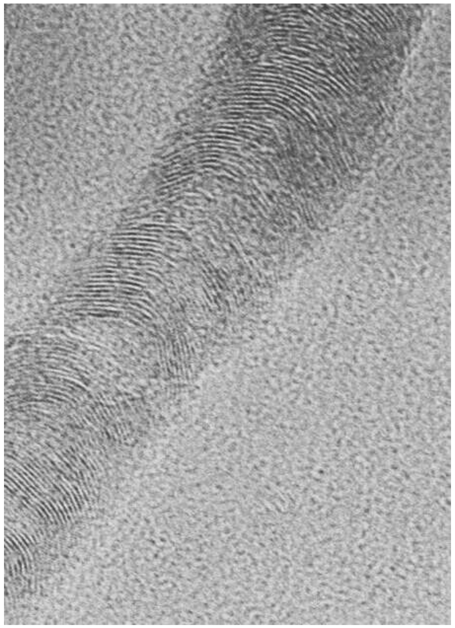
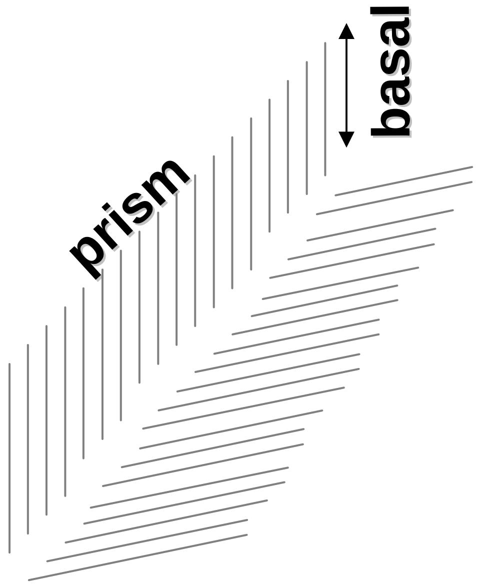
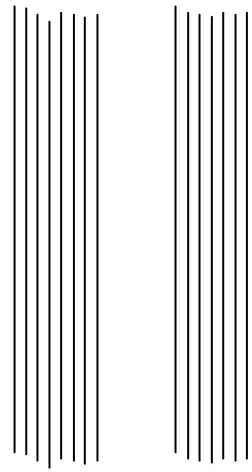
Nanostructured anisotropy

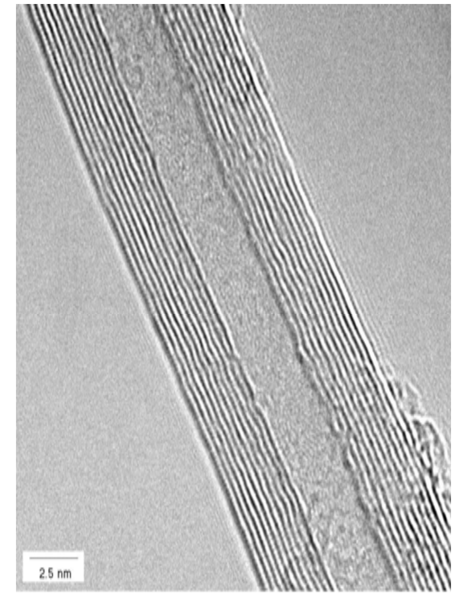




herring
bone
CNF

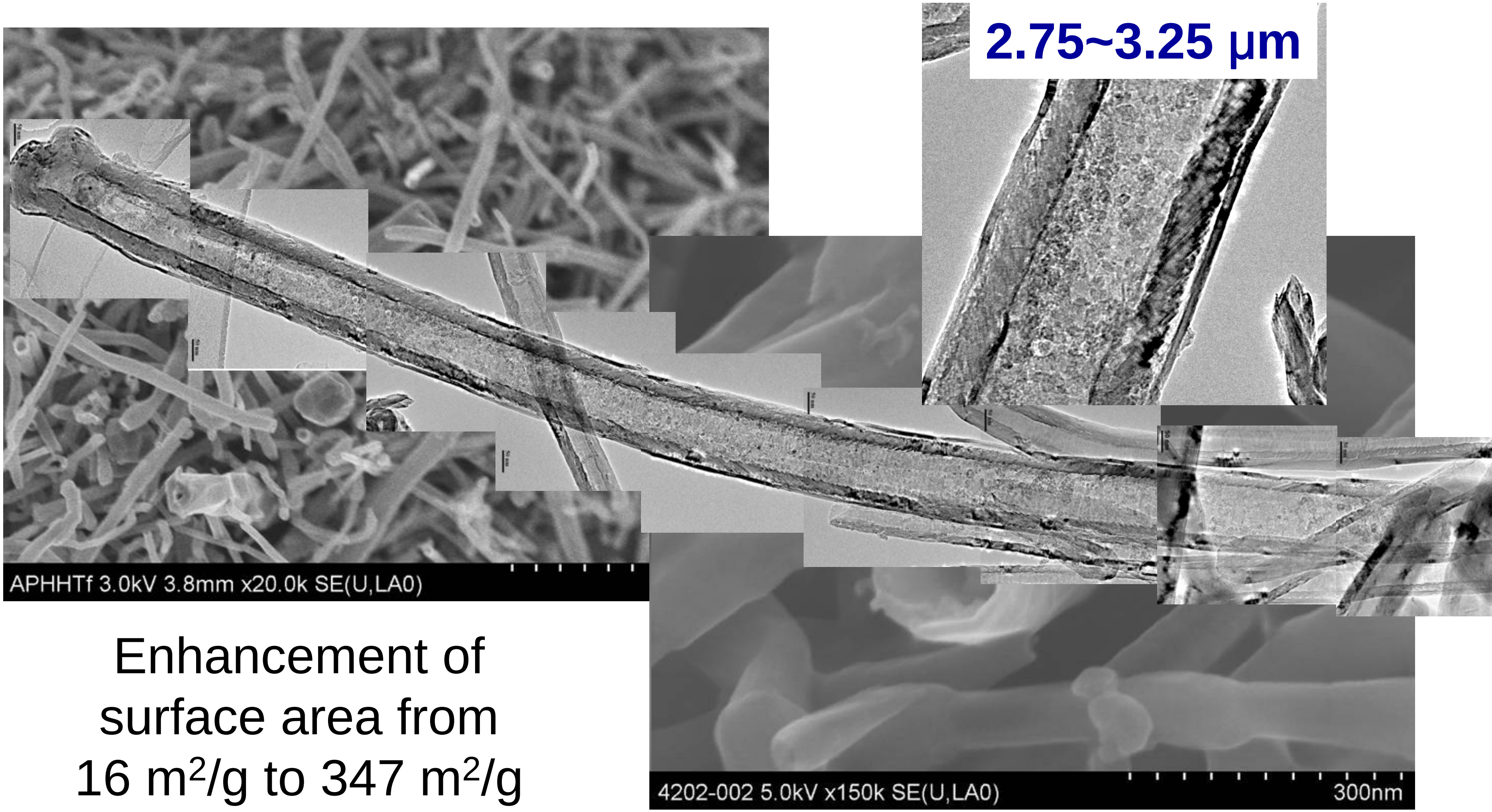


multiwall
CNTs



Nanostructures allow flexibiliy in controlling anisotropy

Graphitic CNT with high surface area



Enhancement of surface area from $16\ m^2/g$ to $347\ m^2/g$

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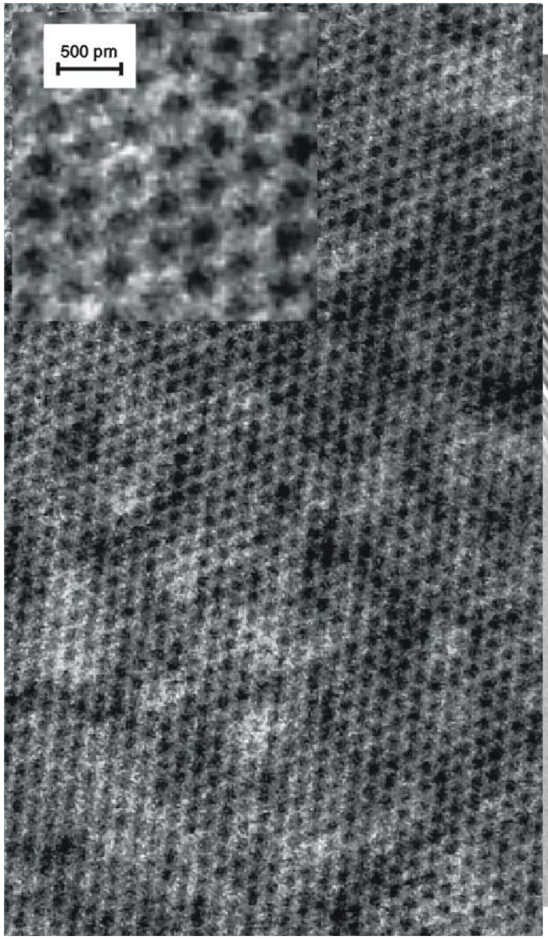
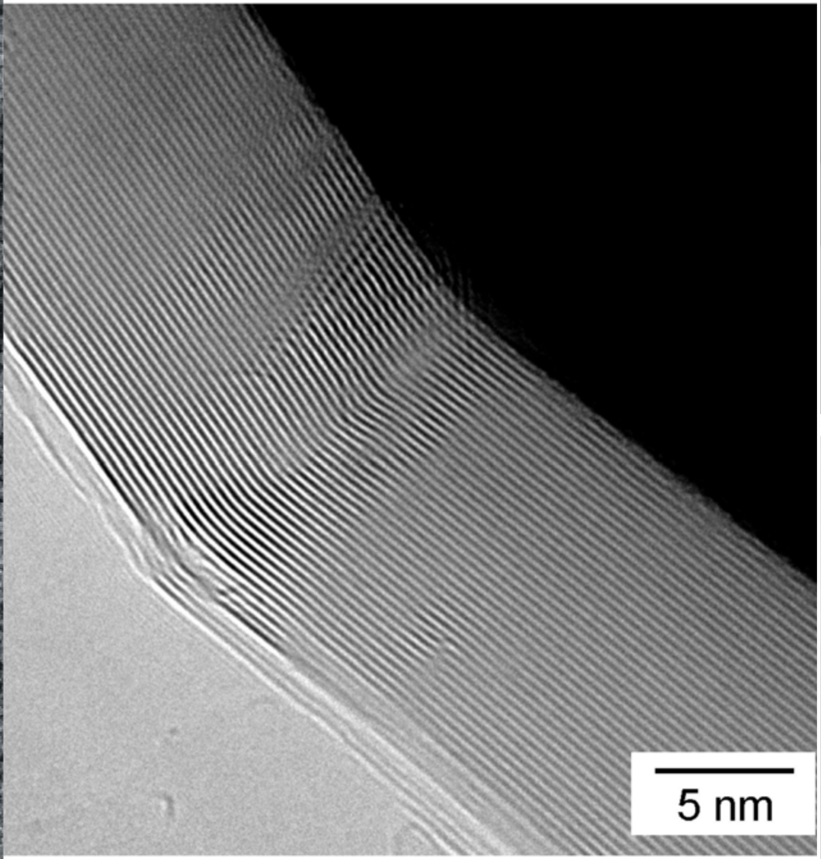
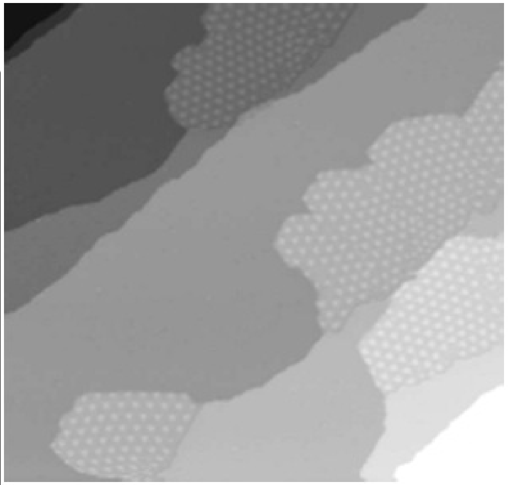
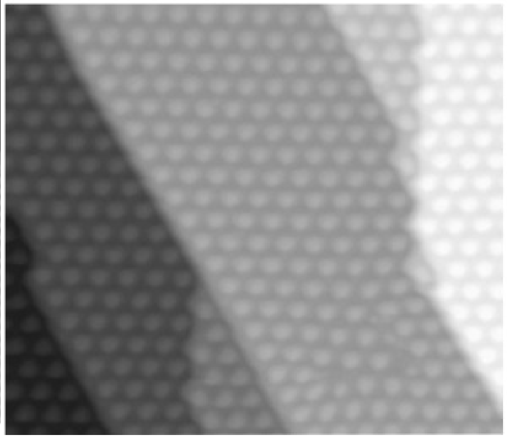
Graphene









100 x 100 nm
Wintterlin et al, PRB, 76, 2007

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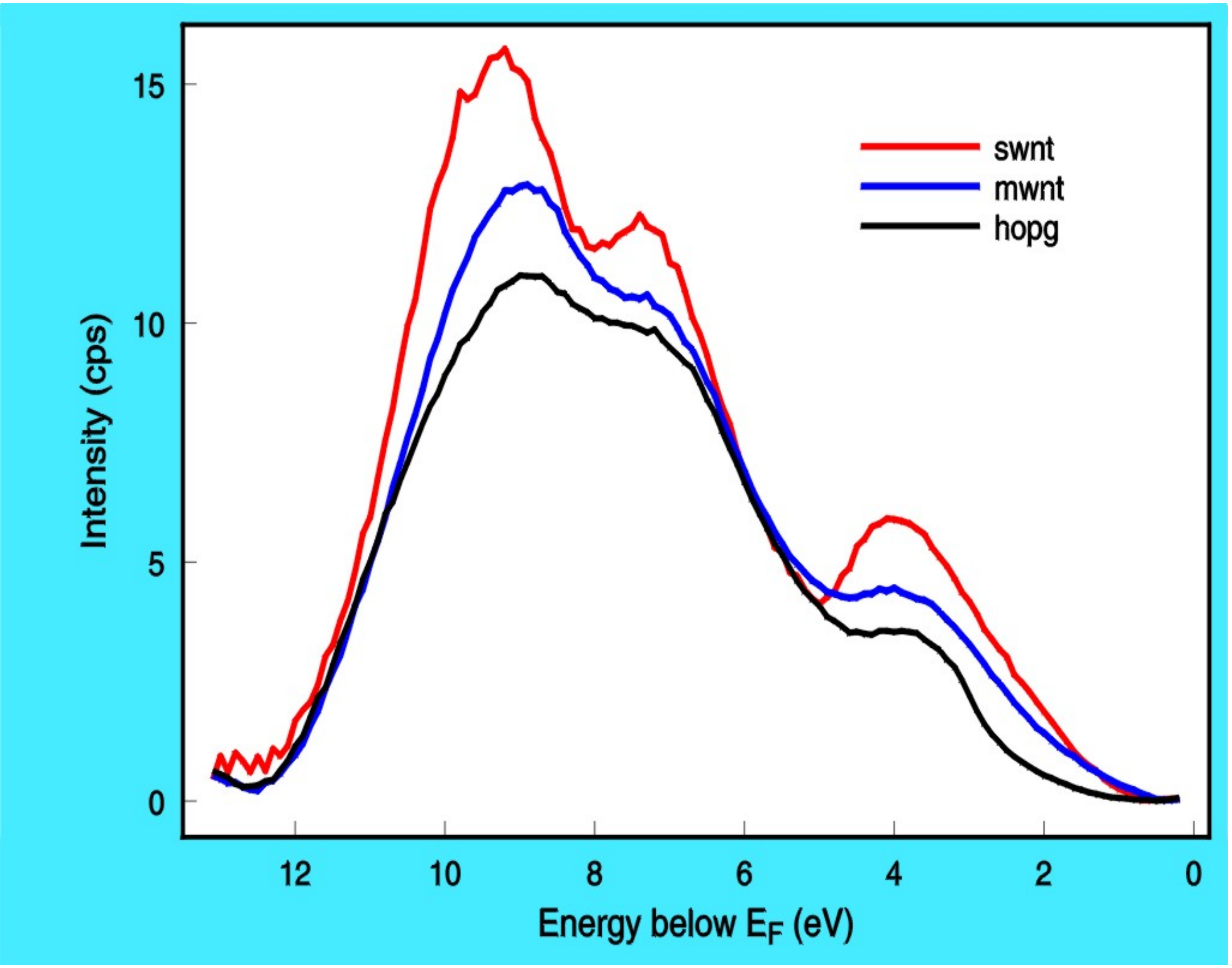
The electronic structure issue



Bending with decreasing diameter causes localization of π states enhancing artificially the “density of states “ of the semimetal graphite

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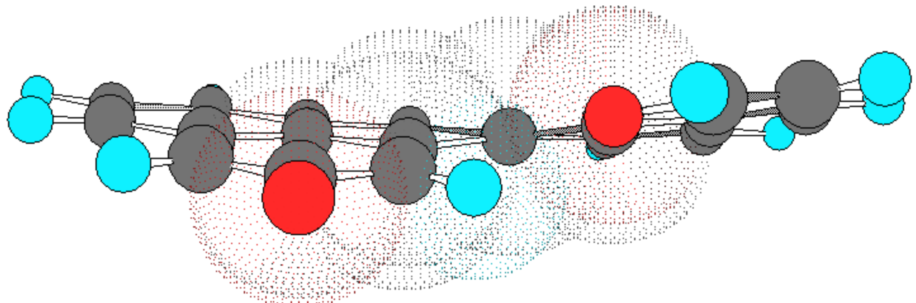
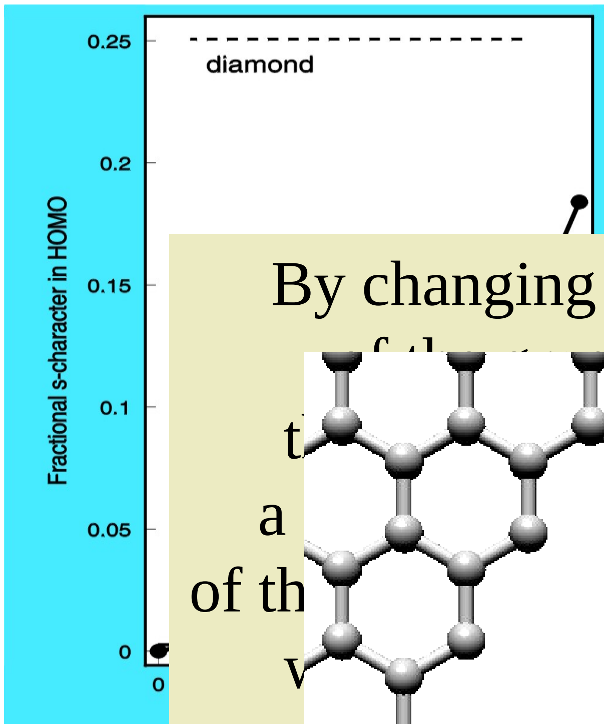
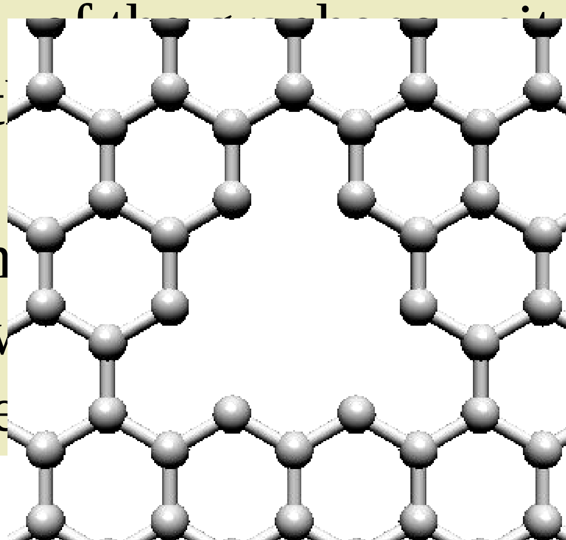
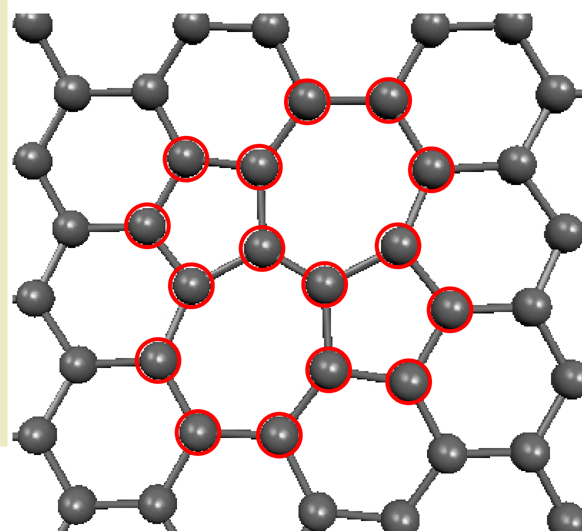
Concept: Tune the C-O bond properties



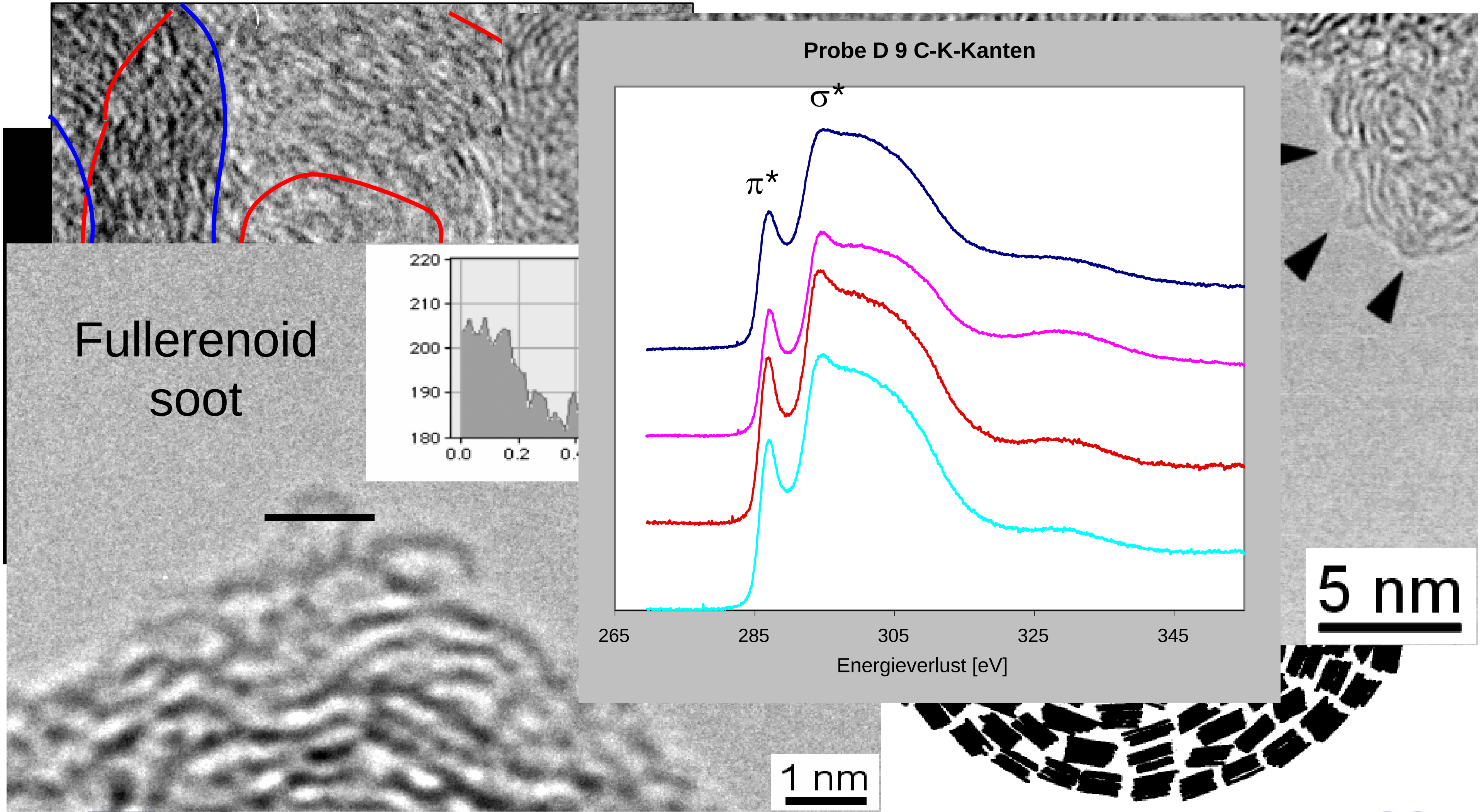


By changing the bending
t... g
a ... on
of th ... bonds
v... l
re... es.





Soot and soot II



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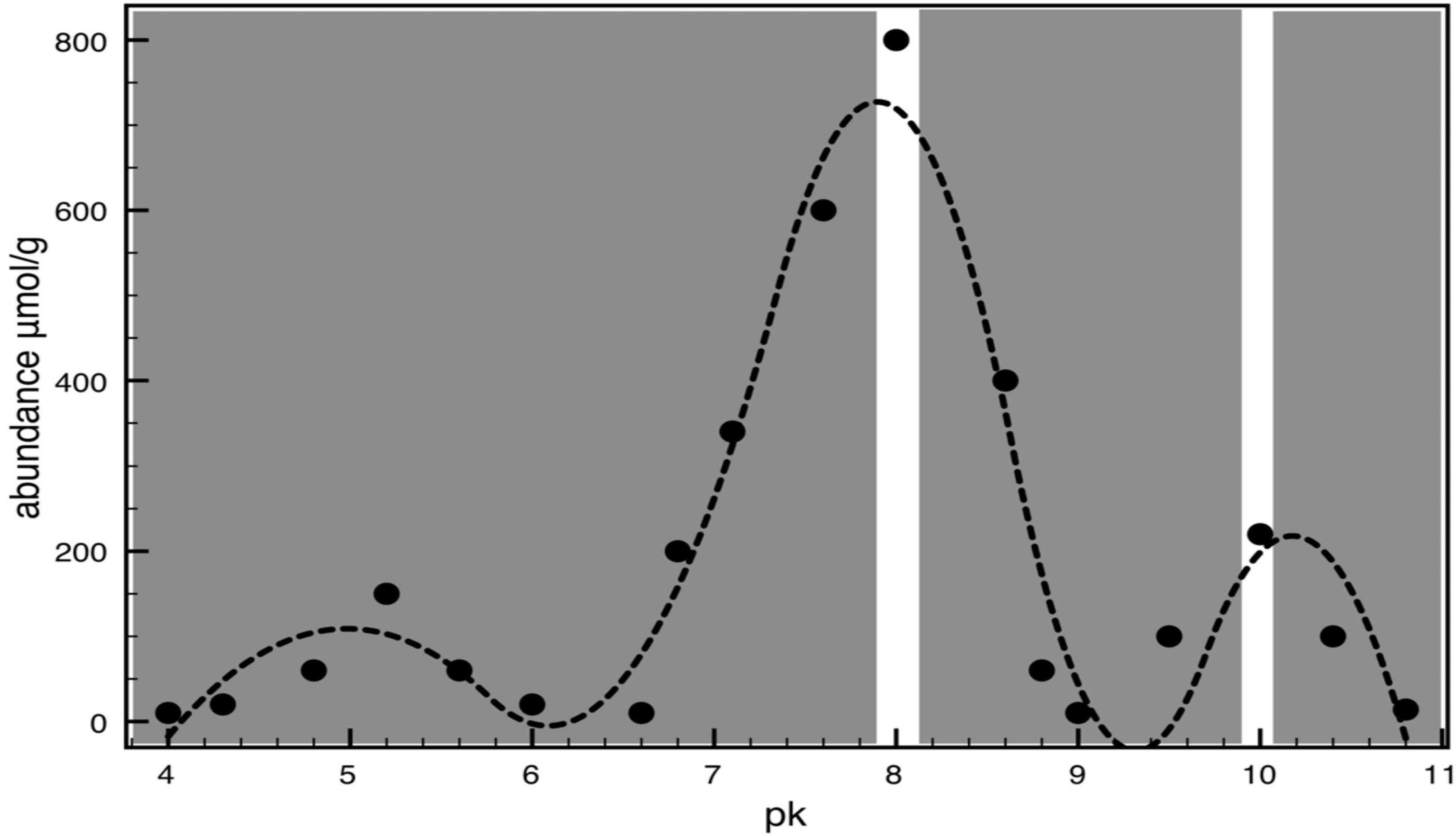
Acid-base groups



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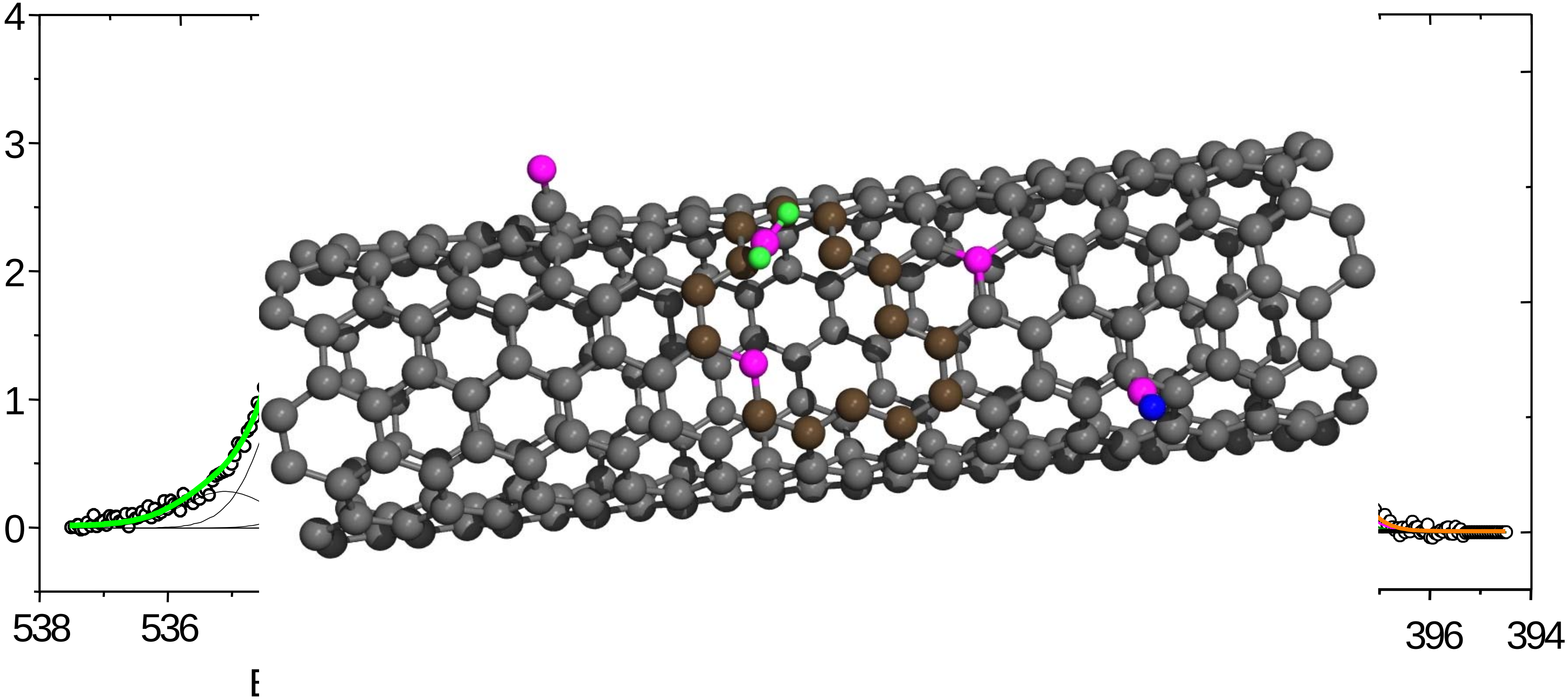
Surface functional groups



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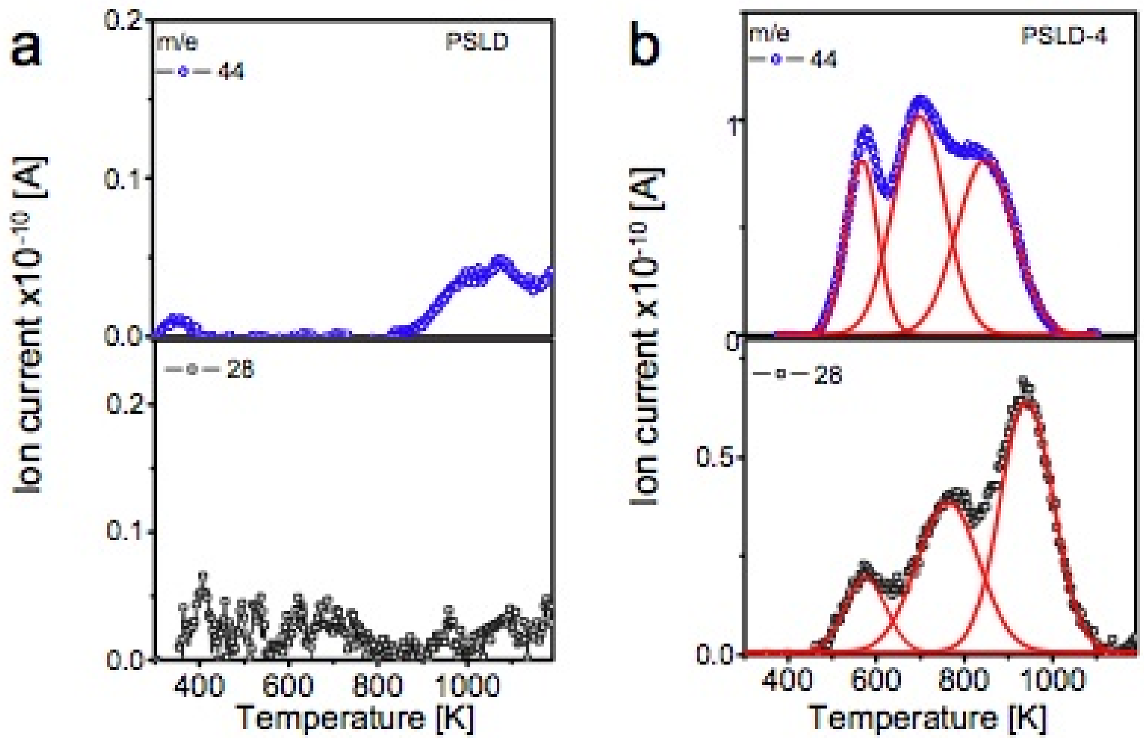
Synthesis of oxygen functional groups



High resolution TPO through slow heating rate and back-mixing-free operation

The combination of fluid phase oxidation followed by calcination to 600 – 900 K generates a specific set of OH-groups

PSLD CNT

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The Li C interaction
Li: a chameleon of chemical bonding

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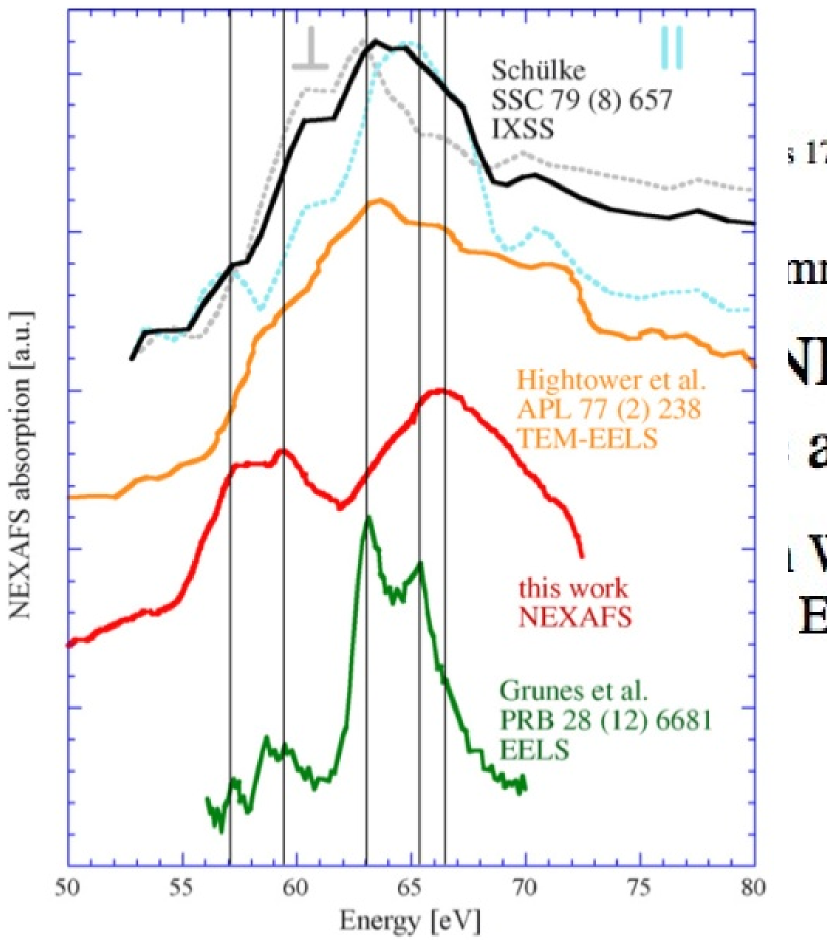
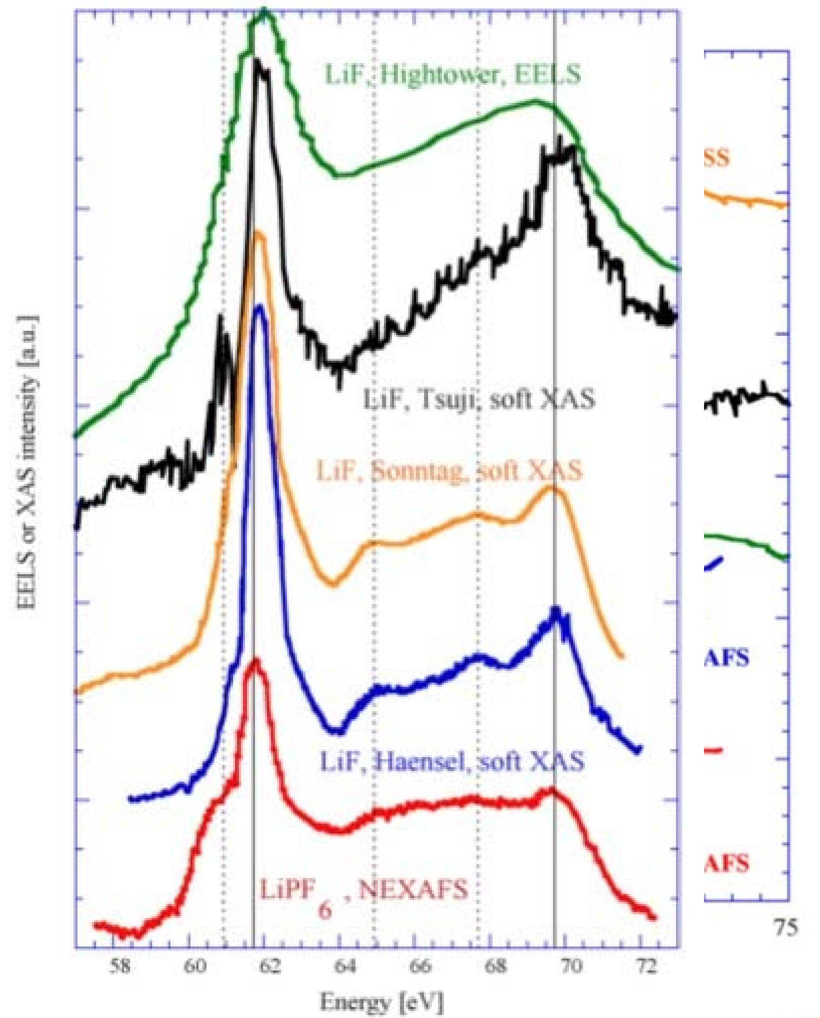
Nature of carbon Li interaction





NEXAFS a critical method

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Nature of Carbon Li interaction

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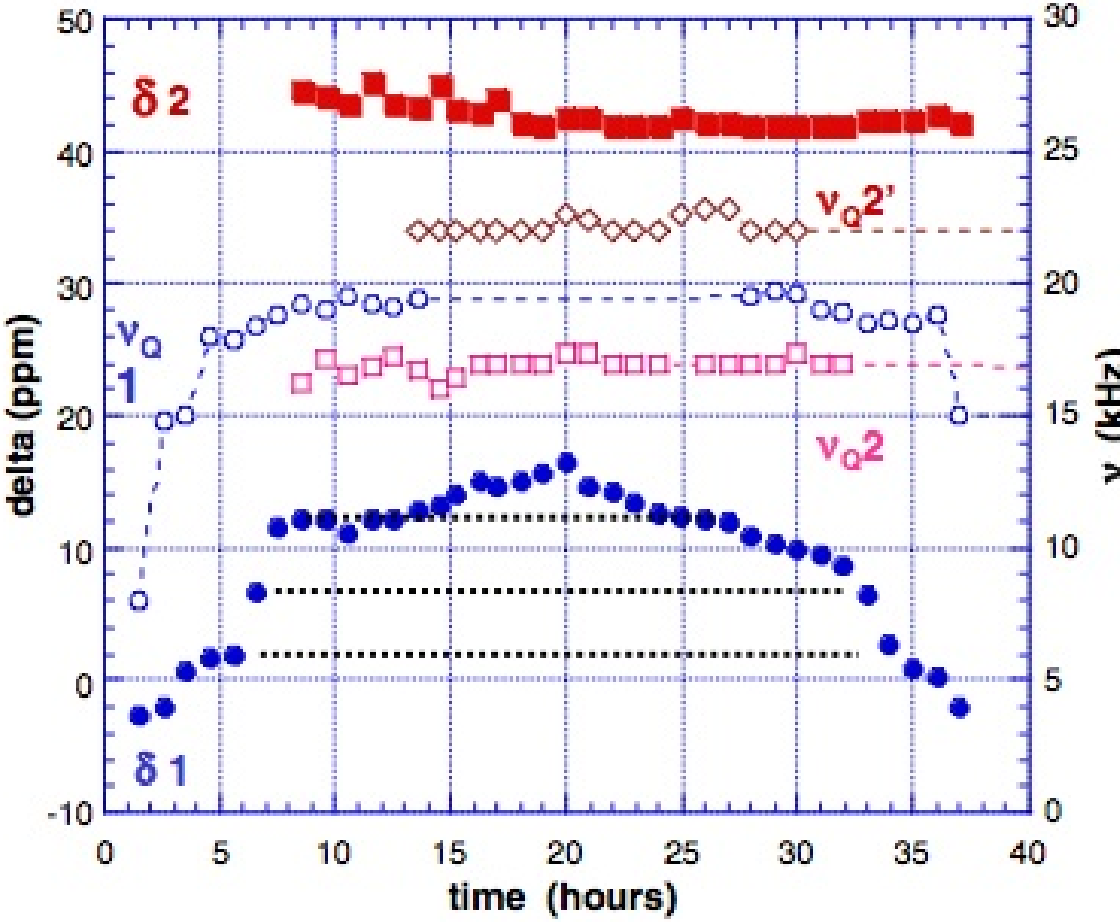
In



servation

l

ette [c]

NMR: co-existence of bonding states

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Nature of carbon Li interaction

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Carbon as Catalyst

metal-free heterogeneous catalysis

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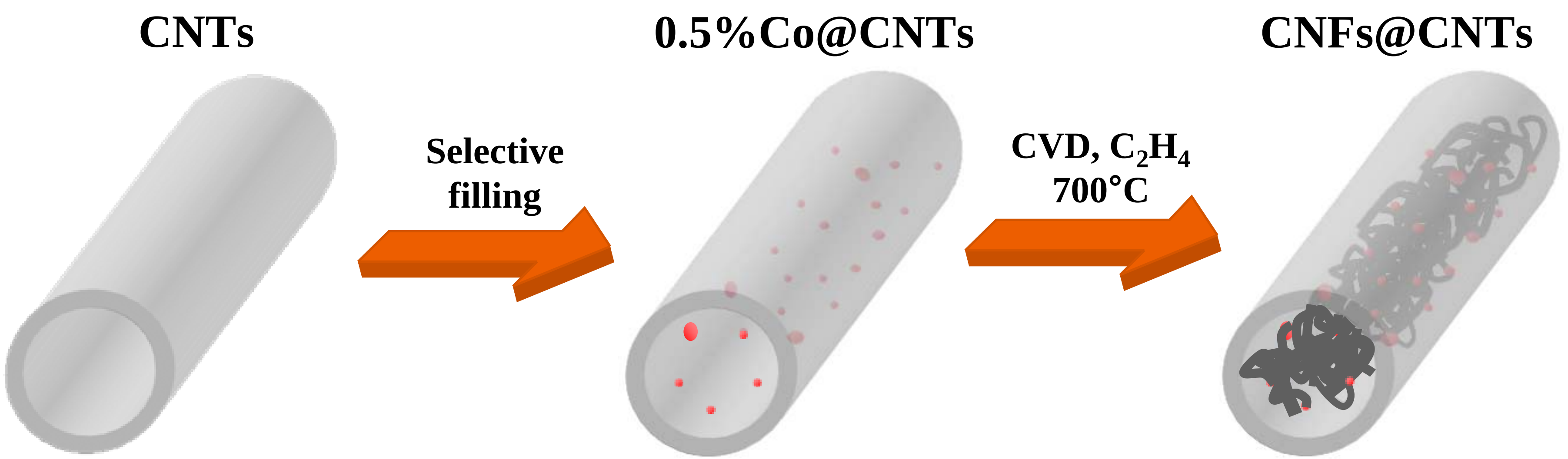
Nano-synthesis for Li-storage

CNFs@CNTs via CVD route



Technical Challenges:

1. Where do metal nanoparticles stay?
2. Can reactant diffuse inside of CNTs?
3. How big are the *children* CNFs

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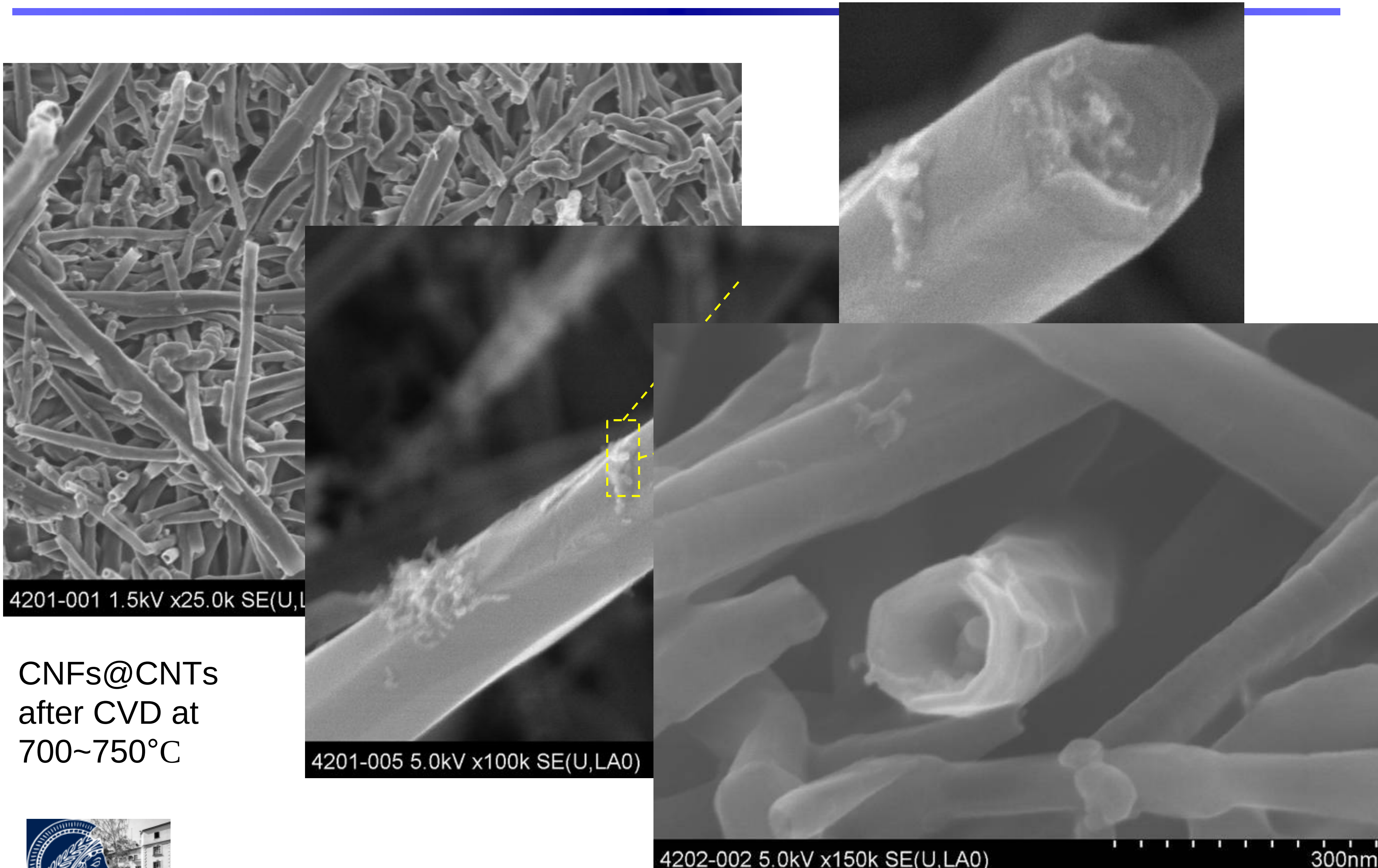
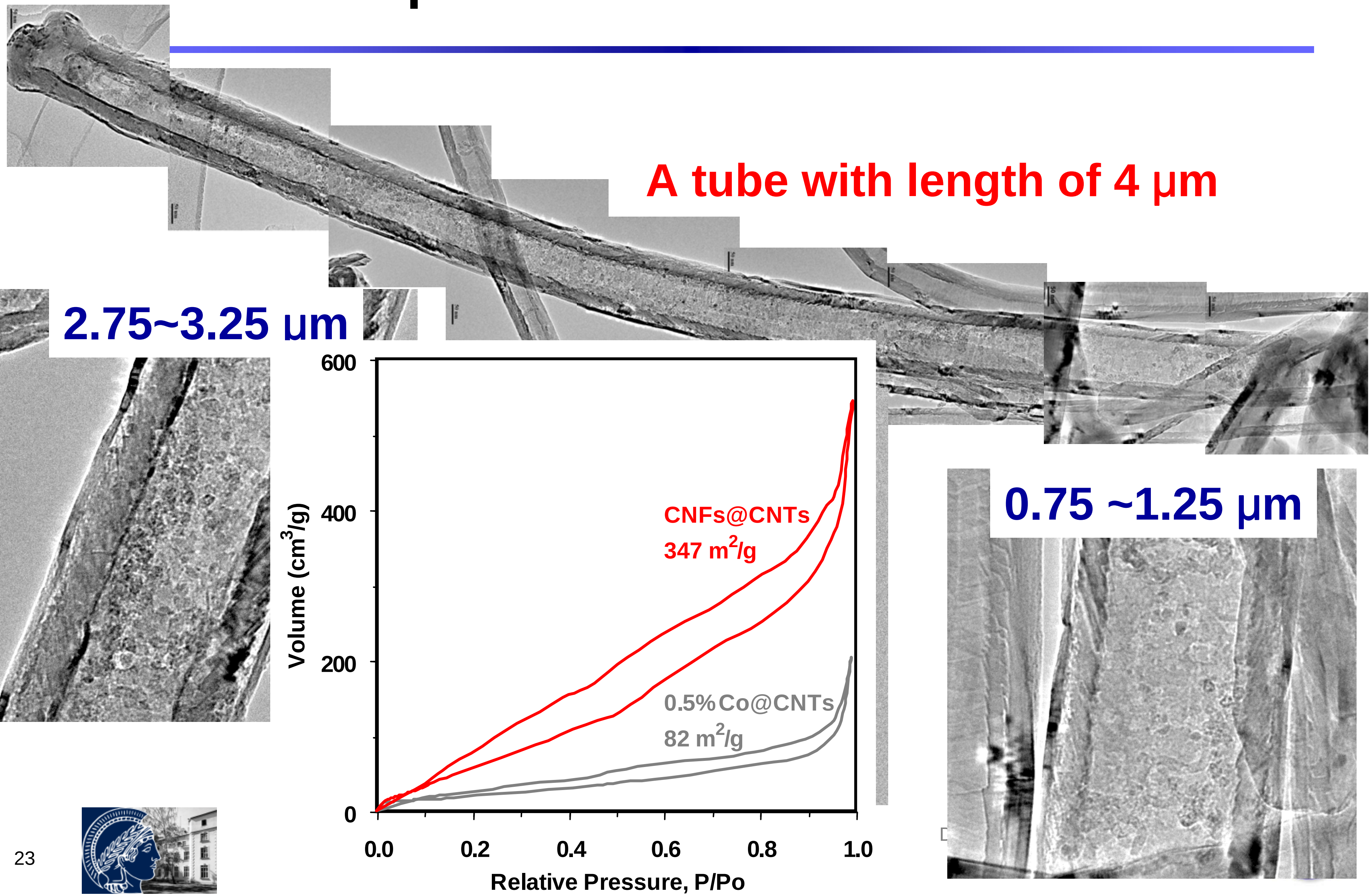
Analytics for controlled synthesis: Li storage

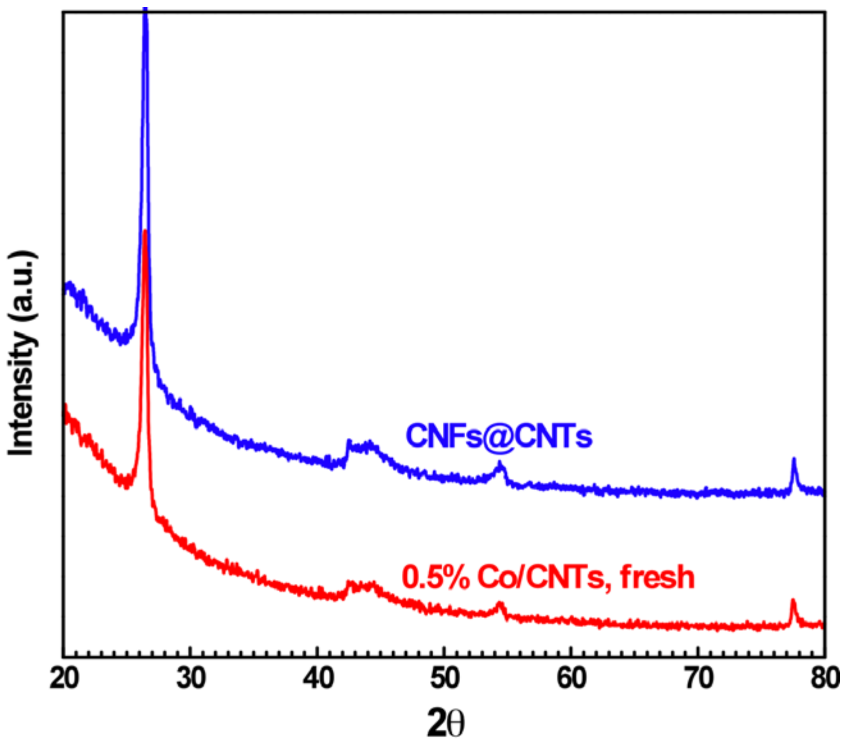


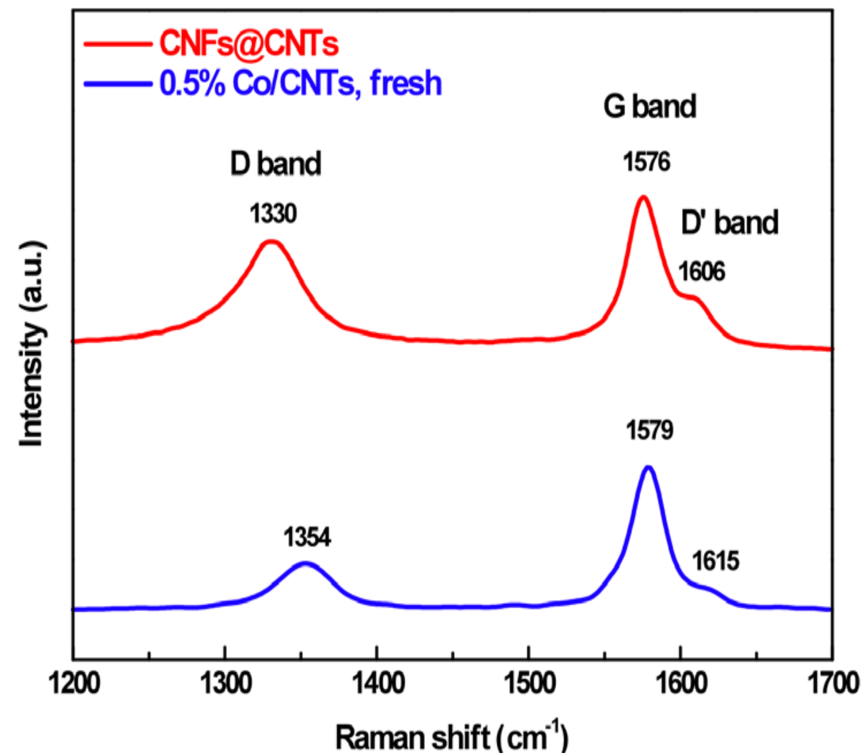
CNFs@CNTs
after CVD at
700~750°C

After optimization: a material



Structure of the C/C composite





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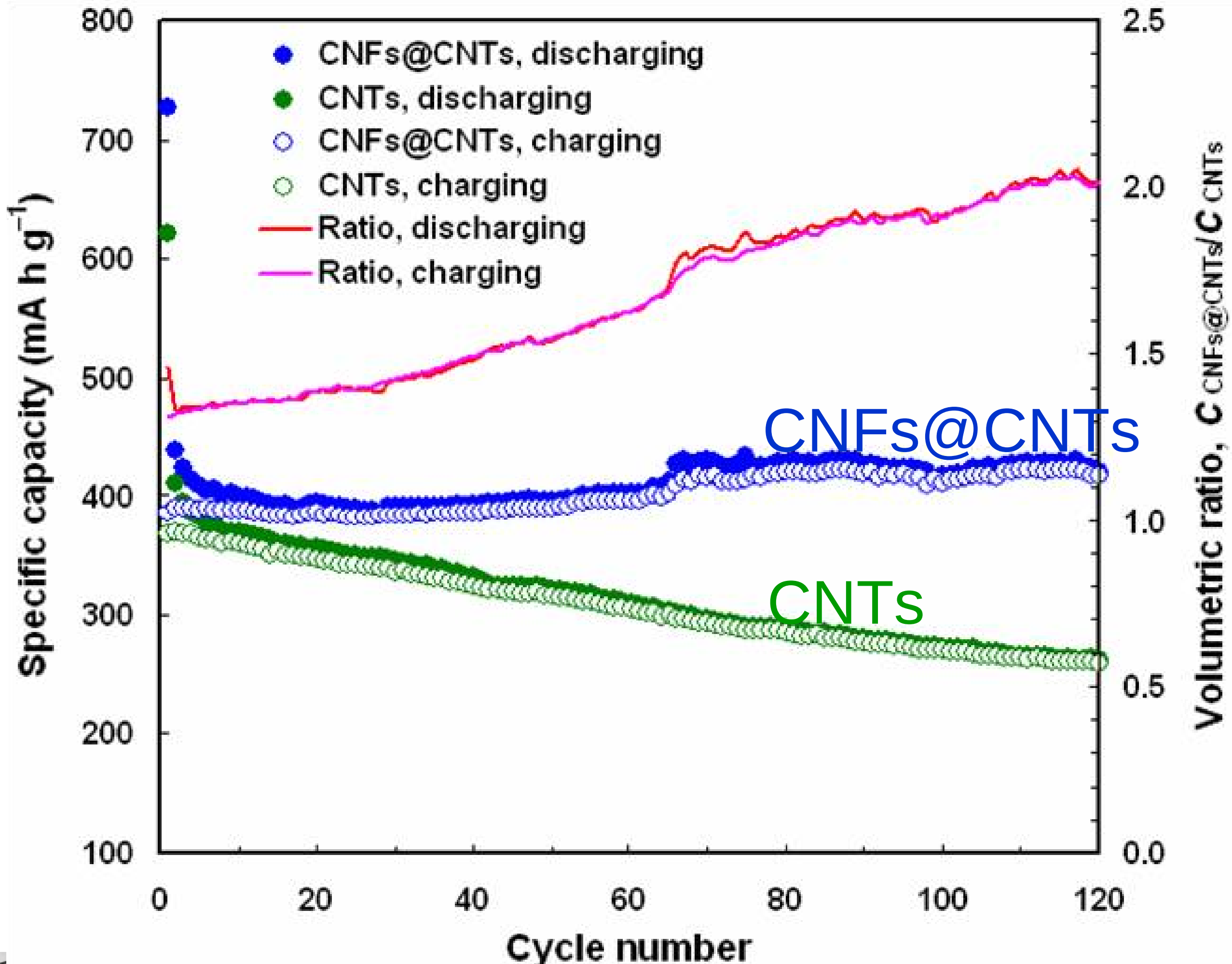
CNFs@CNTs in Li Batteries

Cycling stability in 1 M $LiPF_6$ in EC/DMC solution



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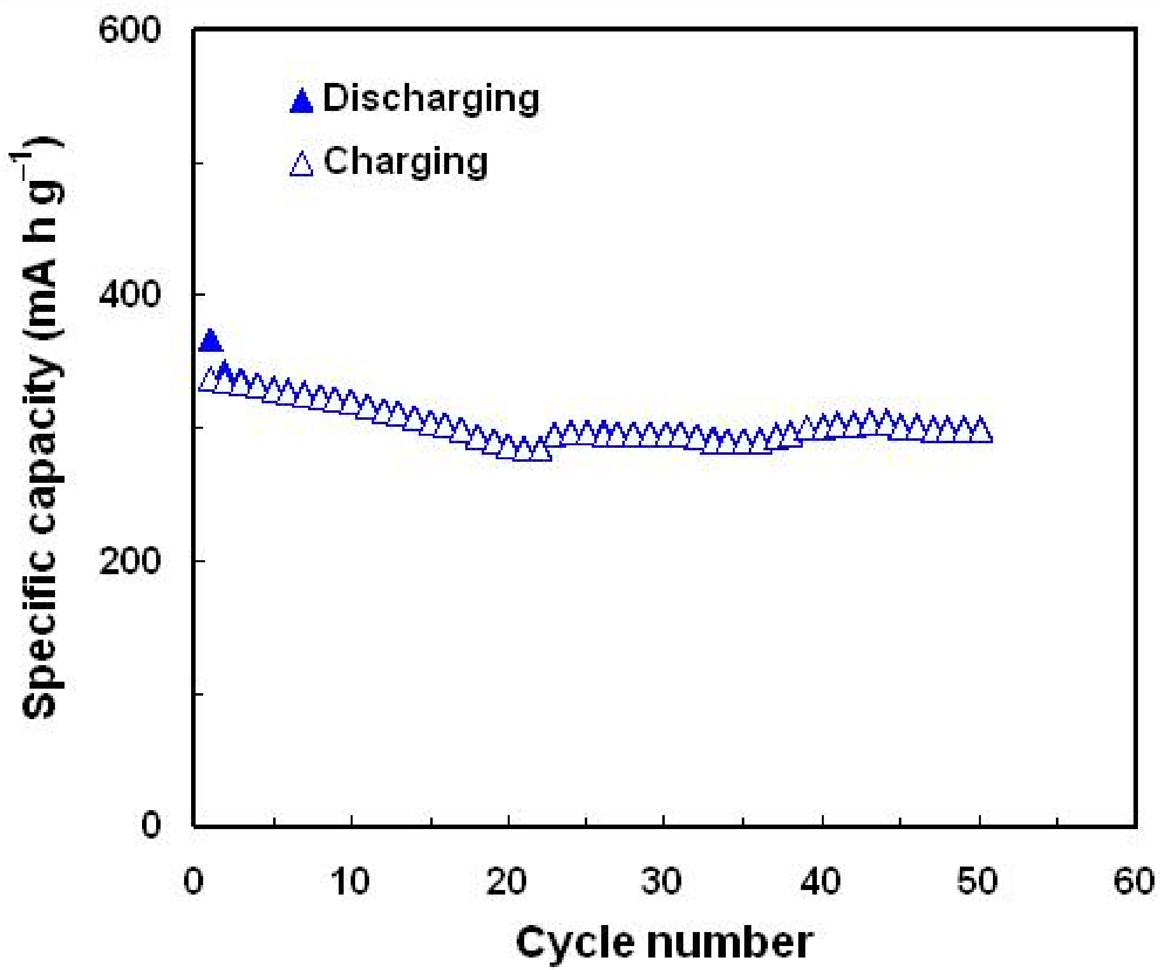
CNFs@CNTs in Li Batteries

Electrochemical stability of CNFs@CNTs in 1 M $LiPF_6$ in EC/DMC solution at 1C after 120 cycles at C/5



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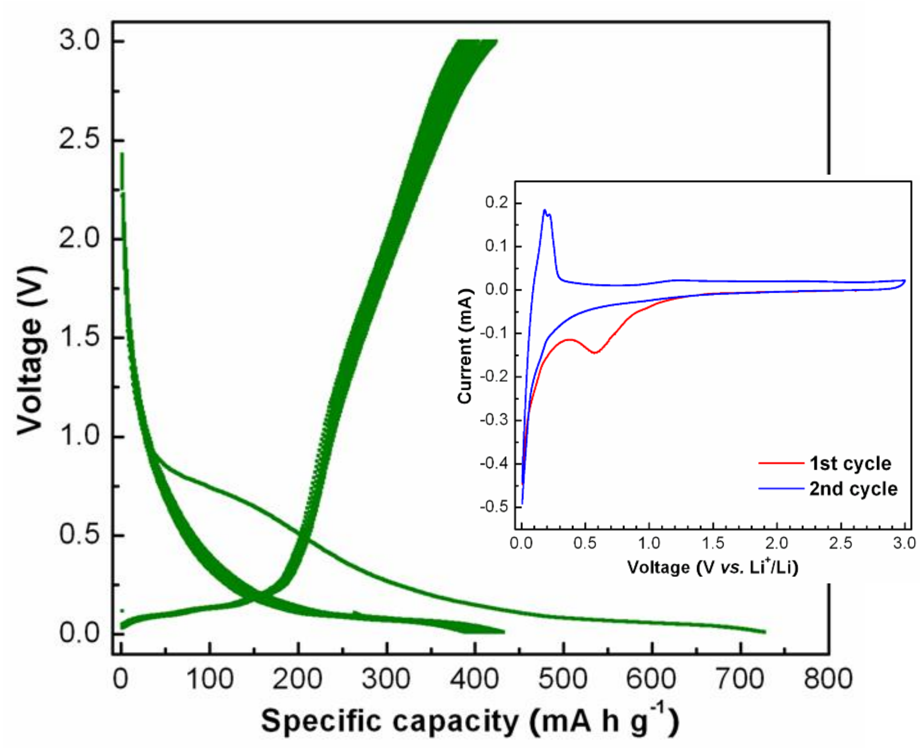
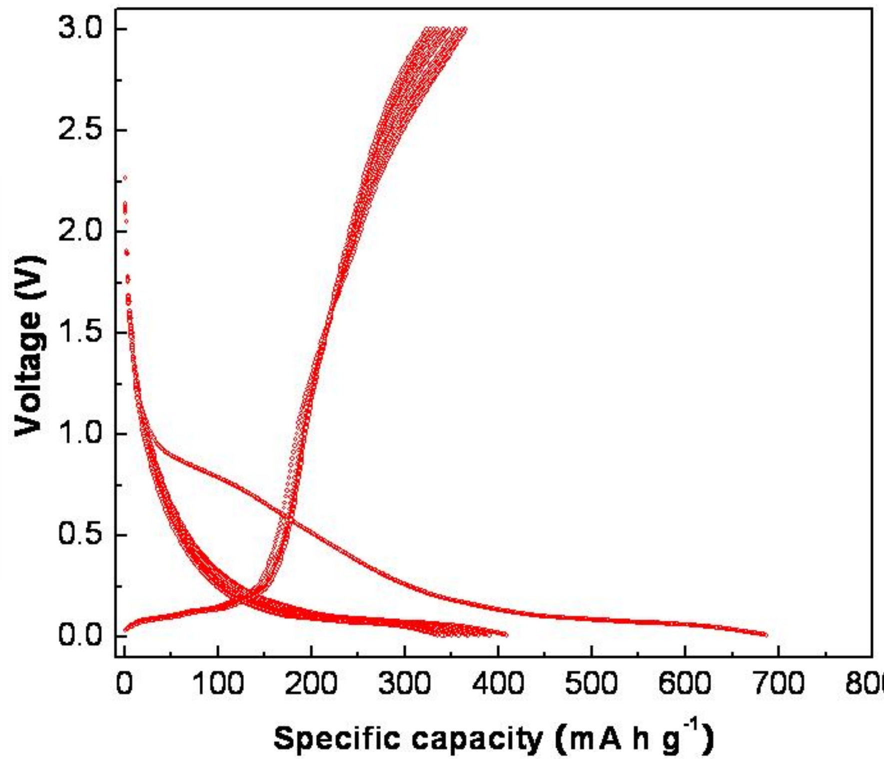
CNFs@CNTs in Li Batteries

Galvanostatic discharge curves of CNFs@CNTs (cycled at a rate of C/5)

in 1 M $LiPF_6$ in EC/DMC solution



in 1 M $LiClO_4$ in PC solution



Unlikely ethylene carbonate (EC), propylene carbonate (PC) is safe at low T.

PC solvent and the solvated Li^+ ions tend to co-intercalate into graphite, accompanied by severe exfoliation of graphite layers and thus destruction of structure !

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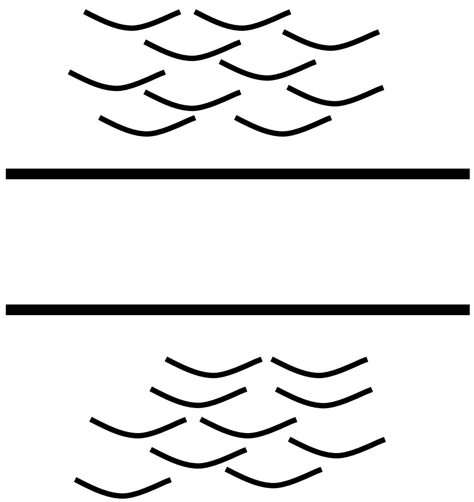
Novel Carbon-2: CTIT

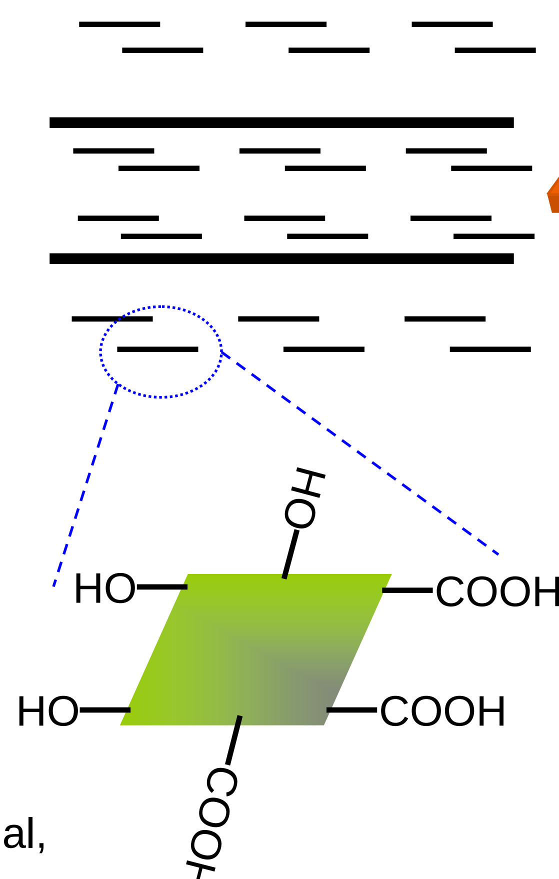
Carbon tube-in-tube via wet chemical assembly

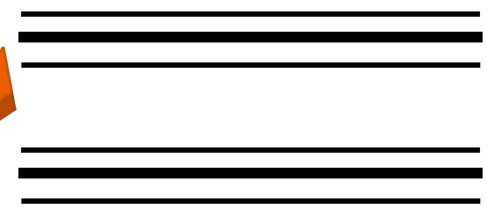
Pristine CNT

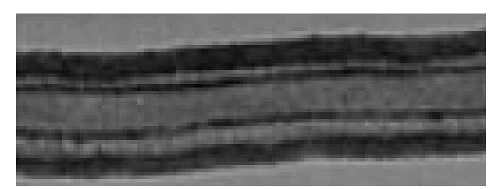
Functionalized

Tube-in-tube









Z.P. Zhu, D.S. Su, G. Weinberg, et al,
Small 1 (2005) 107

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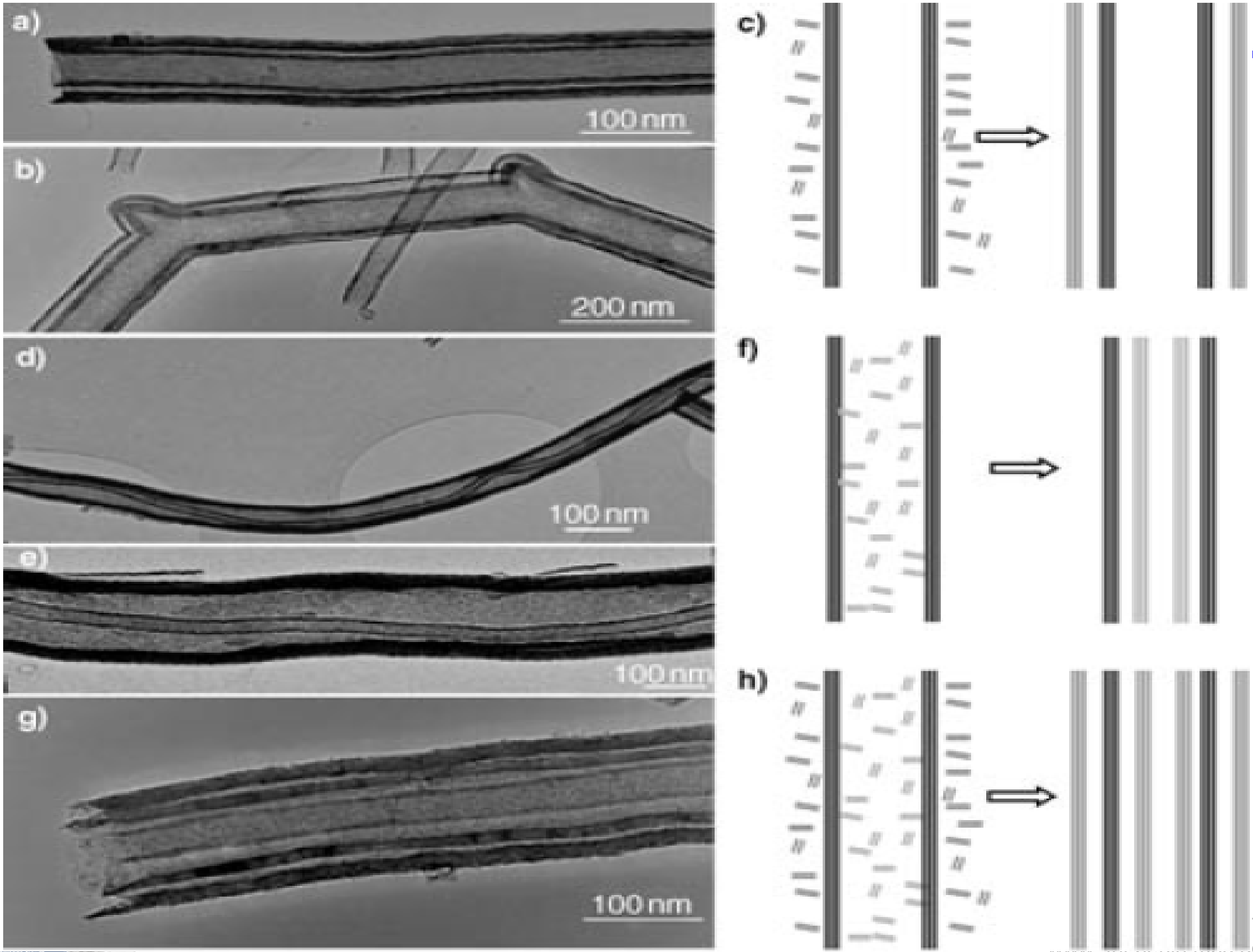
Carbon tube-in-tube (CTIT)



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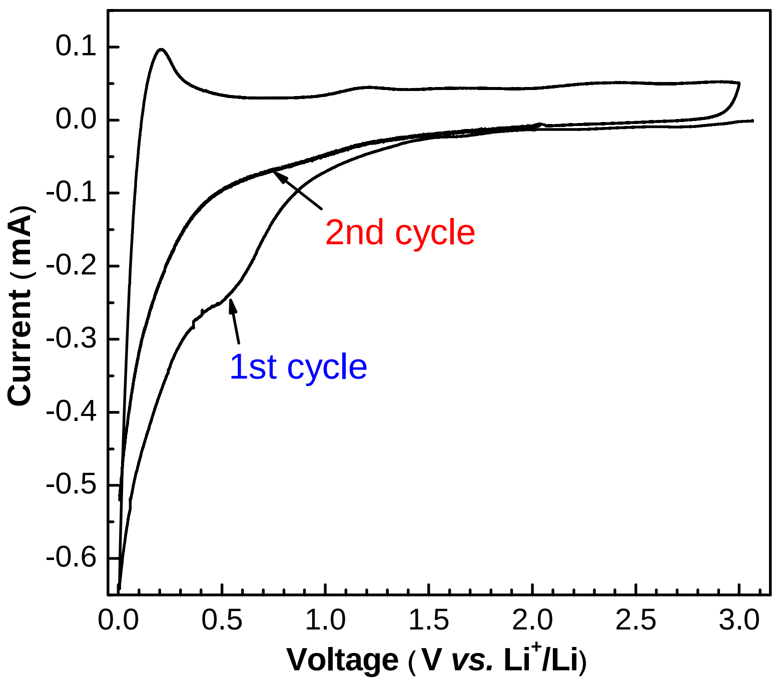
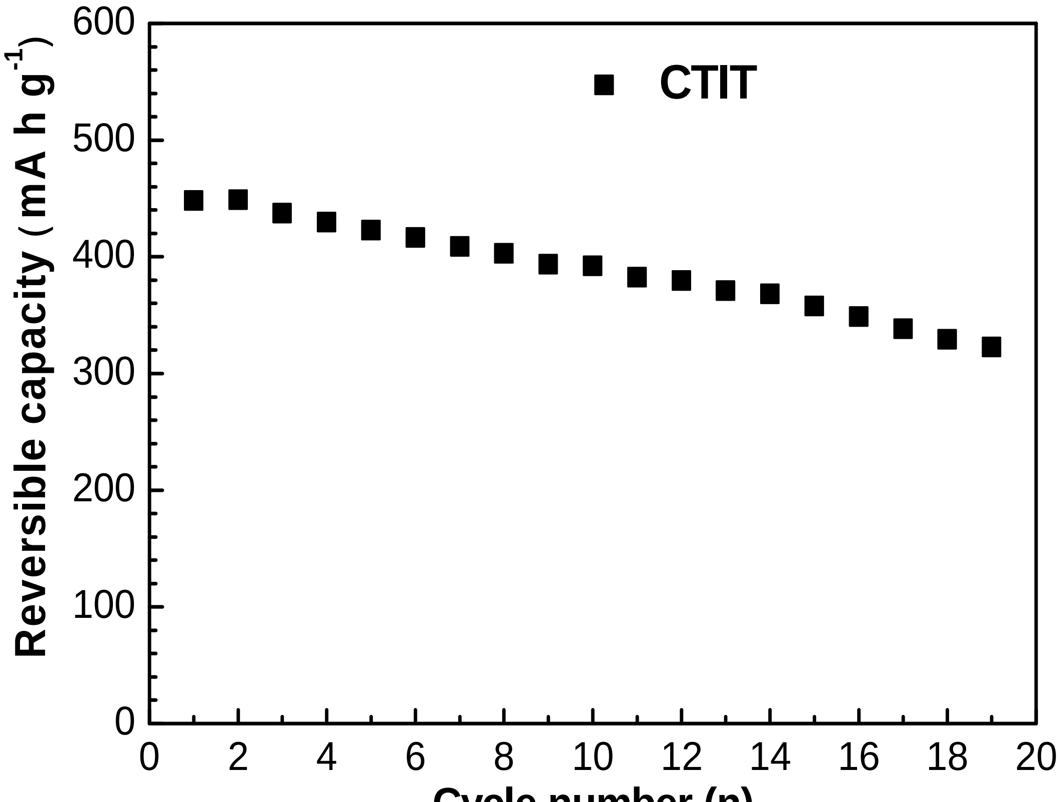
Carbon tube-in-tube (CTIT)

Unfortunately, performance decreased during 20 cycles





Cyclic voltammogram at a scan rate of 0.1 mV s^{-1} in the voltage range of 0.01 and 3 V in 1 M LiPF6 in EC/DMC solution

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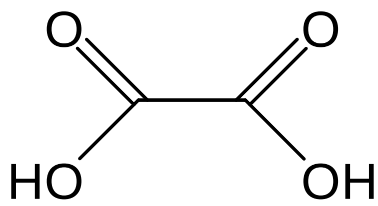
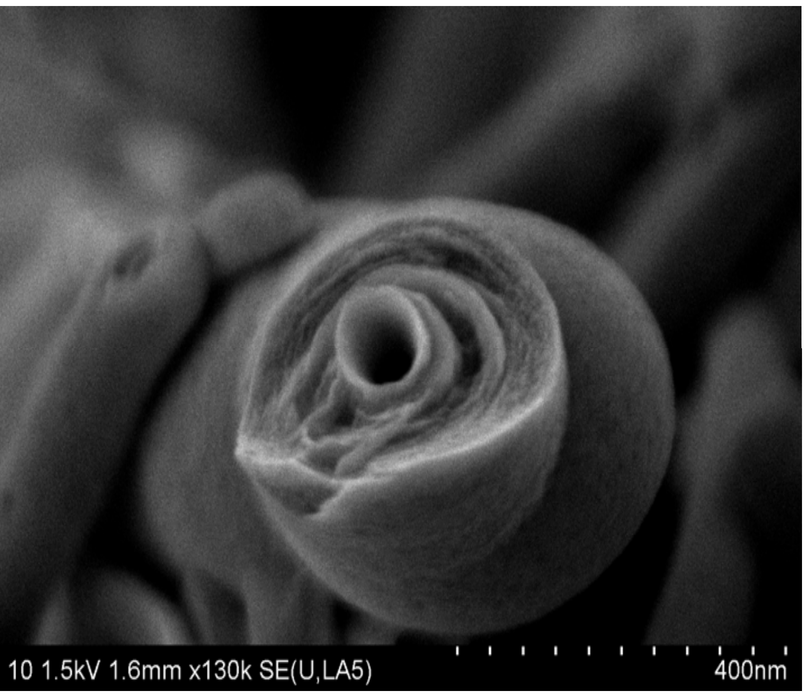
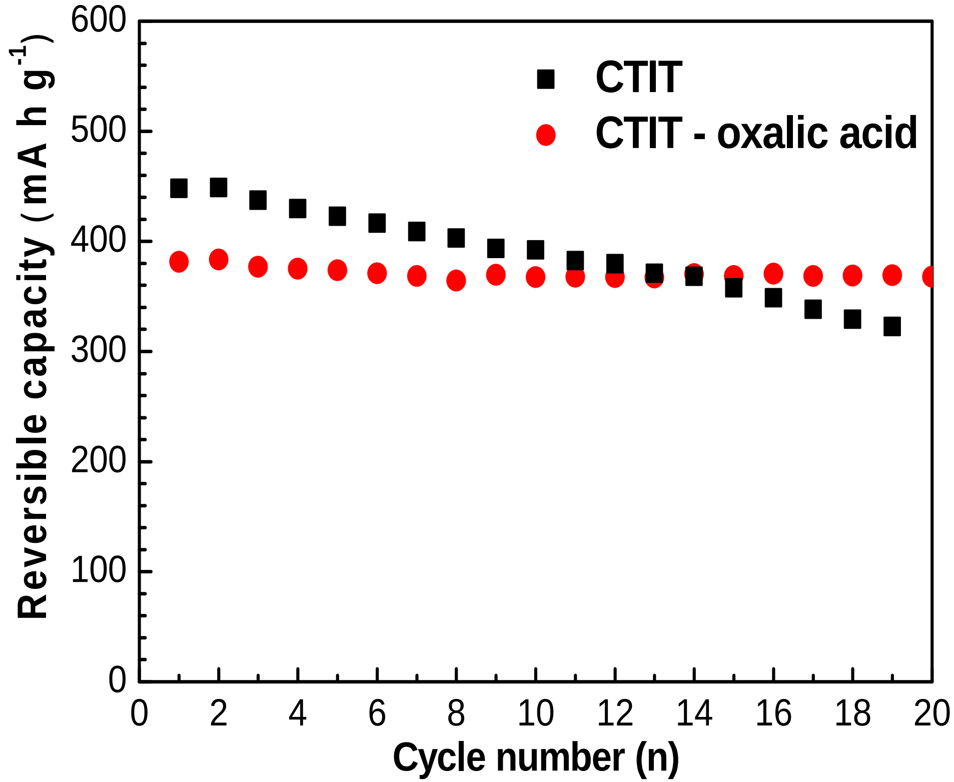
Fixation of oxygenate sites







From TPR: no more chemical reduction of oxygenate sites

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Carbon as Catalyst

metal-free heterogeneous catalysis

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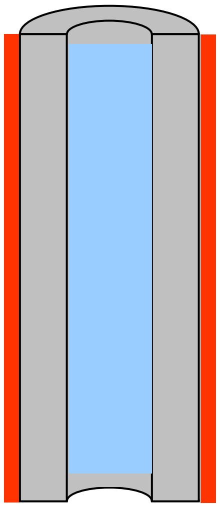
Control of Localization

Oxide particles are killing nanocarbon: limit it to the bare minimum, avoid formation of lumps e.g. in the inner parts of nanotubes

Steps for the selective decoration of the outer surface



1. 250 mg of MWNT treated with HNO_3
2. Filling of the inner cavity with 1.4 ml n-C8 (γ = 21 $mN.m^{-1}$ and low miscibility with water)
3. Impregnation with 1 ml of an aqueous solution containing metal-salt (final loading: 1 wt.%)
4. Drying, calcination. Metal oxide nano particles are only outside.

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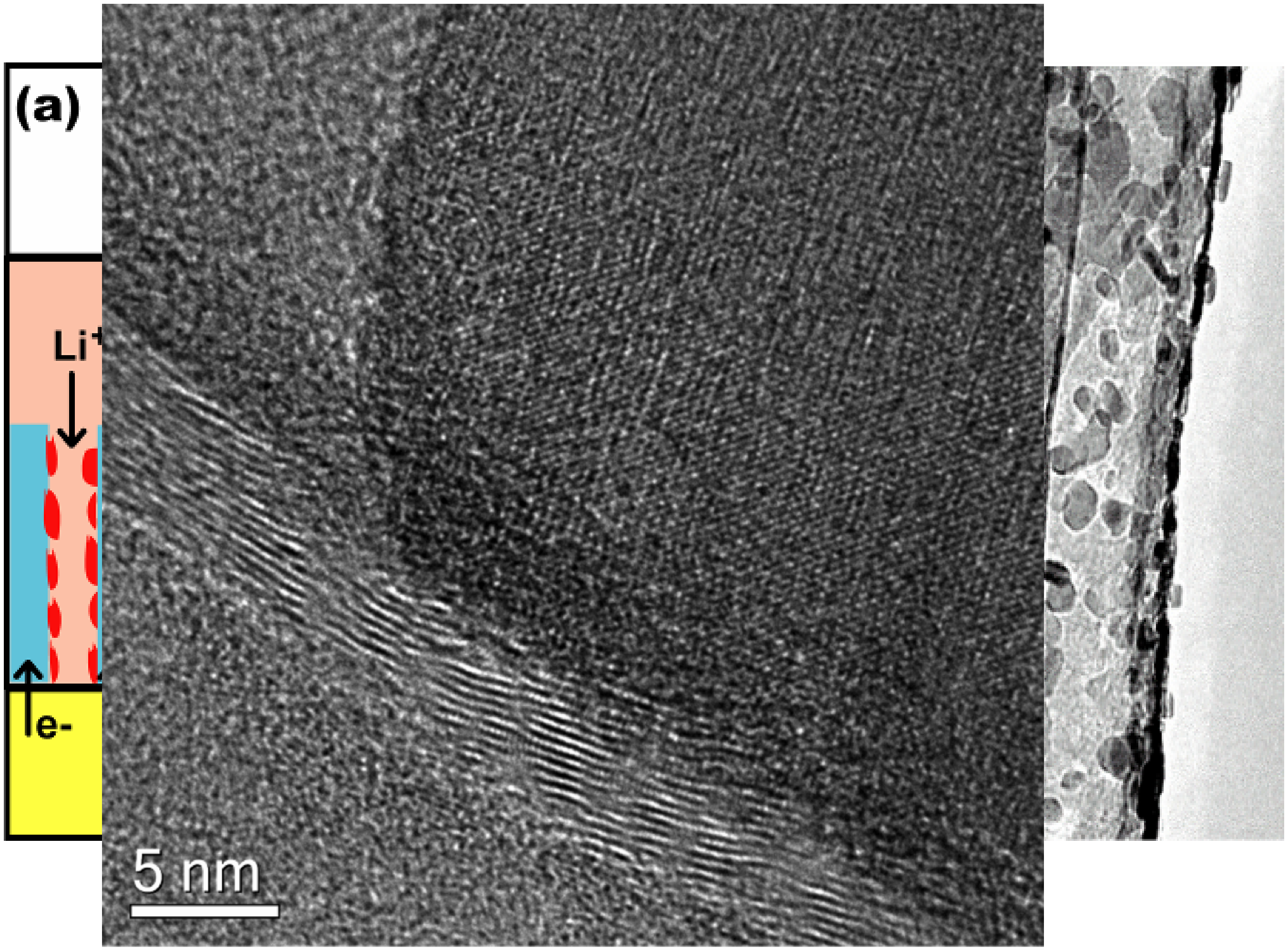
Control of localization with CNT



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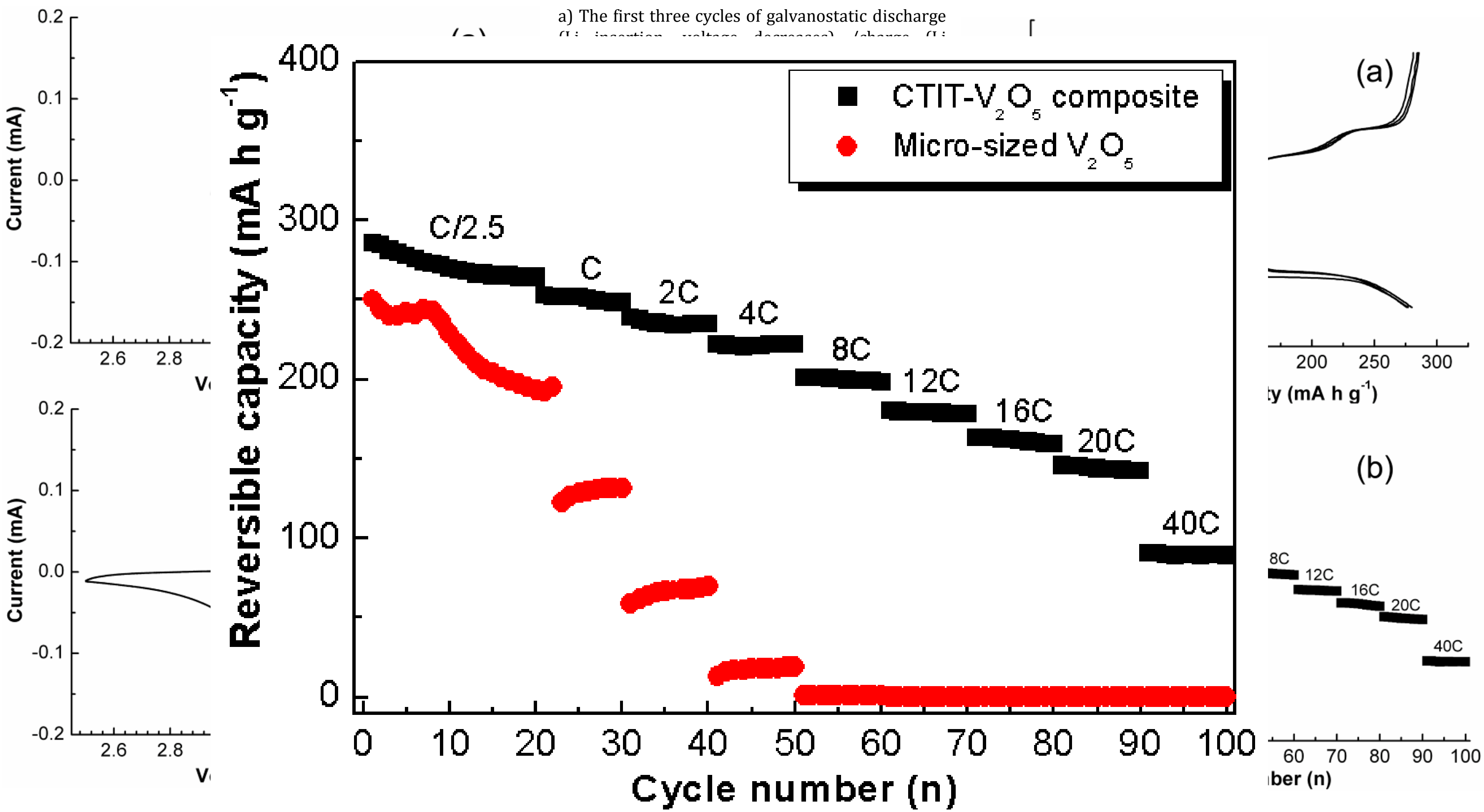
Cathode in Li storage



Cyclic voltammograms of a) the V_2O_5/CTIT nanocomposite and b) micro-sized V_2O_5 at a scan rate of 0.1 mV/s.

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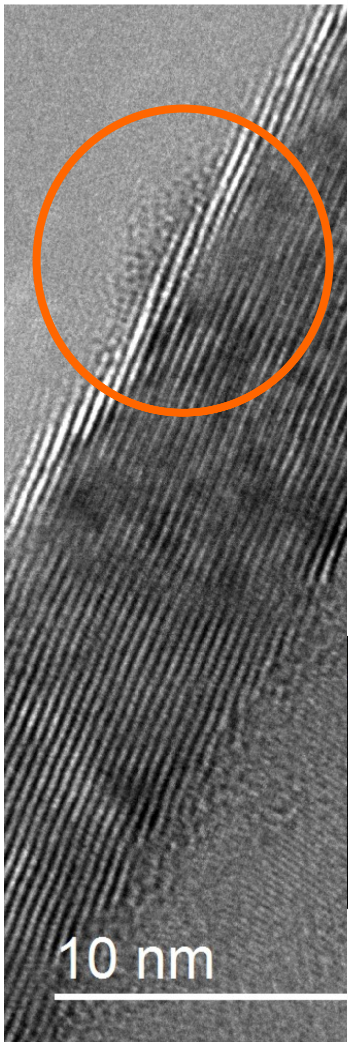
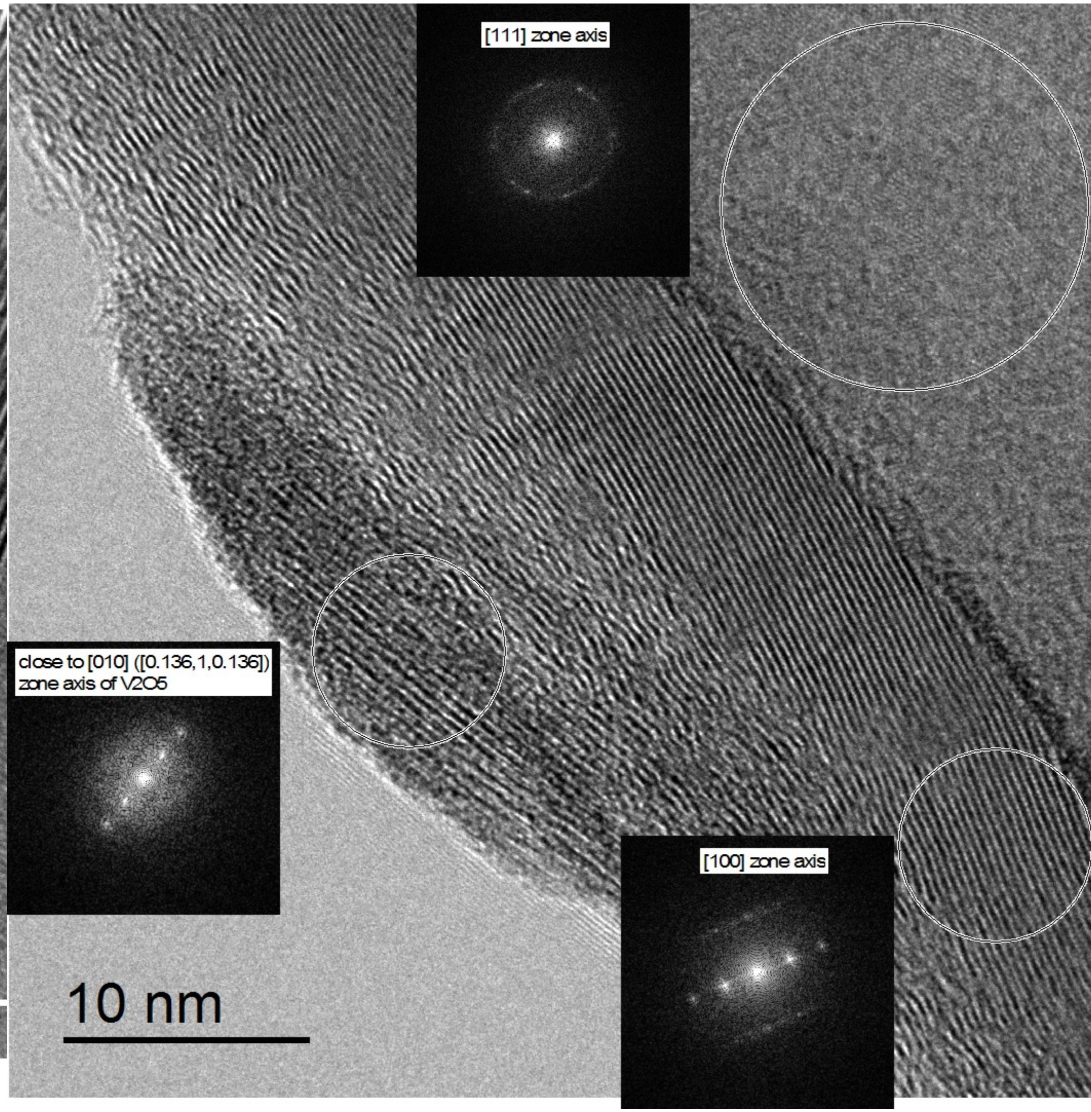
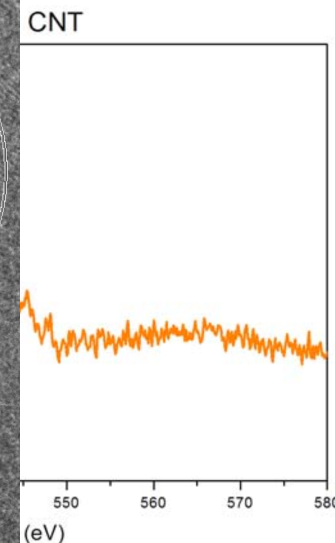
Nano clusters







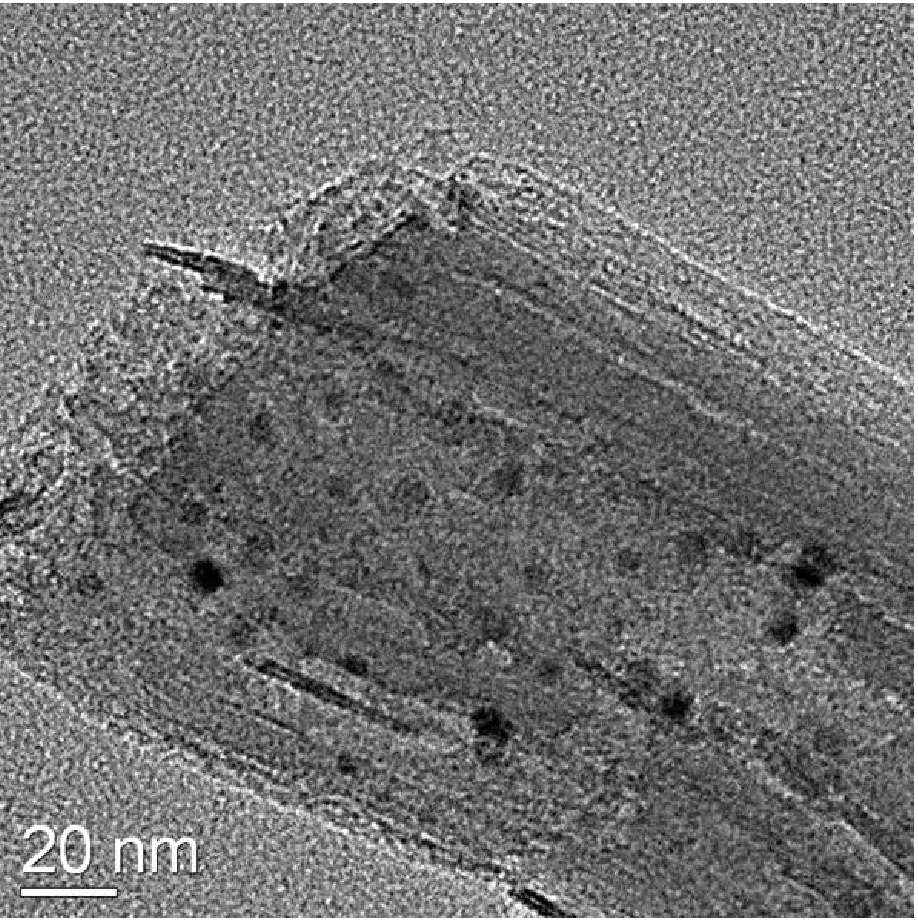
nge structure
structure
(higher
lence)

Nanocarbons represent an attractive family of catalytic materials: metal-free and as supports

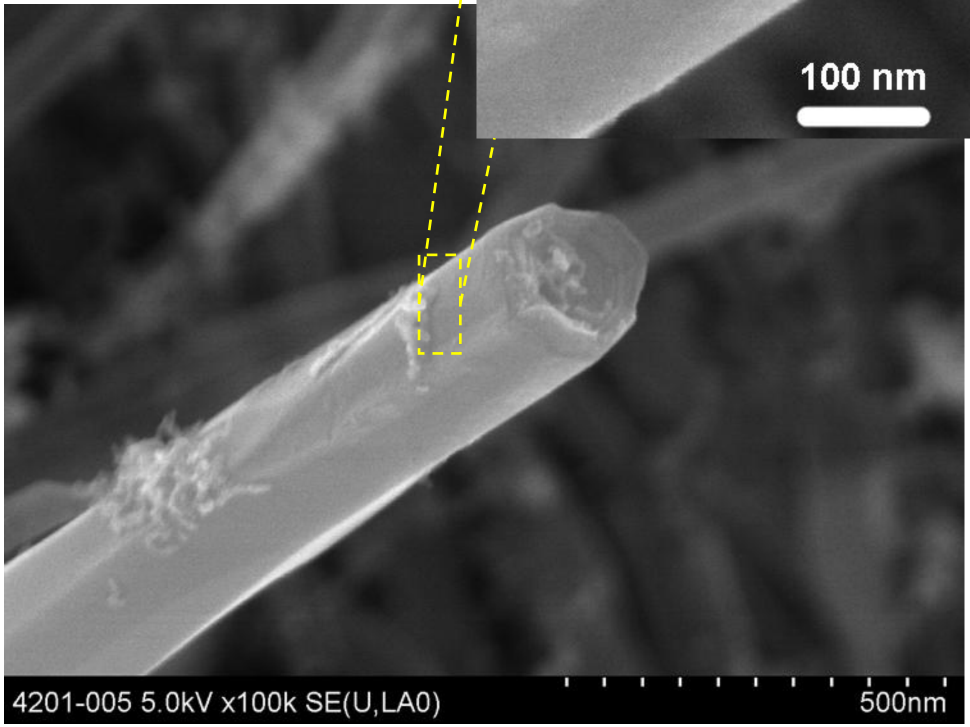
Thank You

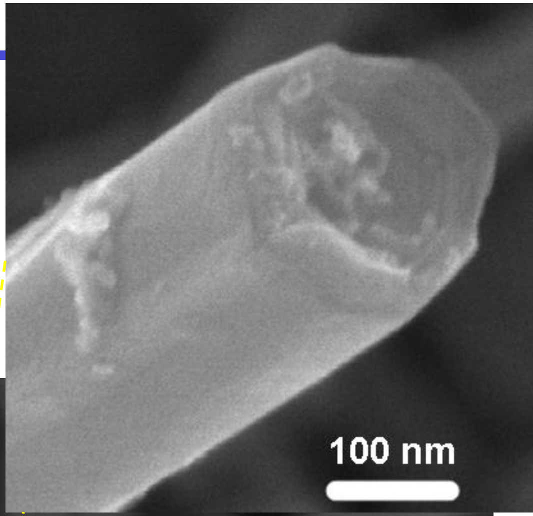
Application: Synthesis of Carbon Nanocomposite

0.5%Co@CNTs



CNFs@CNTs





J. Zhang, Y.S. Hu, J.-P. Tessonnier, G. Weinberg, J. Maier, R. Schlögl, D.S. Su, *Adv. Mater., on line.*