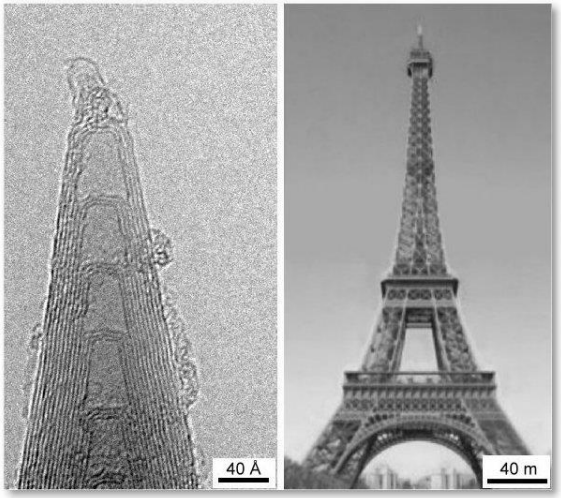

Nanocarbon as catalyst

Potential and Challenges

S.B. Abd Hamid
J. Delgado
D. Su
X. Liu
X. Chen
J.P. Thessonnier
R. Arrigo
S. Abourus
W. Ranke
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Fritz Haber Institut der MPG
Robert Schlögl

nano C
Driving Future Industries

CANAPE
ENERCHEM
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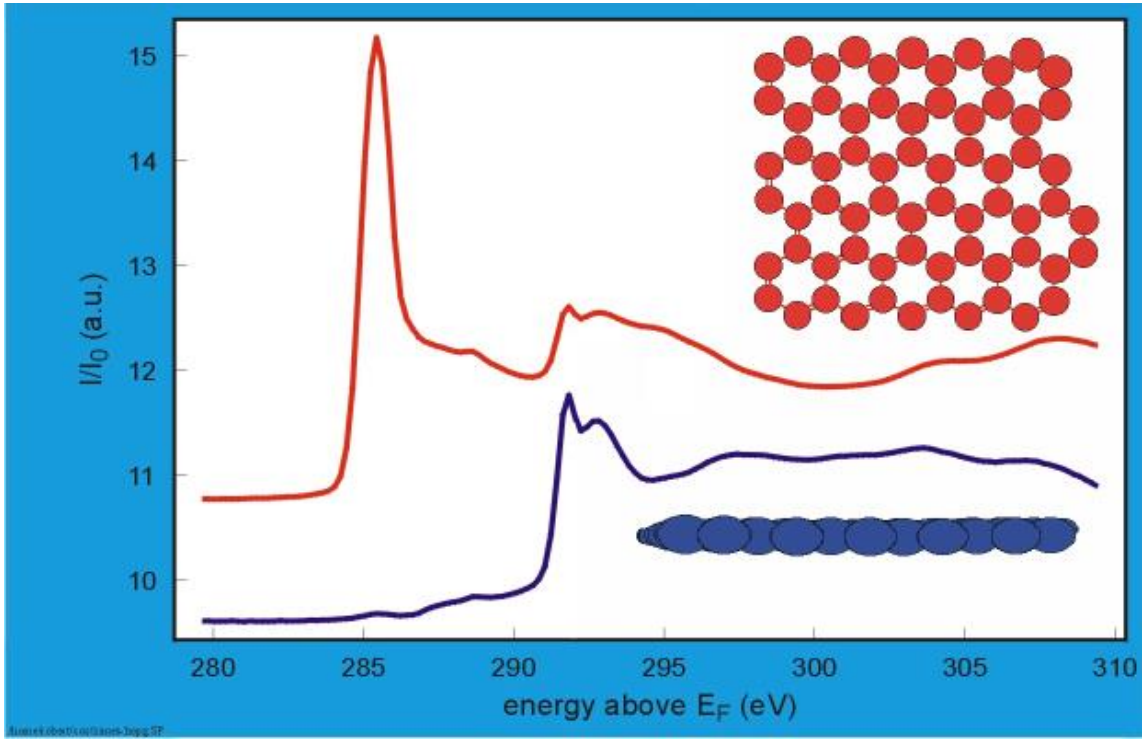
Anisotropy



There is no other material than graphitic carbon showing such pronounced electronic structural anisotropy resulting from the anisotropy of the sp2 bonding: only the (blue) prism face is reactive, the (red) basal plane is metallic inert

Oxidation catalysis: Why CNT/CNF?

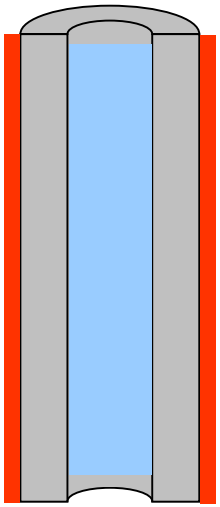
- Alkane activation by oxidation is a core target of chemical transformation
- Suffers from selectivity (burning)
- Conventional systems either destroy molecular structure (metals) or contain too much reactive oxygen (oxides)
- Carbon as perfect (?) alternative with low metallic conductance and very little oxygen content

Ultra-disperse oxides and CNT

Use functionalized CNT as carriers for extremely disperse oxide with defined localization on support

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

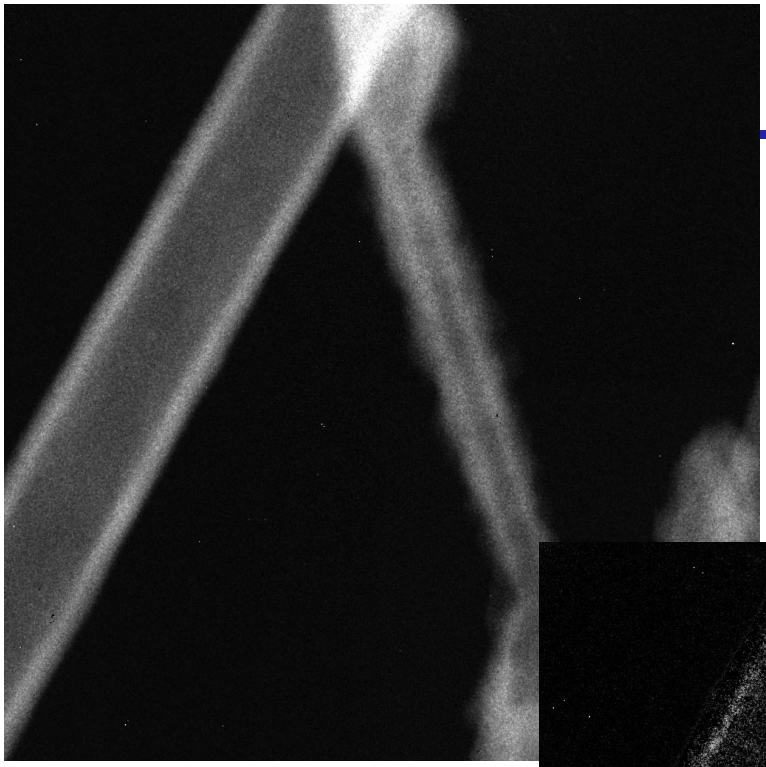


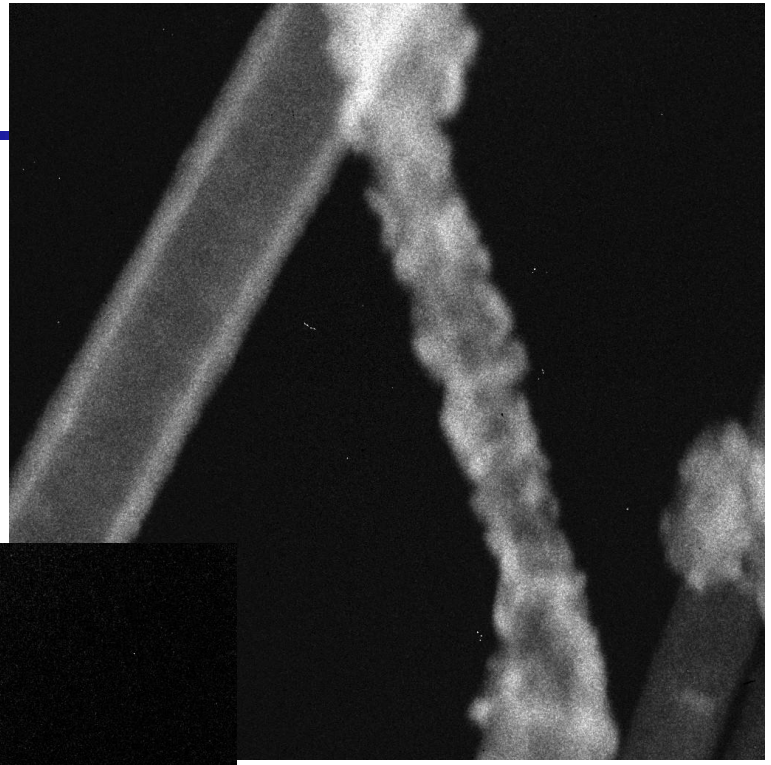
Steps for the selective decoration of the outer surface

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.

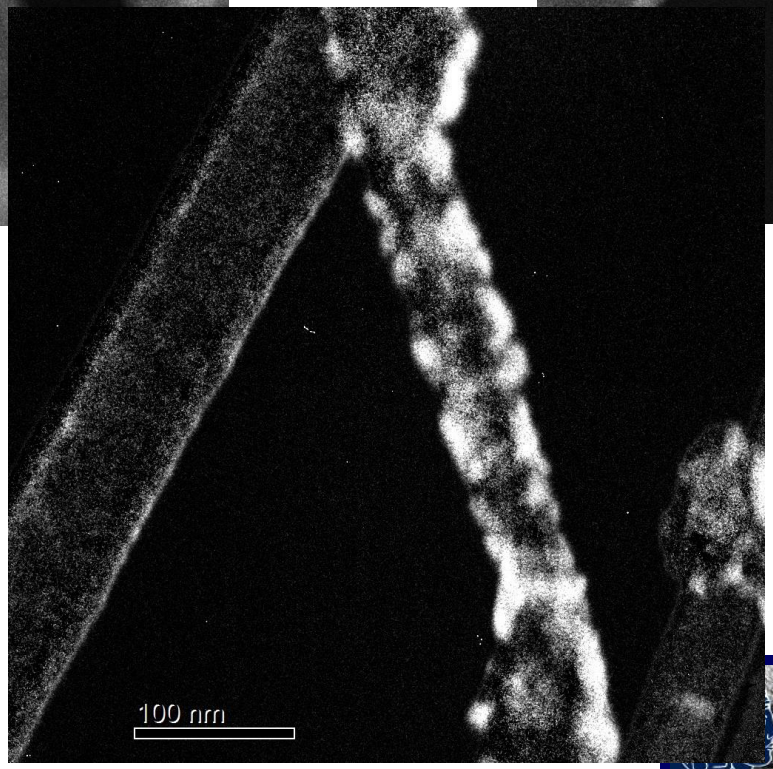
Pre-edge

Post-edge





V-map



The EELS mapping reveals:
There is some Vanadium on all the tubes!

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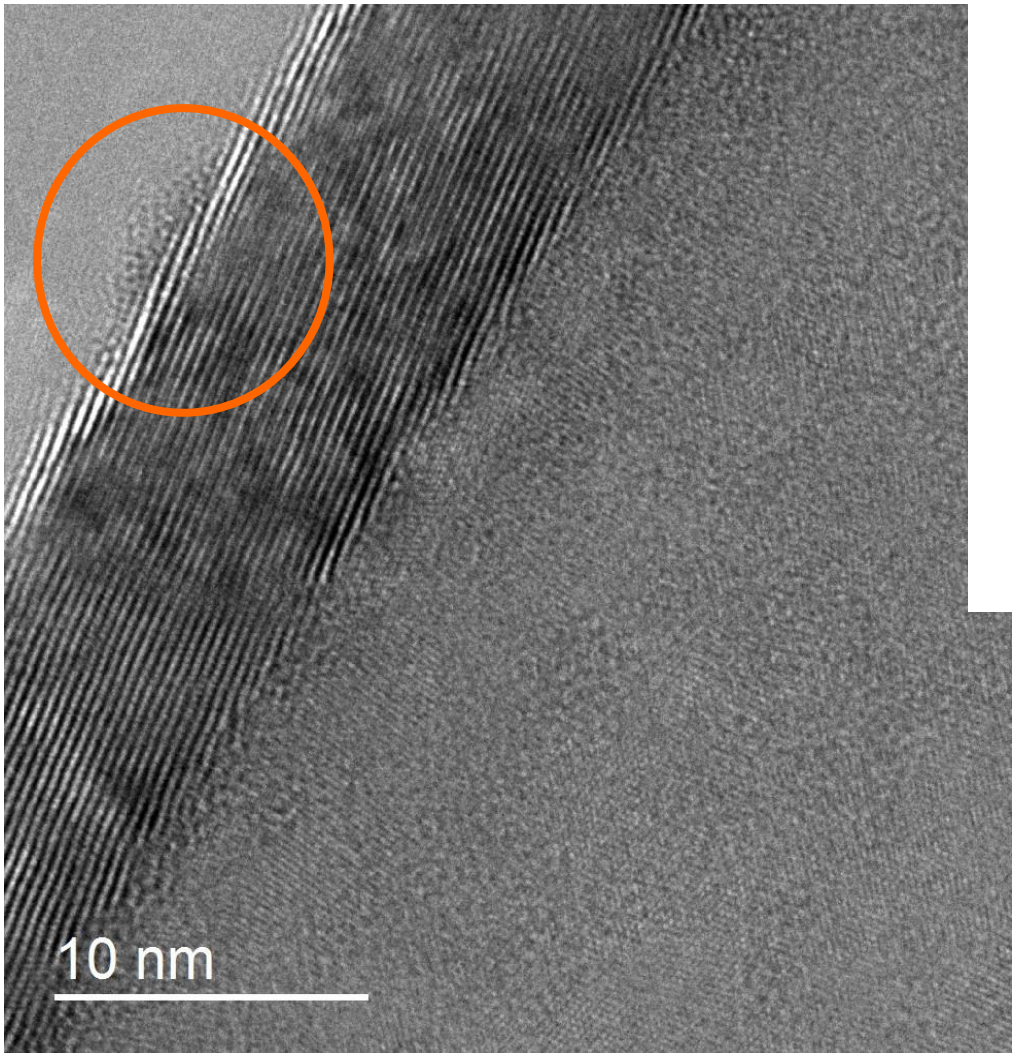
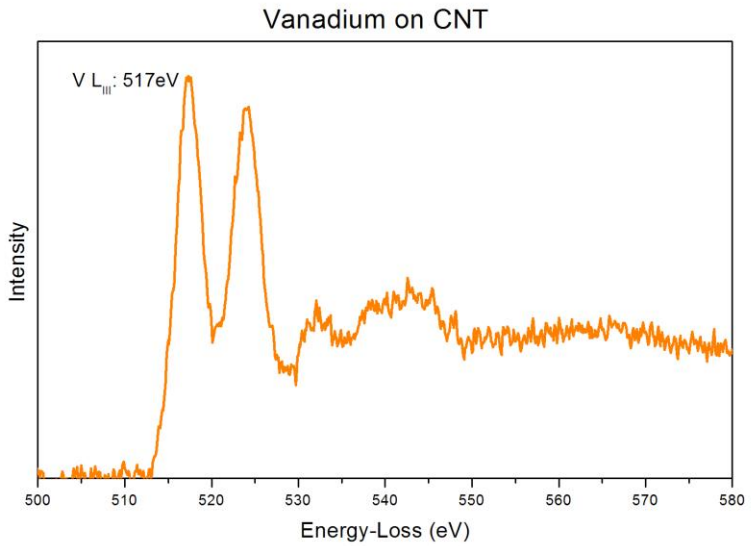
Nano clusters

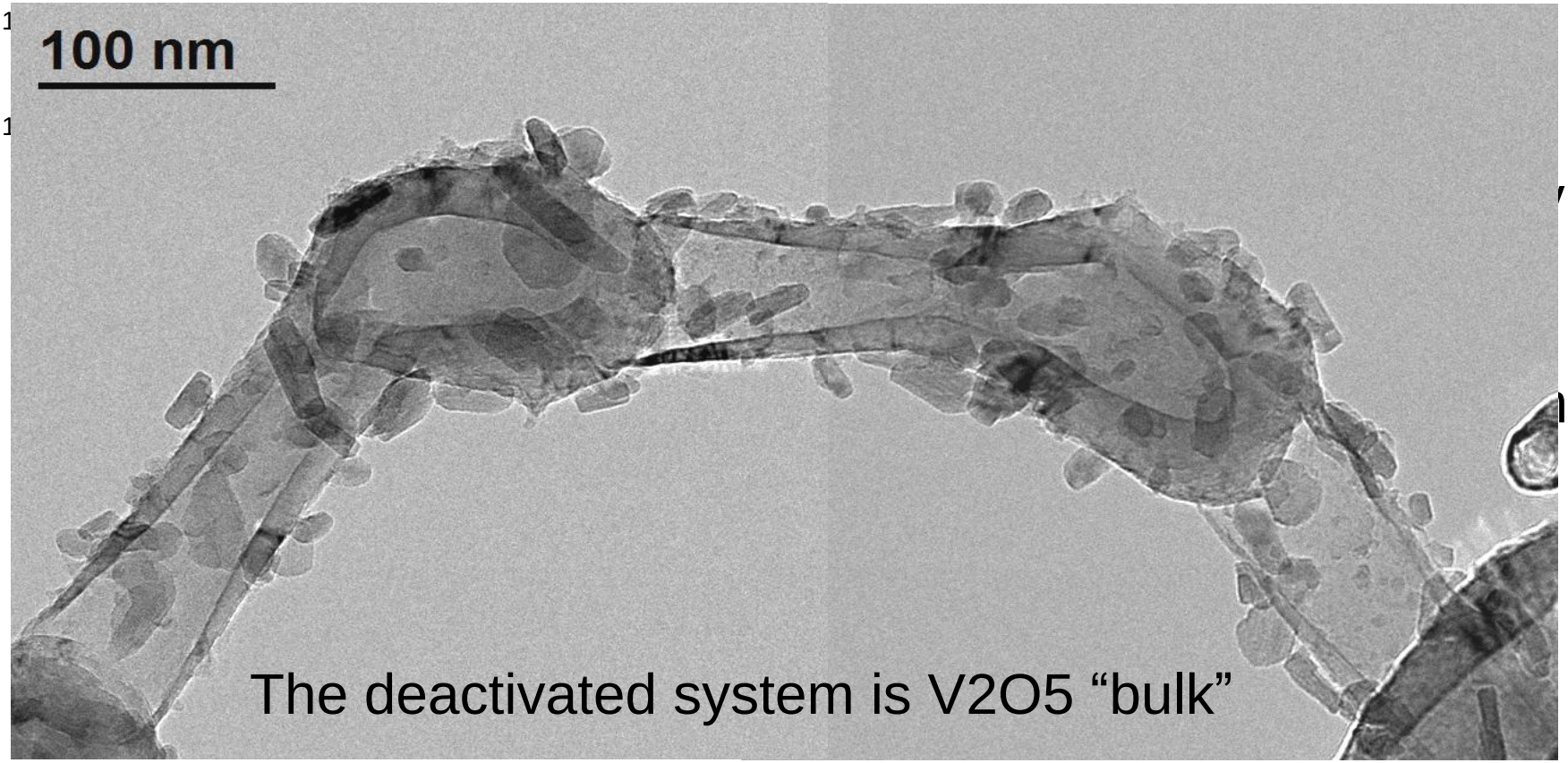




No long-range structure
Electronic structure
V2O3 like (higher average valence)

Catalytic performance

V_xO_y on CNT



concentration (ppb)

ity

nd

The deactivated system is V2O5 “bulk”

Very high activity (better than
any other system studied so far)

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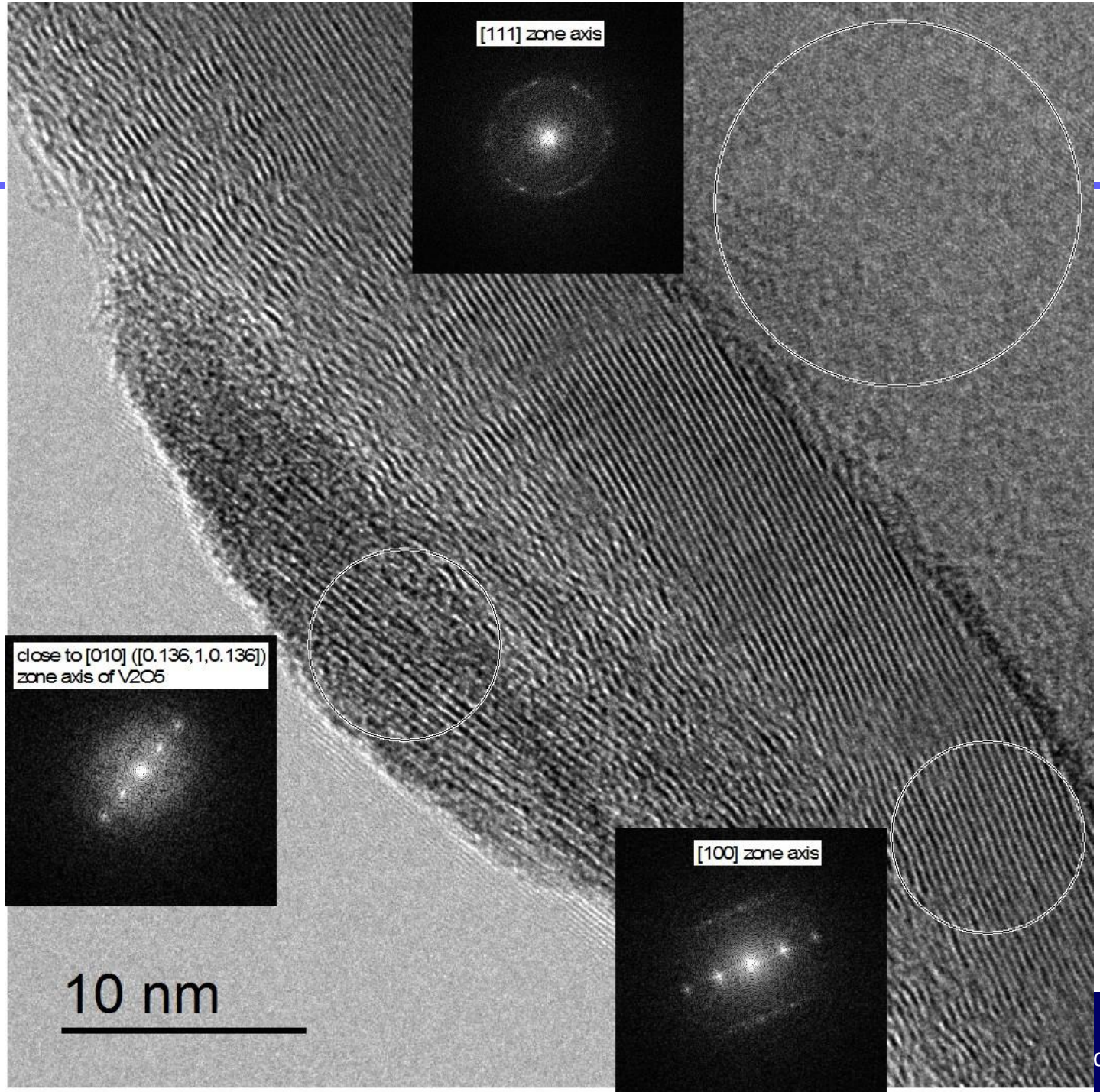
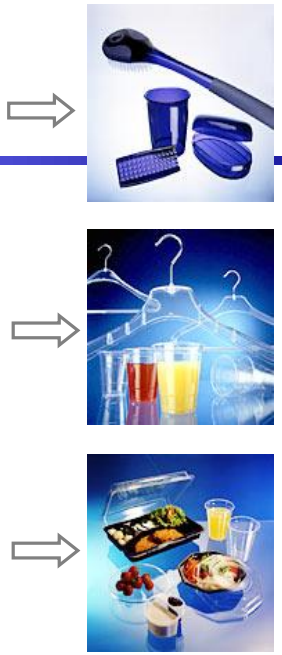

[111] zone axis
close to [010] ([0.136,1,0.136]) zone axis of V2O5
[100] zone axis
10 nm

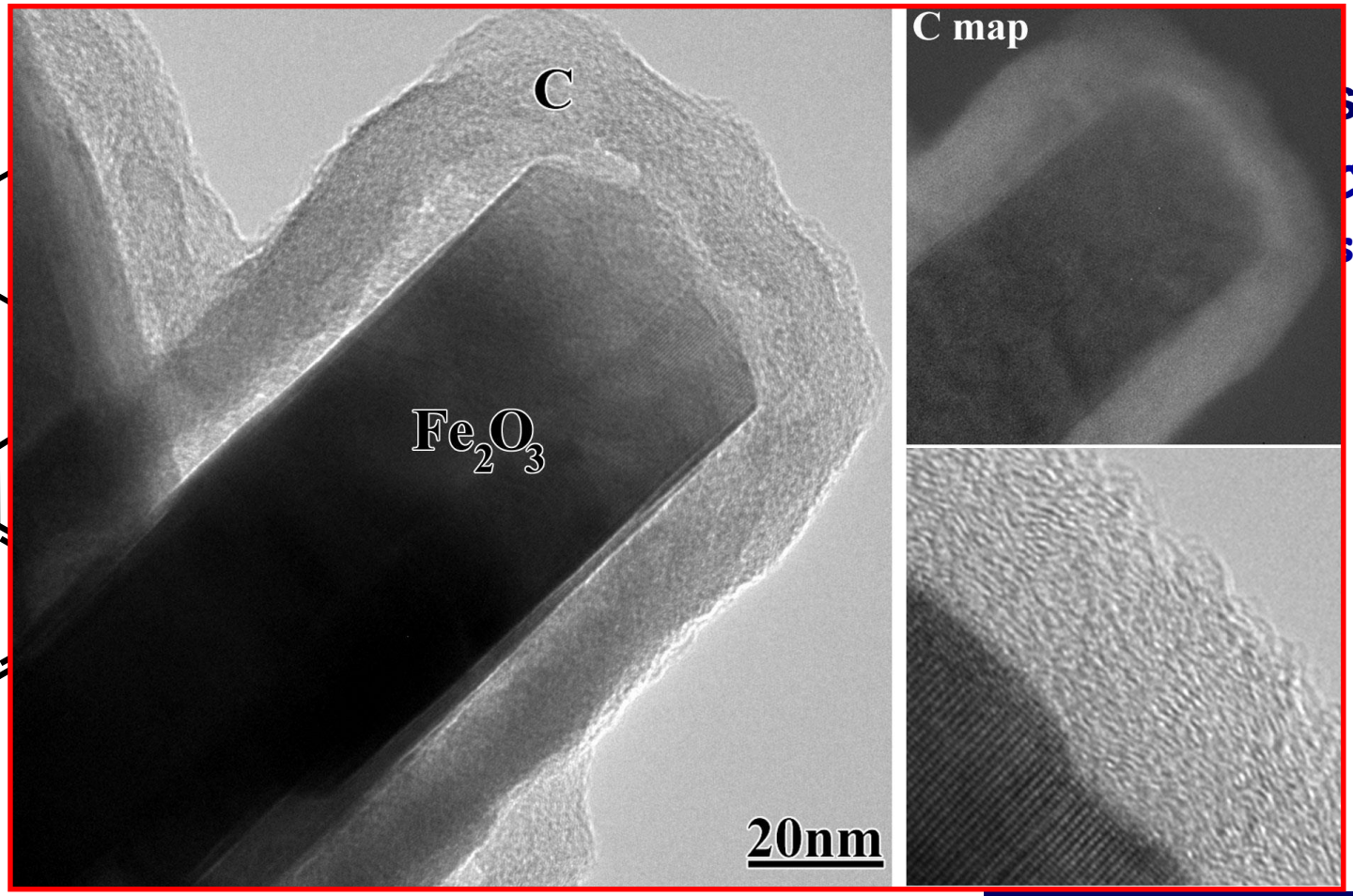


CNT as catalyst

Ethylbenzene to styrene conversion in a new paradigm: no energy input, no steam dilution

A target reaction: 24 Mt/a

Dehydrogenation (non oxidative)



s:

c

steam

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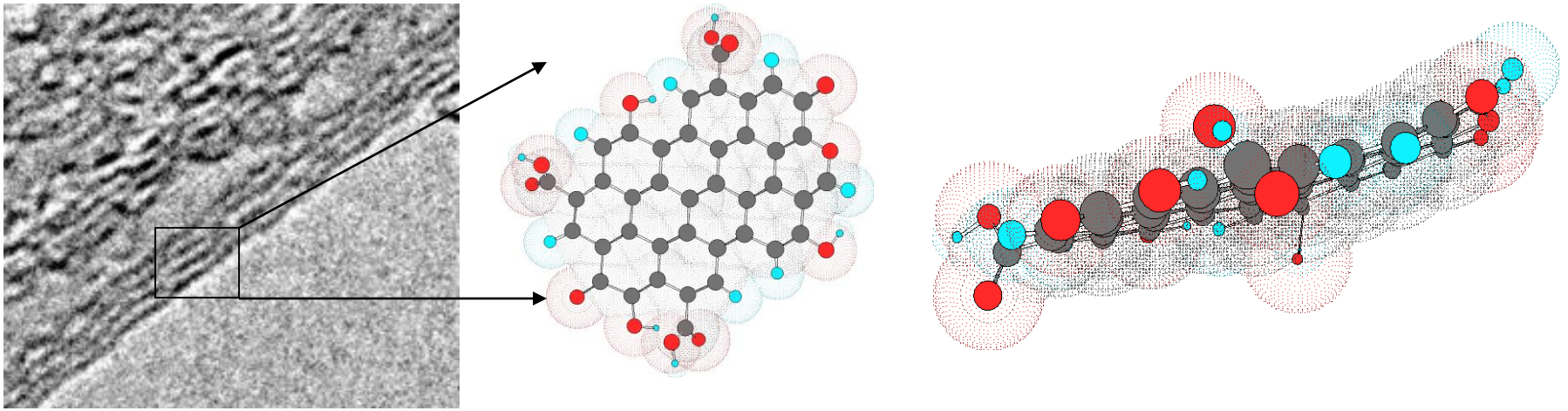
The active site



The BSU of CNT or CNF provide at their periphery sites for functional groups

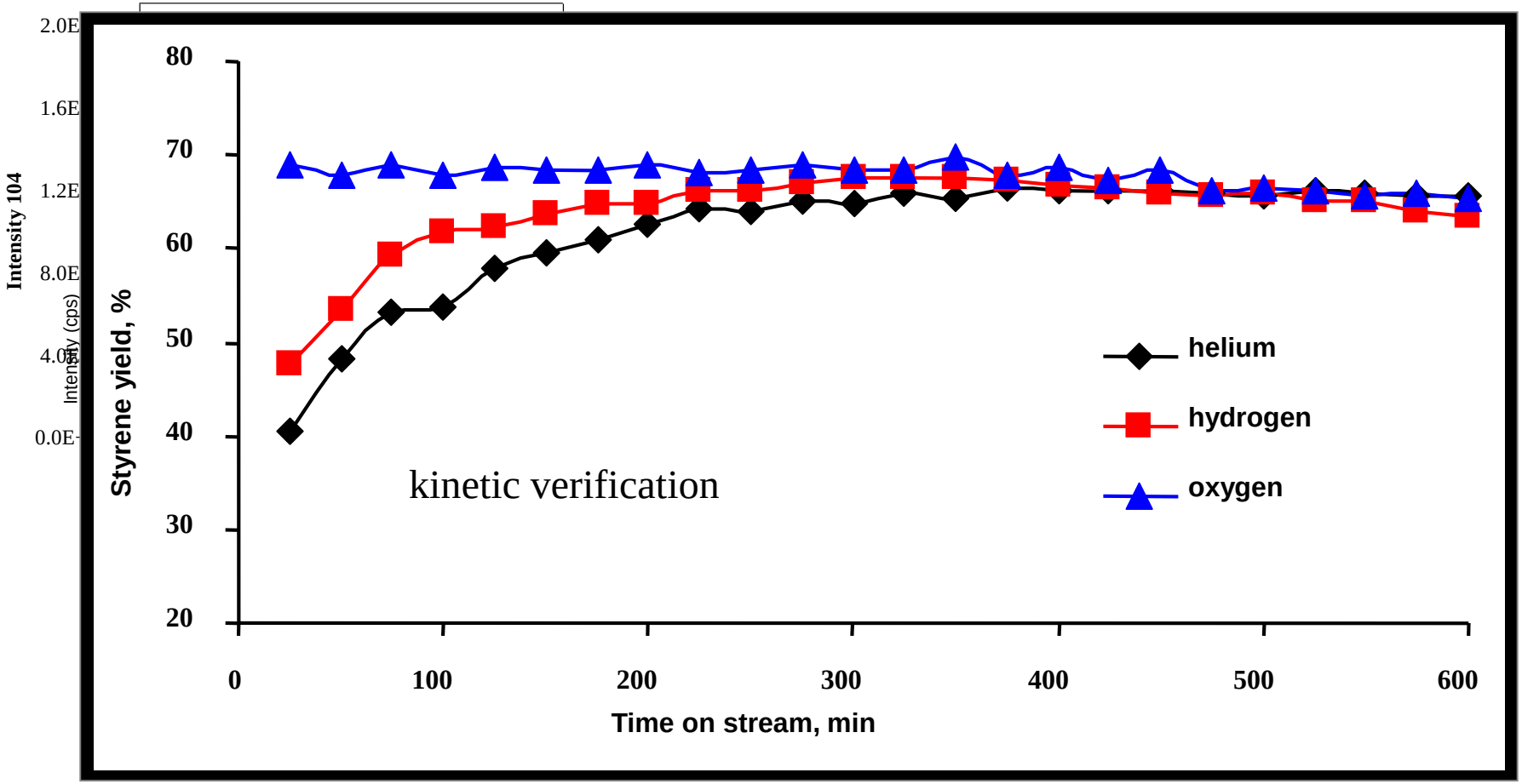
These can be also defects in graphene wraps

Modification of bonding by strain through non-sp2 bonds (both on carbon and heteroatom)

Active are quinone functional oxygen groups abstracting hydrogen and being oxidized to water

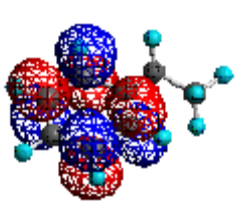
Basic Oxygen Functional Groups

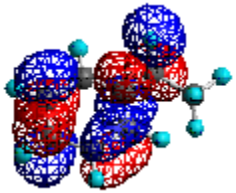
Carrier gas (20% O_2/ 80% N_2), 1.2 % Eb (v), 40 ml/min,

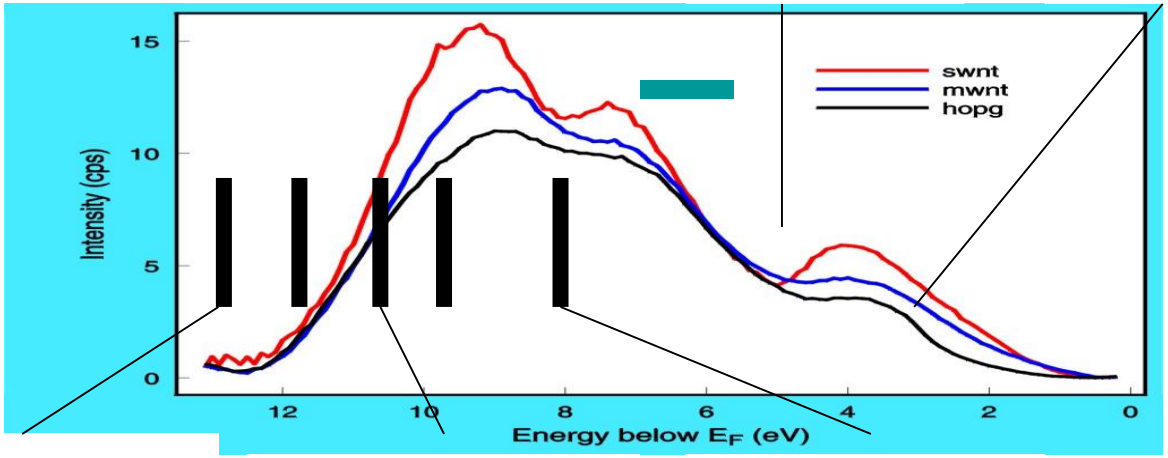


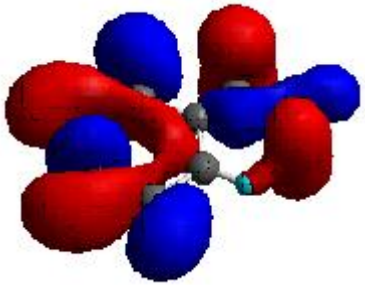
The electronic structure issue

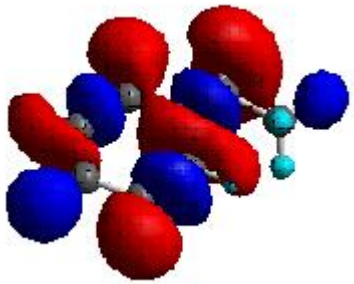
Initialization of reaction by reductive activation

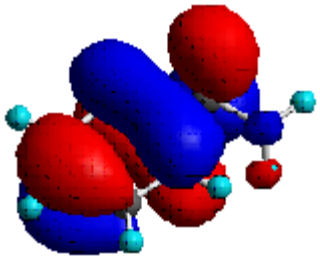




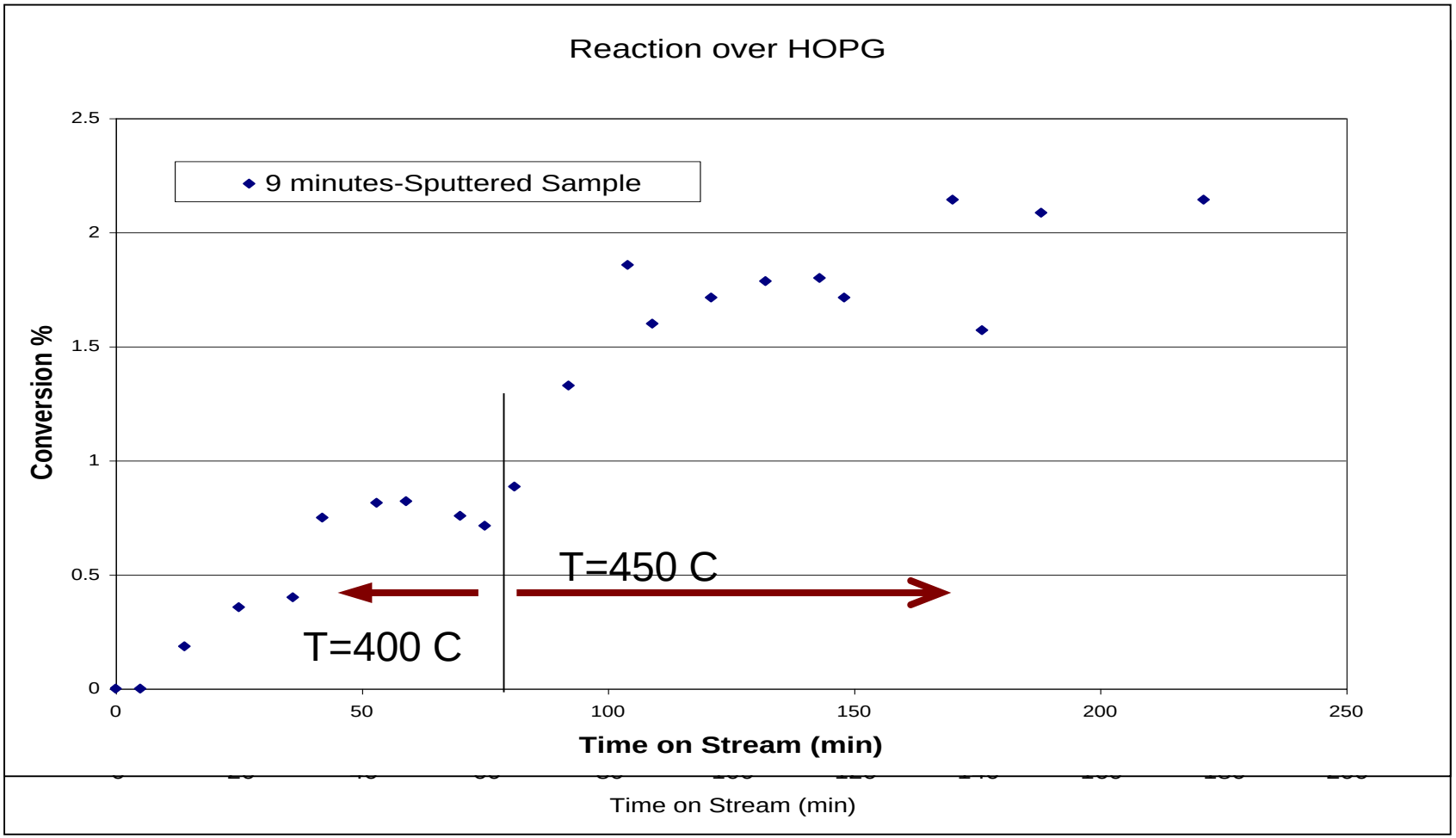




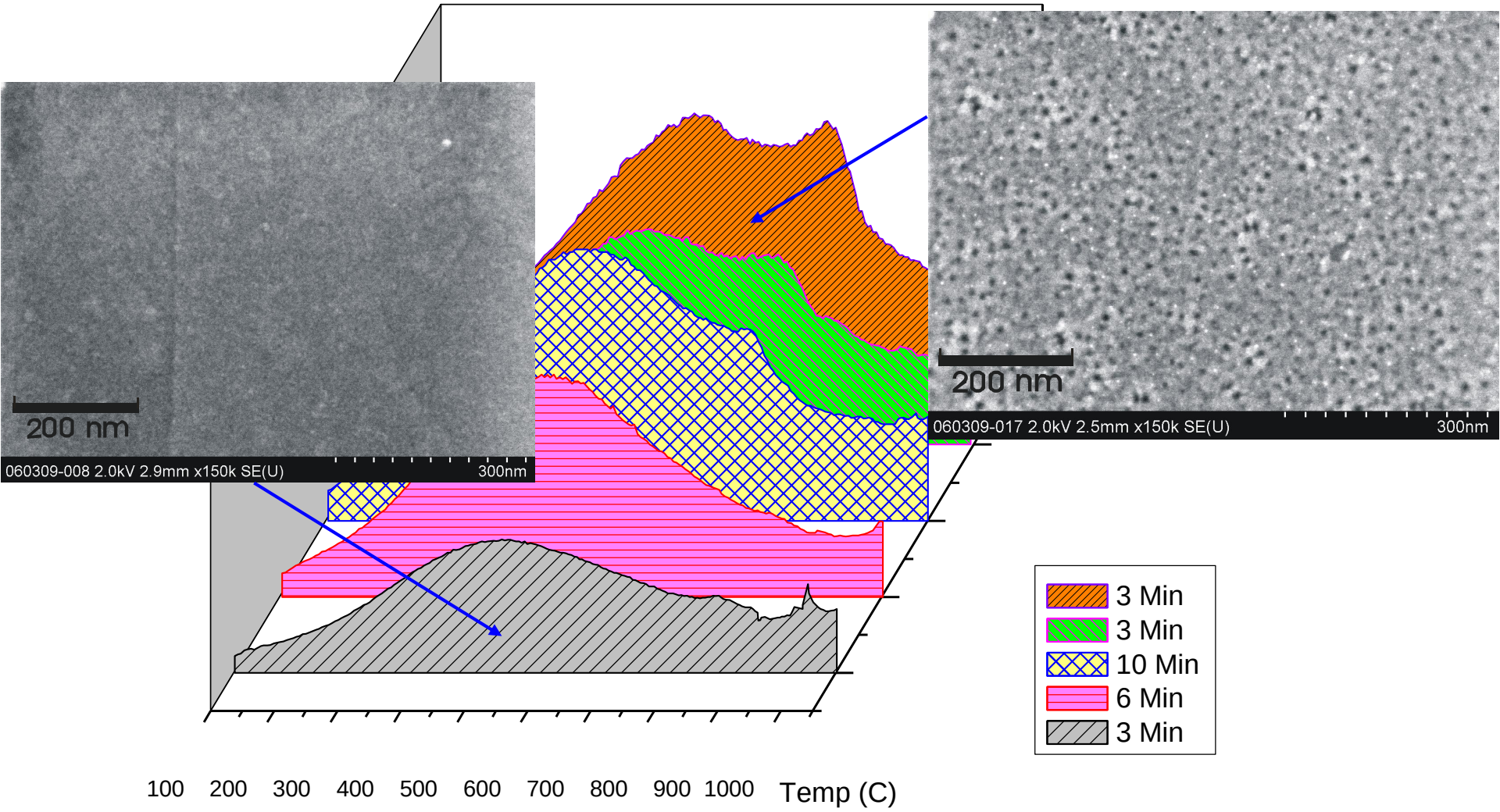


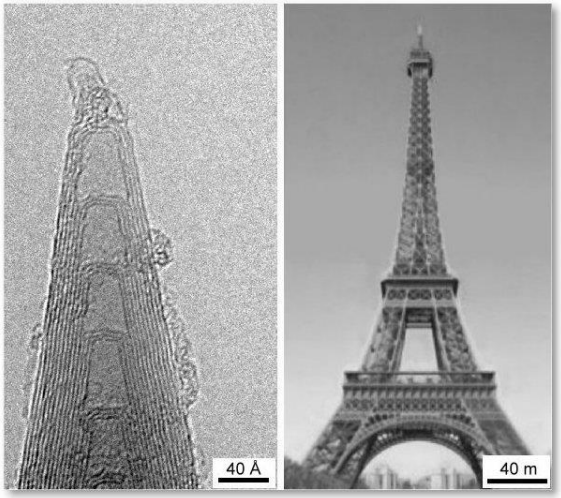


Planar Model: HOPG-oxygen sputtered



Model system: HOPG





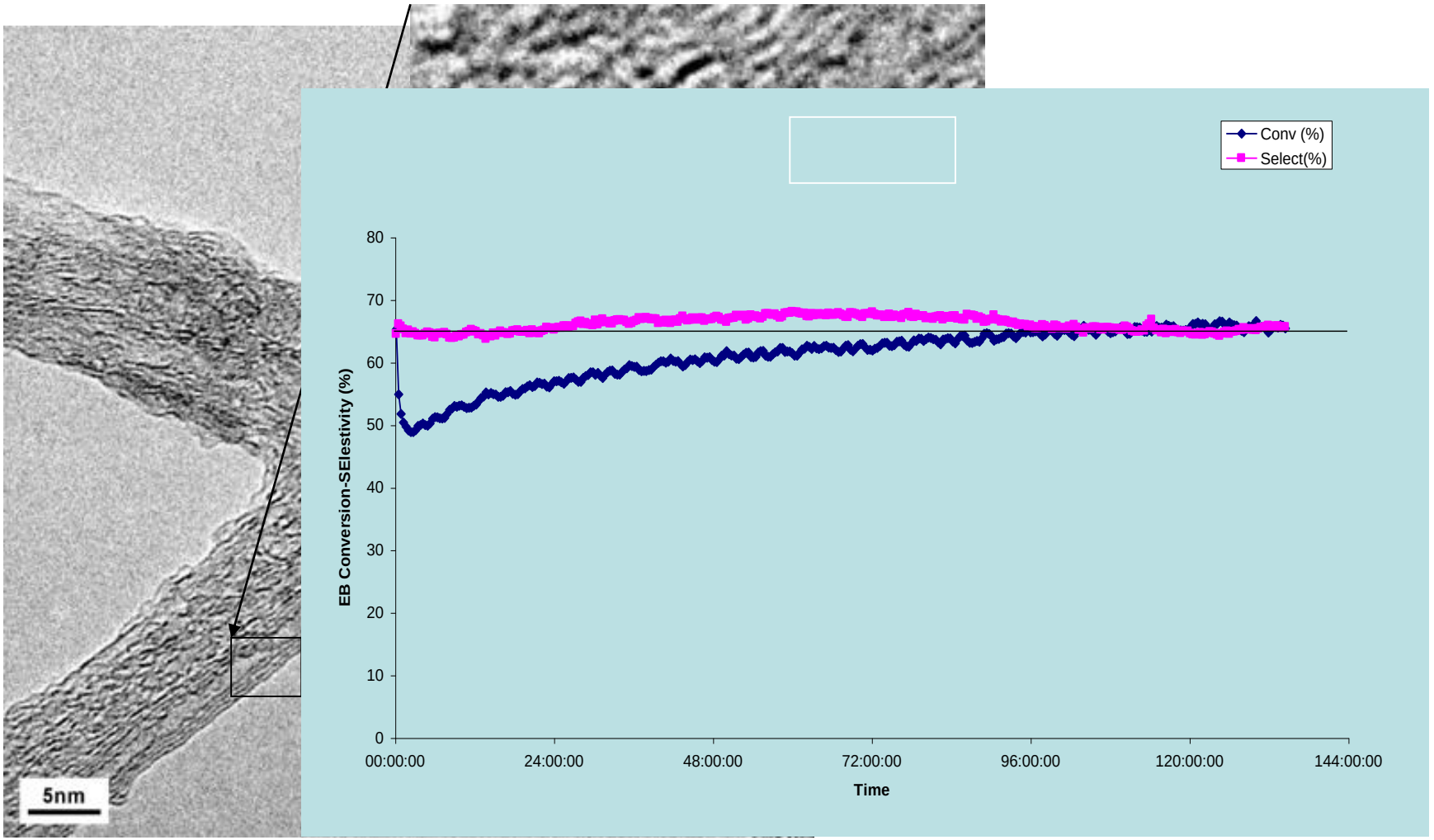
Loose samples

Targets:

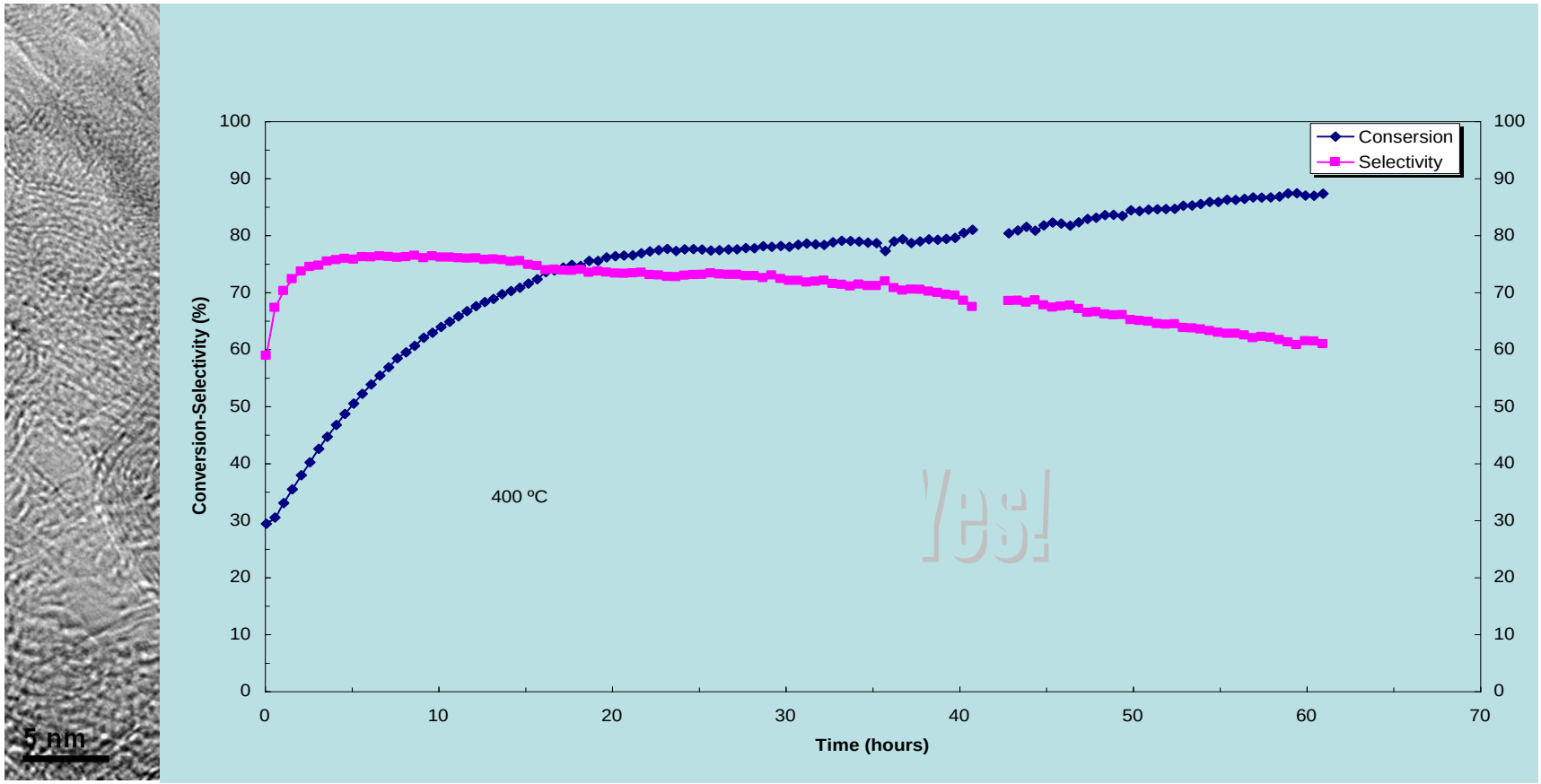
Identification of activity in non-herringbone CNF/CNT

Broaden the material basis and allow for a wider variability in catalyst design

The best “realistic” sample: bundles TS



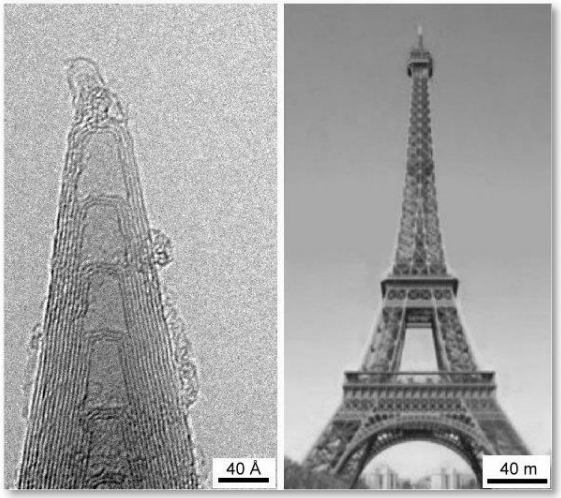
The best “realistic” sample: bundles TS: improvements possible?



Optimisation of defect concentration for maximising basic OH groups and minimizing oxidation on other defects

Consequences

- The high excess of oxygen in the feed necessary for optimum performance
  - Shows the nature of ODH (oxygen in the rds)
  - Requires maximum attention on stability of carbon cat
- The improvement after partial graphitisation shows
  - Adsorption of EB can be optimised
  - Herringbone may not be the best geometry
- Minimisation of defects is the common development target:
  - better adsorption of EB
  - Increased stability vs. Oxygen
- Understand catalytic formation



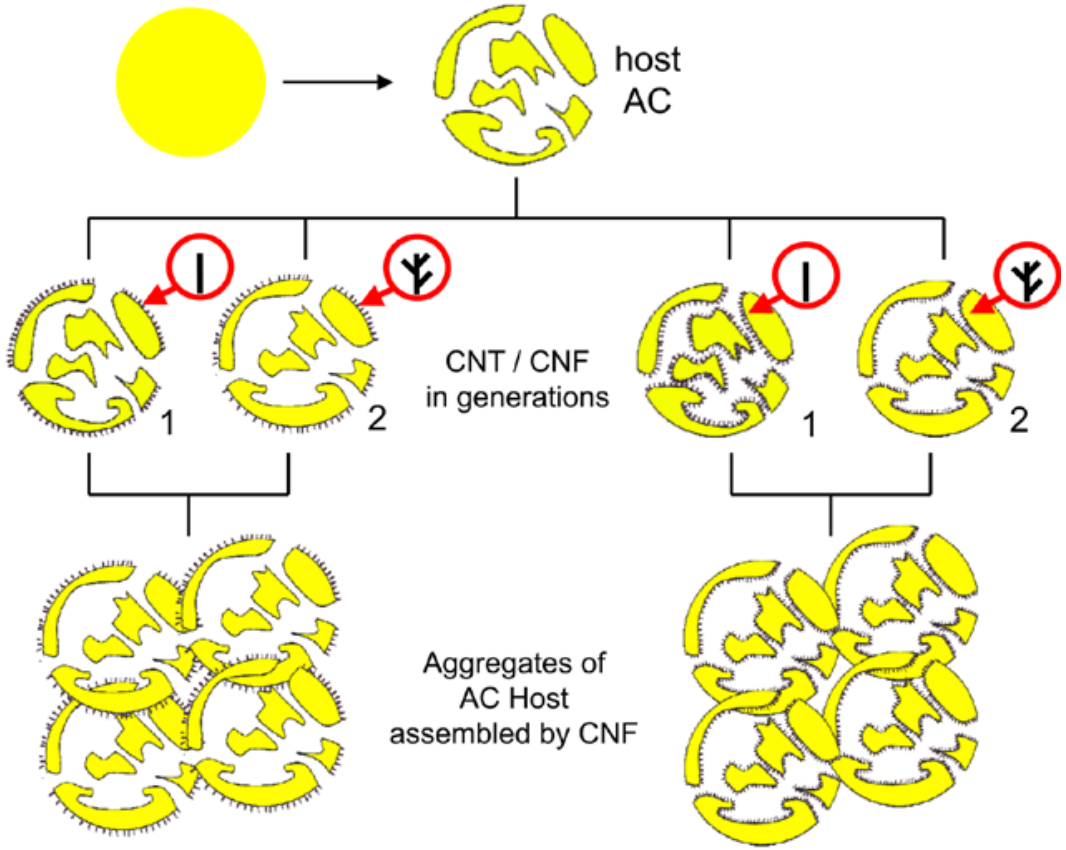
The scale-up issue

The mesoscopic transport problems prevent a simple enlargement of the system into midget scale test systems;

from 20 to 500 mg a hard barrier in performance

: commercialization?

Naturally re-enforced AC support

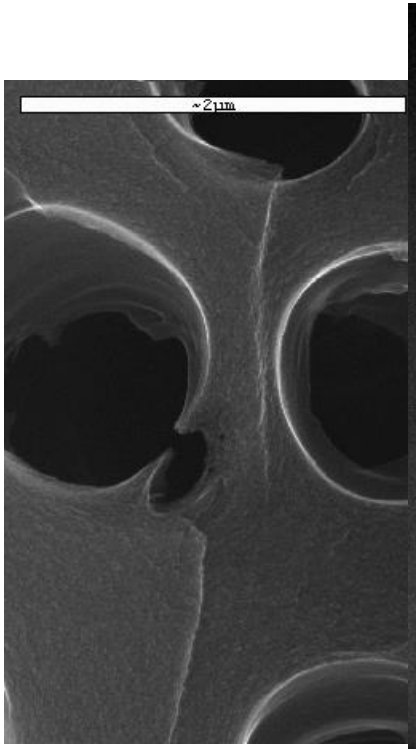


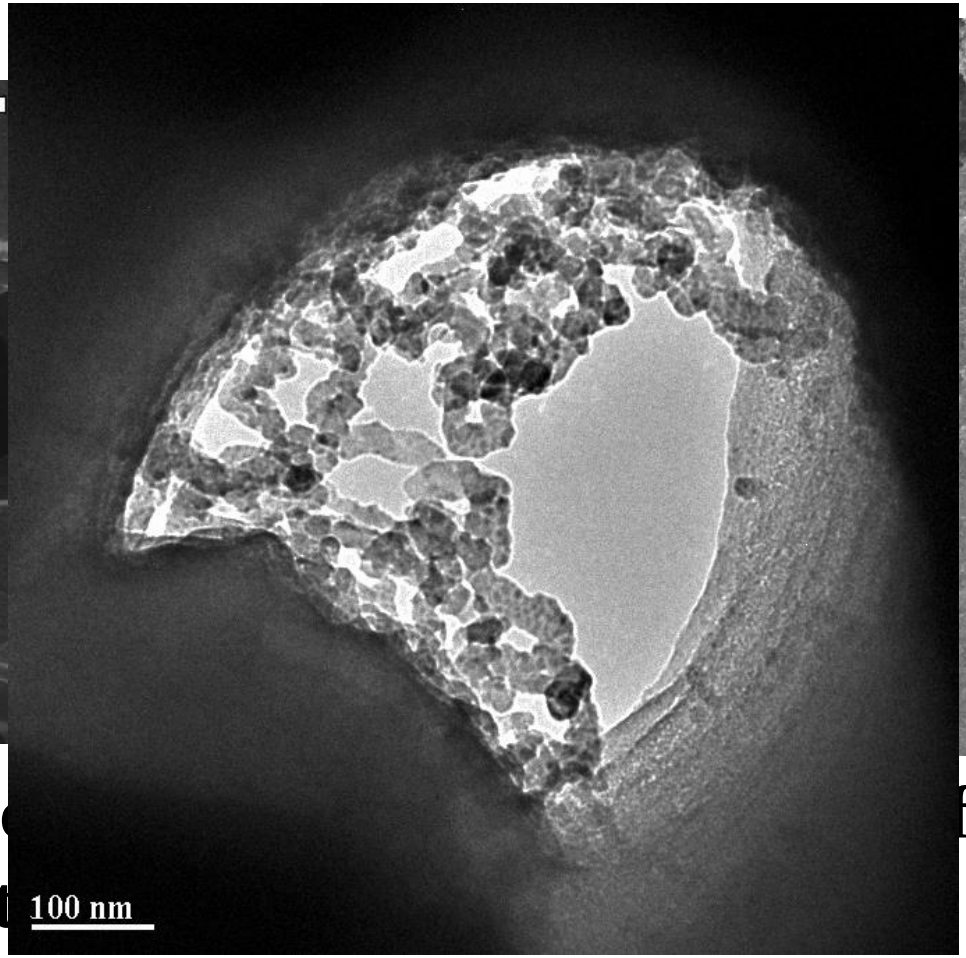
Catalytic nanostructuring and CNF growth: intrinsic catalysts (ash) or by addition

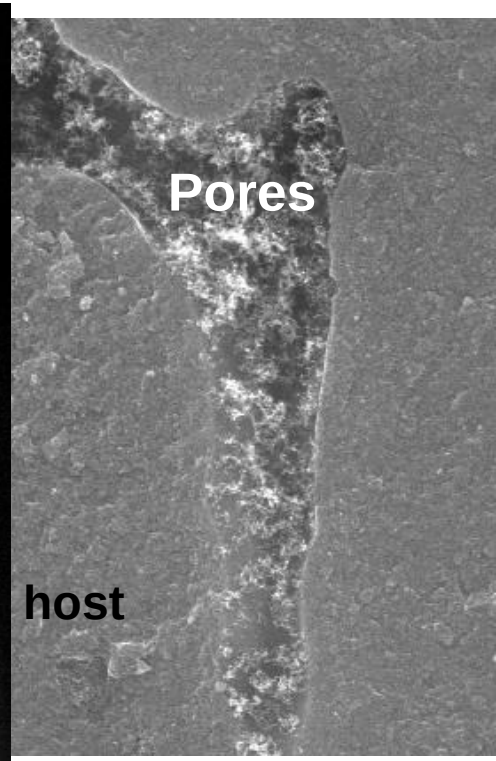
D.S. Su, X. Chen et al.

Angew. Chem. Int. Ed.

Realization of AC-supported CNF







Activated c **from**
calcined at

Some kinetic data

Sample	Ea EB (KJ/mol)	Ea ST (KJ/mol)	n O2	T^a range (°C)	Conversion range	Selectivity range
Mesoporous Carbon	44,5	43	-	350-400	36-70	77
Baytube	76	41	0.23-0.3	325-400	15-48	87-50
Composite	52	35		400-450	27-51	77-62
Applied Science	100	84,7	0.23-0.44	380-425	11,1-38	70-57
Lava/CNT	48,1	50,2		350-400	16-33	65-70
PSLD	63,4	56,6	0.22	350-400	14-36	82-75

DH on promoted iron oxide is 55 kJ/mole

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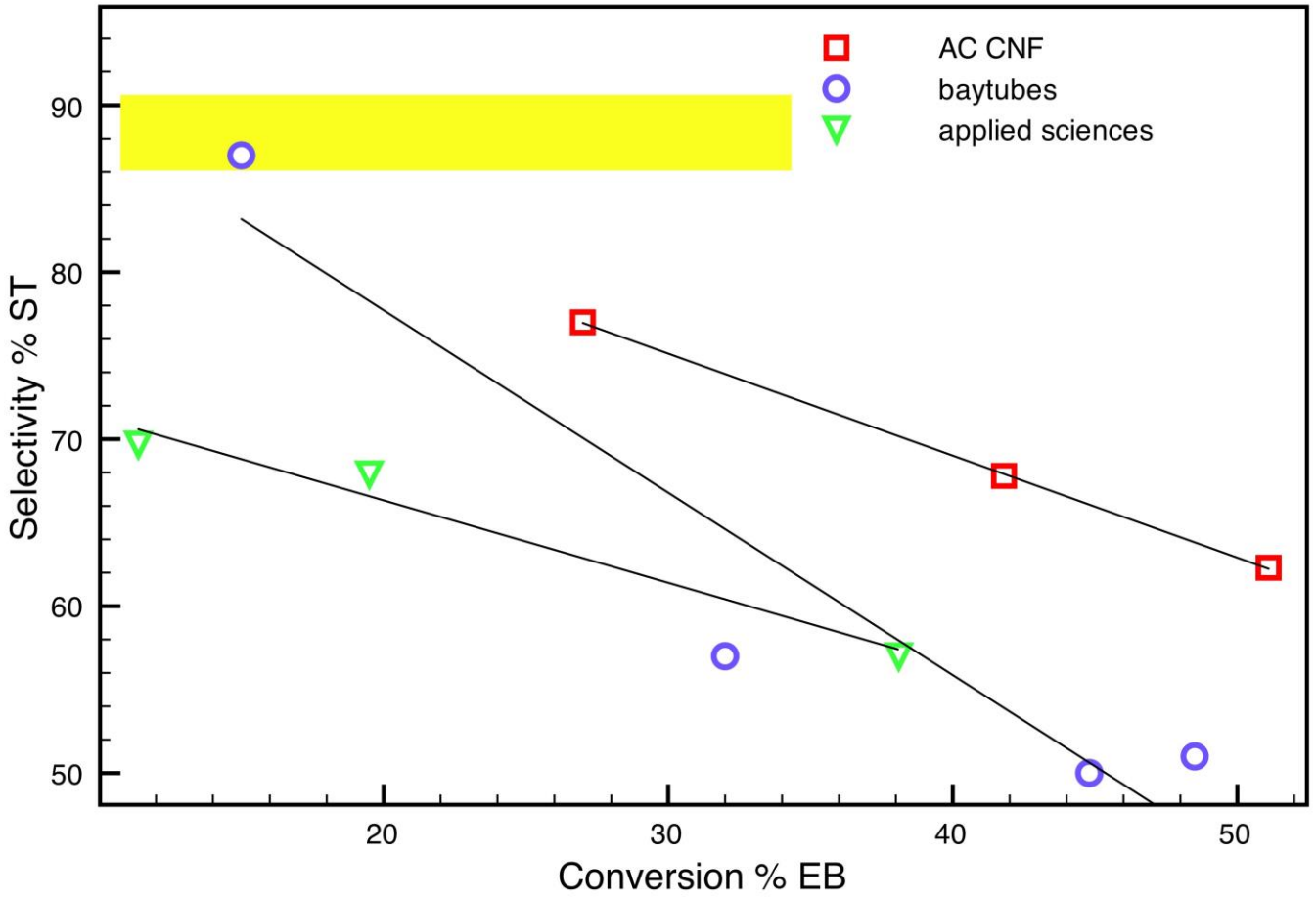
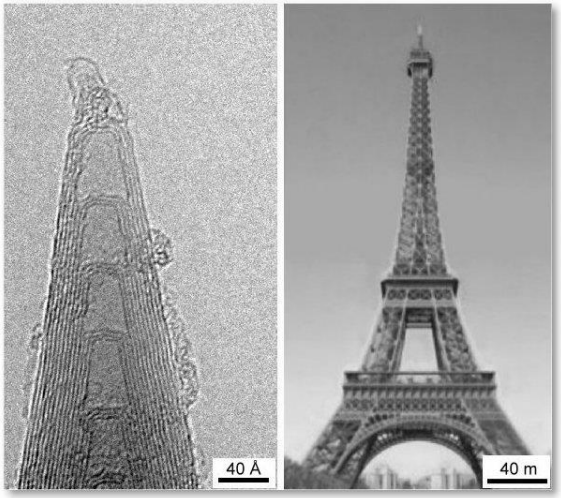
Technical performance possible?



Both systems of CANAPE activities are potentially capable of reaching target



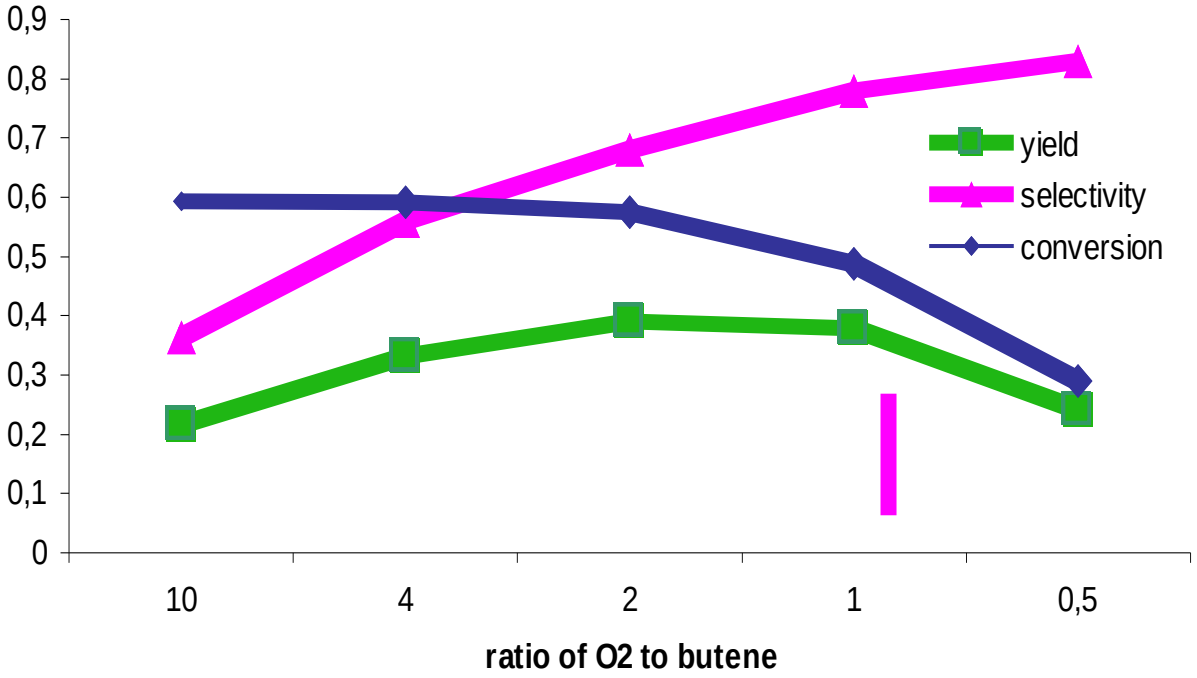
Other ODH Reactions

Butene to Butadiene

Facile as partly activated

Challenge is selectivity not to oxidze system

Butene ODH to Butadiene



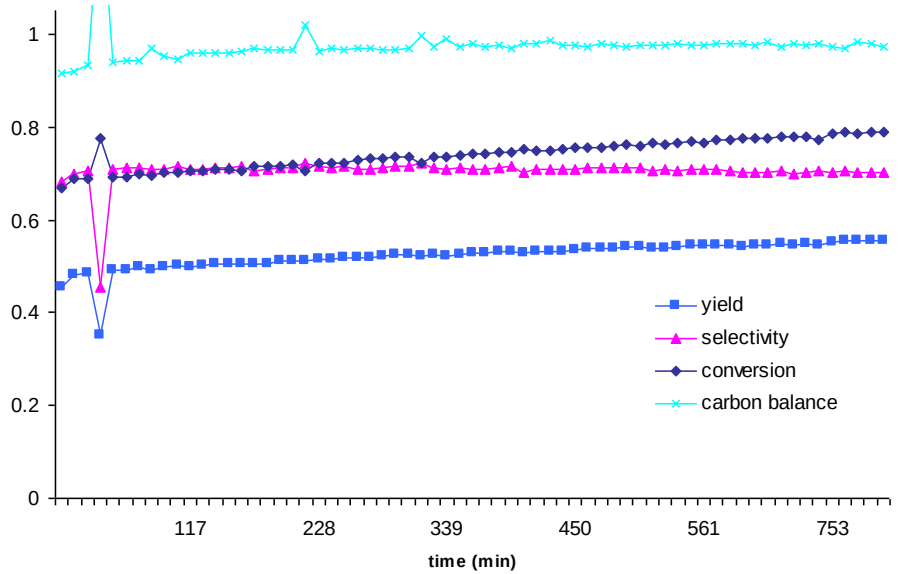
Desired range of operation:

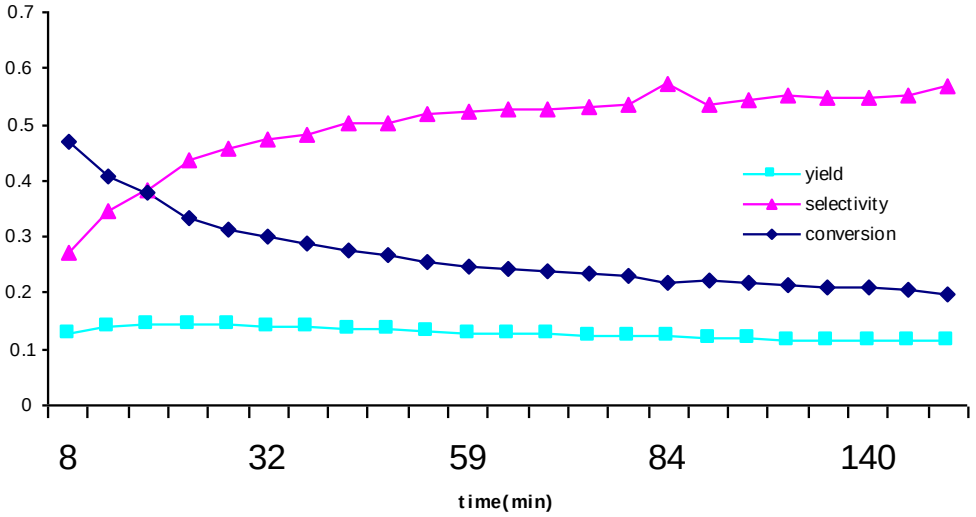
What is the optimum geometry of the nanocarbon for this reaction?

200mg functionalized PSLD, butene 0.1ml/min, O_2 1ml/min, total flow speed 15ml/min

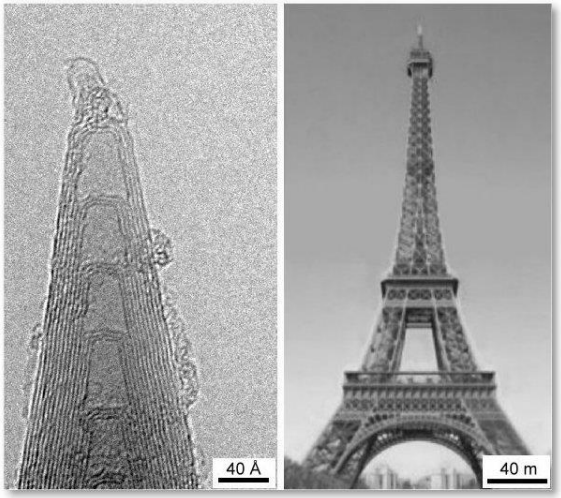
Two modes of operation

673 K: Self-engineering of active sites with carbon from substrate





623 K: pre-fabricated active sites



Formation of CNT

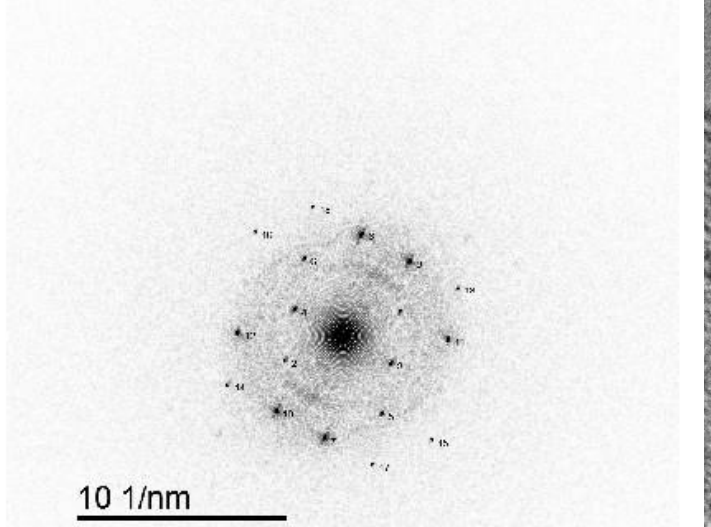
Also catalytic process

Carbon as difficult support for catalyst (application advantages)

Nanostructure of active catalyst

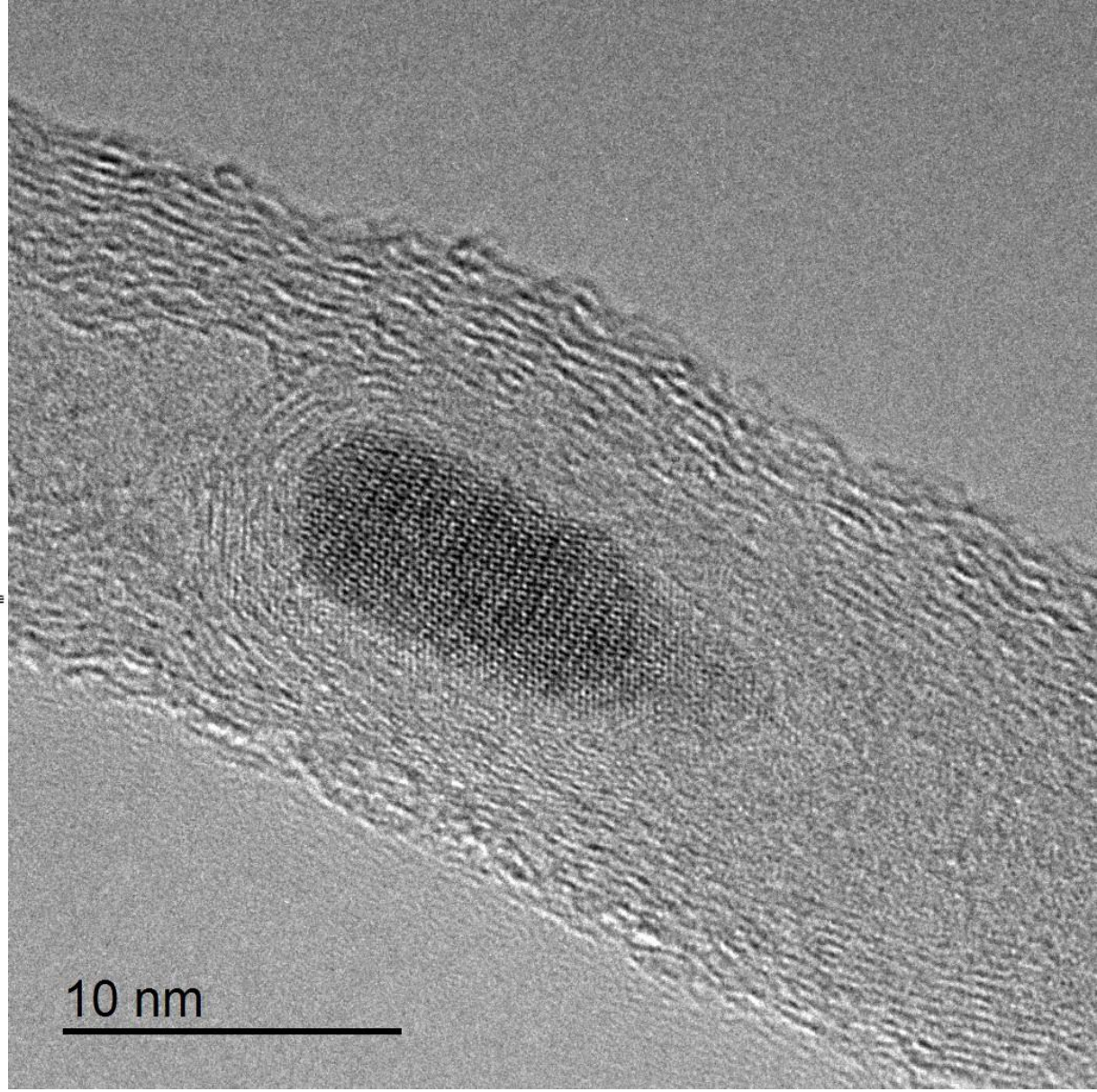
Mechanism of CNT/CNF formation

- Topics to be addressed:
  - Is the catalyst liquid or dynamically solid during operation?
  - Is the carbon activation a surface or a surface-bulk process?
  - May bulk dissolution be part of the active structure formation or is it a spectator process?
  - What are the effects of growth additives like hydrogen, water, ammonia on the catalyst structure?
  - What is the deactivation mechanism of the system (loss of structural dynamics)?



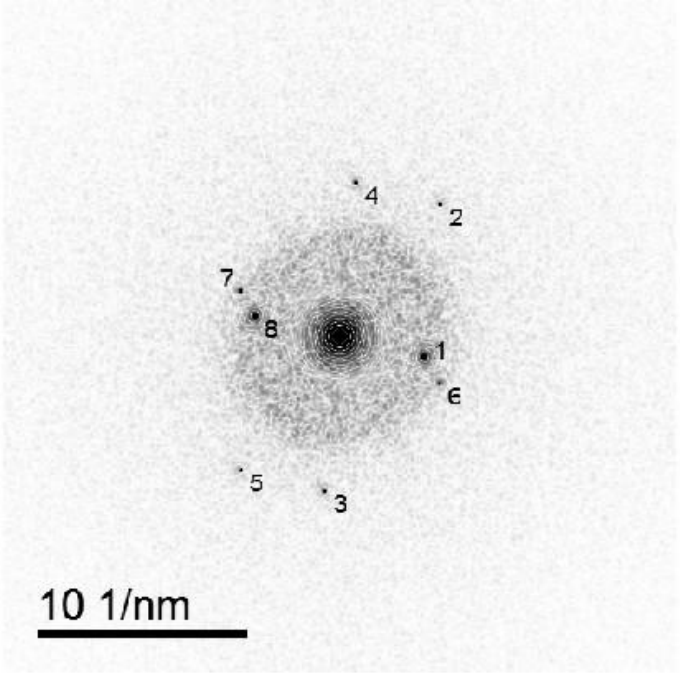
Reduced FFT of CNT-E5-Xiauwei-6

Spot#	d-Spacing (nm)	Rec. Pos. (1/nm)	Degrees to Spot 1	Degrees to x-axis	Amplitude
1	0.3366	2.971	0.00	22.58	202739.45
2	0.3370	2.967	179.55	-156.97	202739.45
3	0.3807	2.627	52.01	-29.43	600835.81
4	0.3832	2.609	128.23	150.80	600835.81
5	0.2426	4.121	85.99	-63.41	458301.38
6	0.2437	4.103	93.96	116.54	458301.38
7	0.2021	4.949	122.95	-100.37	960427.25
8	0.2027	4.935	56.91	79.49	960427.25
9	0.2101	4.761	25.55	48.13	1211165.63
10	0.2098	4.766	154.23	-131.65	1211165.63
11	0.2004	4.991	24.47	-1.89	806274.81
12	0.2008	4.981	155.75	178.33	806274.81
13	0.1688	5.924	0.21	22.79	101694.48
14	0.1690	5.917	179.54	-156.96	101694.48
15	0.1546	6.469	72.33	-49.75	59655.57
16	0.1552	6.445	107.72	130.30	59655.57
17	0.1593	6.279	99.57	-76.99	58603.55
18	0.1597	6.261	80.37	102.95	58603.55



[-1,1,1] zone axis

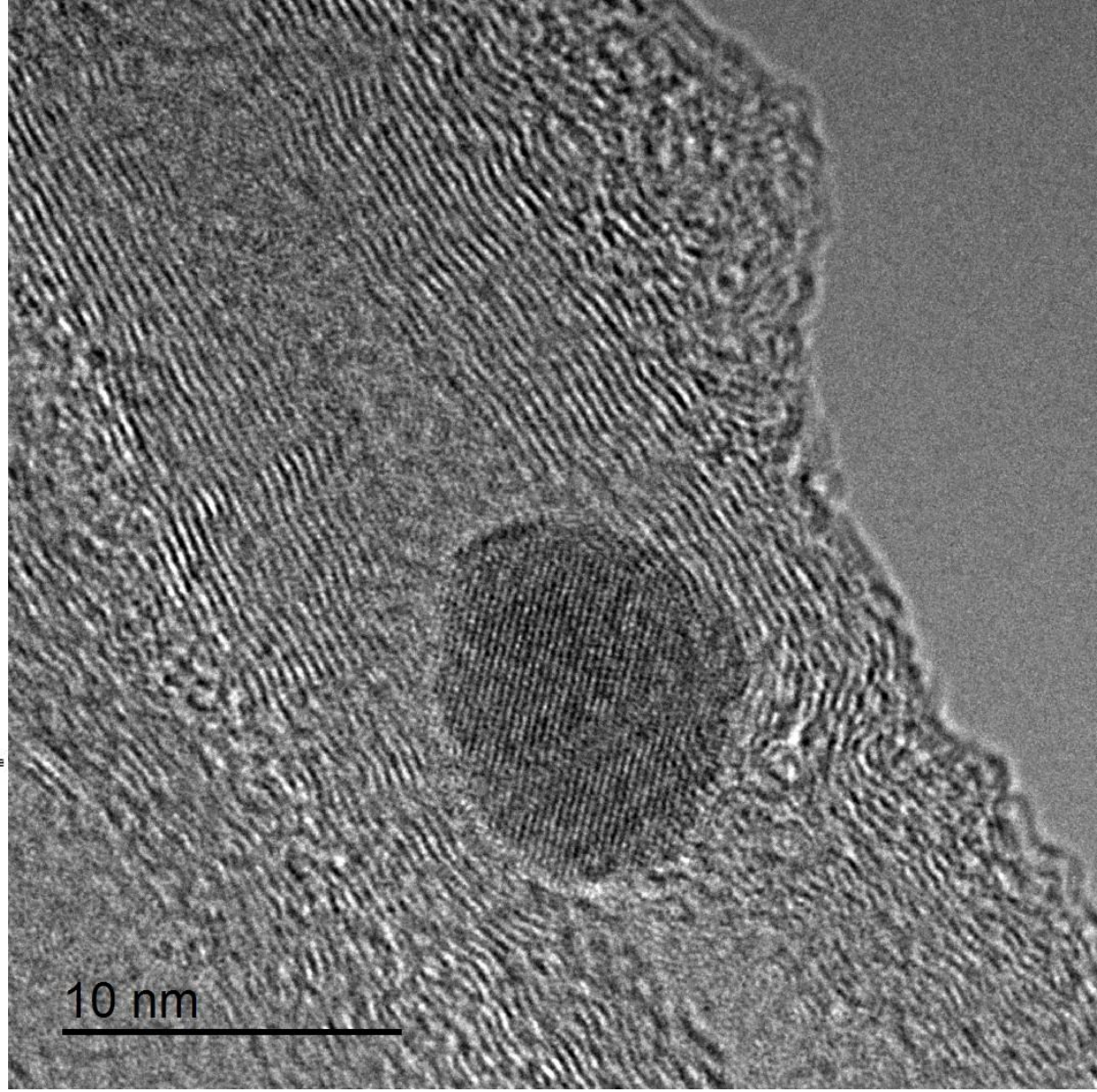
CNT-E5-Xiauwei-6



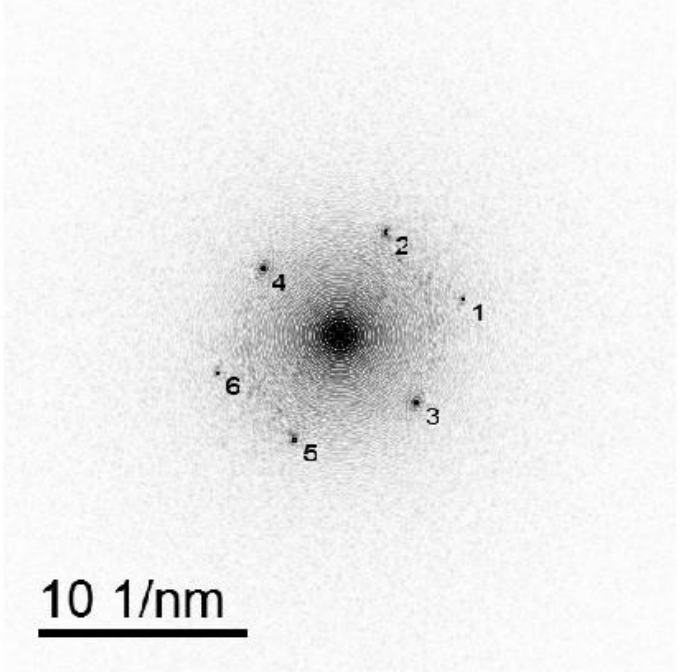
CNT-E5-Xiauwei-10-FFT

Spot#	d-Spacing (nm)	Rec. Pos. (1/nm)	Degrees to Spot 1	Degrees to x-axis	Amplitude
1	0.2411	4.149	0.00	-13.70	908391.41
2	0.1269	7.879	66.60	52.90	47465.01
3	0.1356	7.377	82.02	-95.72	109456.46
4	0.1359	7.357	97.78	84.09	109456.46
5	0.1268	7.884	113.13	-126.83	47465.01
6	0.1916	5.220	11.51	-25.20	117231.57
7	0.1932	5.176	168.87	155.18	118010.60
8	0.2427	4.120	179.75	166.56	908391.41

[1,0,1] zone axis

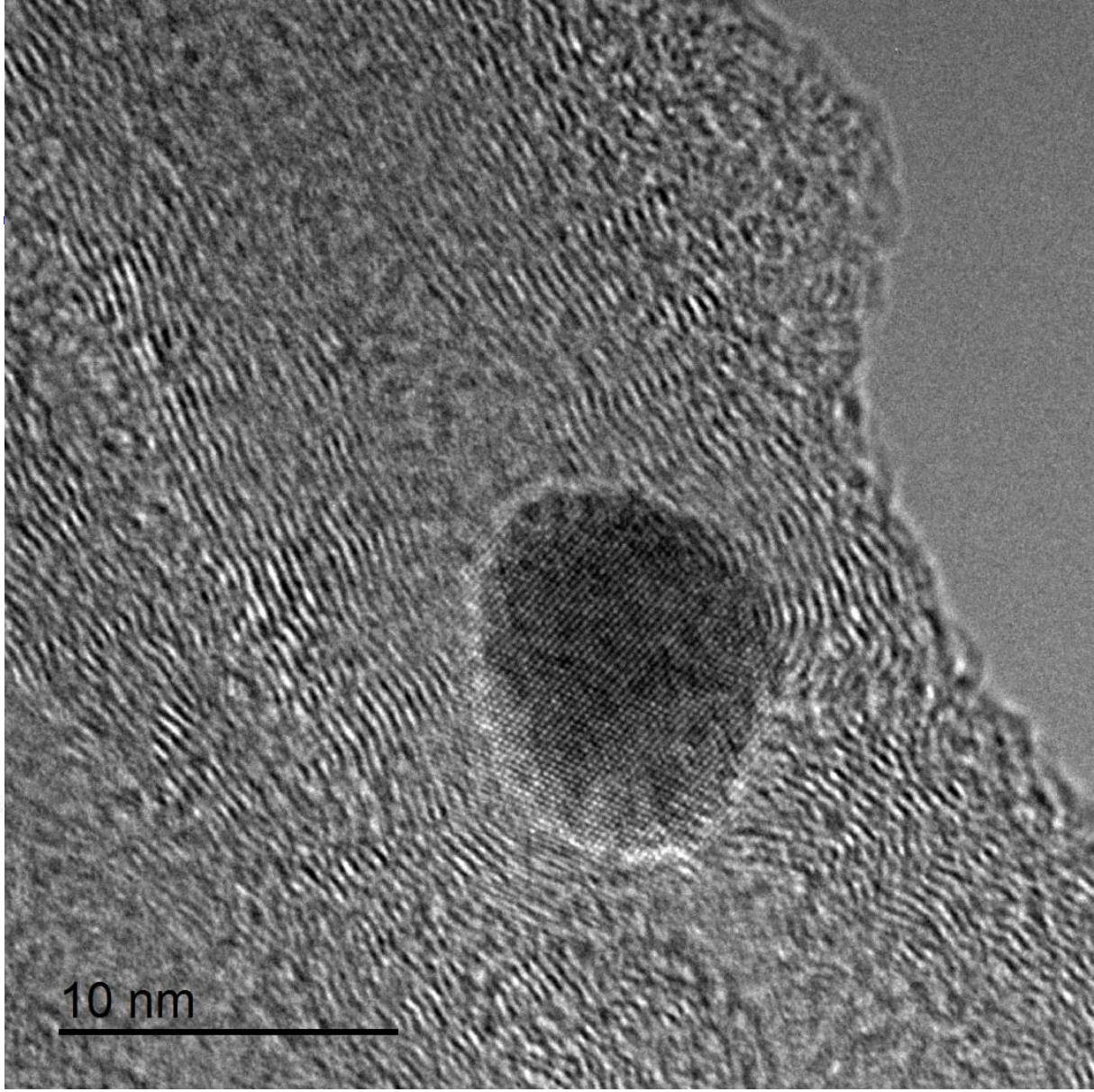


CNT-E5-Xiauwei-10



CNT-E5-Xiauwei-11-FFT

Spot#	d-Spacing (nm)	Rec. Pos. (1/nm)	Degrees to Spot 1	Degrees to x-axis	Amplitude
1	0.1640	6.096	0.00	16.51	109004.81
2	0.1856	5.387	49.39	65.91	278100.72
3	0.2060	4.854	57.68	-41.17	992573.88
4	0.2072	4.827	122.35	138.86	992573.88
5	0.1852	5.399	130.34	-113.83	278100.72
6	0.1644	6.082	179.72	-163.21	109004.81



[5,2,6] zone axis

CNT-E5-Xiauwei-11

Take home messages

- Synthetic variability of nanocarbon is useful for designing local electronic structure for active sites
- Key problem: sticking of non-activated reagents vs. stability in reactant atmosphere
- Defect control and functionalisation need to be improved: understand catalysis of CVD formation
- Designed surface and auto-structuring: CNT as template for autogeneous catalyst formation
- Besides the usual support function nanocarbons are well capable of acting on their own as catalyst for oxidation (and hydrogenation) reactions