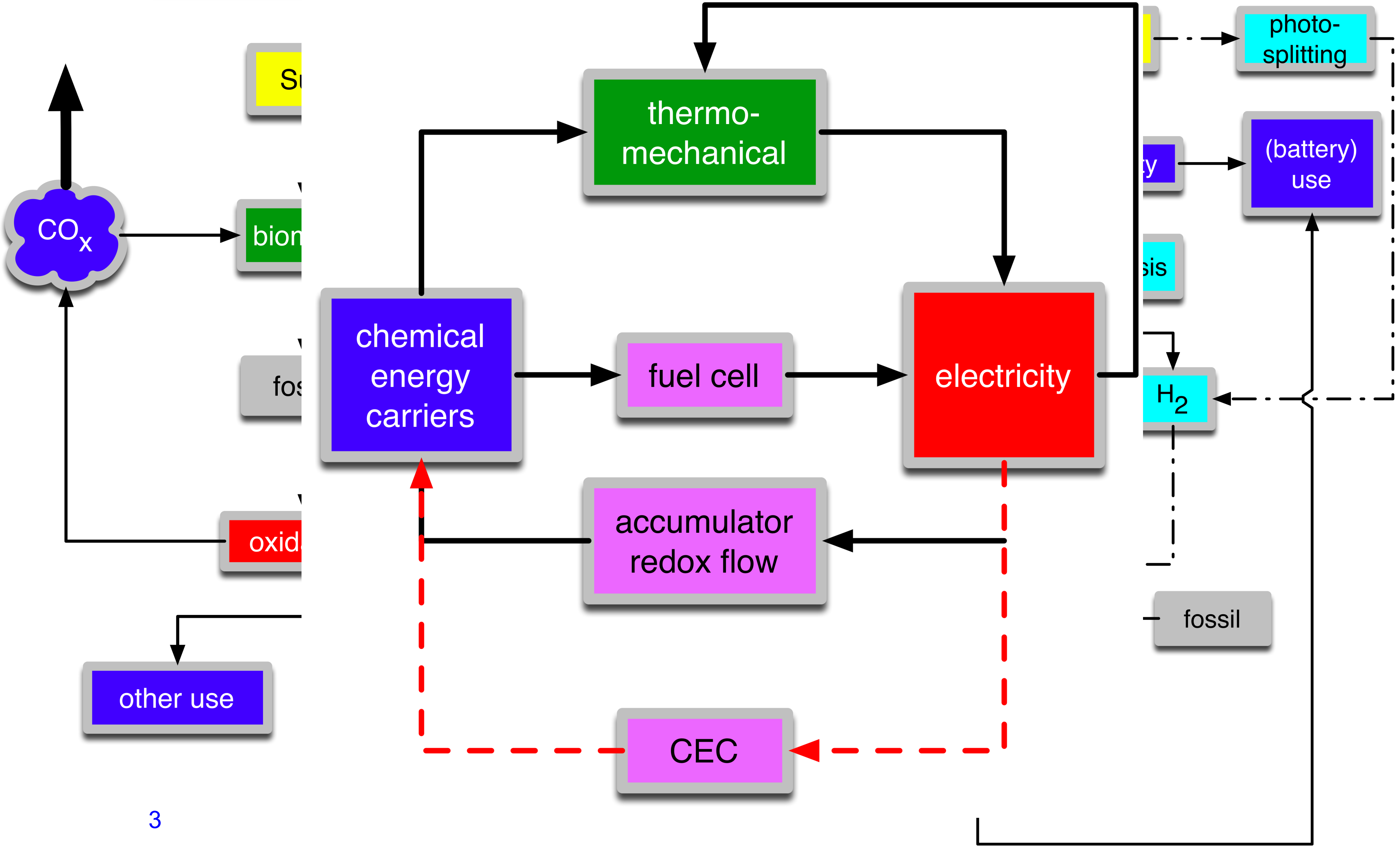
Nanostructured Carbons

Energy systems: sustainability



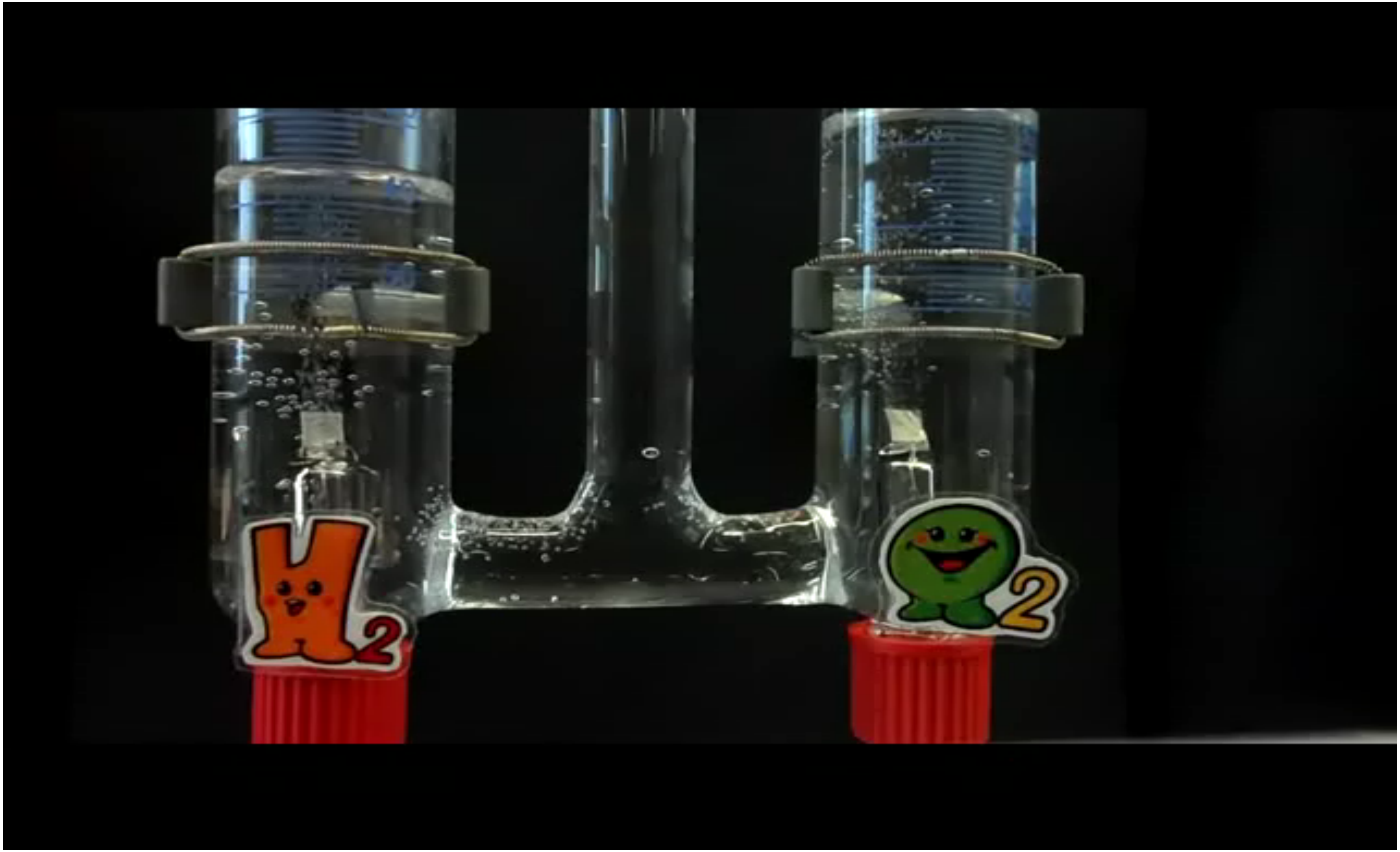
Nanocarbon in Chemistry

- Carbon in its sp2 allotrope forms a large number of „pseudo-phases“ called „nanocarbon or „SCA“.
- These are semimetals or semiconductors.
- They exhibit extreme chemical anisotropy.
- Chemical reactivity occurs at localized double bonds or aromatic terminal sites.
- The basal planes are active for chemisorption but not for covalent bonding.
- The 3-dimensional stacking or warping creates spaces for intercalation.
- Electrocatalysis is a premier application area followed by metal-free heterogeneous catalysis.

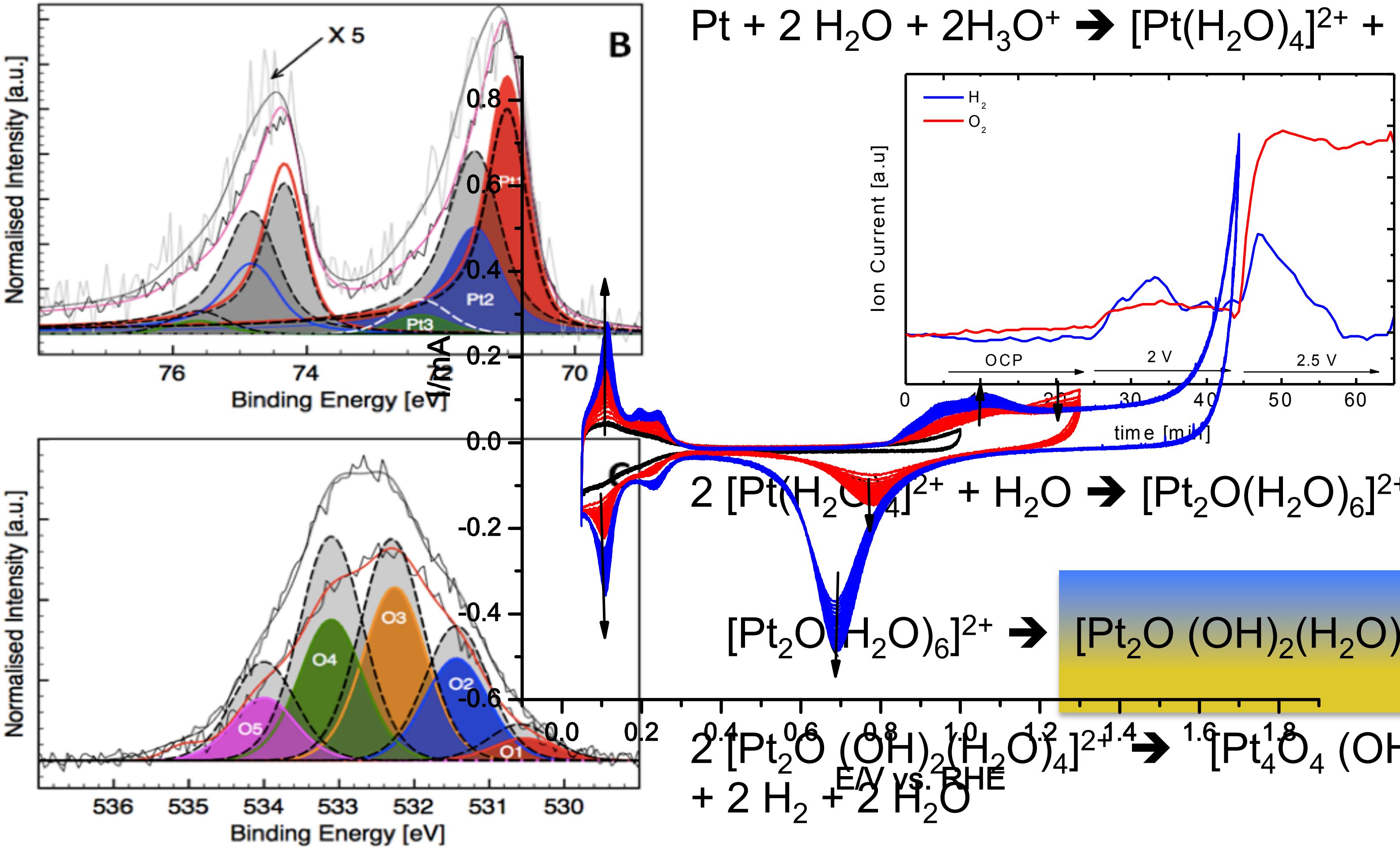
Electrochemistry

Requirements for nanocarbons

System chemistry:
Water splitting



Surface Chemistry of OER
Pt as prototype for a „noble“ electrode



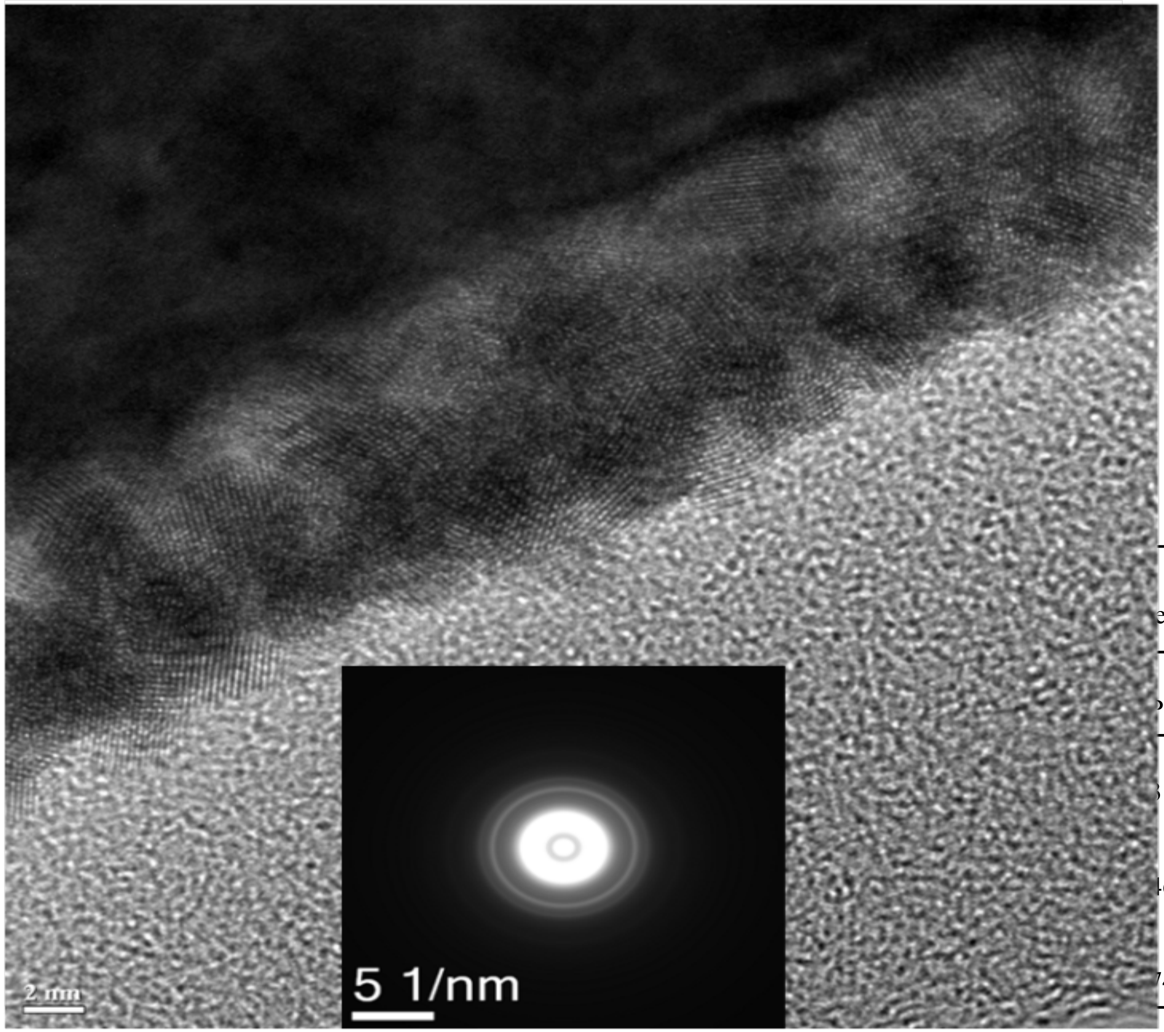
$Pt + 2\,H_2O + 2H_3O^+ \rightarrow [Pt(H_2O)_4]^{2+} + H_2$

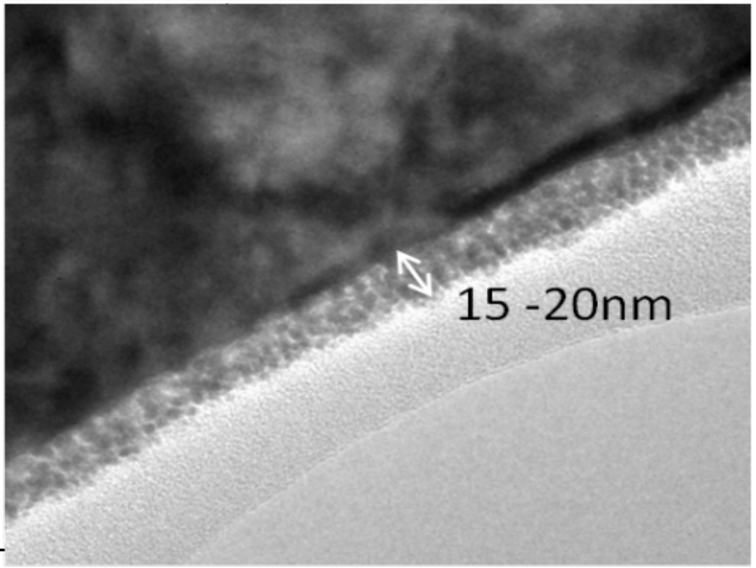
$2\,[Pt(H_2O)_4]^{2+} + H_2O \rightarrow [Pt_2O(H_2O)_6]^{2+} + 2\,H_3O^+$

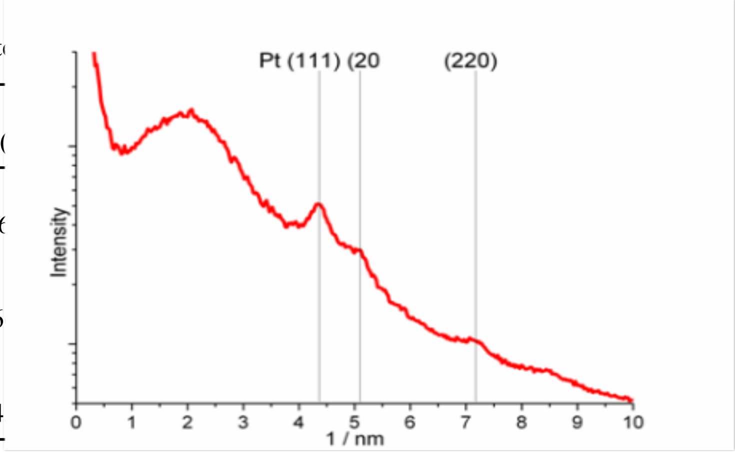
$[Pt_2O(H_2O)_6]^{2+} \rightarrow [Pt_2O\,(OH)_2(H_2O)_4]^{2+} + H_2$

$2\,[Pt_2O\,(OH)_2(H_2O)_4]^{2+} \rightarrow [Pt_4O_4\,(OH)_4(H_2O)_4]^{4+} + 2\,H_2 + 2\,H_2O$

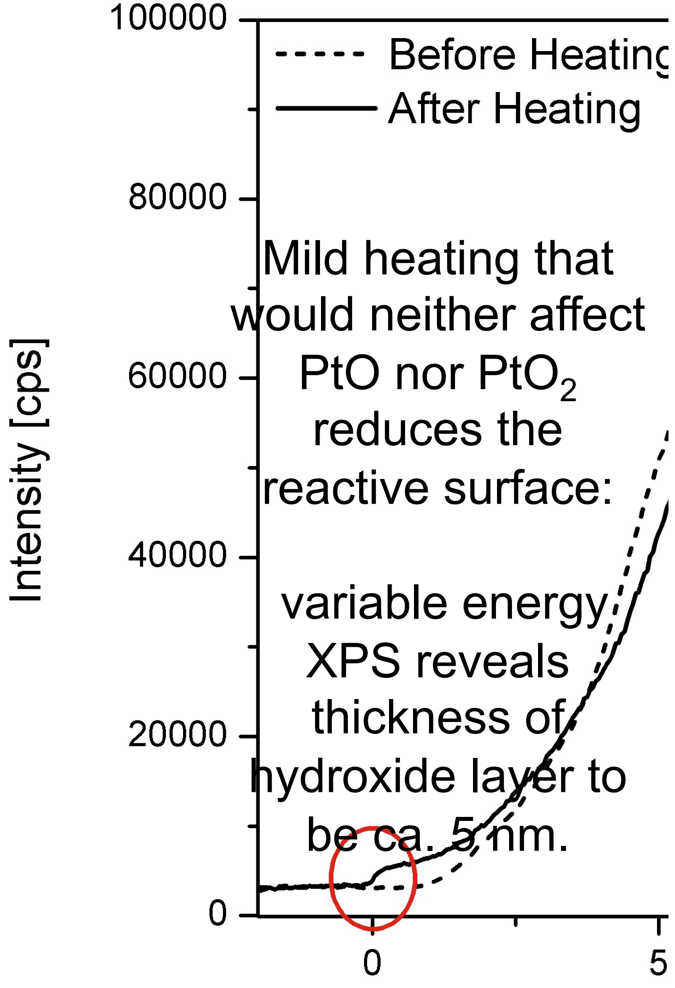
Pt single crystals as reference OER electrodes
Chemistry at the interface: dynamics





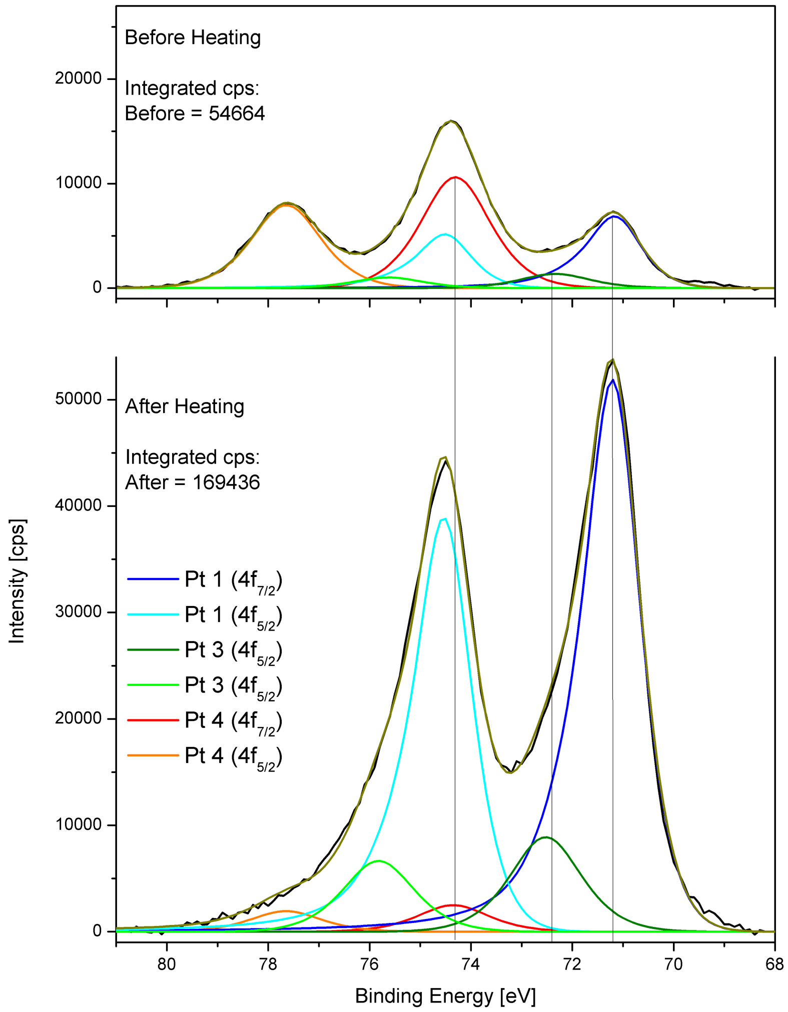


Photoelectron spectroscopy on emersed Pt after 3 h at 1.6 V RHE

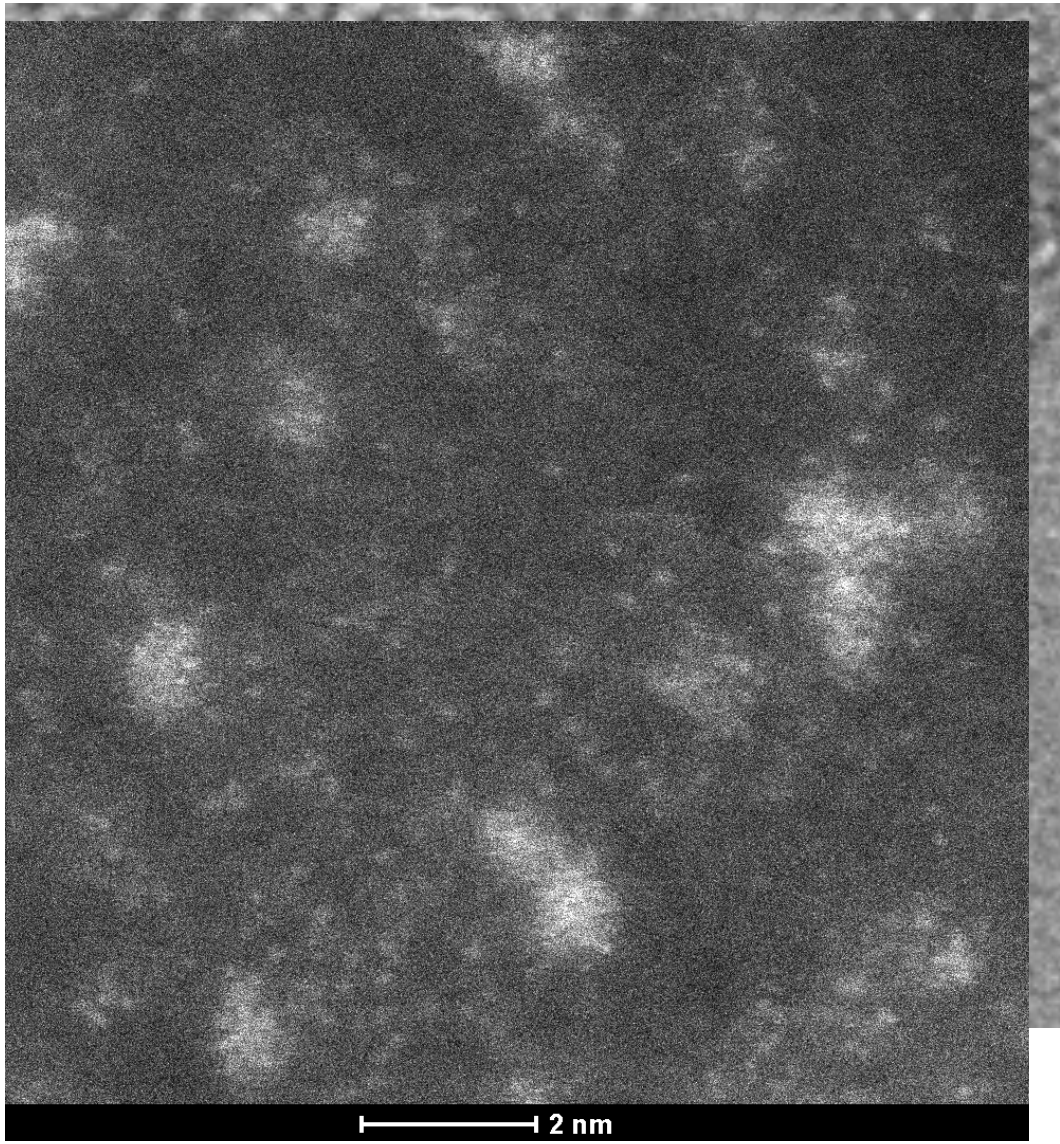


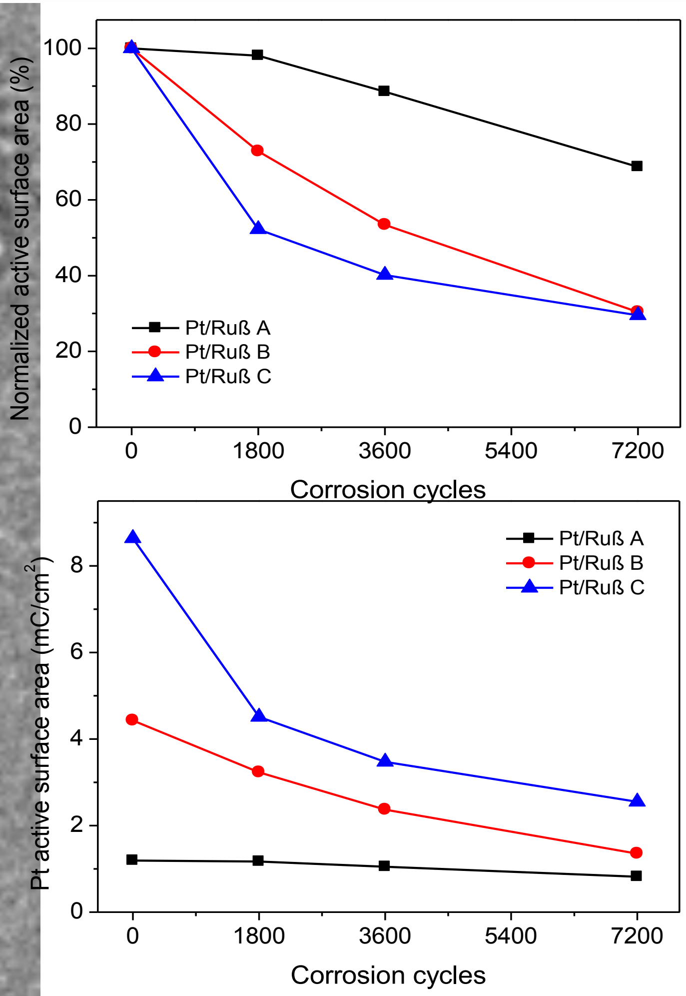
Mild heating that would neither affect PtO nor PtO_2 reduces the reactive surface:

variable energy XPS reveals thickness of hydroxide layer to be ca. 5 nm.

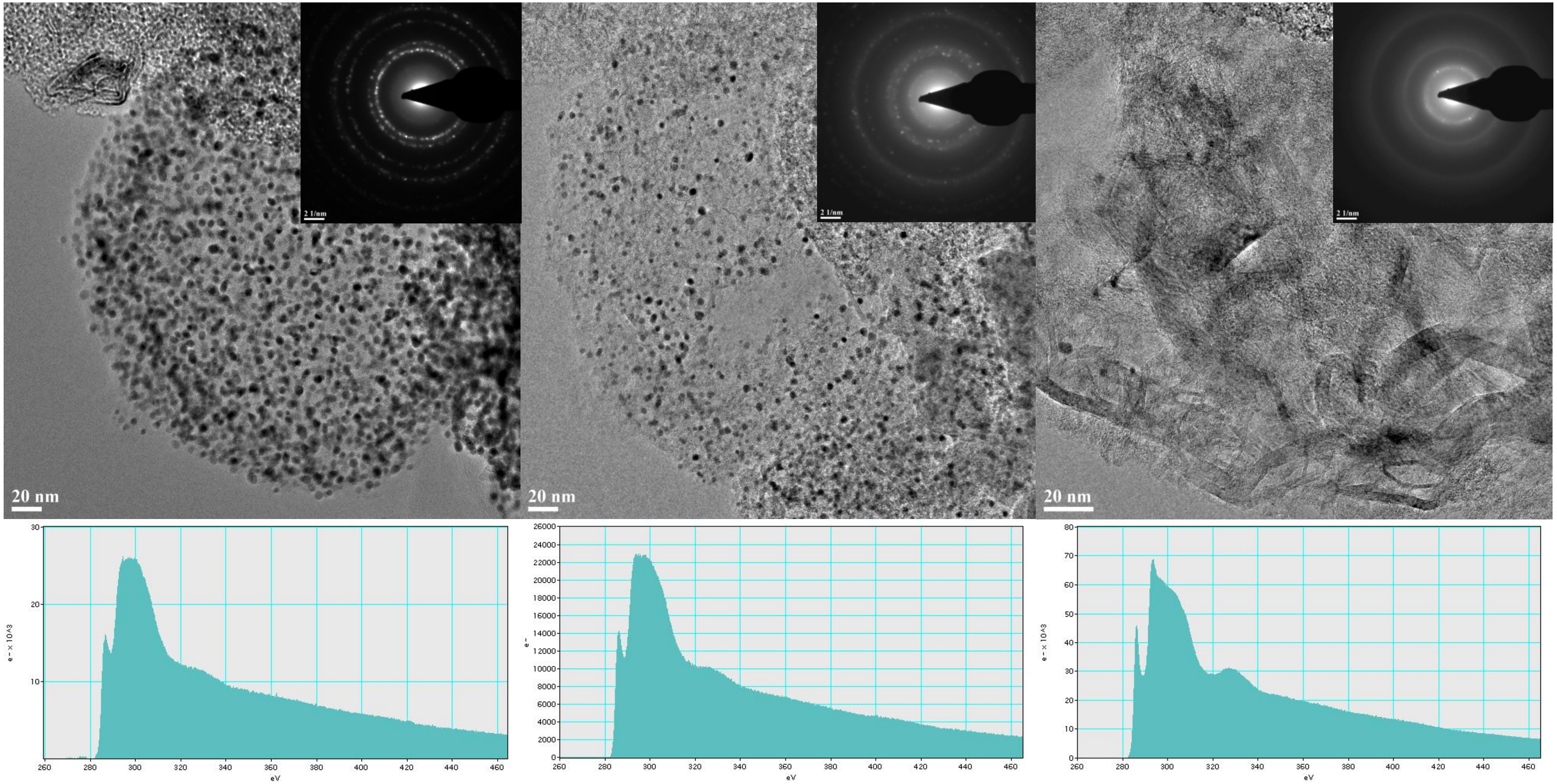


Pt- carbon for water electrolysis: the reference

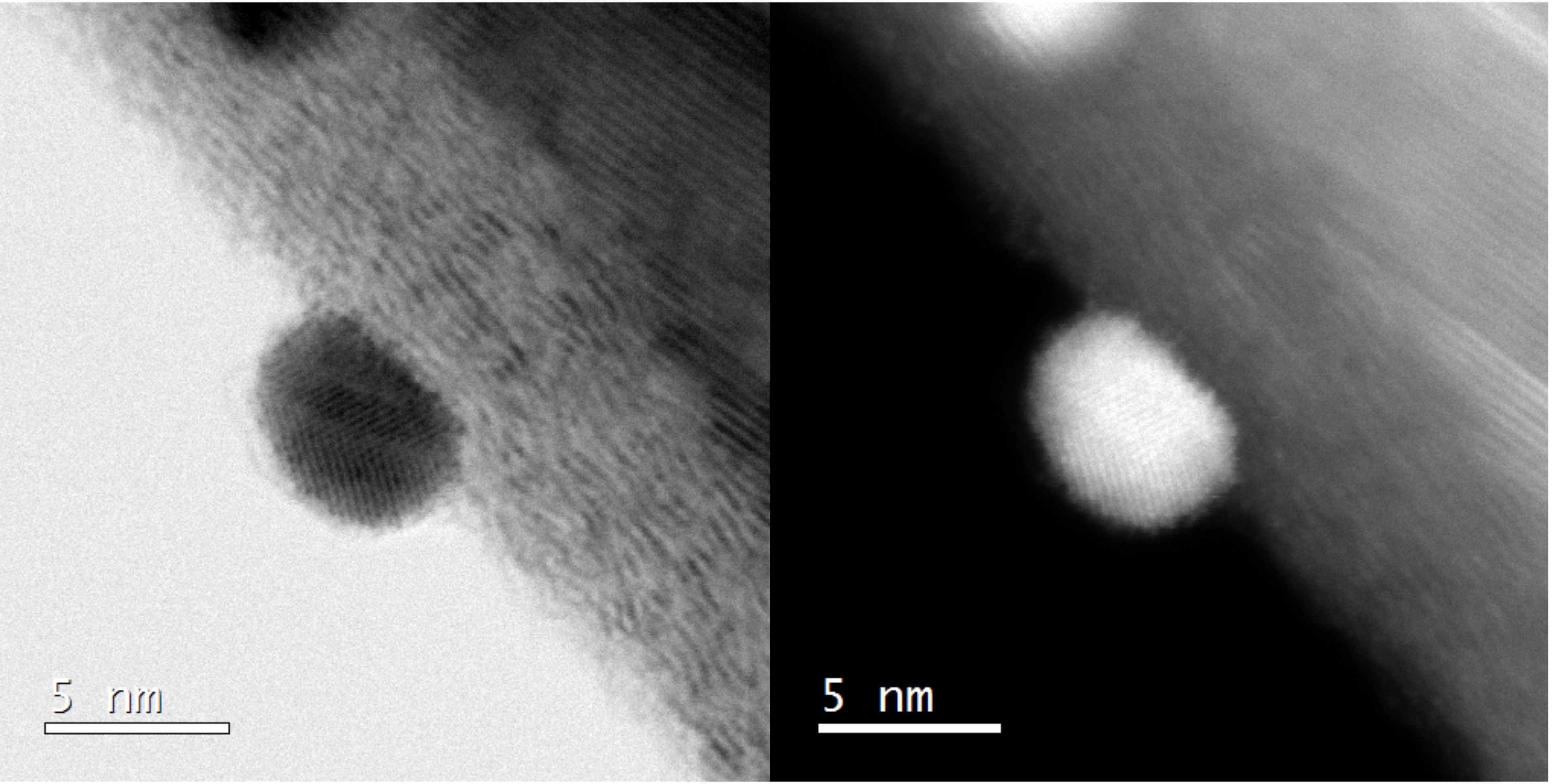




The role of the support structure

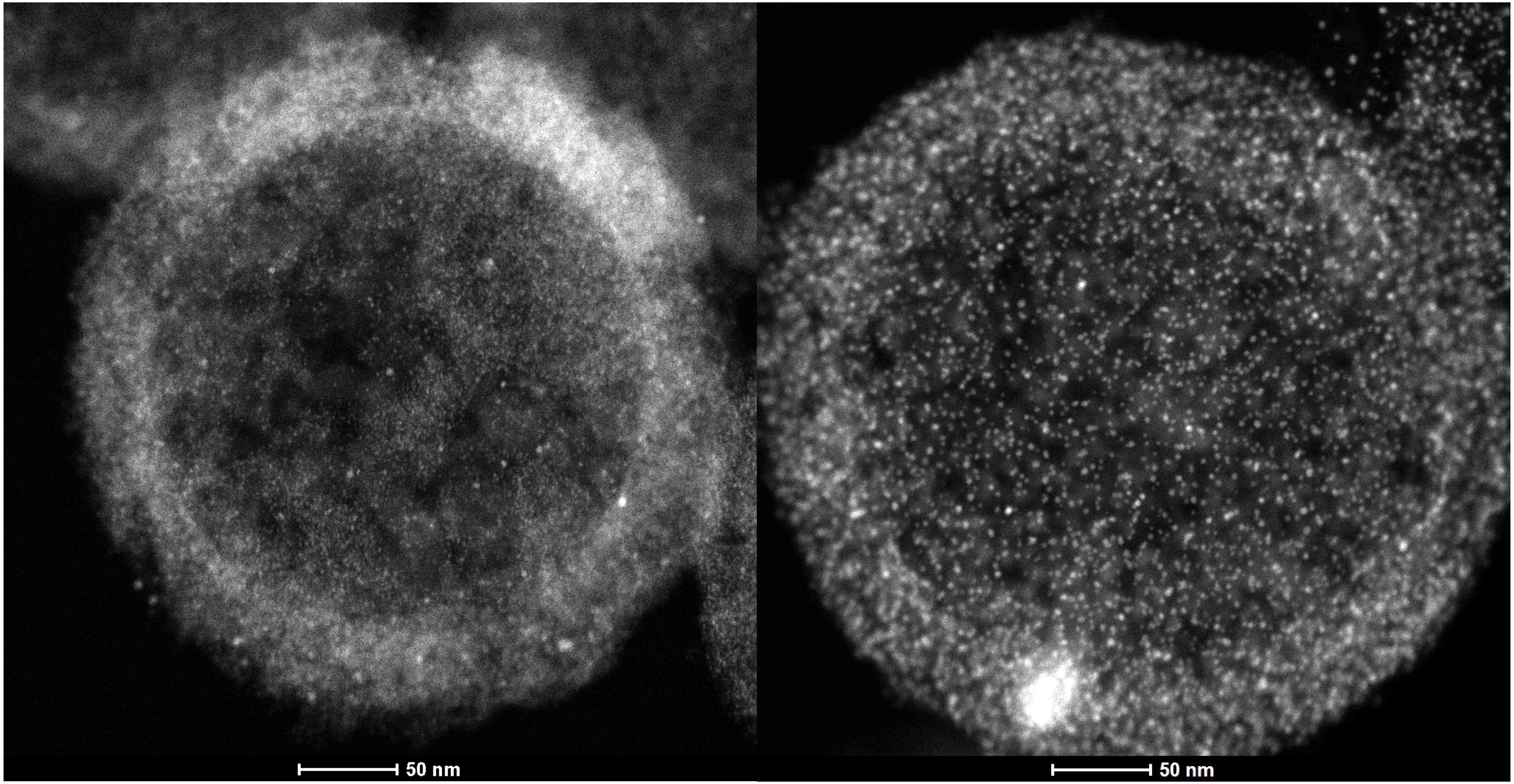


Origin of good sticking of the metal:
point defects of carbon plus functional groups

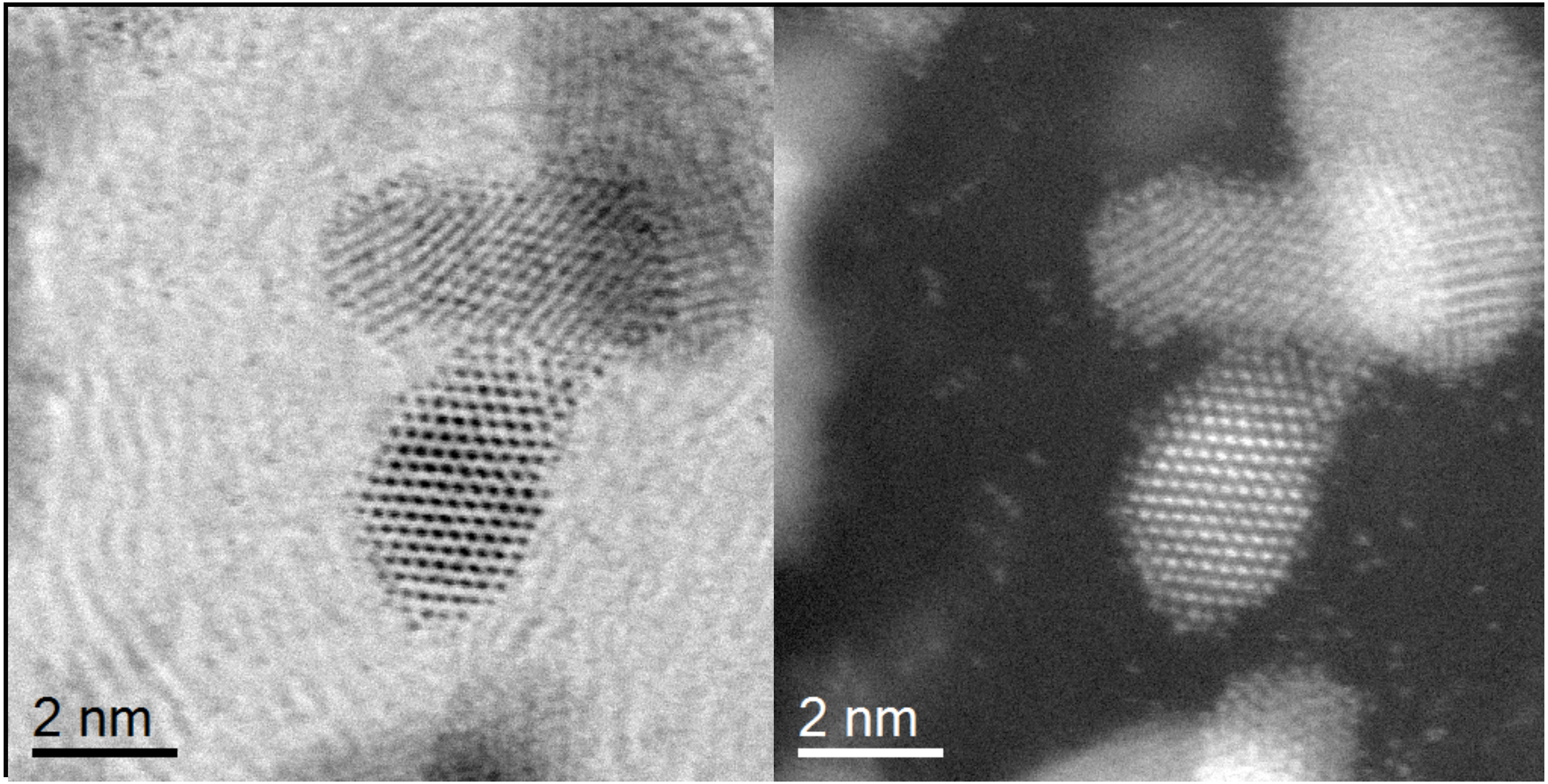


Nanocarbon as support in OER electrodes

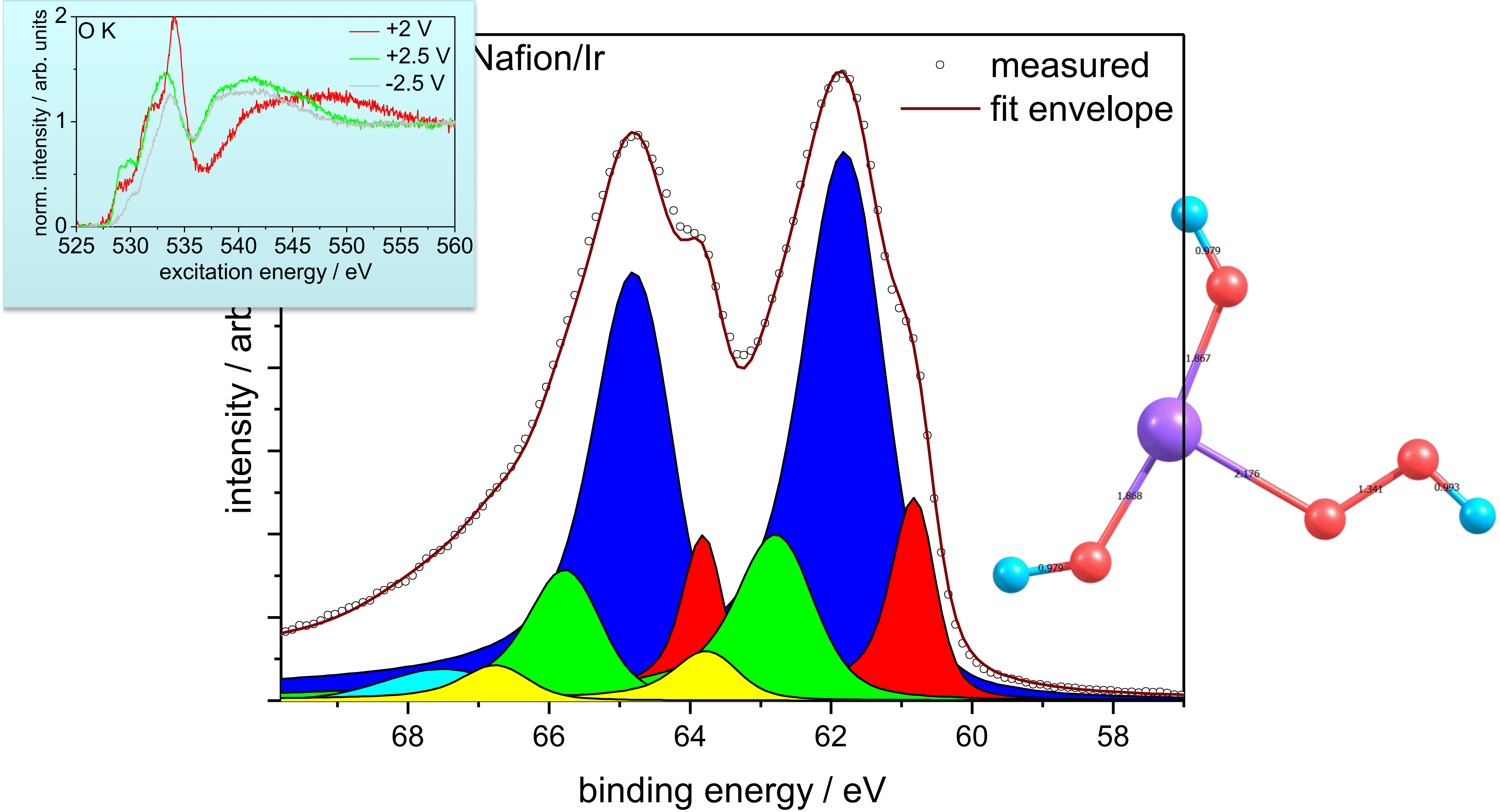
(with F. Schueth, KOFO)



Pt- Carbon
How electrocataylsts look like

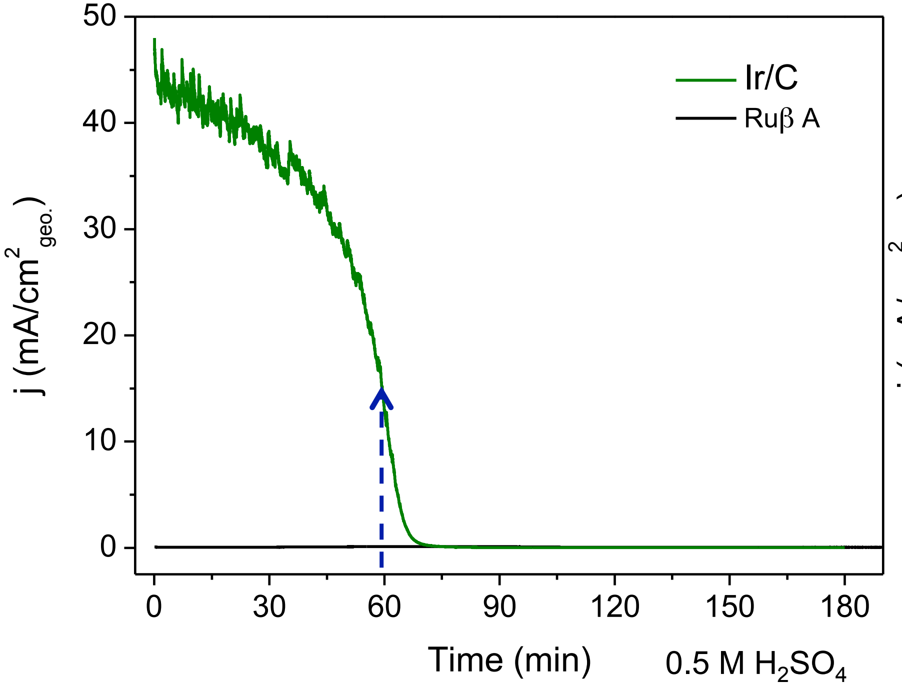


Speciation at reaction conditions



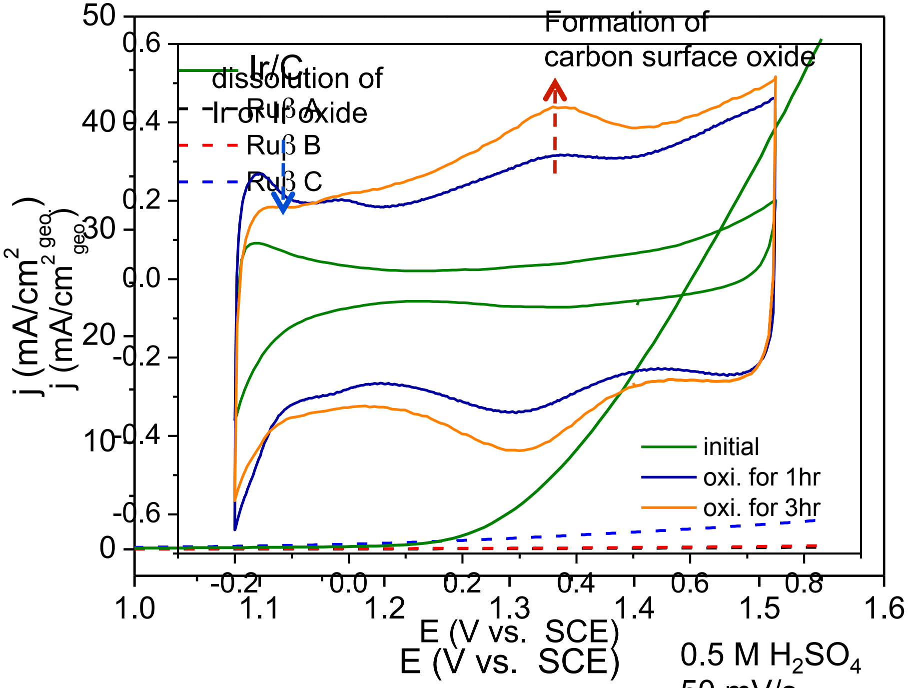
Stability: a main challenge

Chronoamperometry at 1.6 V RHE



0.5 M H_2SO_4
1.55 V vs. SCE

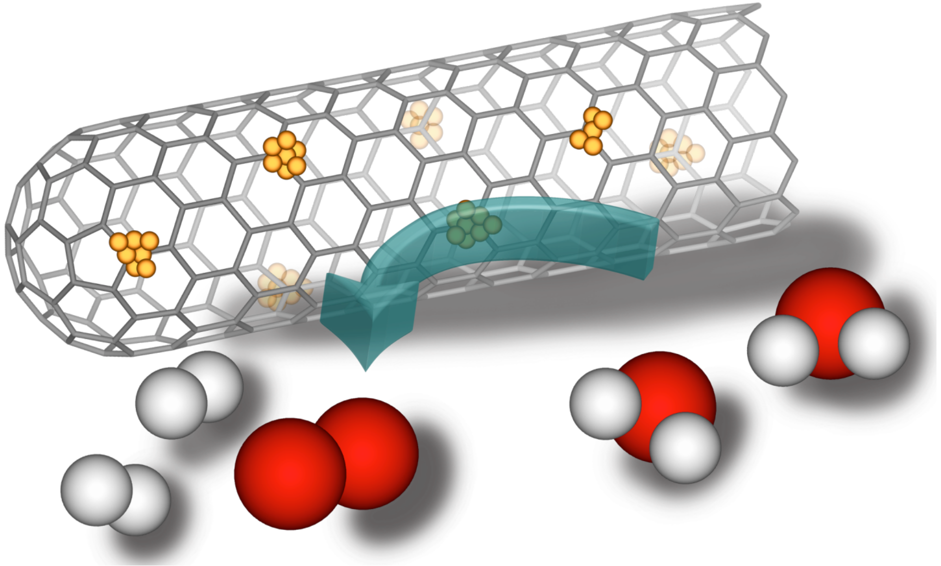
Cyclovoltammetry in H_2SO_4

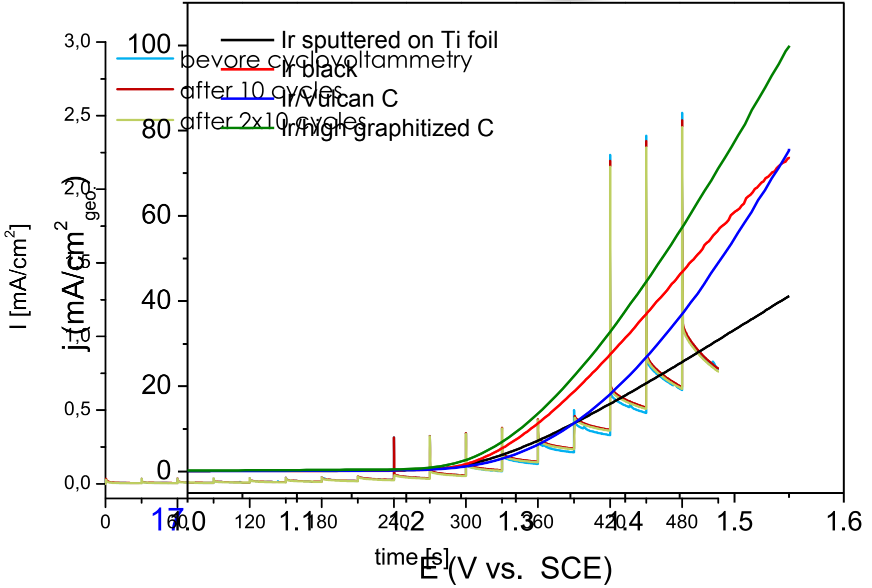


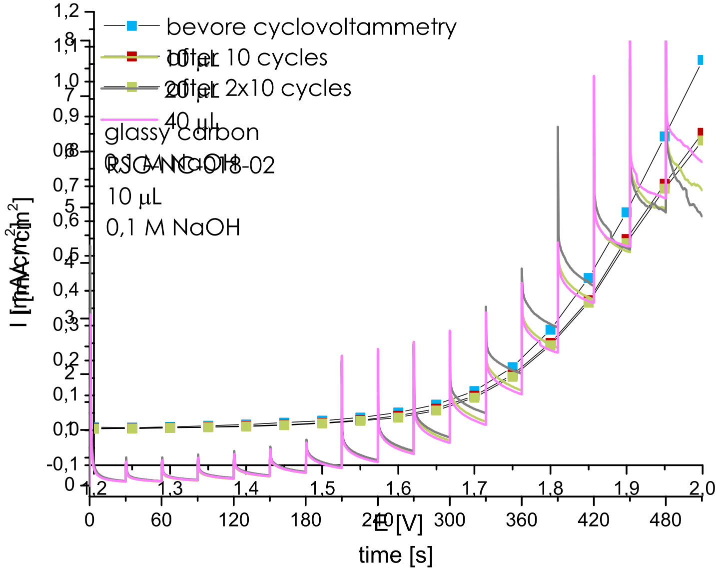
0.5 M H_2SO_4
50 mV/s

The performance of the best OER catalyst is quite insufficient at relevant current densities: massive electrodes at low current densities as technical „solution“

Carbon an electrode for water oxidation?
What about some help with a co-catalyst?



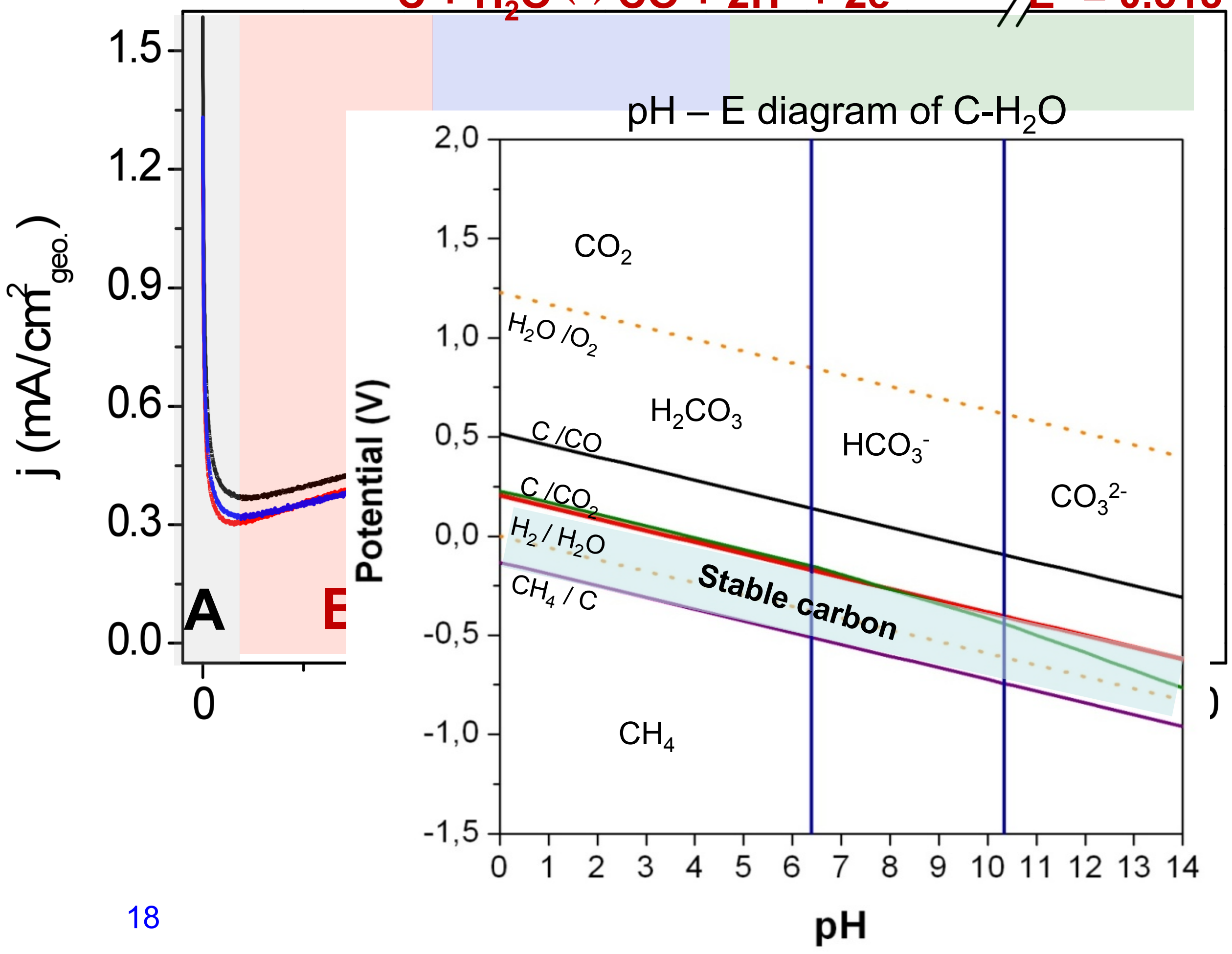




Electro-corrosion of carbon supports

$C + 2H_2O \leftrightarrow CO_2 + 4H^+ + 4e^-$ $E^0 = 0.207$ V

$C + H_2O \leftrightarrow CO + 2H^+ + 2e^-$ $E^0 = 0.518$ V



pH – E diagram of $C-H_2O$

A: capacitance and oxidation of surface

B: pitting corrosion

C: gradual passivation

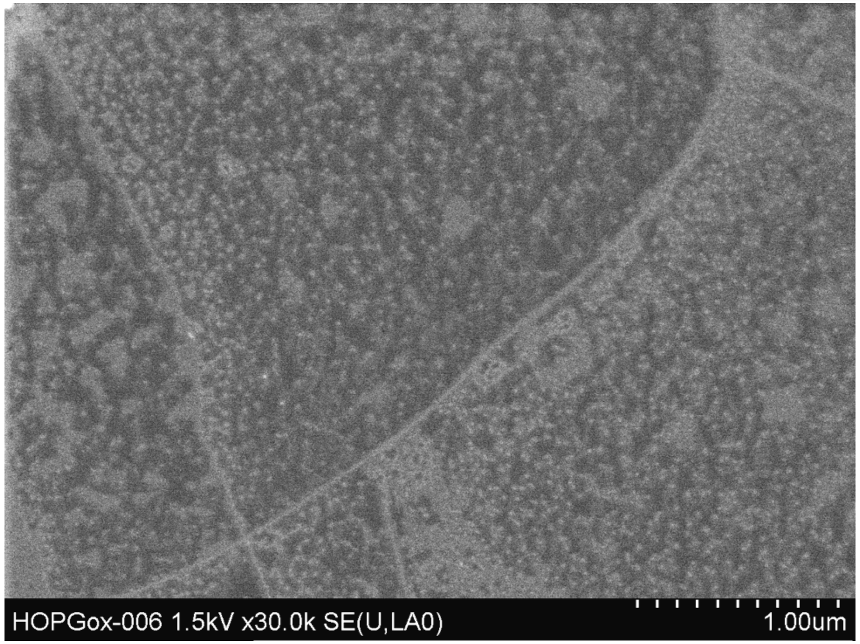
D: passive carbon

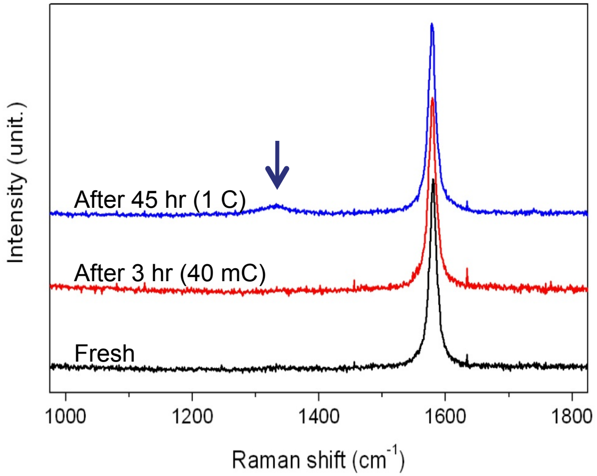
Carbon is thermodynamically unstable against dissolution in non-acidic water; mineral waters.

Kinetically strongly inhibited by C-H termination

At 1.8 V vs. RHE
0.5 M H_2SO_4

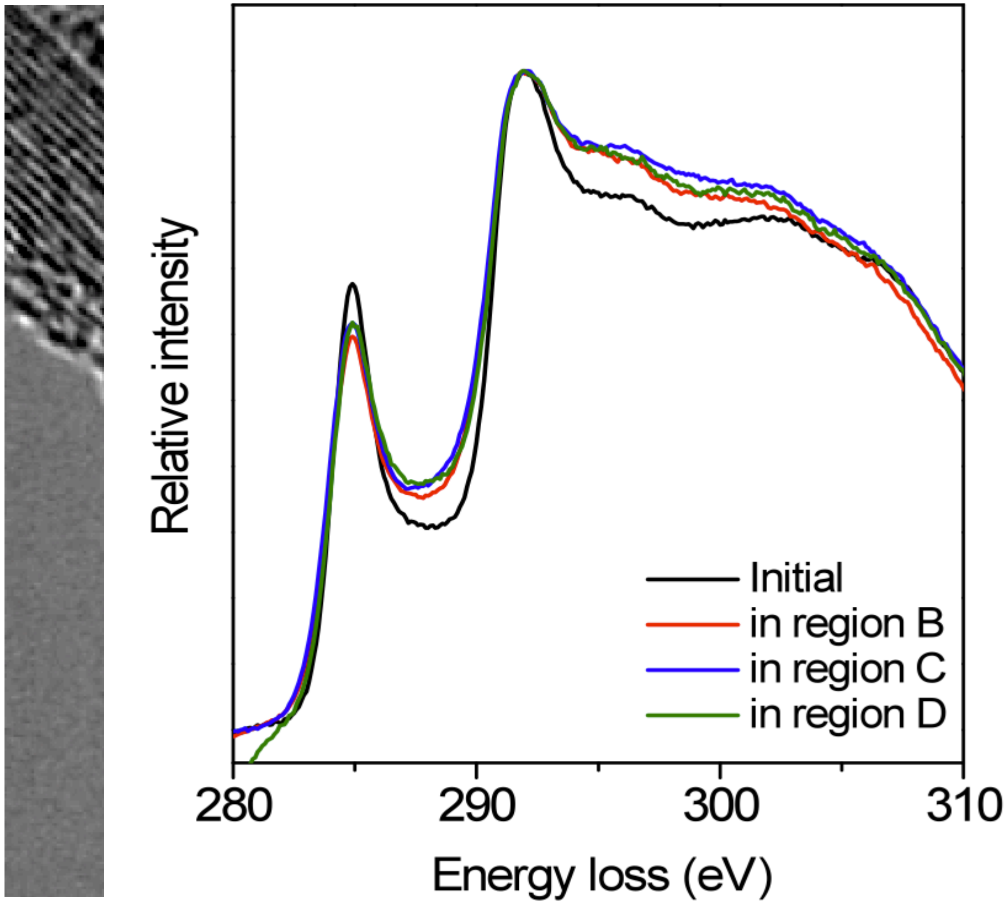
Reference HOPG electroxidation

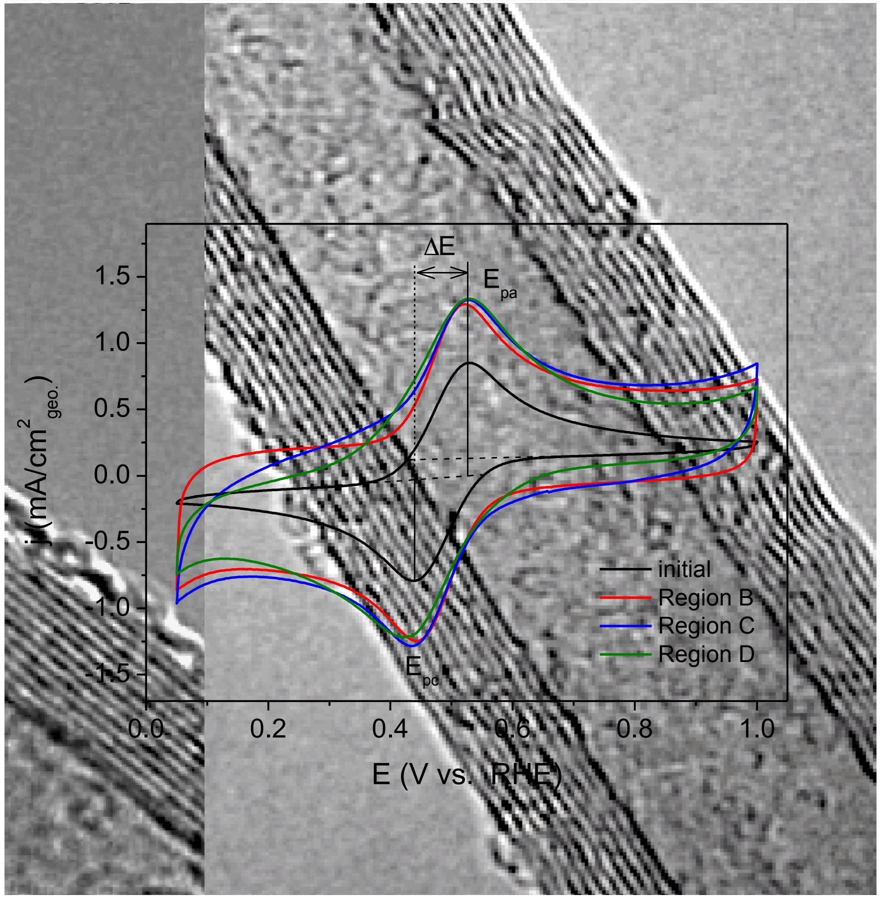




Not trivial to detect damage as product is volatile and carbon defects accumulate only as intermediates

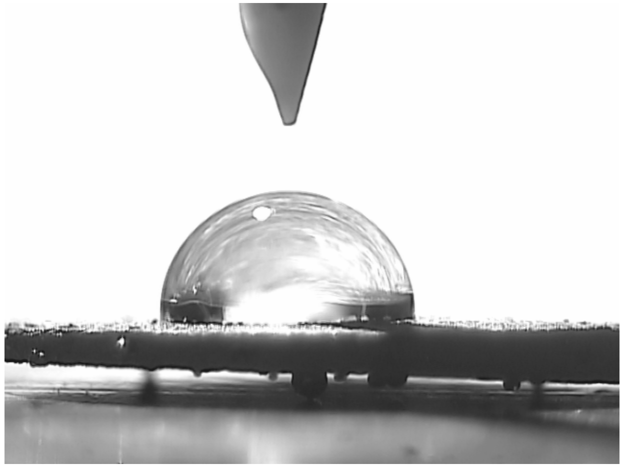
Electron flow through carbon



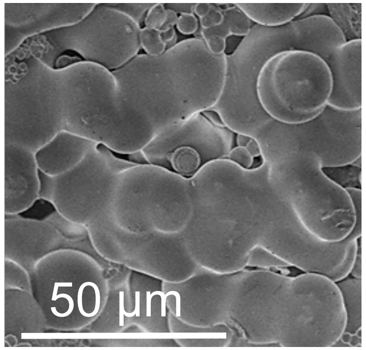


At 1.4 V and 1C flow of electrons substantial damage through formation of C-O hetero-bonds leading to warped graphene BSU

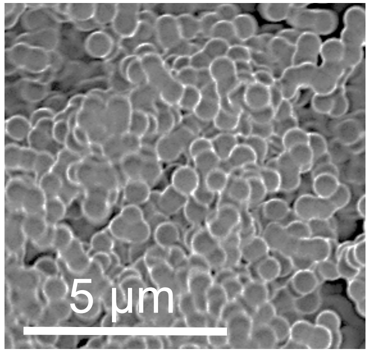
Contact with water ?



319: pH 0
contact angle : 86°



320: pH 6
contact angle : 21°



This critical property for electrochemistry depends sensitively on the surface termination.

HTC_900°C					
pH	SN	C [wt %]	H [wt%]	N [wt%]	O [wt%]
0	**#349**	**92.5**	**1.7**	**2.9**	**3.0**
3	#480	97.7	0.45	0.48	1.4
6	**#508**	**93.9**	**0.82**	**0.2**	**5.1**

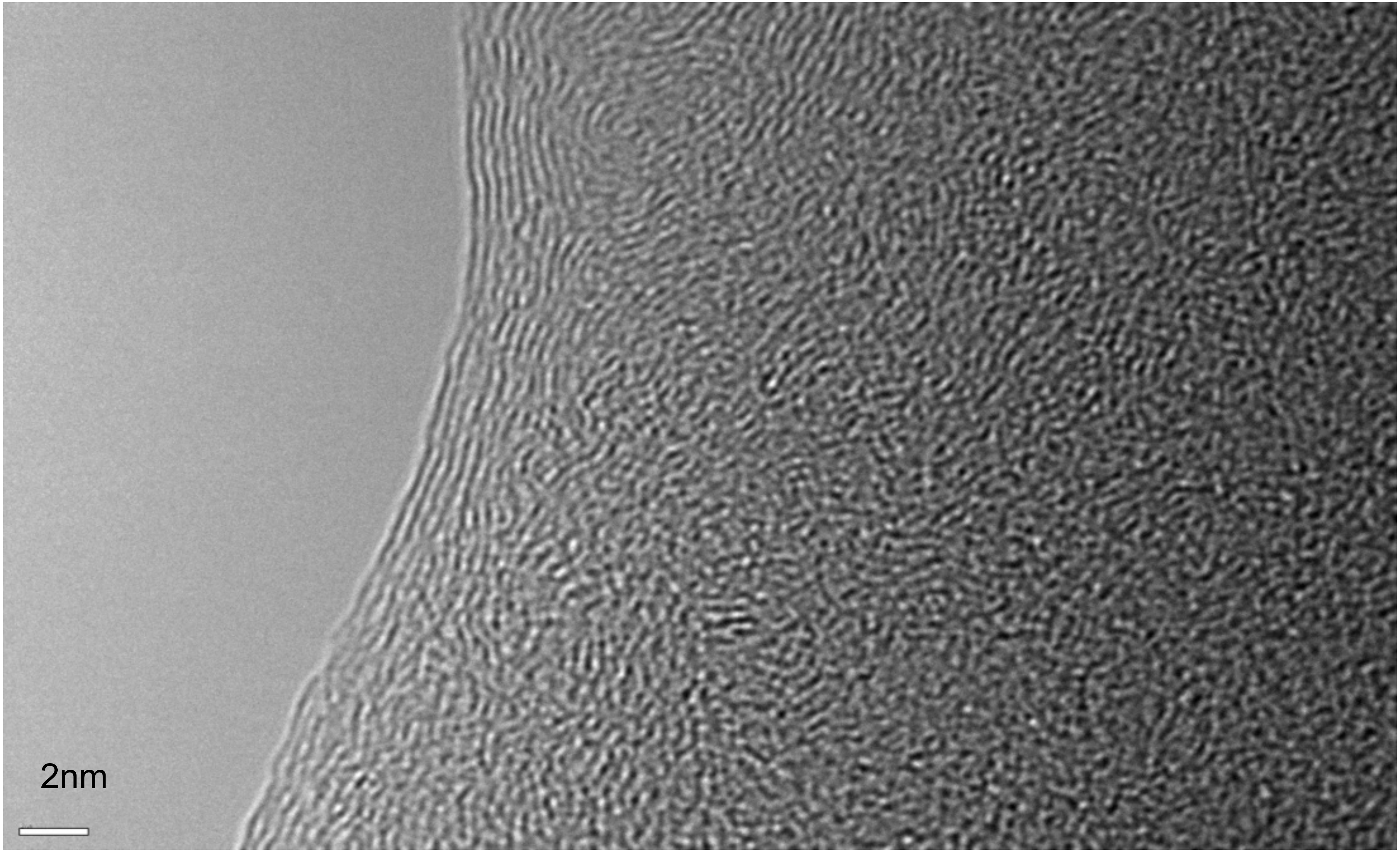
Synthesis controls the properties but no simple correlation.

Synthesis and typology of NC

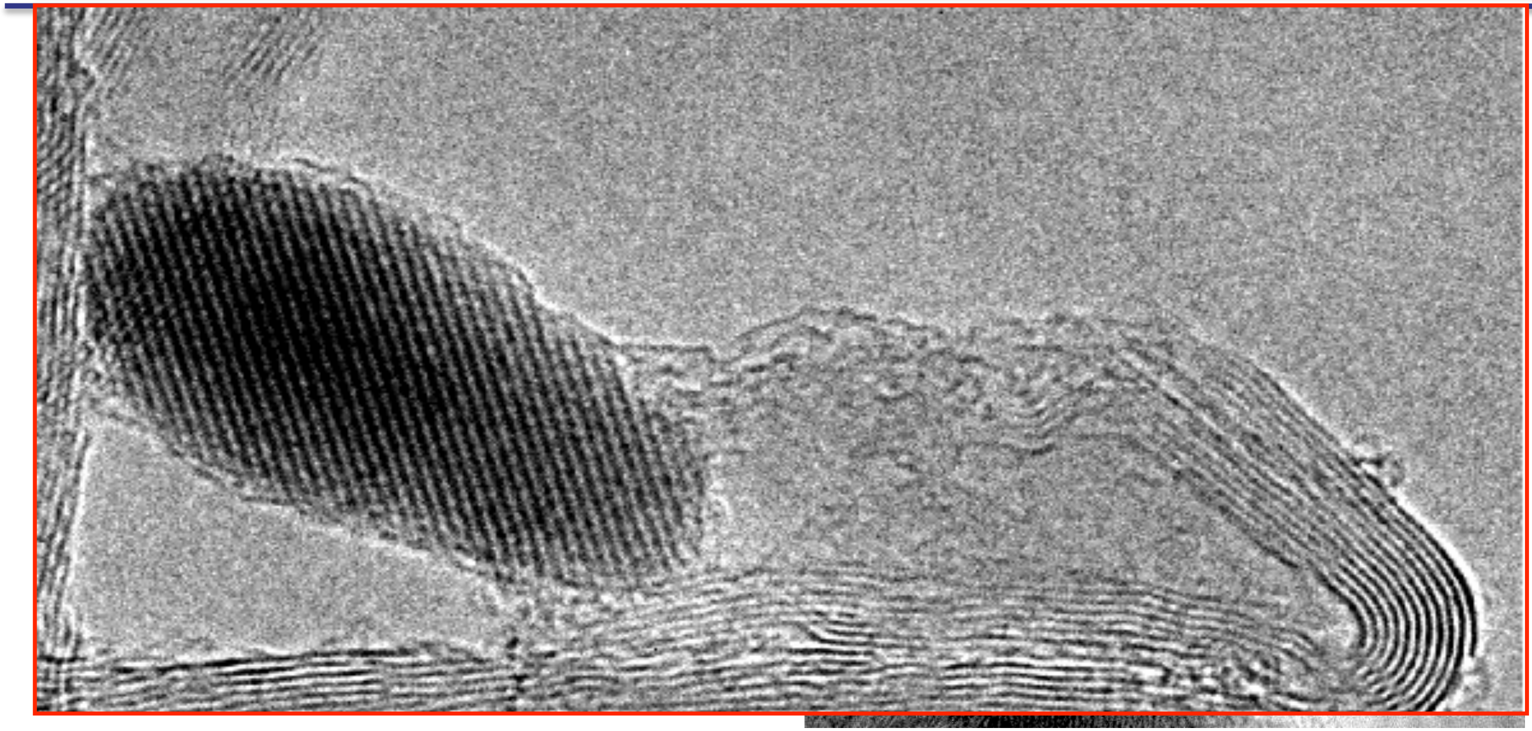
There are many variants ,

few of them are „materials“

How we generate nanocarbons



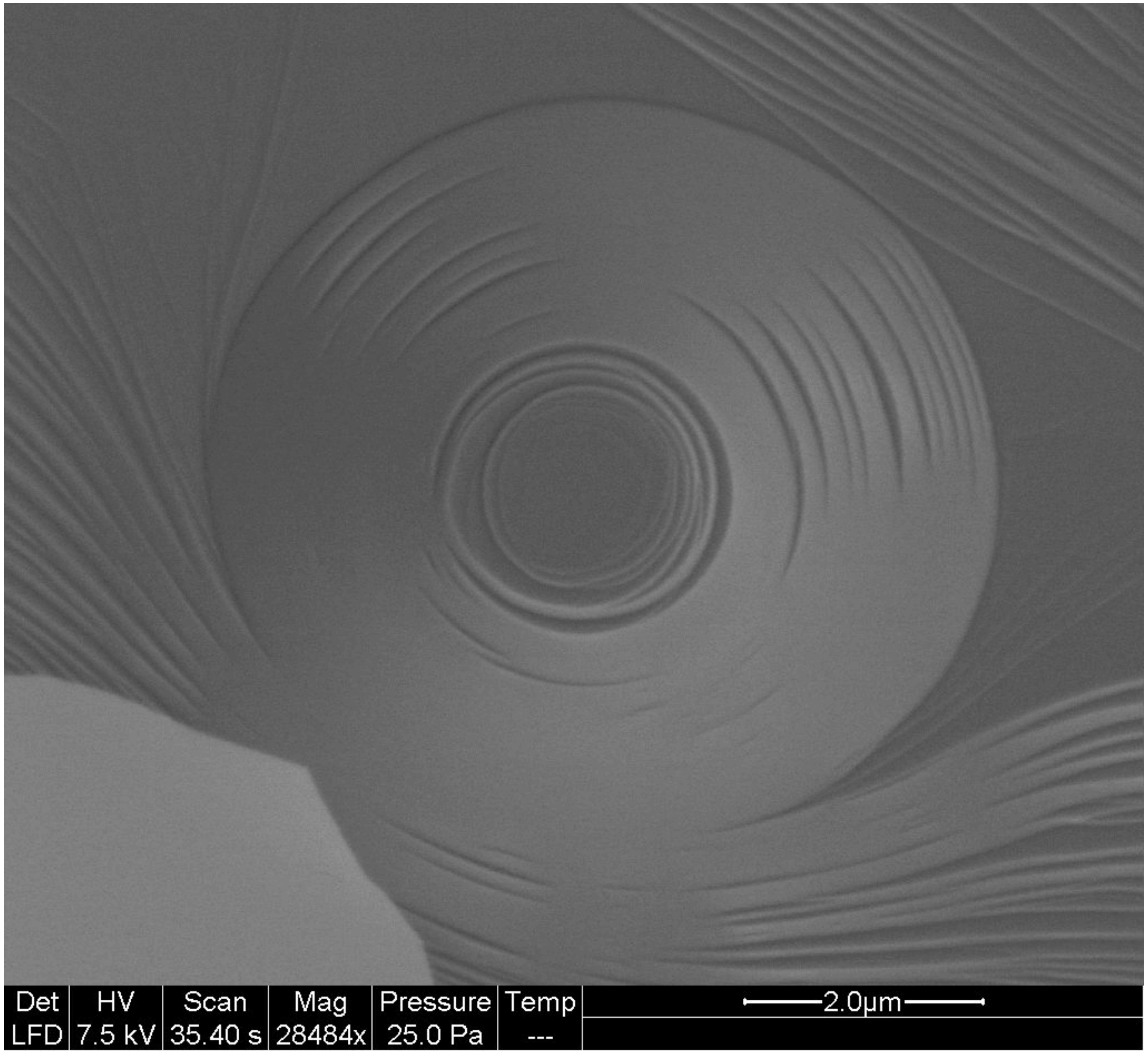
Catalytic carbon synthesis



A metal catalyst dissolves carbon from a molecular source and segregates it on ist (111) terraces via steps as graphene layers: Topotactic formation of nanocarbon given through the size and shape of the metal particle.

Poisoning and hindrance through reaction of dissolved carbon with the catalyst: carbide freezes carbon casting: re-activation thermally or through redox reaction (water hydrogen) with the carbide.

Reaction anisotropy

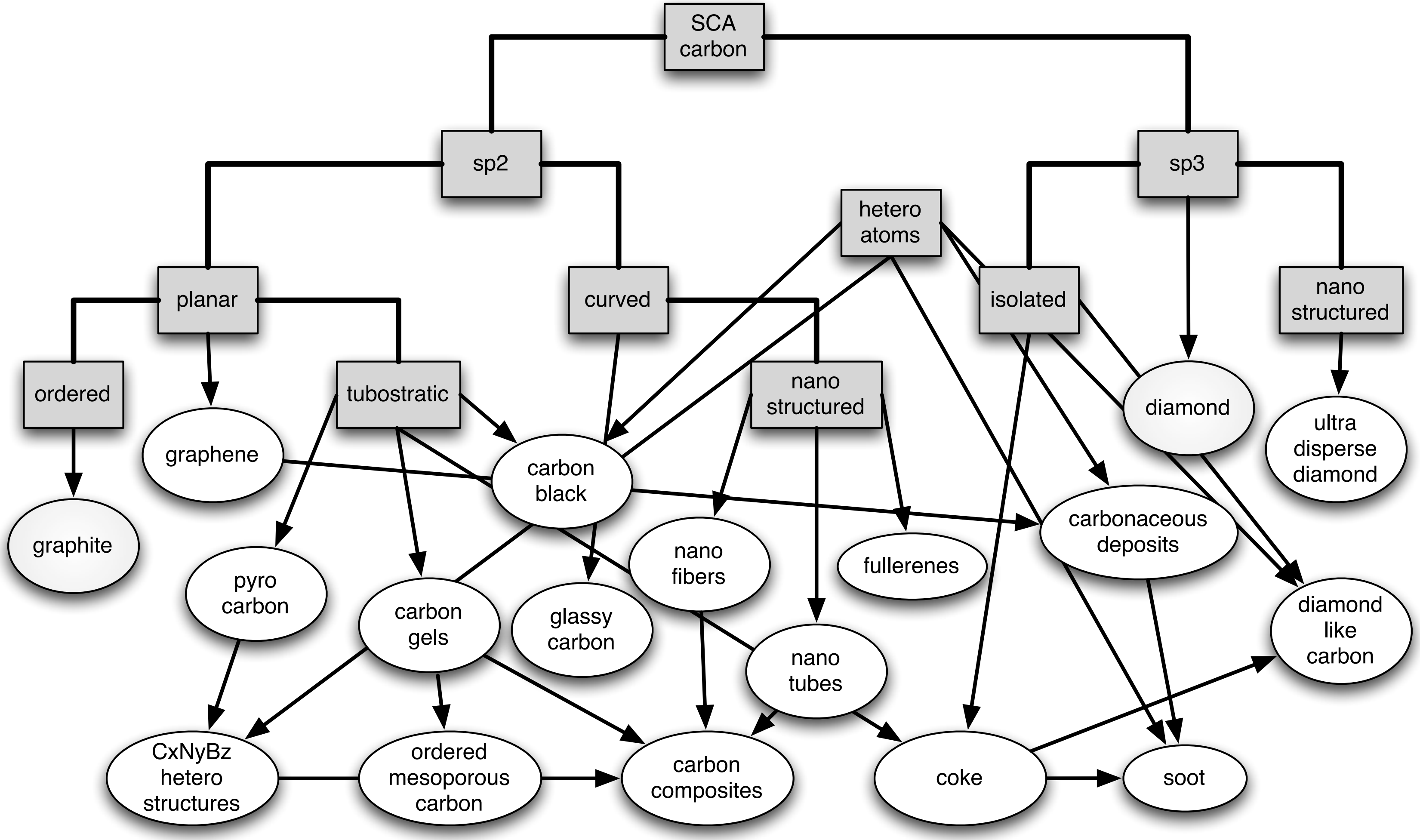


Catalytic methanation at 1273 K observed in situ in pure hydrogen:

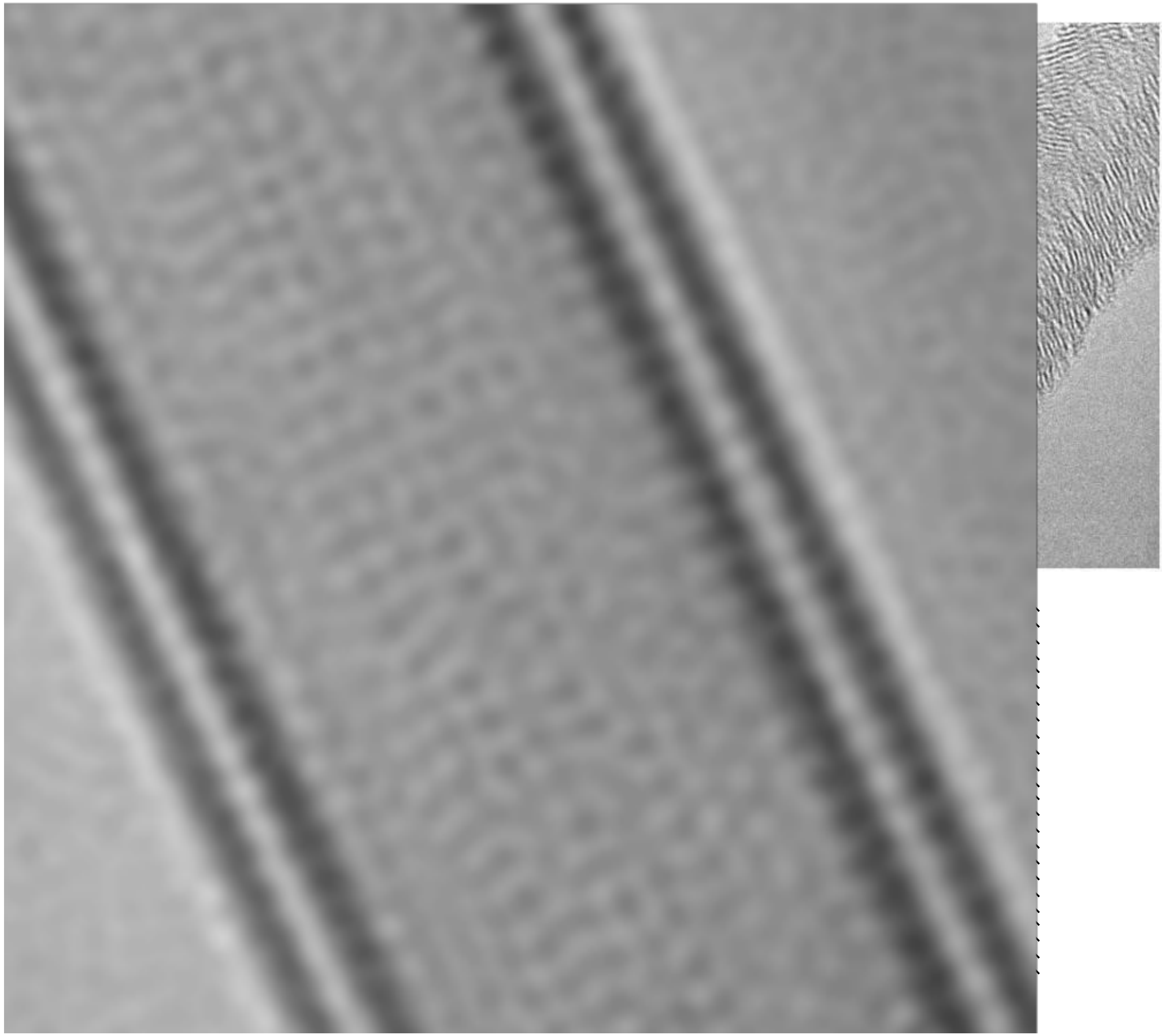
Strict reaction at the interface carbon-catalyst, no direct attack.

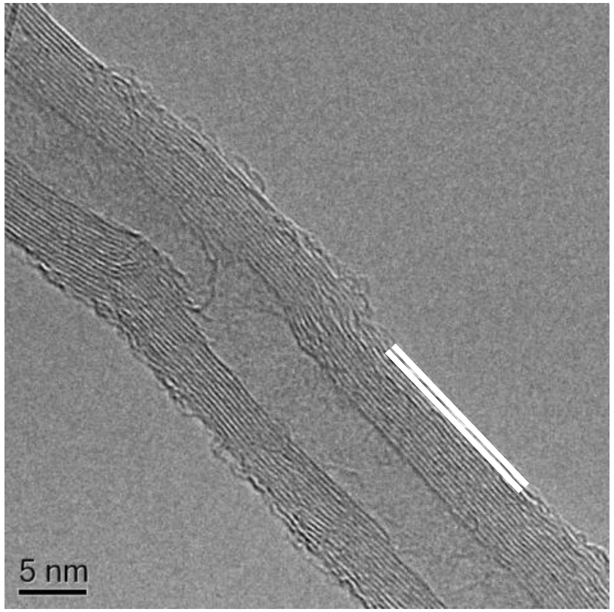
Note the reconstruction of the Pt catalyst due to graphene adsorption.

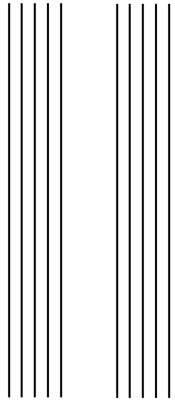
Carbon: nanostructure creates variability



Topology and real surface

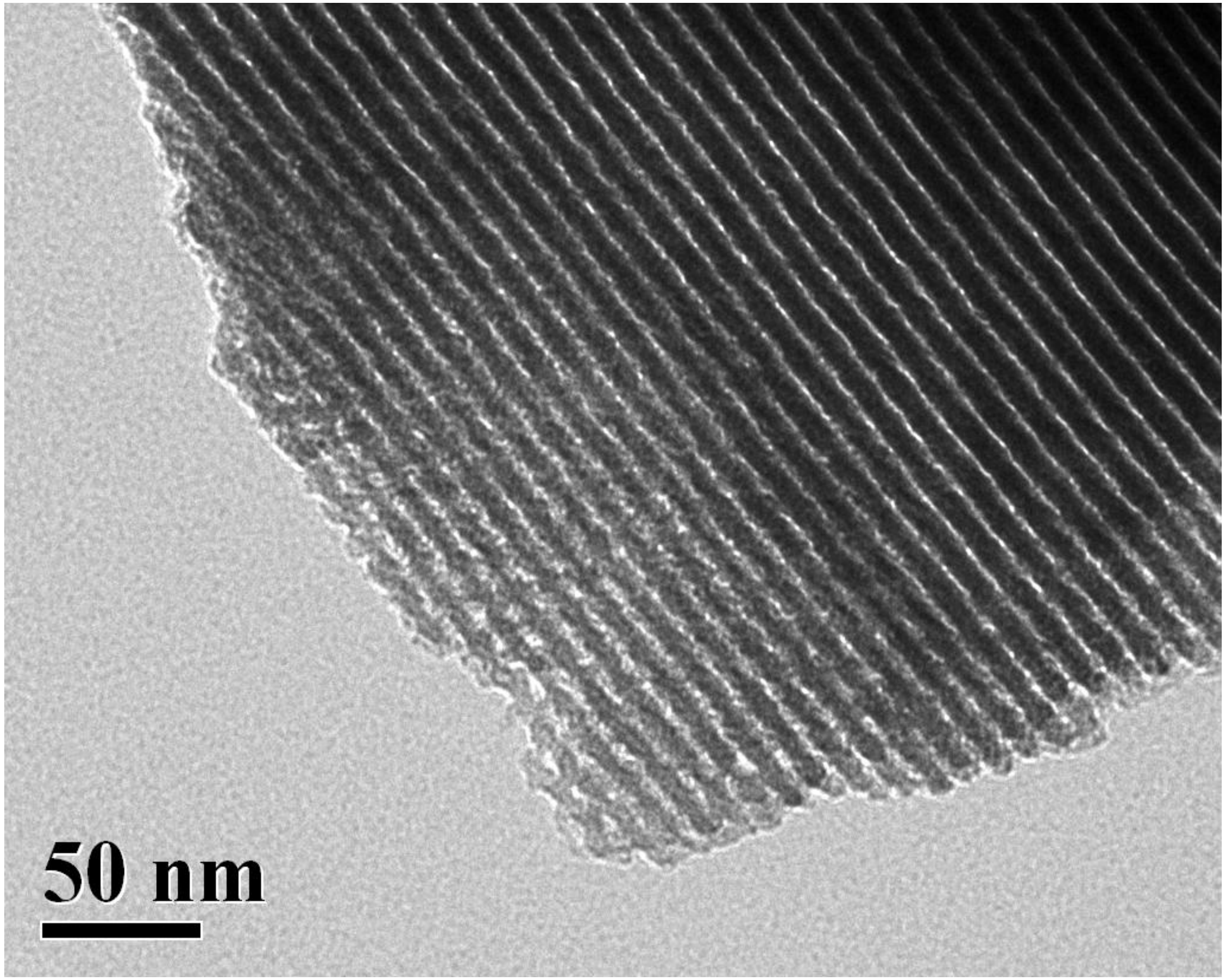






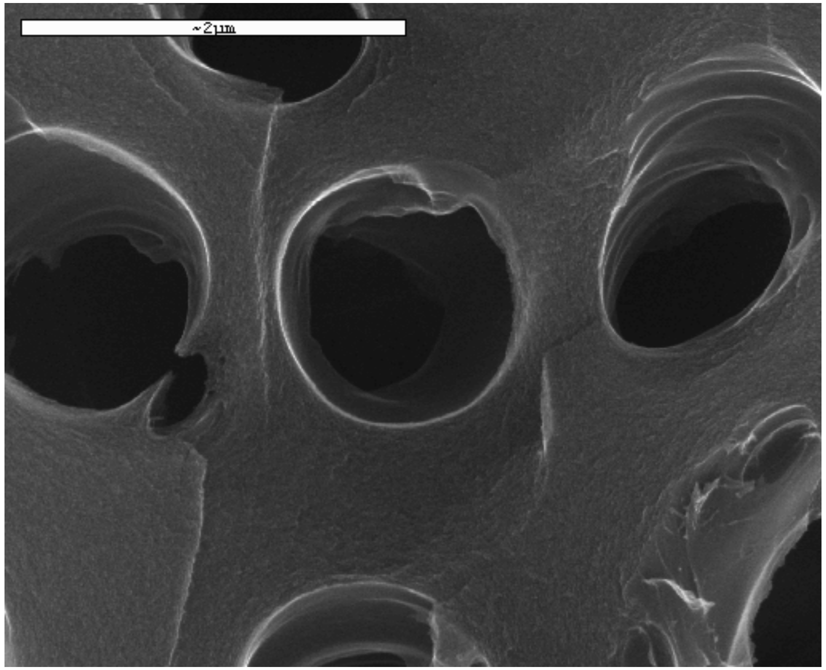
MWCNT

Highly functionalized nanocarbon

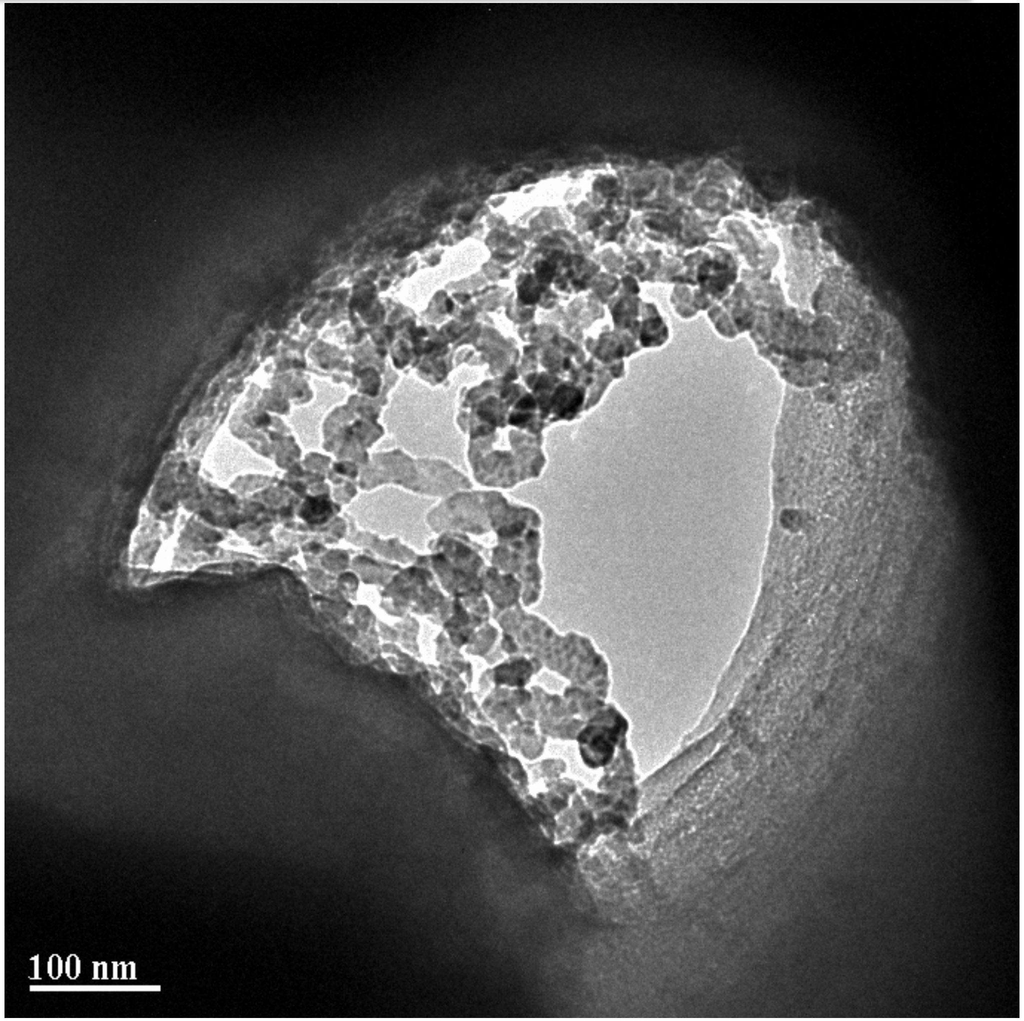


Xiaochen Zhao,
Chem. Mater.
2010, *22*, 5463–
5473

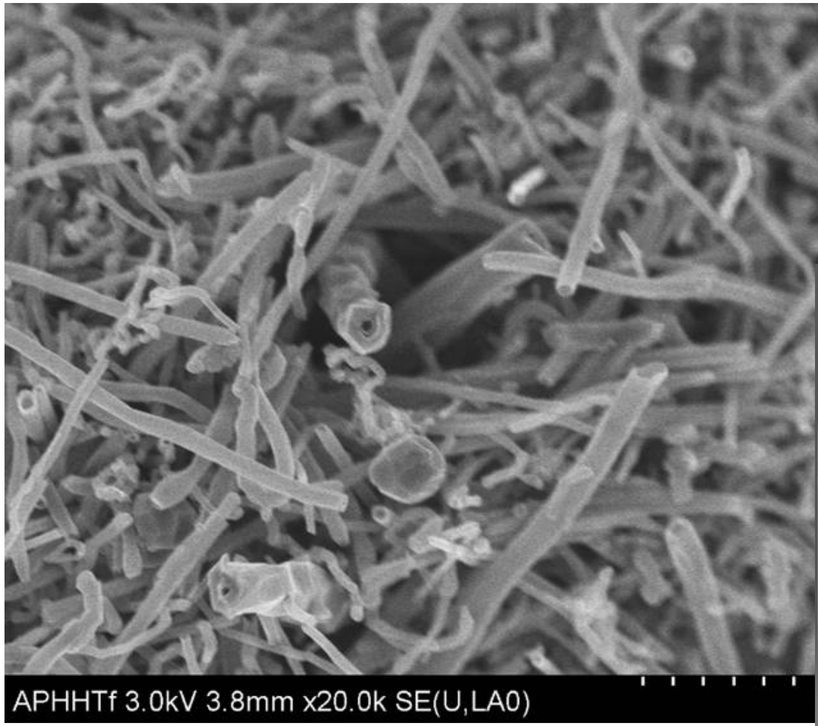
Realization of AC-supported CNF



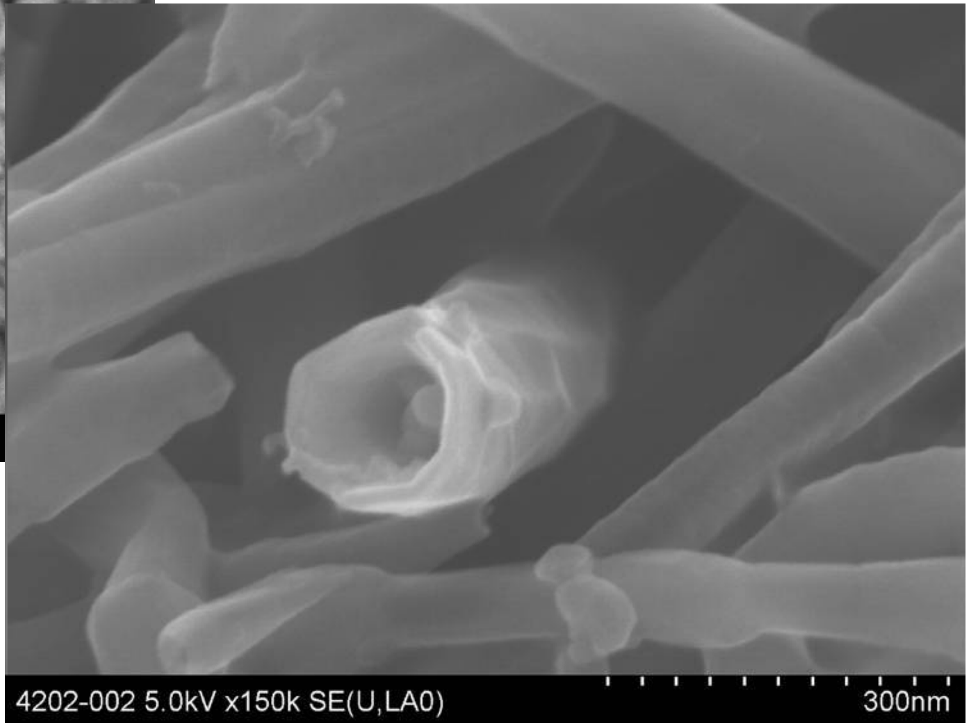
Activated carbon calcined at 673 K



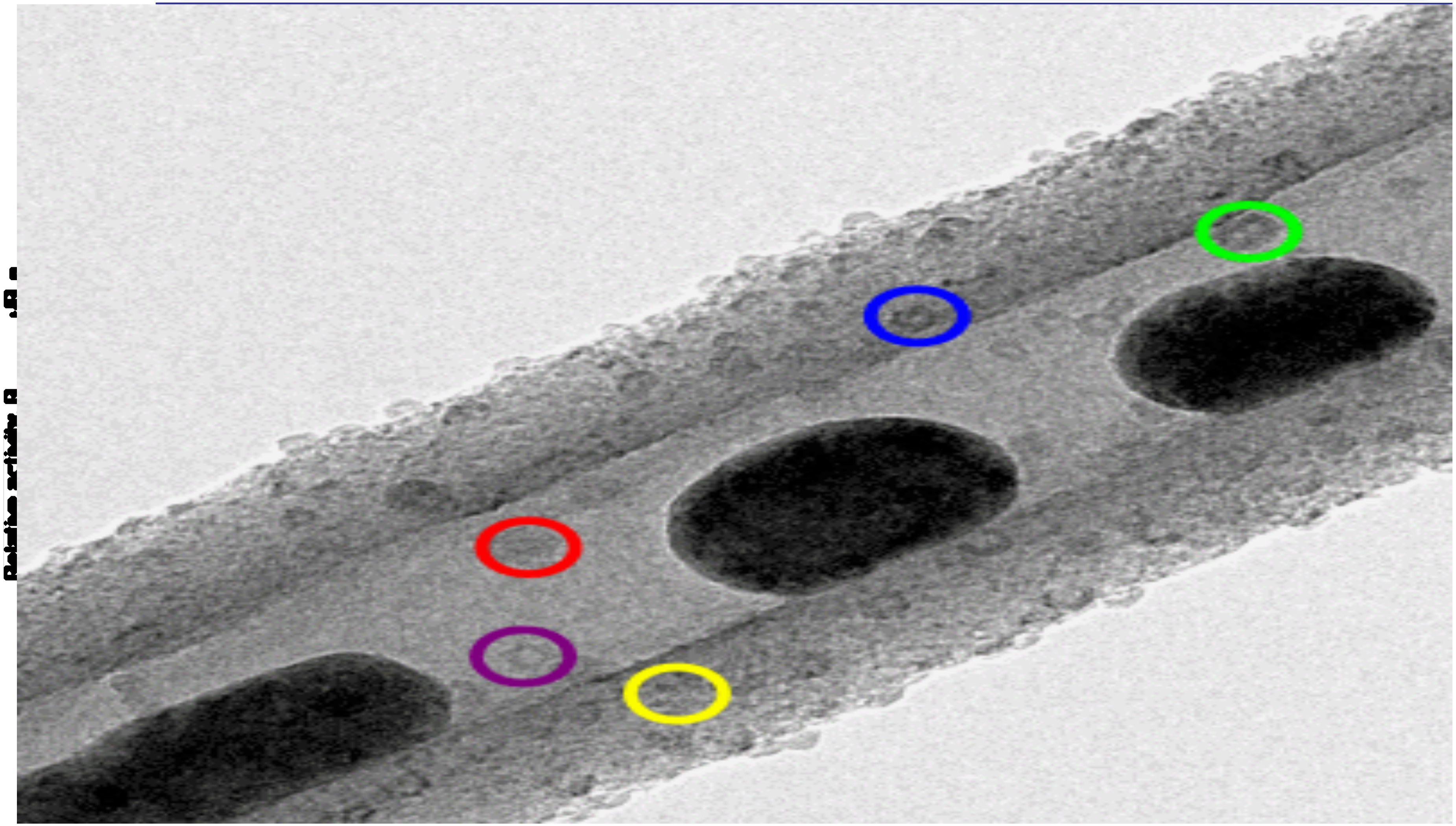
Graphitic CNT with high surface area



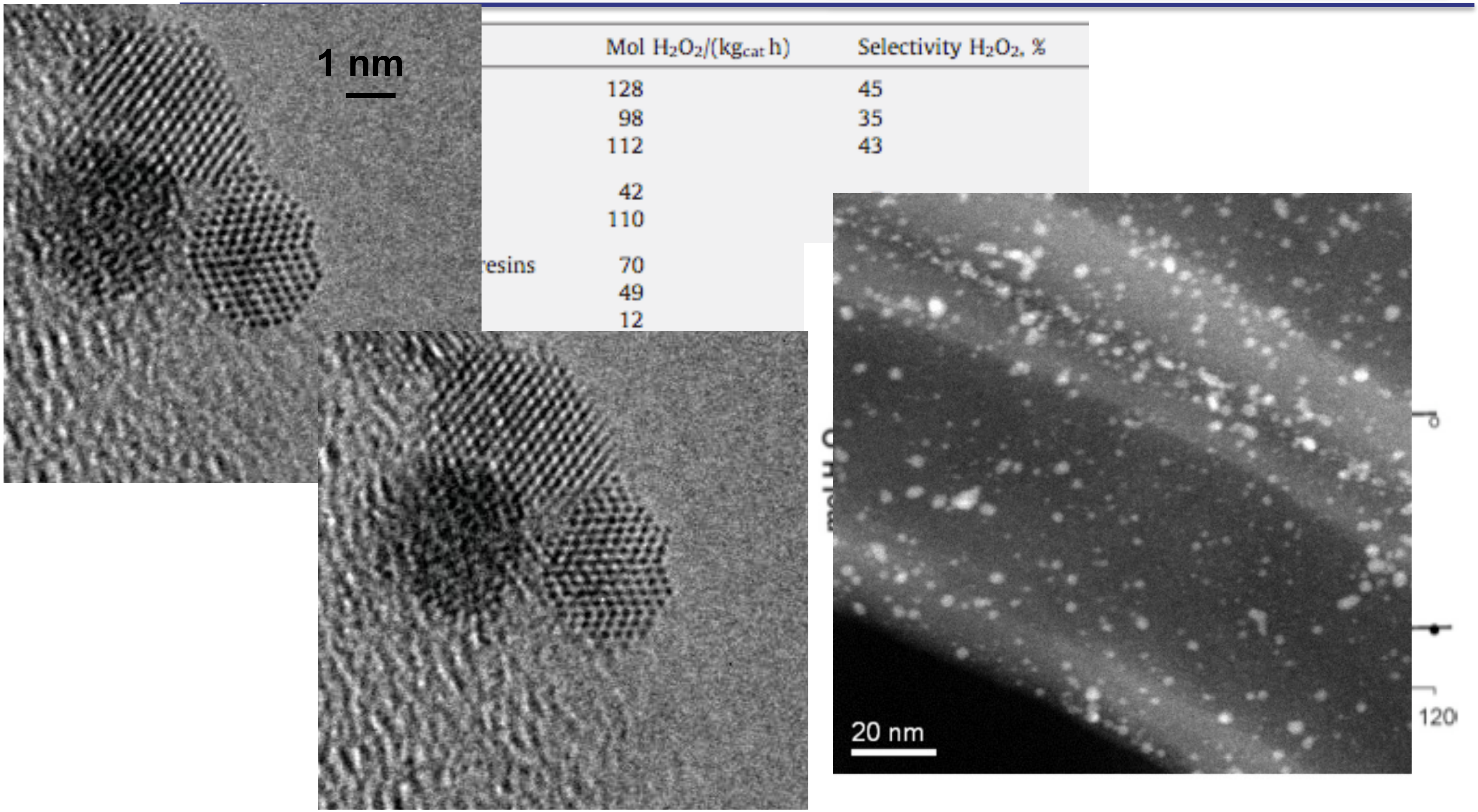
Enhancement of surface area from 16 m²/g to 347 m²/g



Ammonia splitting for hydrogen storage carbon as dimensionally stable support

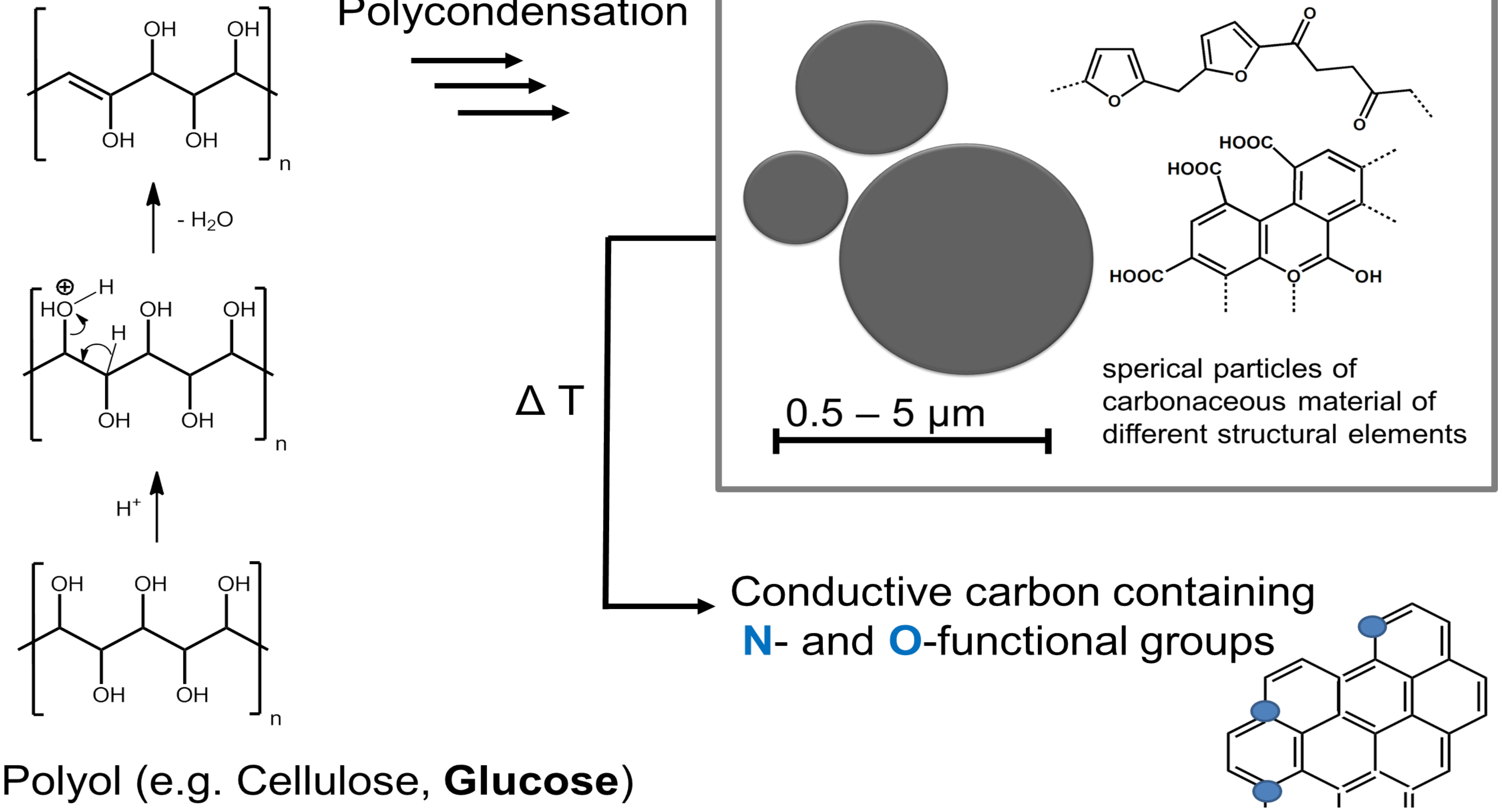


Pd/CNT in H_2O_2 synthesis
also a test reaction for water splitting



	Mol H_2O_2/(kg_{cat} h)	Selectivity H_2O_2, %
	128	45
	98	35
	112	43
	42	
	110	
esins	70	
	49	
	12	

Bottom-up synthesis
from „black stuff“ to designer carbon



Dehydration

Polycondensation

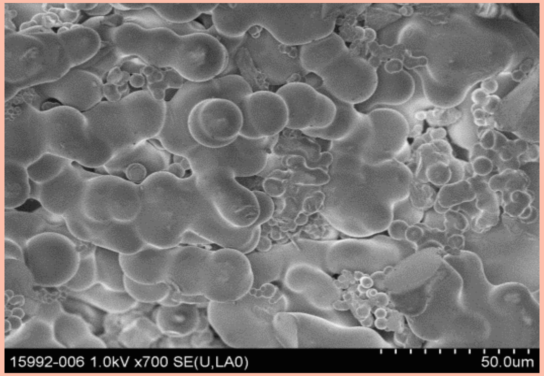
Polyol (e.g. Cellulose, **Glucose**)

Hydrothermal Carbon (HTC)

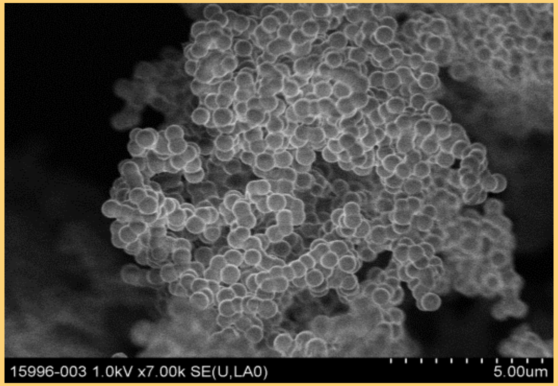
sperical particles of carbonaceous material of different structural elements

Conductive carbon containing **N**- and **O**-functional groups

Solvothermal synthesis
a scalable concept for de-novo carbon

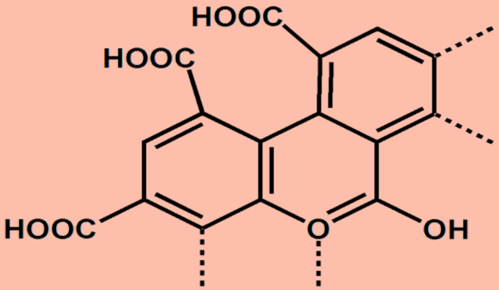


50 µm



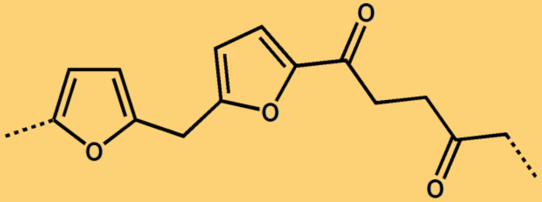
5 µm

Low pH



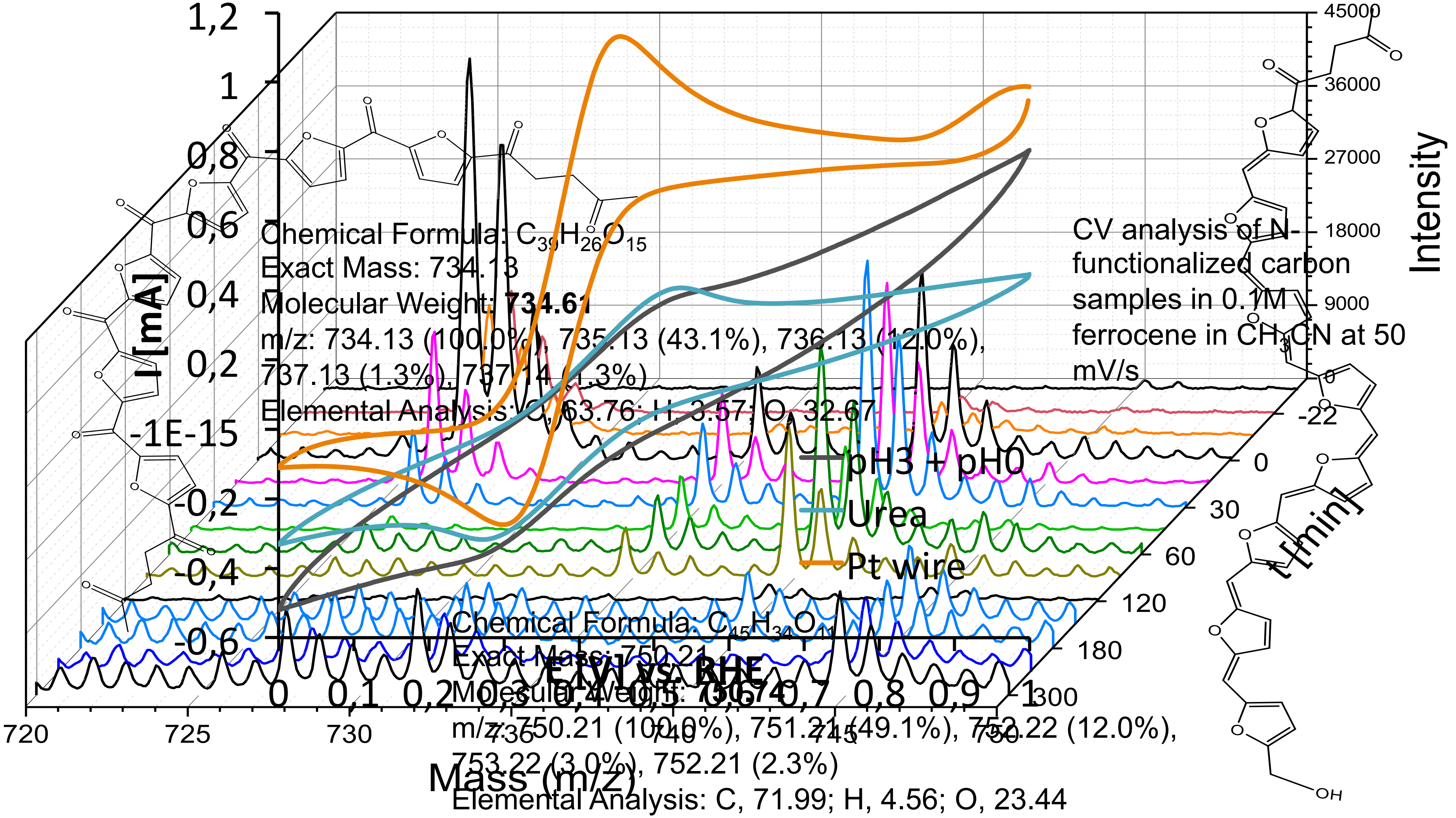
higher fraction of

Higher pH



higher fraction of

Control of synthesis and doping



Chemical Formula: $C_{39}H_{26}O_{15}$
Exact Mass: 734.13
Molecular Weight: **734.61**
m/z: 734.13 (100.0%), 735.13 (43.1%), 736.13 (12.0%), 737.13 (1.3%), 737.14 (1.3%)
Elemental Analysis: C, 63.76; H, 3.57; O, 32.67

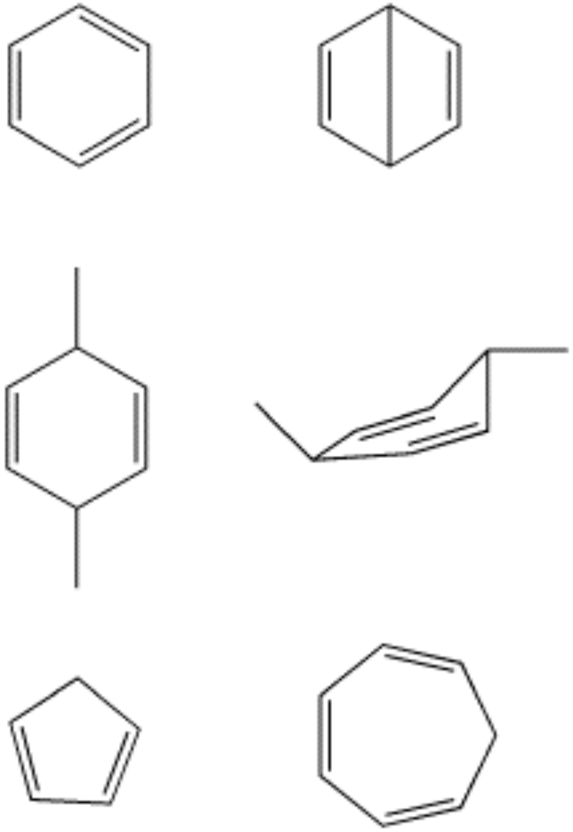
Chemical Formula: $C_{45}H_{34}O_{11}$
Exact Mass: 750.21
Molecular Weight: 750.74
m/z: 750.21 (100.0%), 751.21 (49.1%), 752.22 (12.0%), 753.22 (3.0%), 752.21 (2.3%)
Elemental Analysis: C, 71.99; H, 4.56; O, 23.44

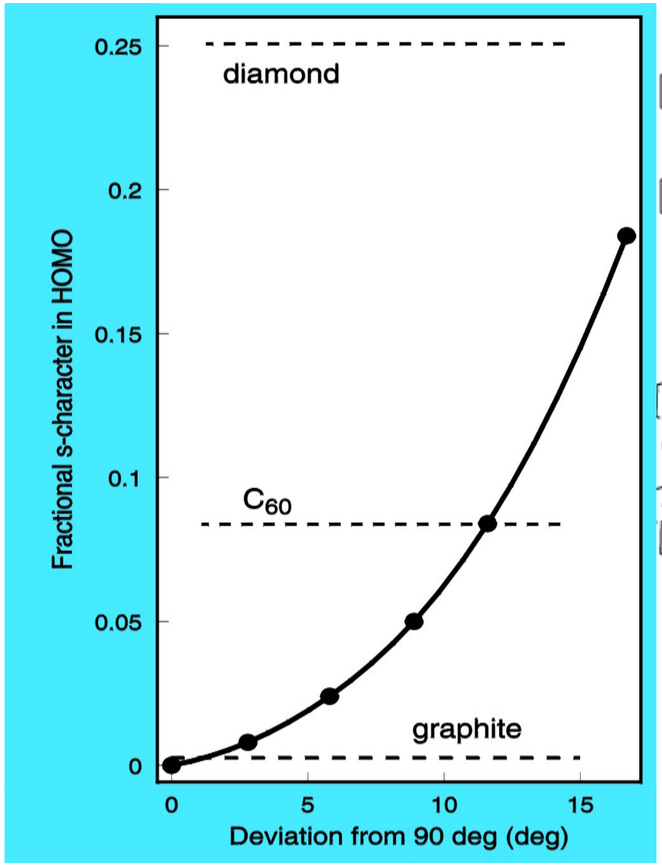
CV analysis of N-functionalized carbon samples in 0.1M ferrocene in CH_3CN at 50 mV/s

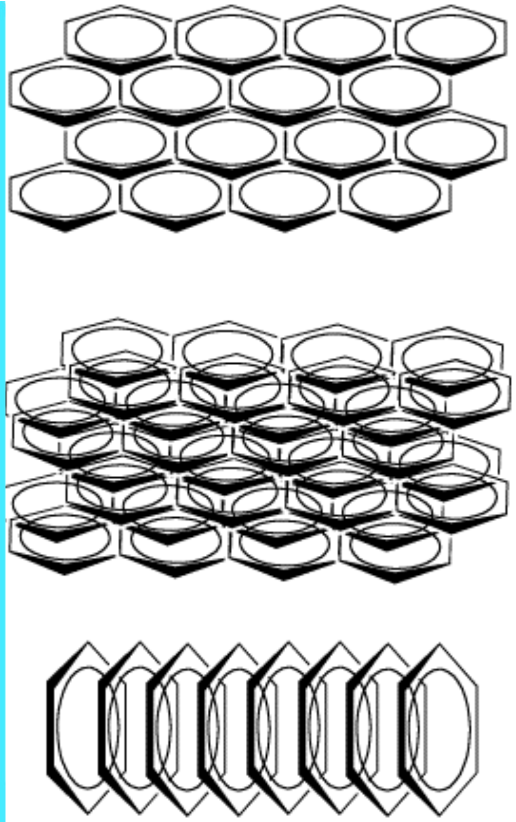
Electronic structure

The origin of the use of nanocarbons in (electro)catalysis

Hierarchical bonding properties: nanostructurung is more than a (past) fashion





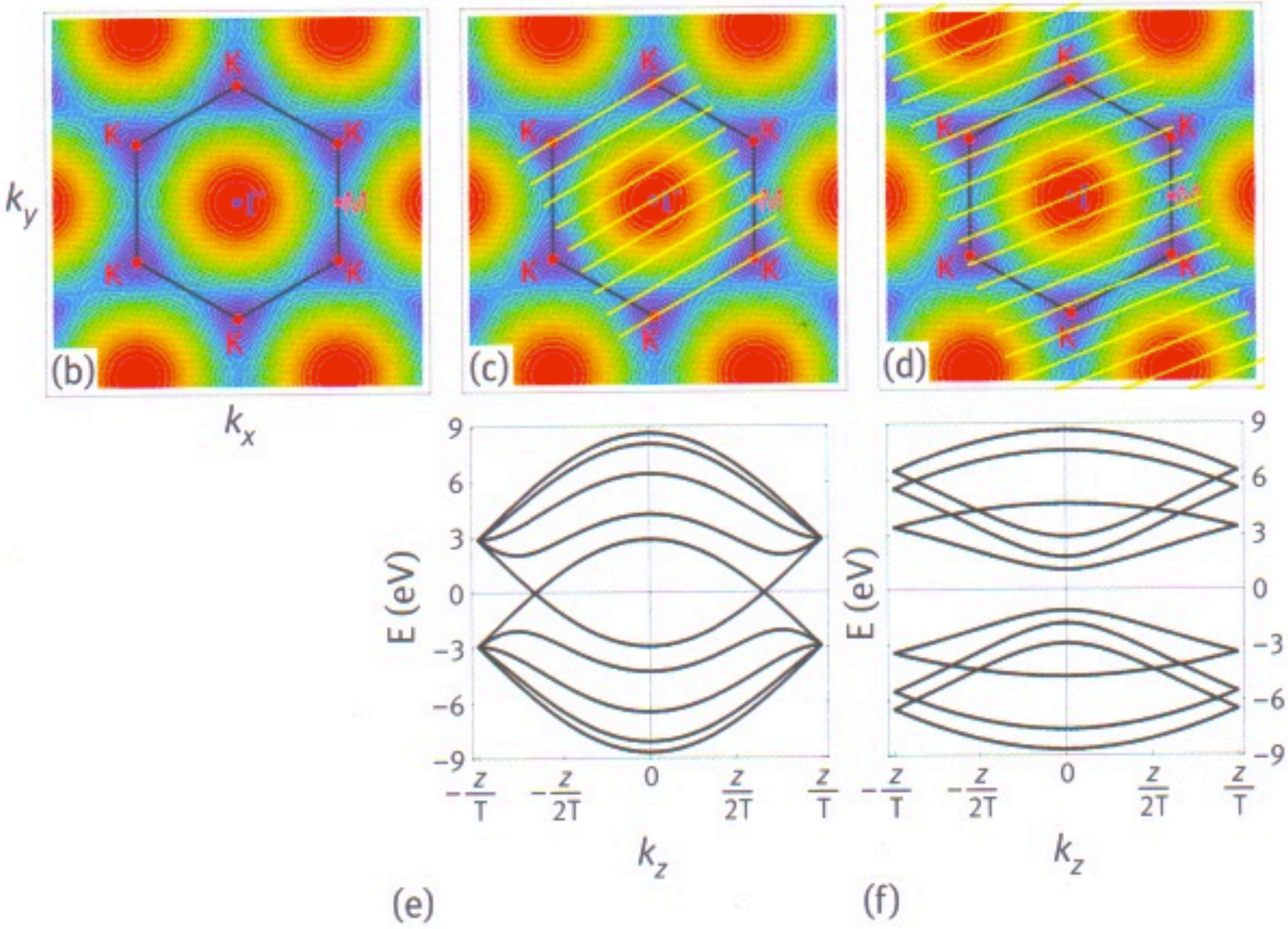


Local bonding:
From metallic („aromatic“)
to excitonic (poly-ene)

Mesosopic:
Curvature,
surface termination

Extended:
Basal vs prism faces
Van-der-Waals vs covalent

Band structure of graphene and nanocarbon



Electronic anisotropy:
the role of "defects" as centers of reactivity

With M. Scheffler and team

J. T. TITANTAH, K. JORISSEN, AND D. LAMOEN PRB 2004

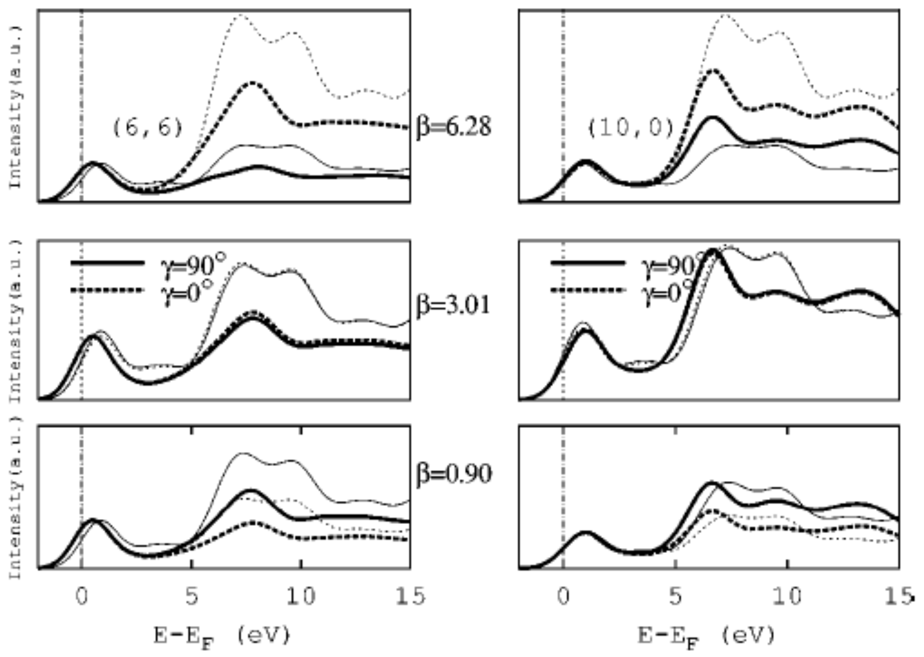
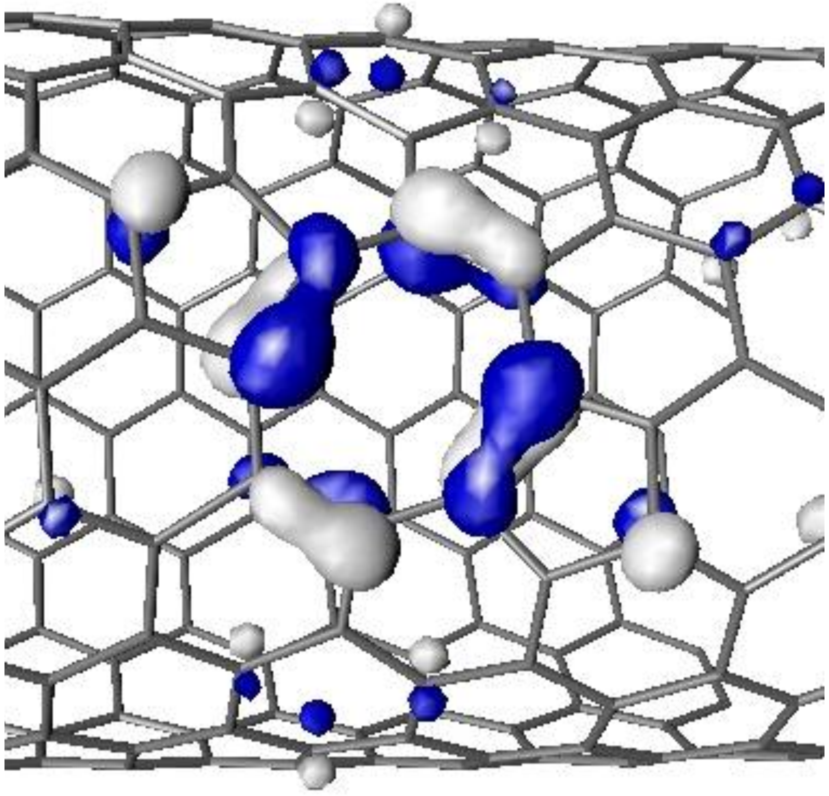


FIG. 12. Orientation resolved ELNES of (6,6) and (10,0) tubes (bold line) and comparison with graphite (thin line). The spectra for $\gamma=0°$ (dashed line) and $\gamma=90°$ (full line) coincide exactly over all energies for $\beta=3.01$ mrad but no such coincidence is seen for $\beta=6.28$ mrad and $\beta=0.90$ mrad. The vertical line indicates the Fermi level.



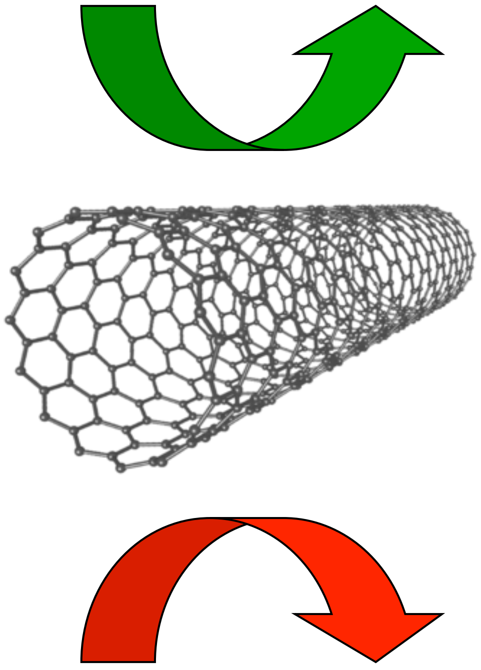
m the anisotropy of the sp^2 bonding:
nctionalization, the (red) basal plane
low electron density.

Functional groups

The main reason for making nanocarbons in chemical applications:

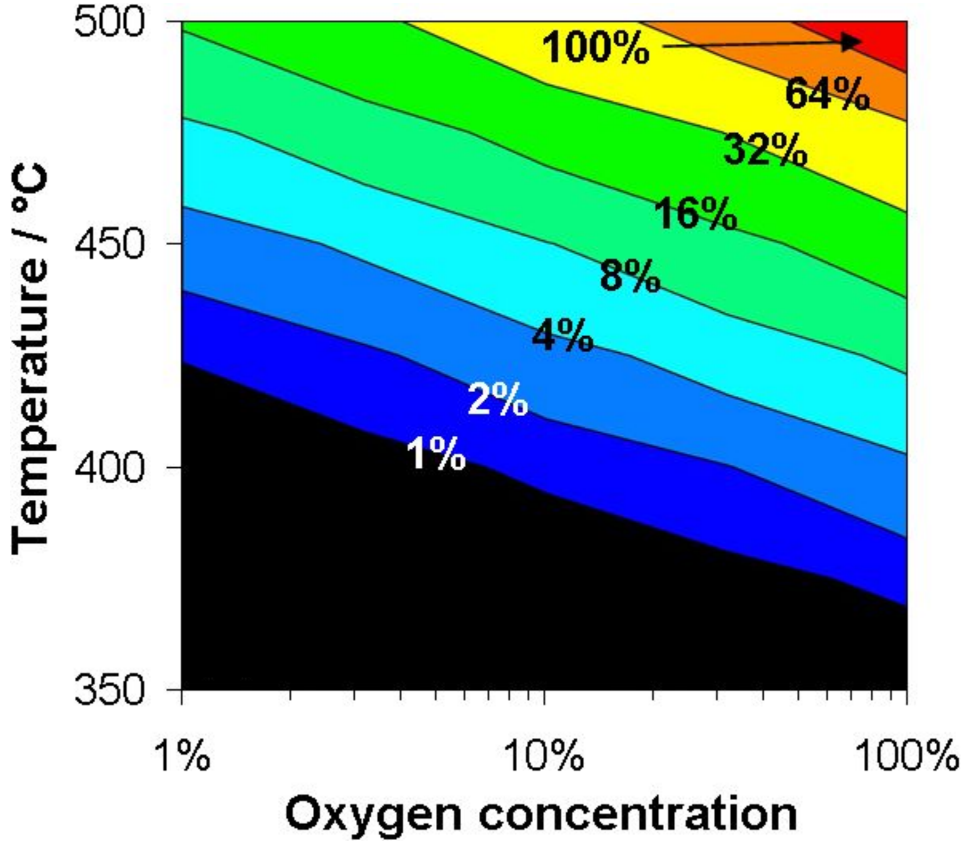
Exist only at defects of the graphene structure!

Oxidative stability:
HC increase the stability up to 100 K



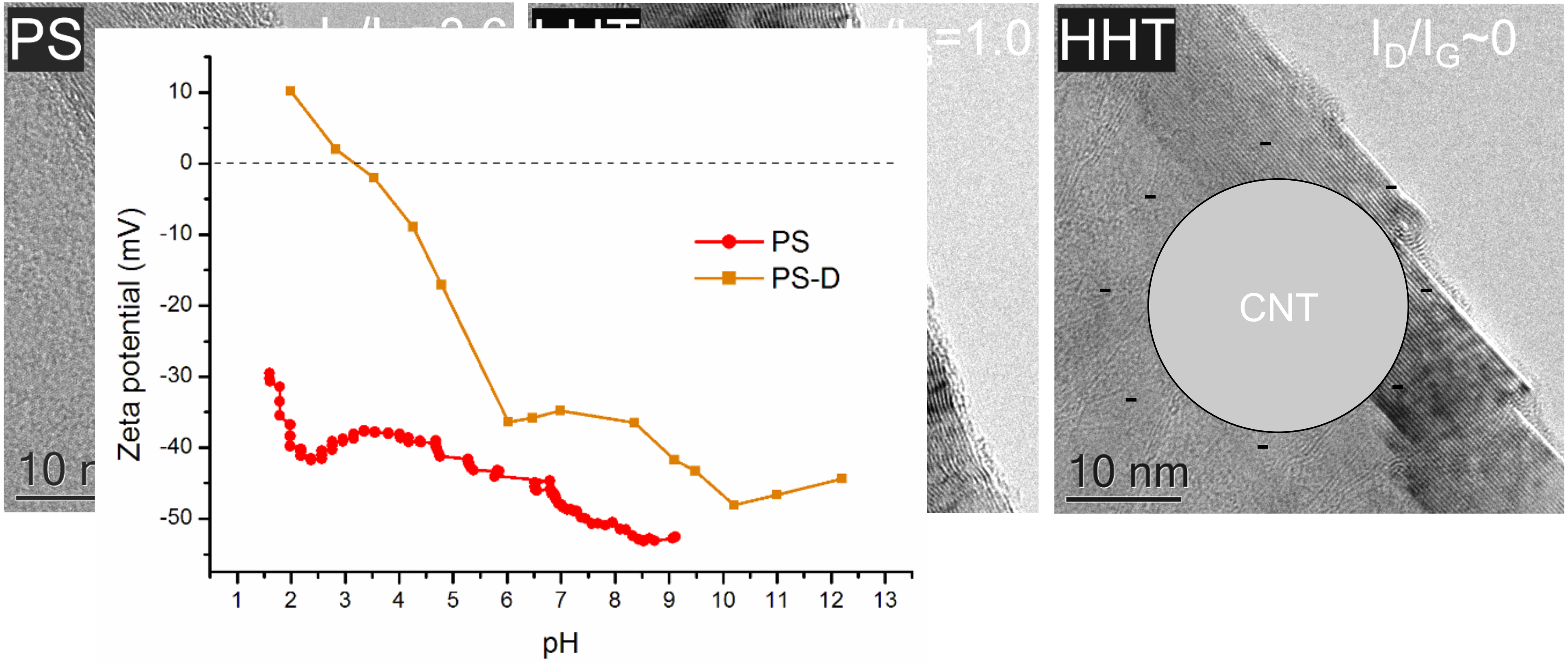
$Alkane + O_2$ $Alkene + H_2O$

O_2 CO_2



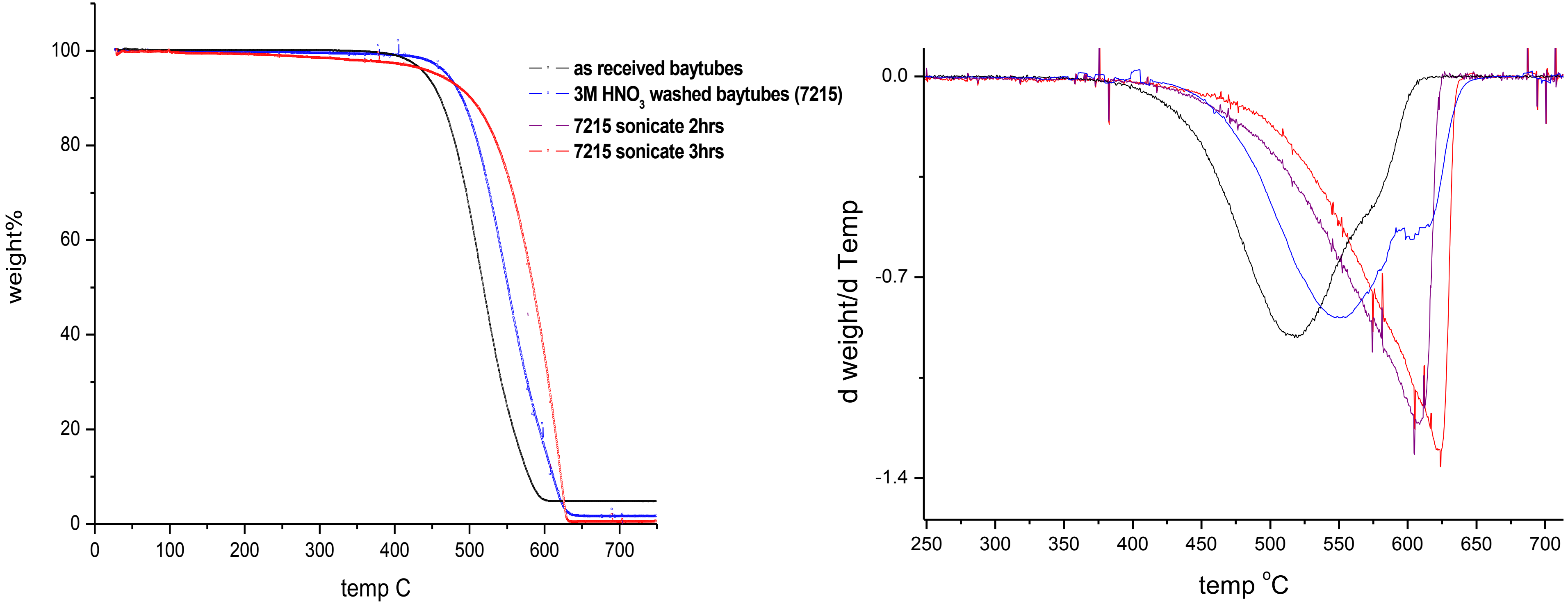
Fraction of B-oCNTs burned after 24 h TOS *without* hydrocarbon

Surface quality



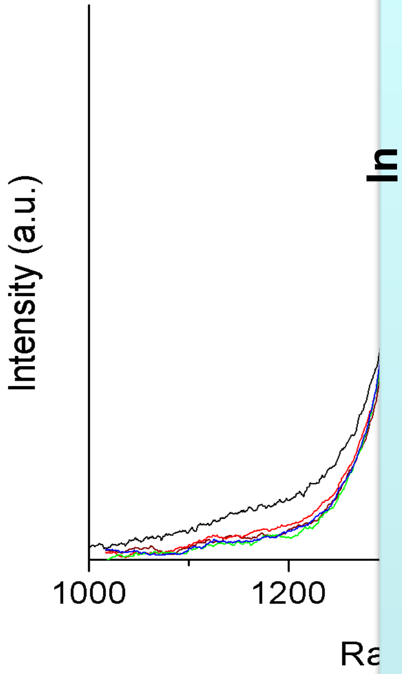
The surface charge coming from functional groups controls chemisorptive properties and hydrophilicity

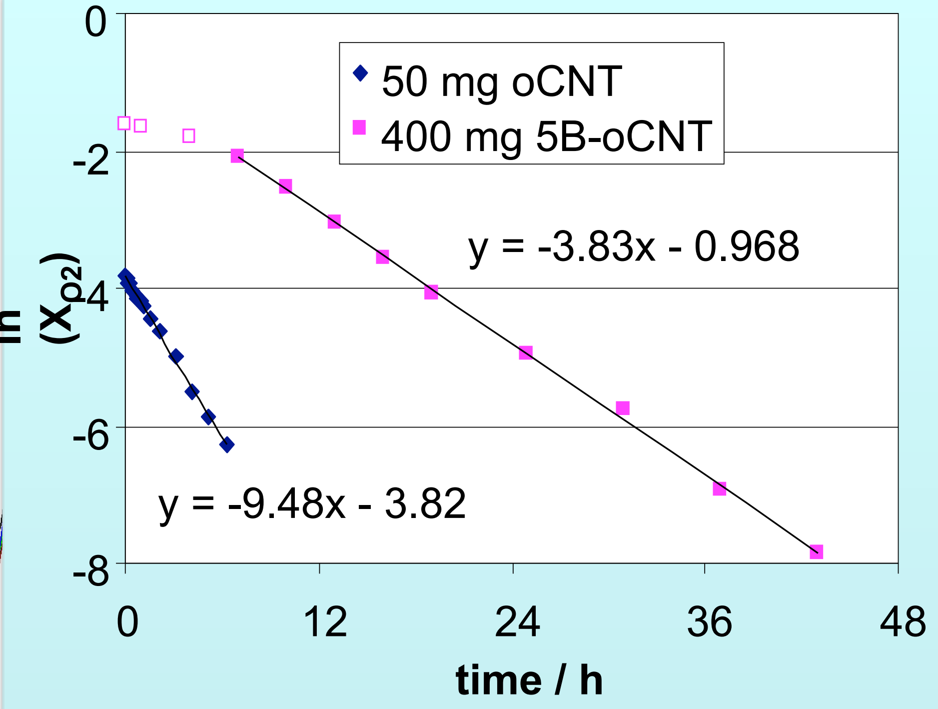
Combustion:
A valuable analytical tool describing the ordering state



Combustion that is conducted such that not oxygen limitation controls the kinetics allows detained insight into the nature of the burning carbon: the reaction is only possible at defects and edge sites.

The basis of all functional sites: mechanism of oxidation

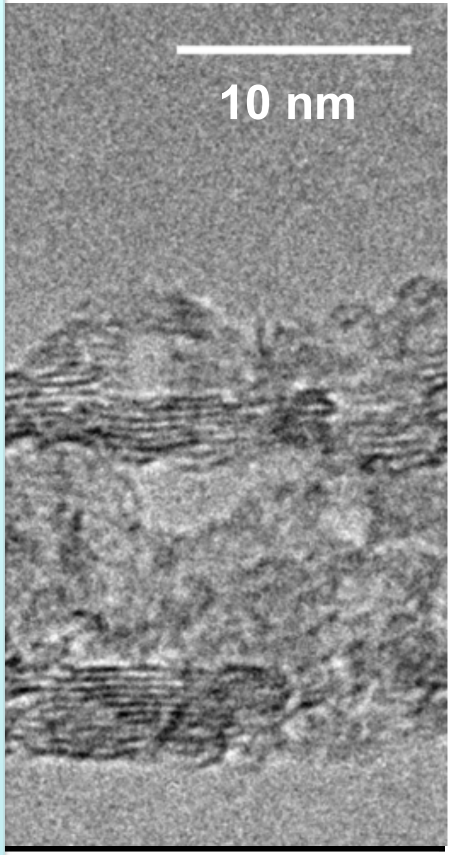




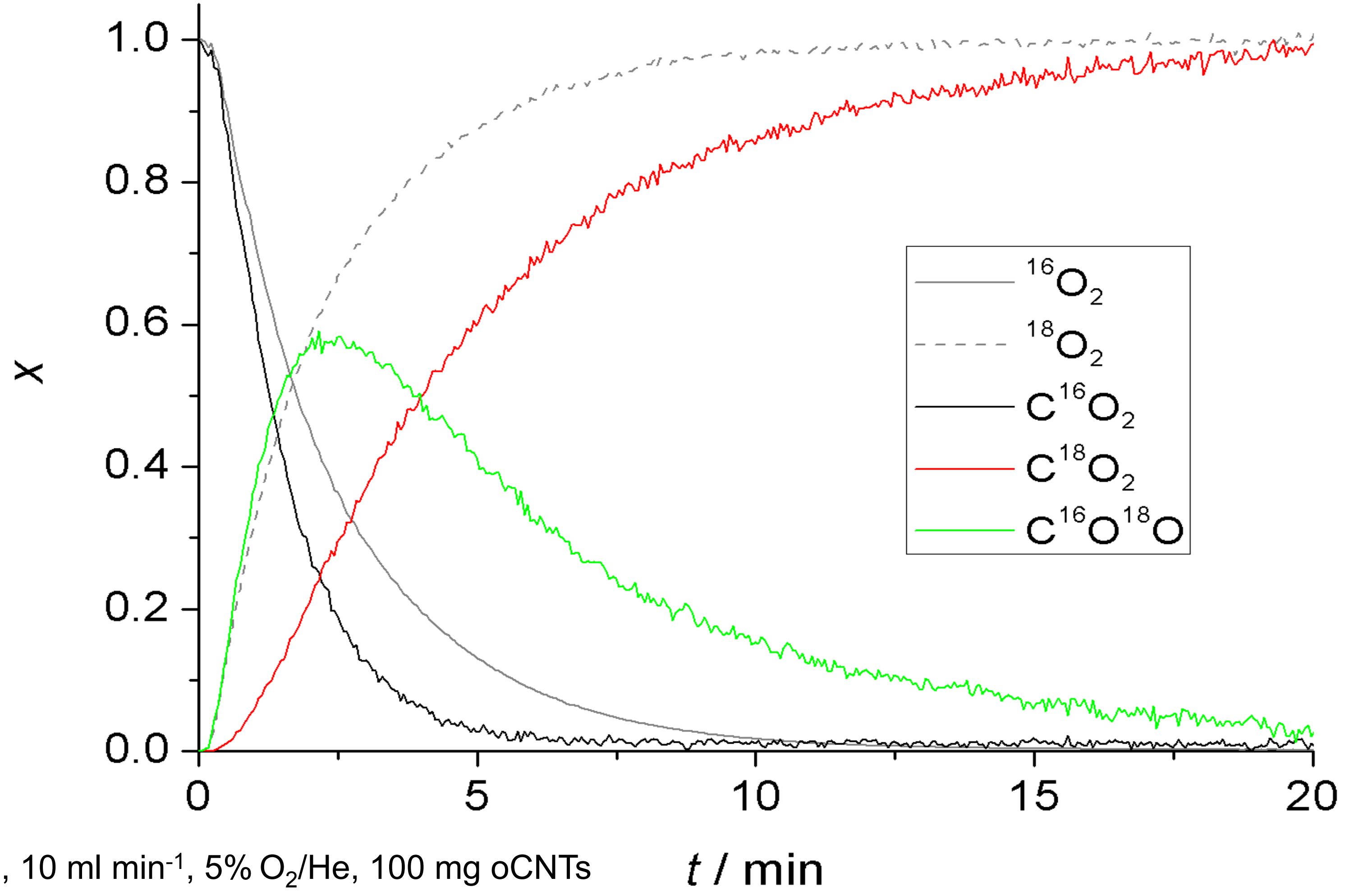
First order in oxygen

Rate proportional to $pO_2^{0.5}$

B,P promotion reduces number of active sites

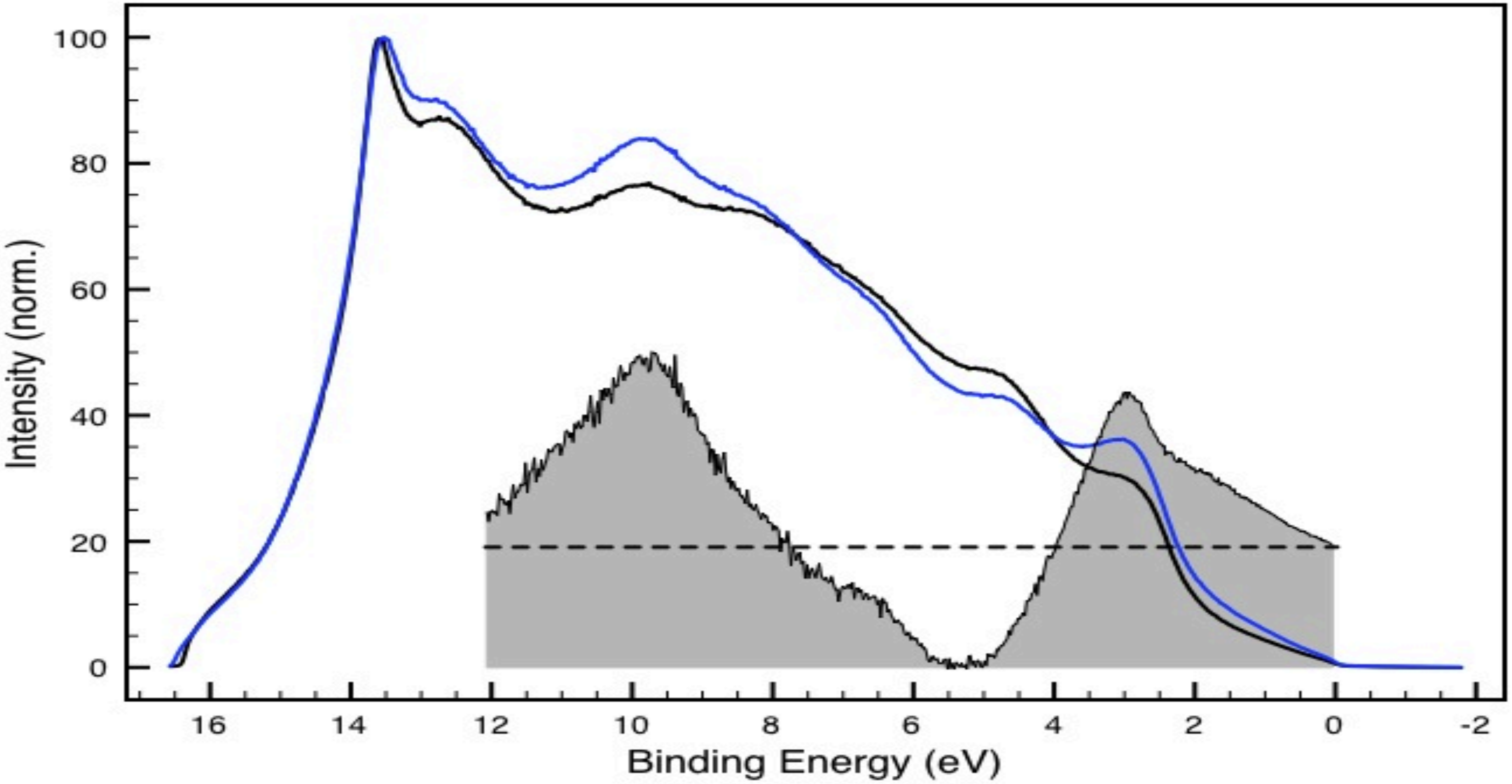


What happens during carbon oxidation



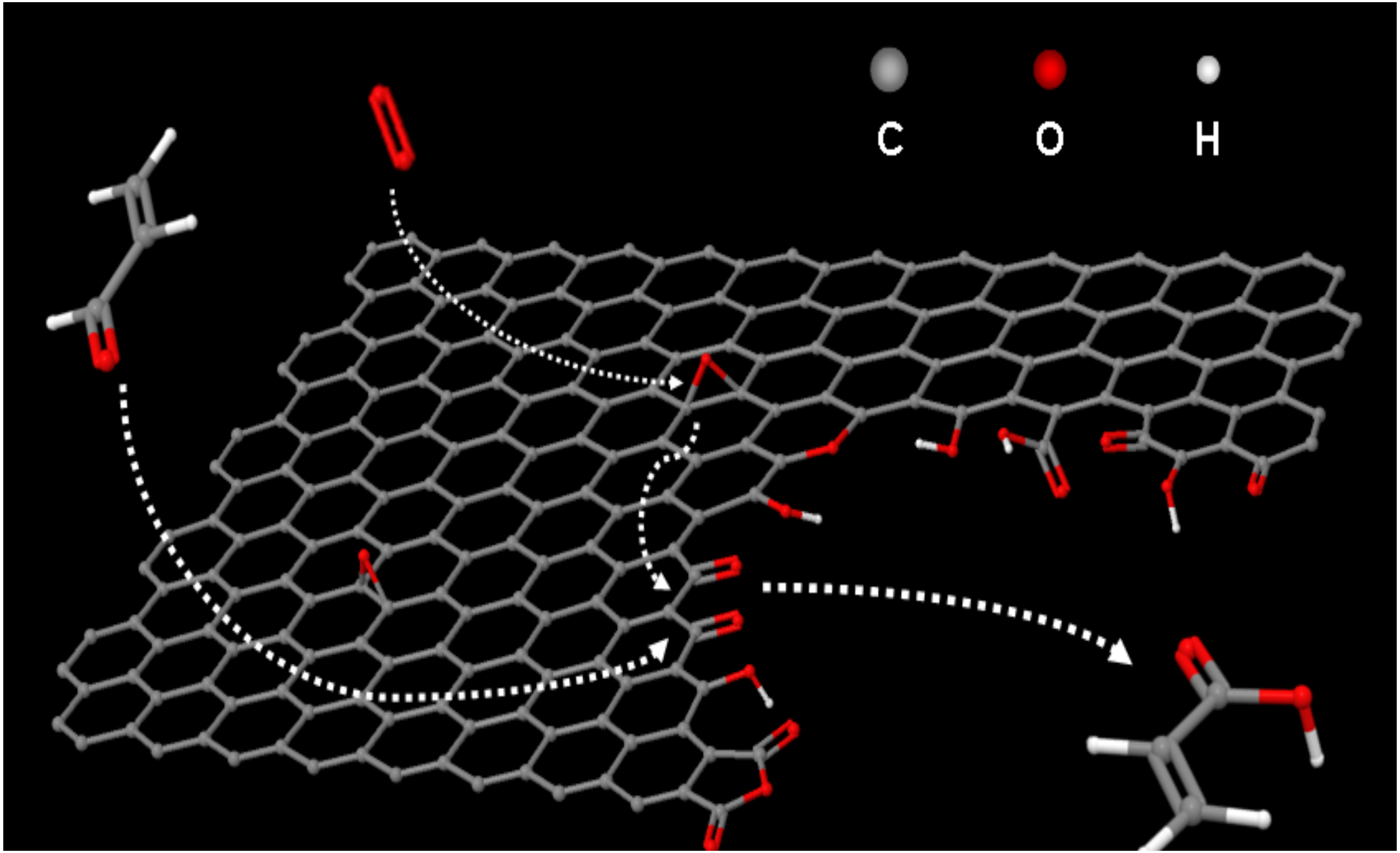
400 °C, 10 ml min^{-1}, 5% O_2/He, 100 mg oCNTs

Electronic structure and nanostructure: How is oxygen stored on carbon?

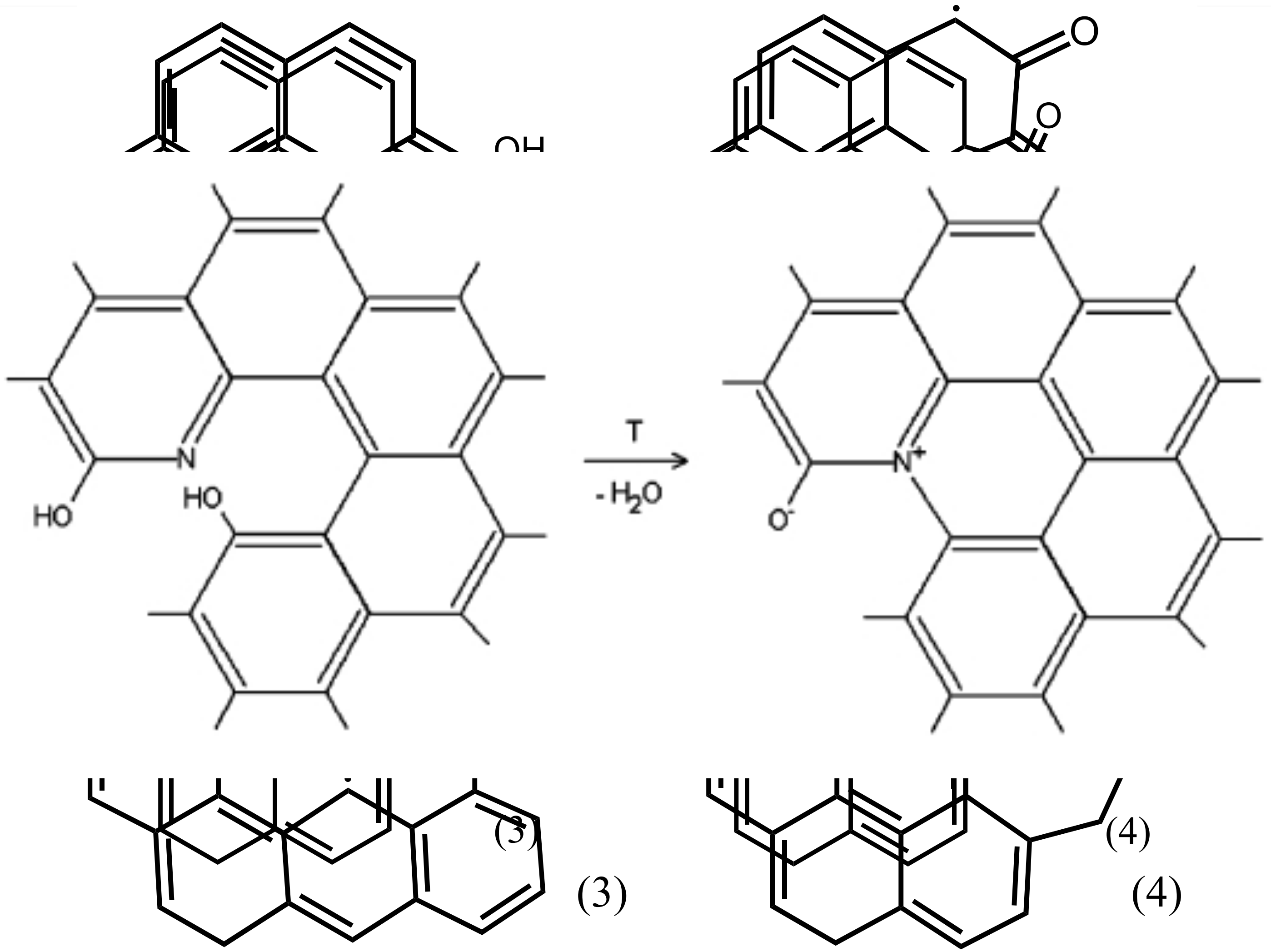


Binding Energy (eV)

A concept



Termination



Calibration of functional group analysis

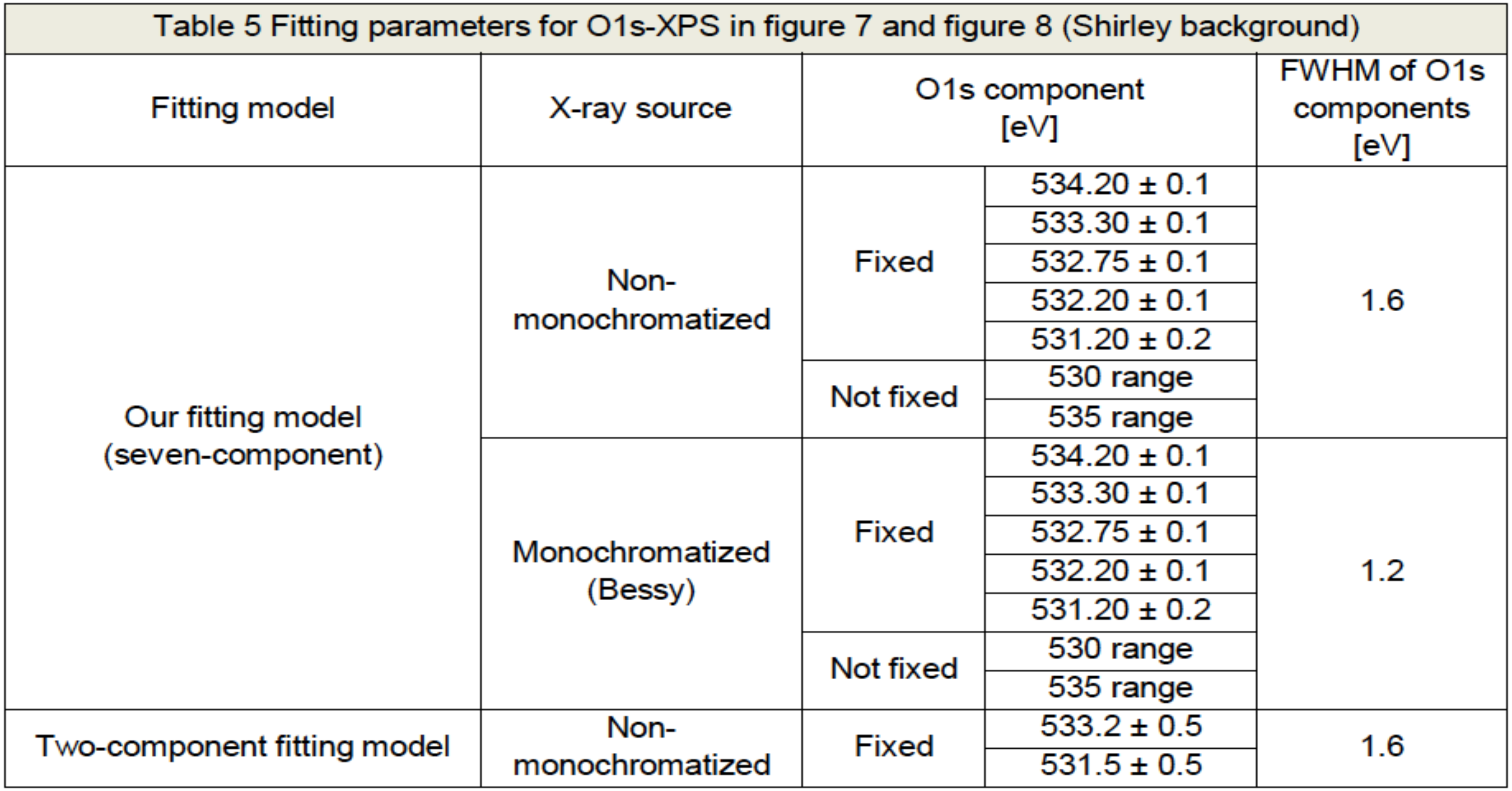
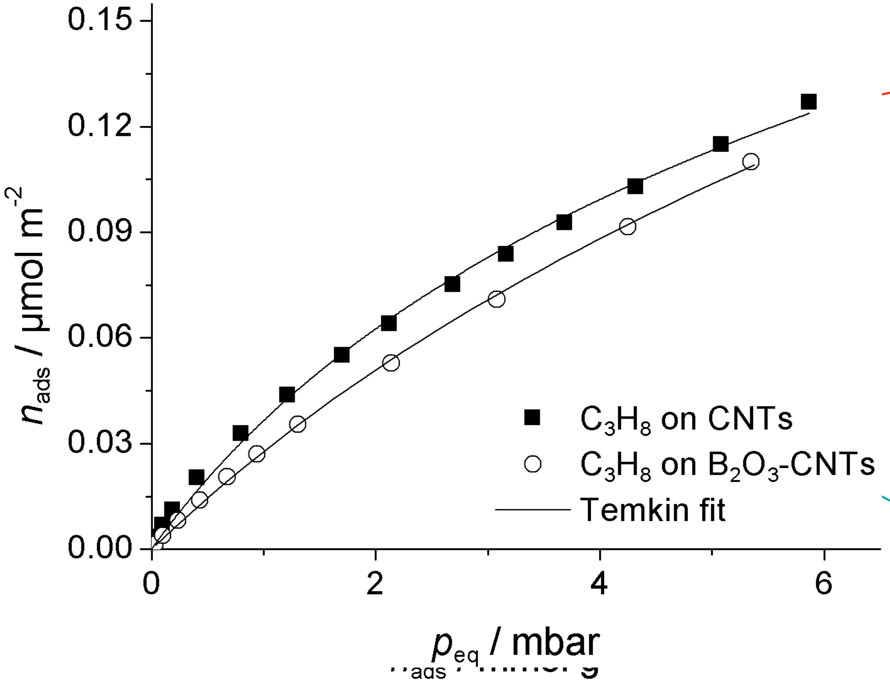


Table 5 Fitting parameters for O1s-XPS in figure 7 and figure 8 (Shirley background)

Fitting model	X-ray source	O1s component [eV]		FWHM of O1s components [eV]
Our fitting model (seven-component)	Non-monochromatized	Fixed	534.20 ± 0.1	1.6
			533.30 ± 0.1	
			532.75 ± 0.1	
			532.20 ± 0.1	
			531.20 ± 0.2	
		Not fixed	530 range	
			535 range	
	Monochromatized (Bessy)	Fixed	534.20 ± 0.1	1.2
			533.30 ± 0.1	
			532.75 ± 0.1	
			532.20 ± 0.1	
			531.20 ± 0.2	
		Not fixed	530 range	
			535 range	
Two-component fitting model	Non-monochromatized	Fixed	533.2 ± 0.5	1.6
			531.5 ± 0.5	

Adsorption as probe for reactive sites: 0,1 % B CNT and propane



Energetically uniform sites
→ Langmuir model

$$\theta = \frac{K p}{1 + K p}$$

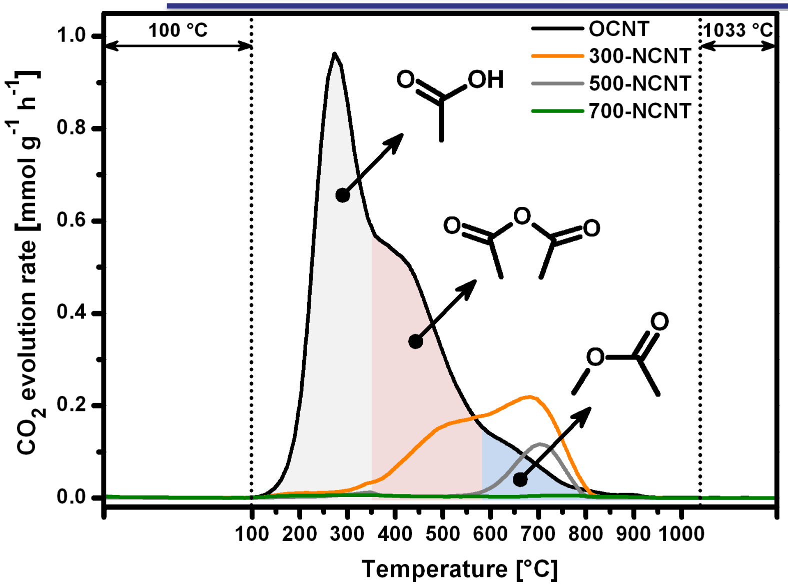
Adsorption probes about 0.1% of geometric surface

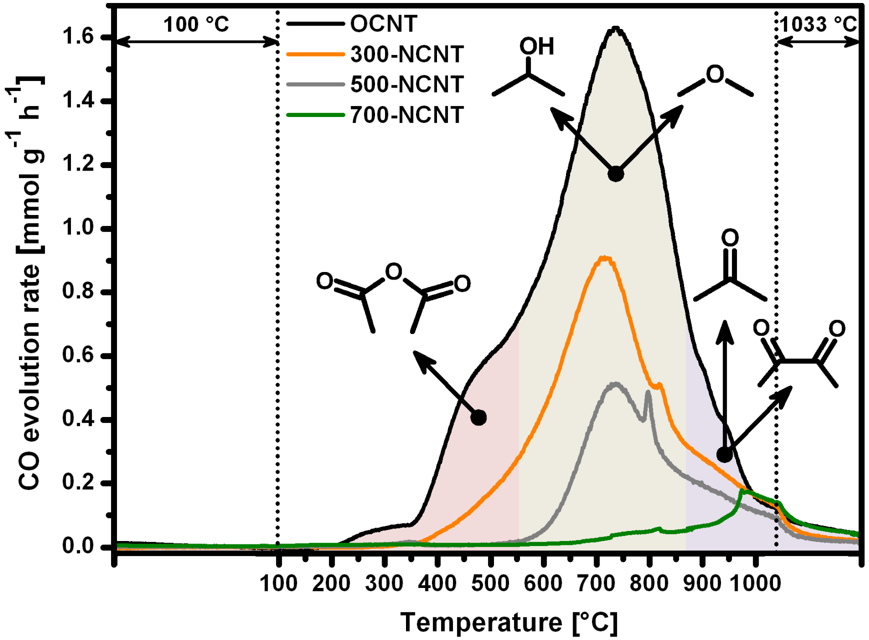
$$\theta = \frac{R\,T}{q_{ads}^{(\theta=0)} - q_{ads}^{(\theta=1)}} \ln\left(\frac{1 + \frac{p}{p^*}\exp\frac{q_{ads}^{(\theta=0)}}{R\,T}}{1 + \frac{p}{p^*}\exp\frac{q_{ads}^{(\theta=1)}}{R\,T}} \right)$$

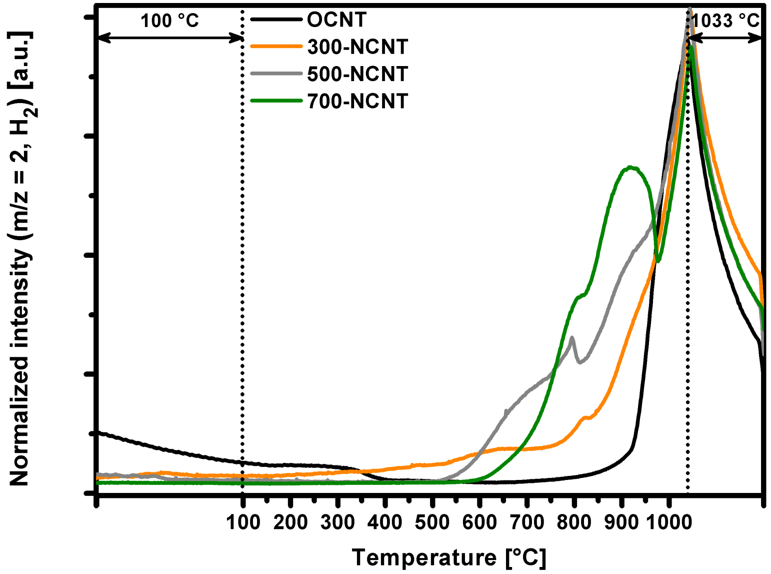
Energetically non-uniform sites (decay of q_{ads} with increasing coverage) → Temkin model

	***K* (Langmuir adsorption constant)**	***p** (Temkin factor)**
oCNT	2250 bar^{-1}	0.0065 bar
B_2O_3-oCNT	370 bar^{-1}	0.048 bar

How to identify surface groups?
Thermal desorption

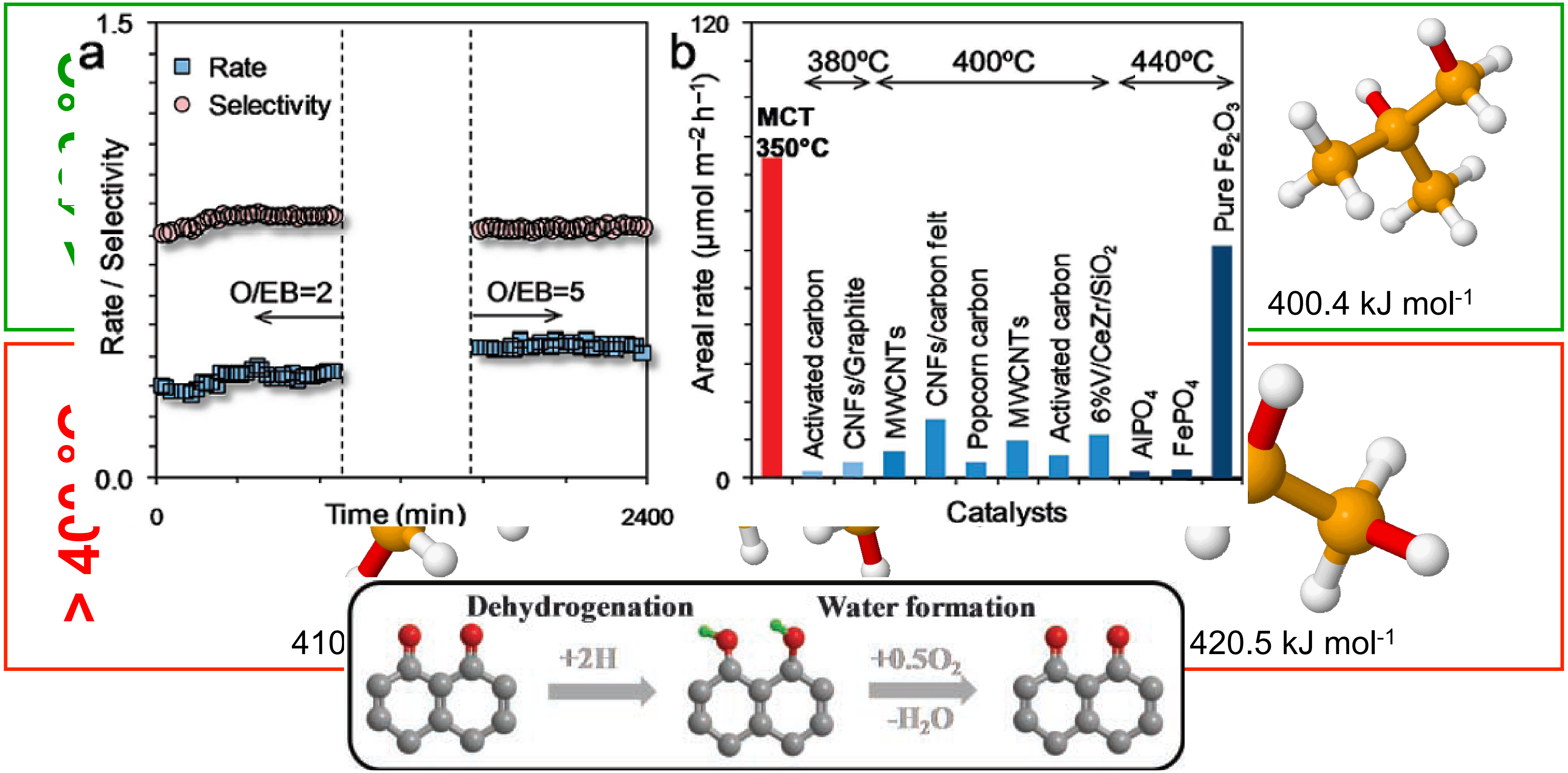






Careful and isothermal thermal desorption yields high chemical resolution of functional groups: Mind their stability!

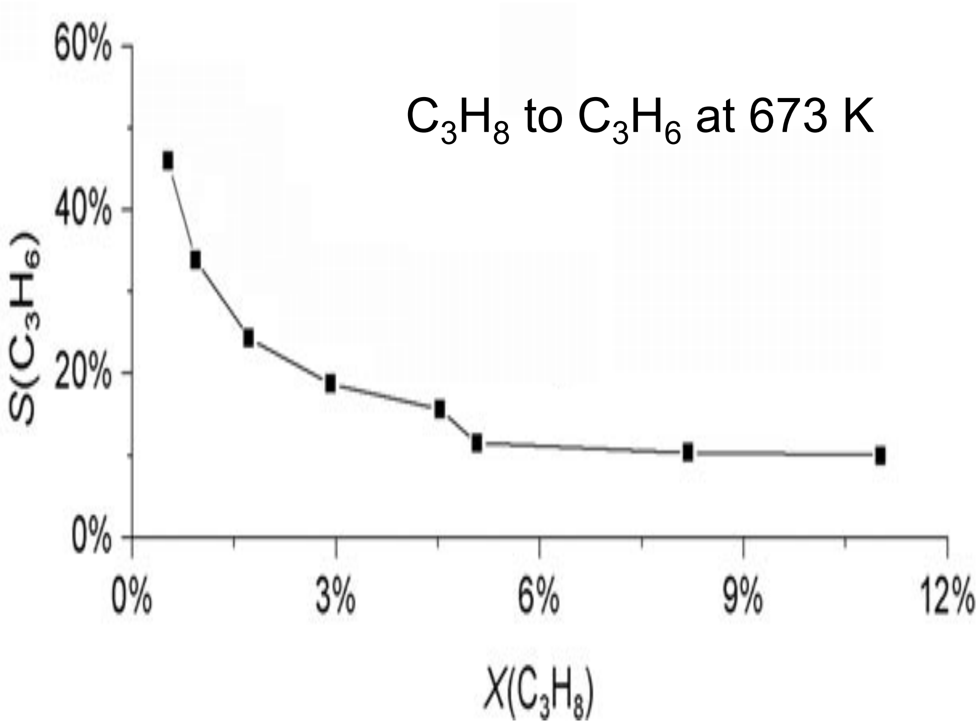
Concept: can we use carbon as selective cataylst for oxidation reactions?

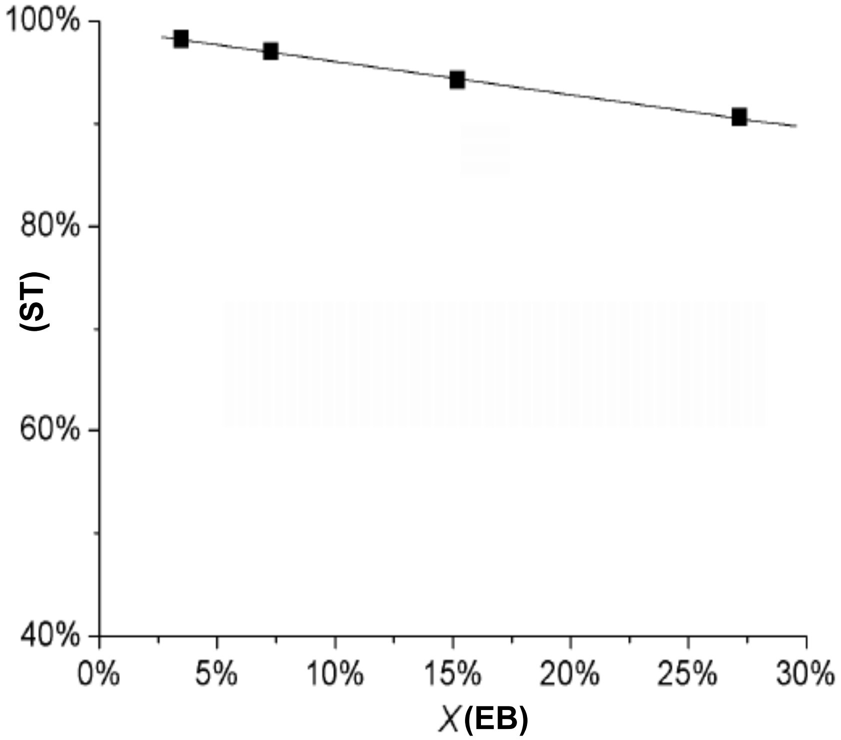


With K. Müllen and team

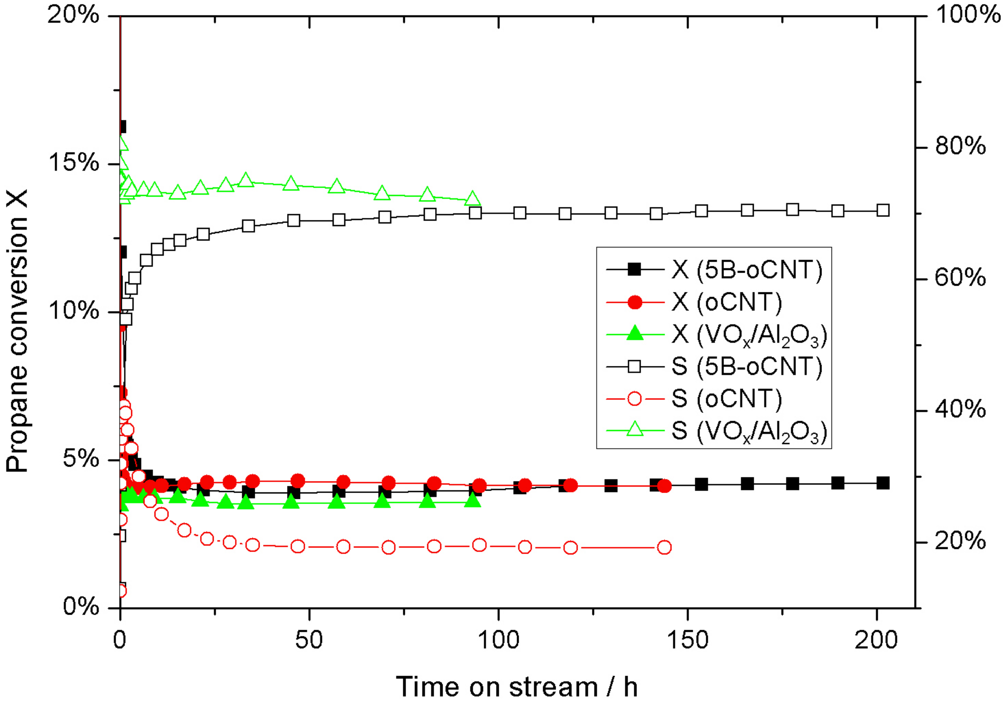
Comparison of ODH reactions over MWCNT

50 mg HNO_3 treated MWCNTs (NC3100), 400°C
$C_3H_8/O_2/He$ = 5/5/90, 60...1000 ml g^{-1} min^{-1}
$EB/O_2/He$ = 2.1/2.1/95.8, 300...2000 ml g^{-1} min^{-1}


C_3H_8 to C_3H_6 at 673 K


EB to sty at 673 K

Propane ODH: compare metal oxide to metal-free MWCNT

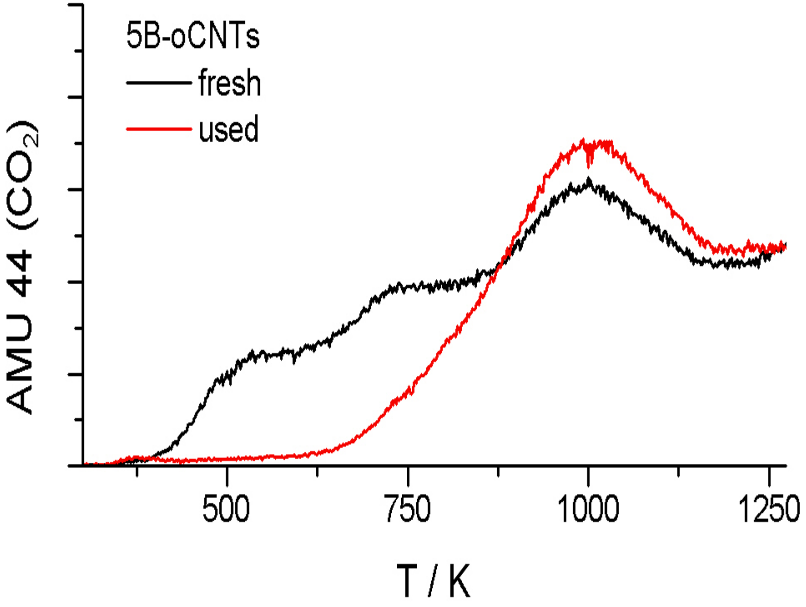


100 mg (oCNTs, VO$_x$/Al$_2$O$_3$)/500 mg (5B-oCNTs), 15 ml min^{-1}, C$_3$H$_8$/O$_2$/He = 1:1:48, 673 K

As well performing as long-developed oxide grafted catalysts: No „lattice oxygen“

Thermal analysis reveals that a restructuring occurs removing acidic sites and leaving strongly bound C-O groups intact:

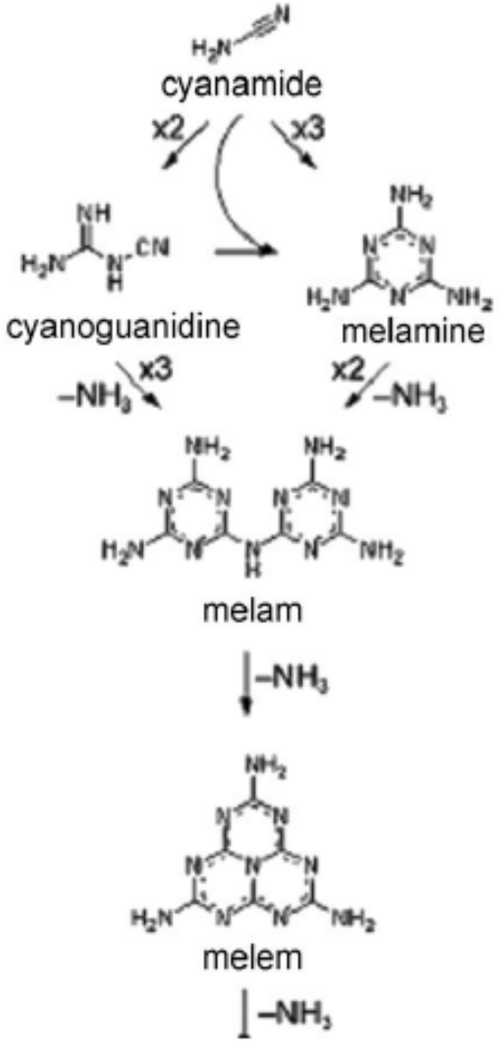
The boron (phosphorous) oxide pre-treatment is essential to suppress continuous oxidation

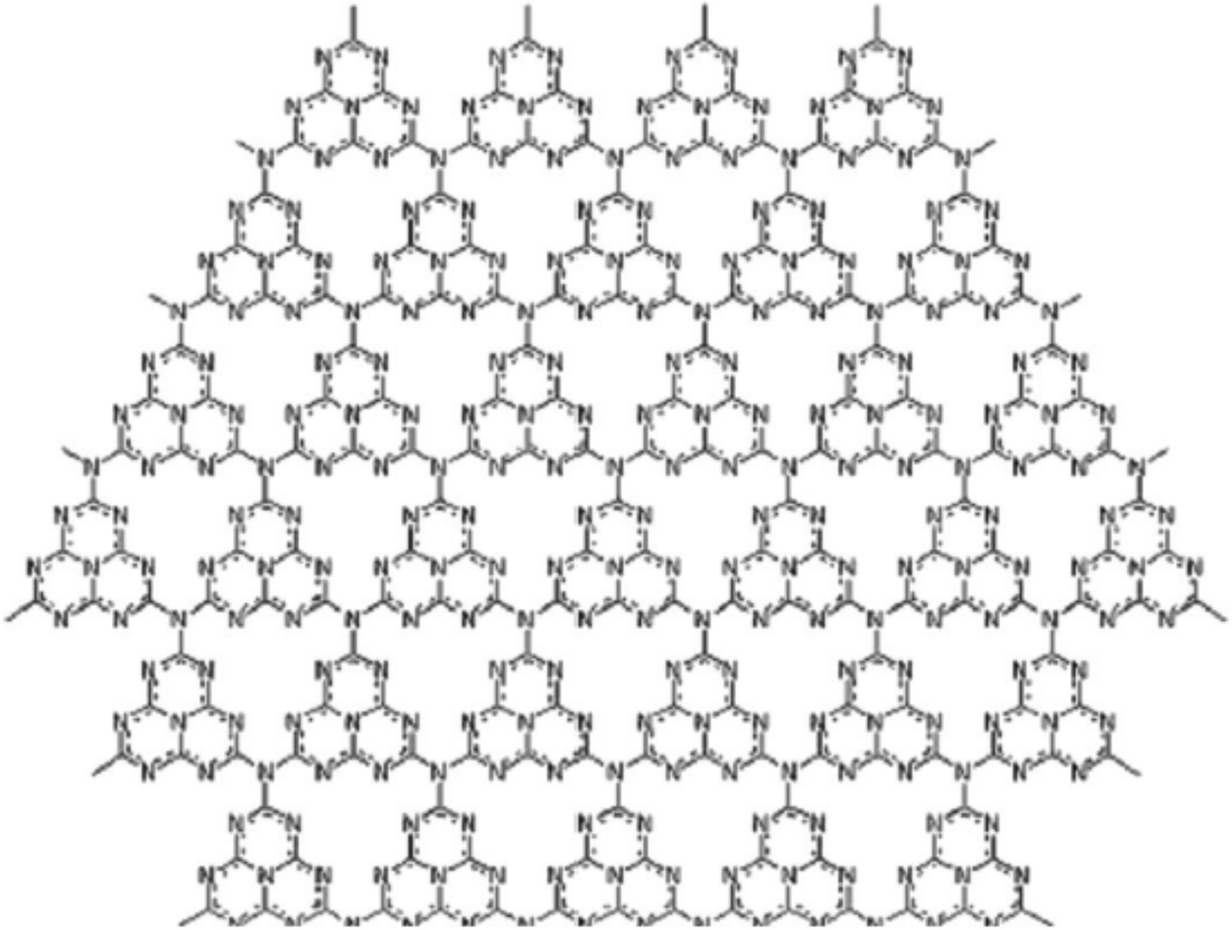


N- CNT
„dernier crie“

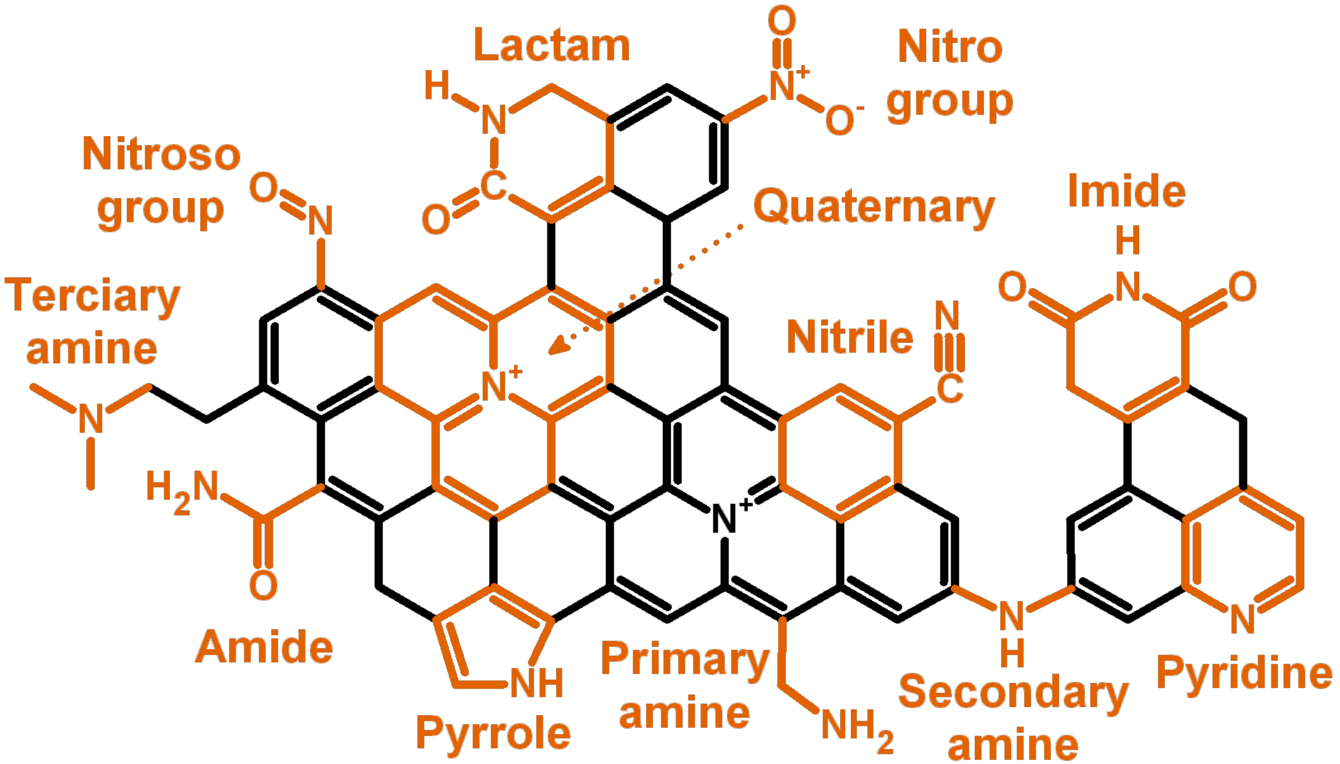
The concept of „doping“ is not as simple as zhought: many experiments still limited convergence

A nitrogen-rich form of carbon: mpg-C3N4





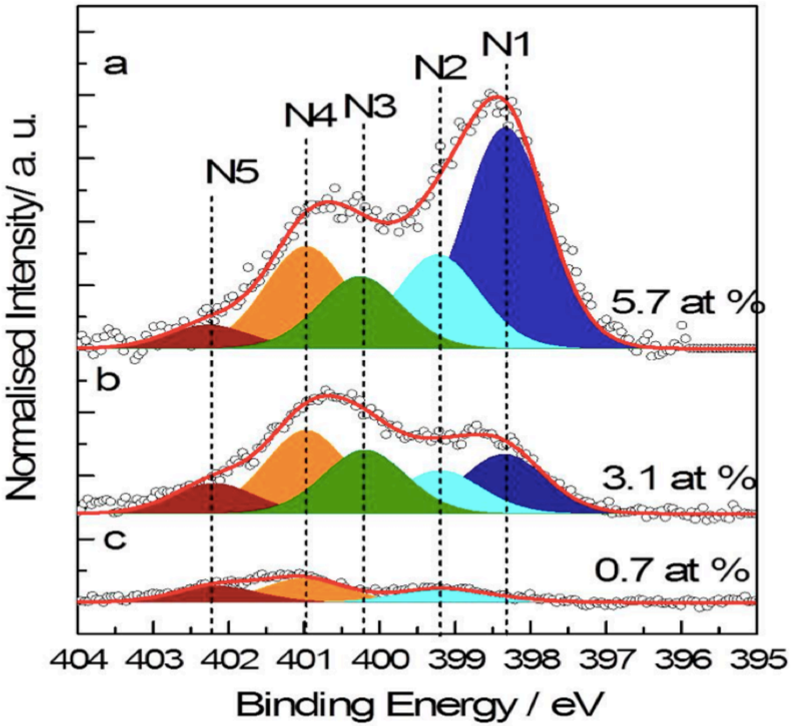
C-N chemistry of the poor man: Elusive in carbons

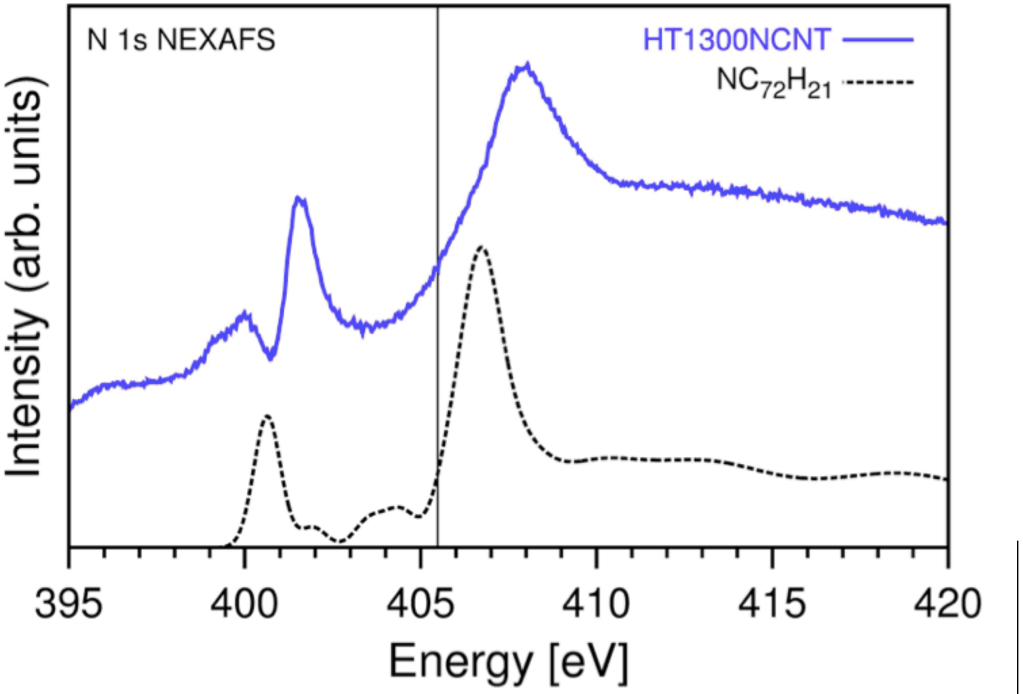


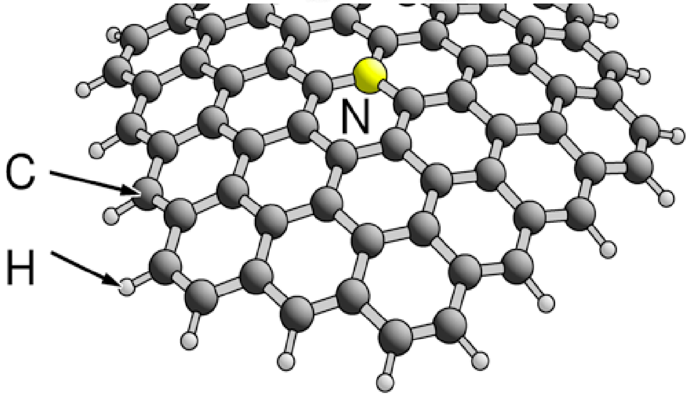
Since decades the N-substitution of sp2 C is a challenge: functional groups are facile, the true „graphenic“ N is a challenge.

Motivations are „n-doping“ of carbon and the predicted superior mechanical properties of (CN)x

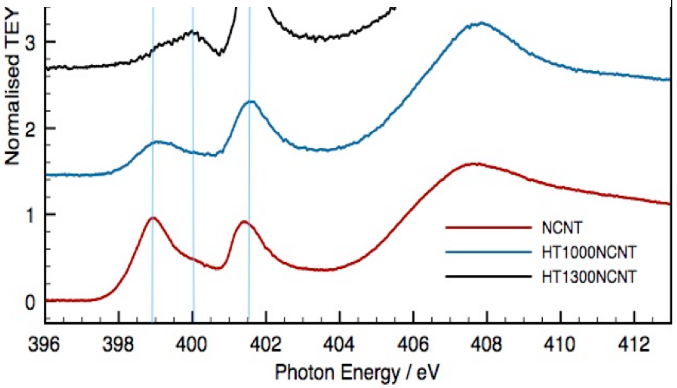
Doping:
Nitrogen in carbon „graphenic N“







donating effect and leads to strong charge localization

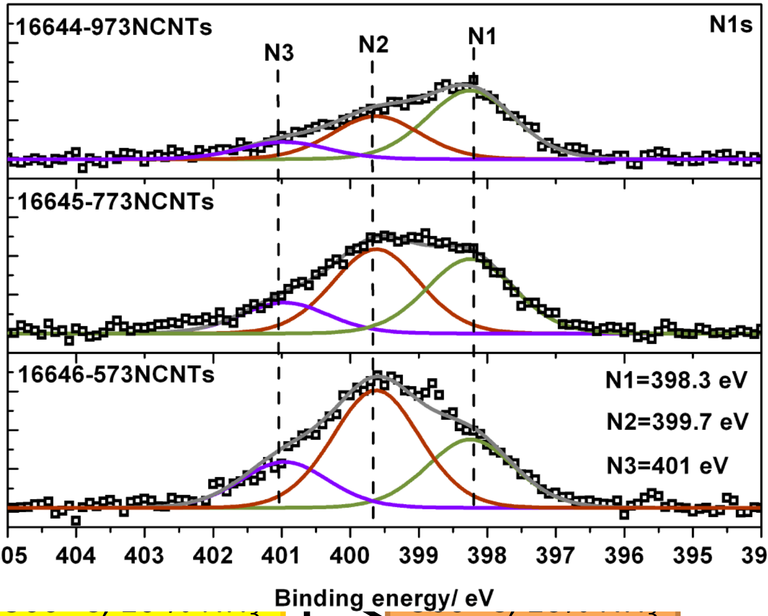


Carbon functionalization is key
Basic nitrogen: how much of what species?

700°C

500°C

300°C



(16393)

(16433)

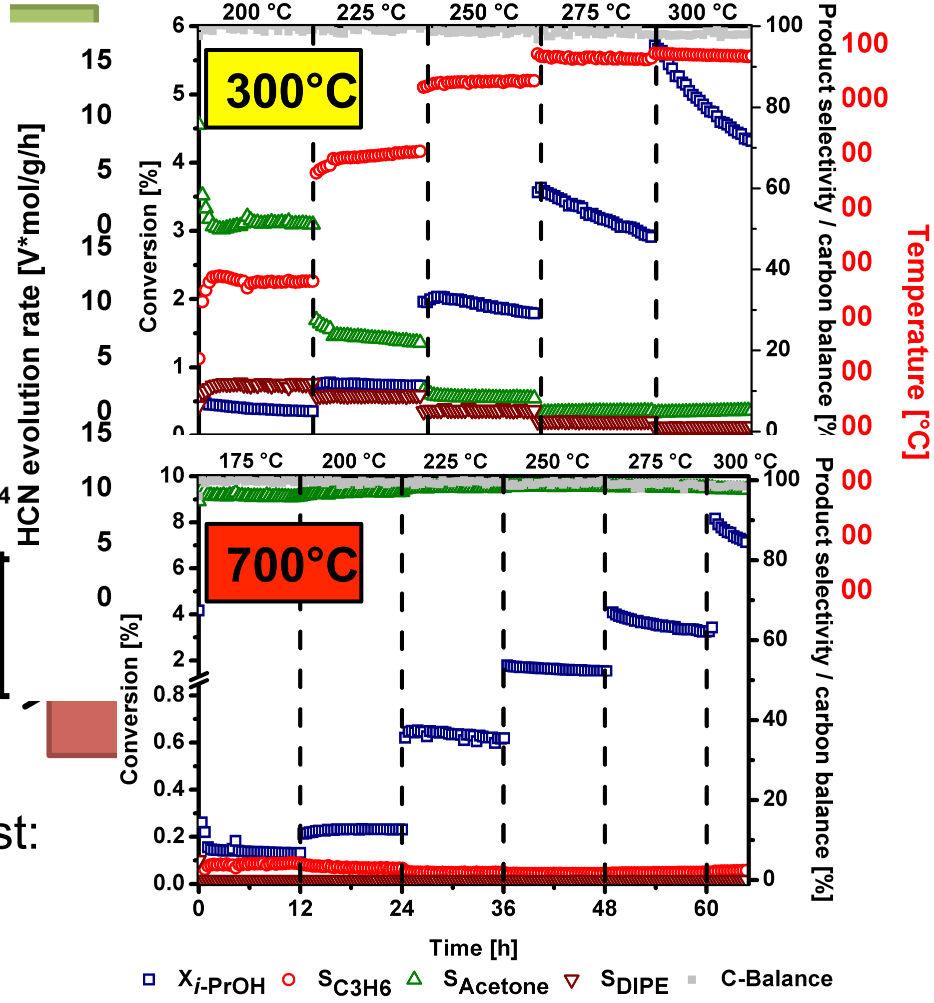
700 °C, 10% NH_3
(16432)

N1: pyridine

N2: pyrrole/pyridone/imide

N3: quaternary

Multiple types of functional groups co-exist:
„Chemical spectroscopy“ needed.



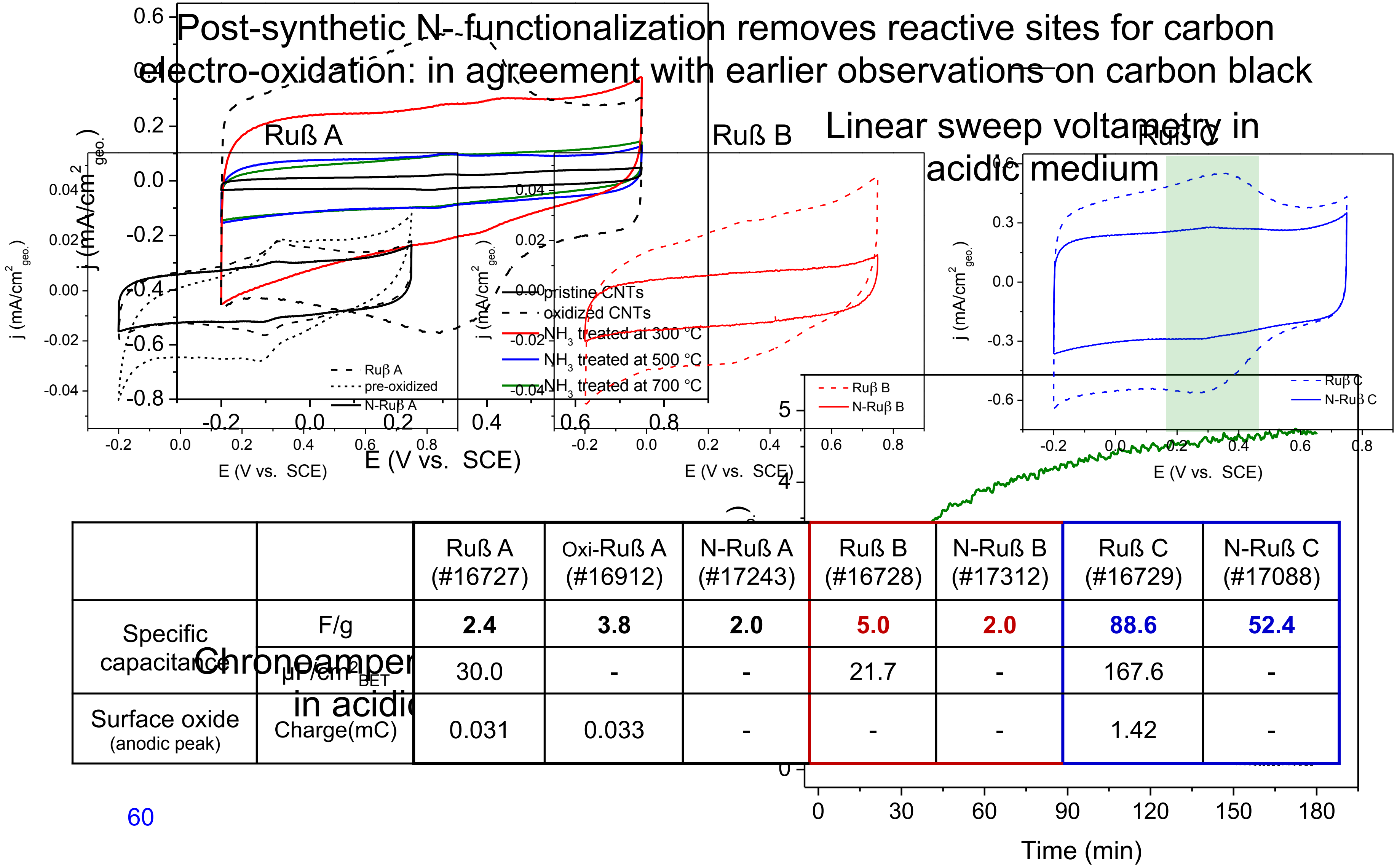
N-CNT electrochemistry

Post-synthetic N-functionalization removes reactive sites for carbon electro-oxidation: in agreement with earlier observations on carbon black

Linear sweep voltammetry in acidic medium

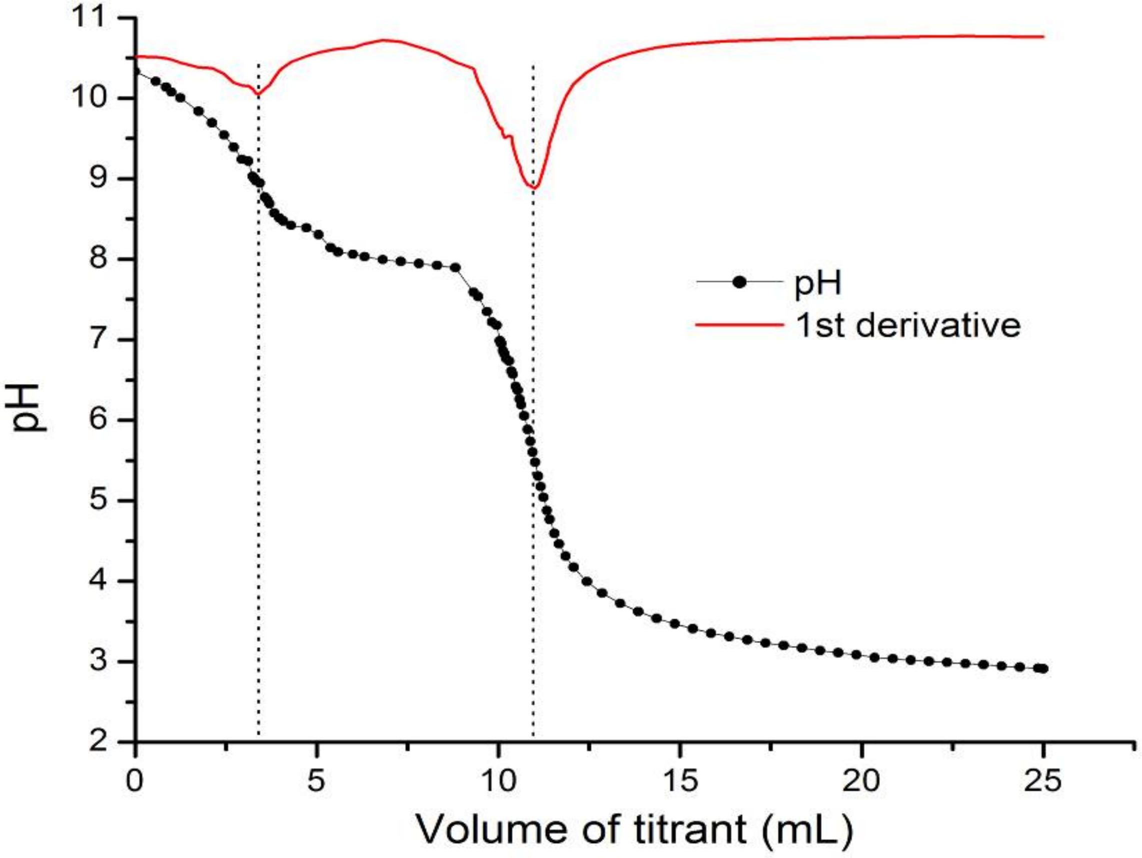
Chroneamper

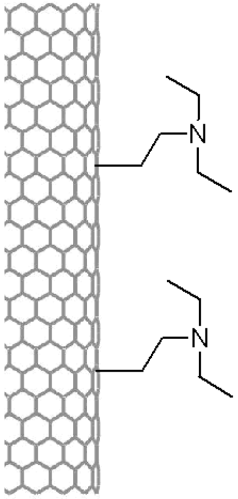
in acidi

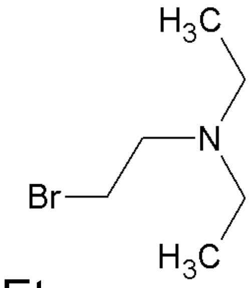


		Ruß A (#16727)	Oxi-Ruß A (#16912)	N-Ruß A (#17243)	Ruß B (#16728)	N-Ruß B (#17312)	Ruß C (#16729)	N-Ruß C (#17088)
Specific capacitance	F/g	**2.4**	**3.8**	**2.0**	**5.0**	**2.0**	**88.6**	**52.4**
	µF/cm$^2_{BET}$	30.0	-	-	21.7	-	167.6	-
Surface oxide (anodic peak)	Charge(mC)	0.031	0.033	-	-	-	1.42	-

Synthetic functionalization

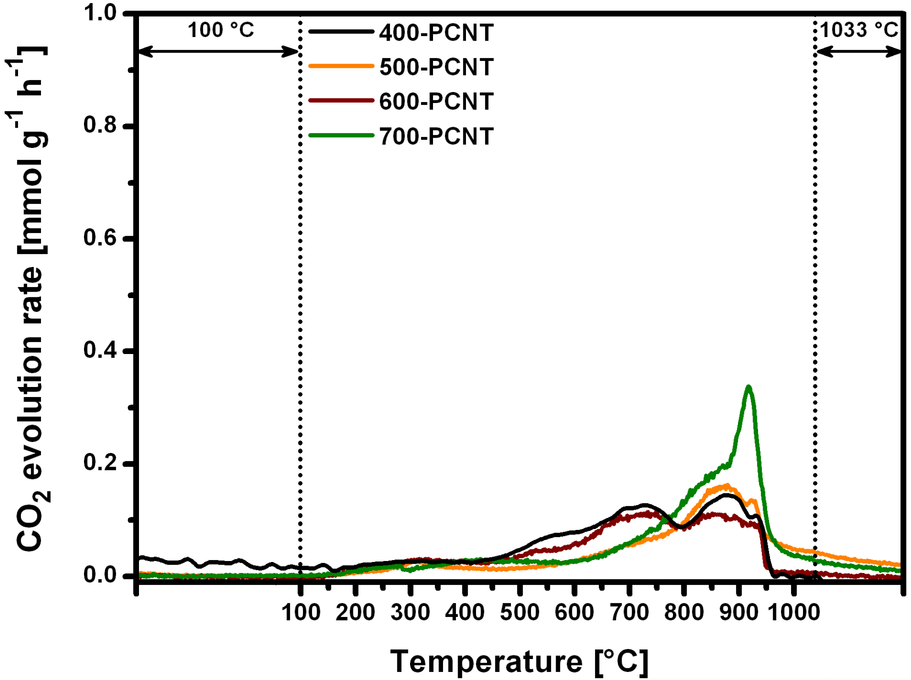


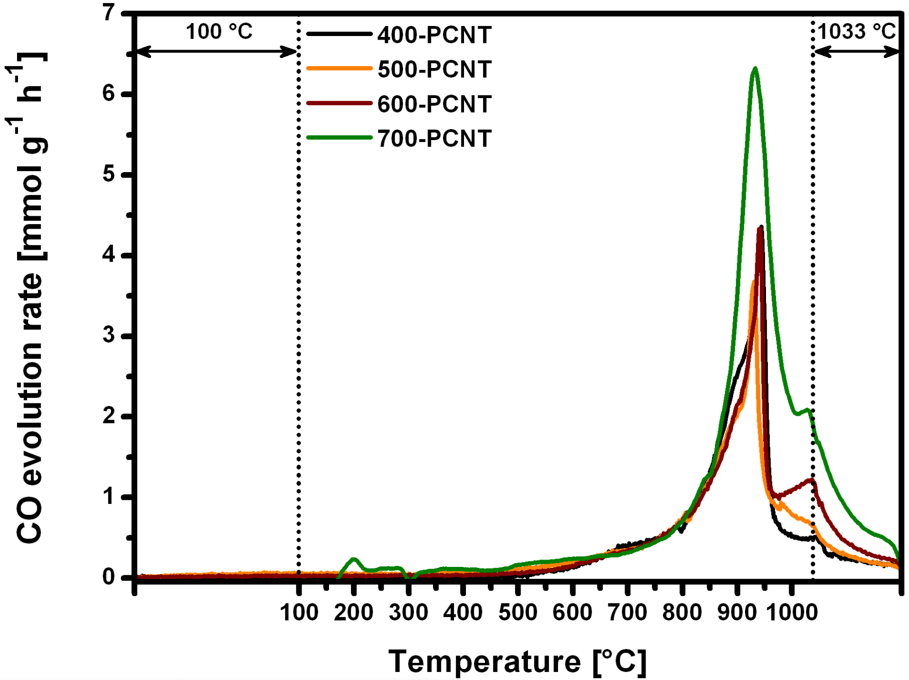


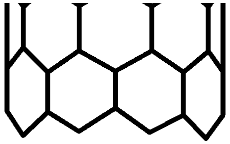


Br-NEt_3 :

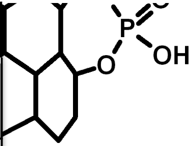
De-activation of functional groups: P- CNT







Sample	CO$_2$ [µmol/g$_{CNT}$]	CO [µmol/g$_{CNT}$]
400-PCNT	205	1631
500-PCNT	162	1669
600-PCNT	153	1842
700-PCNT	202	2928



To take away

- Nanocarbons are non-equilibrium variants of graphene.
- Semimetal with topological fractional double bond localization.
- Defect chemistry as „functional groups“.
- Most frequent are –H and C_2O, all other forms are rare but important for chemical reactivity.
- On basal planes no chemical reactivity but electron transfer upon potential gradient.
- Thermodynamical unstable in electro-oxidation: kinetic stabilization.
- Multiple applications as metal-free catalysts or as support.
- Role of “N-doping” complex and still under study: non-trivial.

Dem Anwenden muss das Erkennen vorausgehen

Max Planck

Thank You