C/N-Katalysatoren : Artifizielle Photosynthesis, Heterogeneous Organokatalyse und die CO2 Aktivierung

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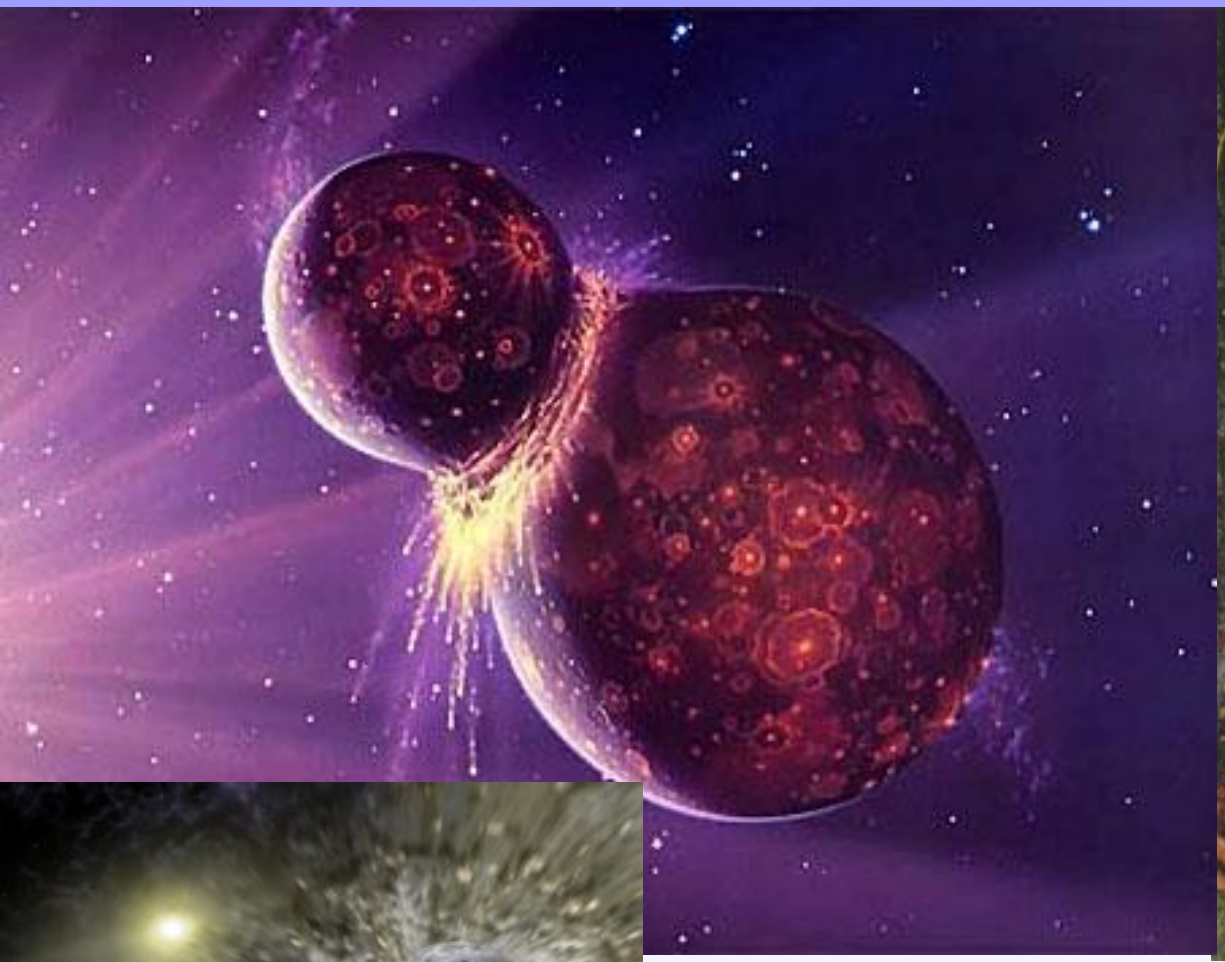
Biomimetic Materials Research (BMR)

Nature: an endless source of inspiration

mimicking molecules, chemical systems, larger hierarchies, whole cells, intellectual principles…

HERE: Photosynthesis, CO_2-Activation

Alpha to omega (nothing before is left..)



Theia and Hyperion:

The birth of Earth and Moon

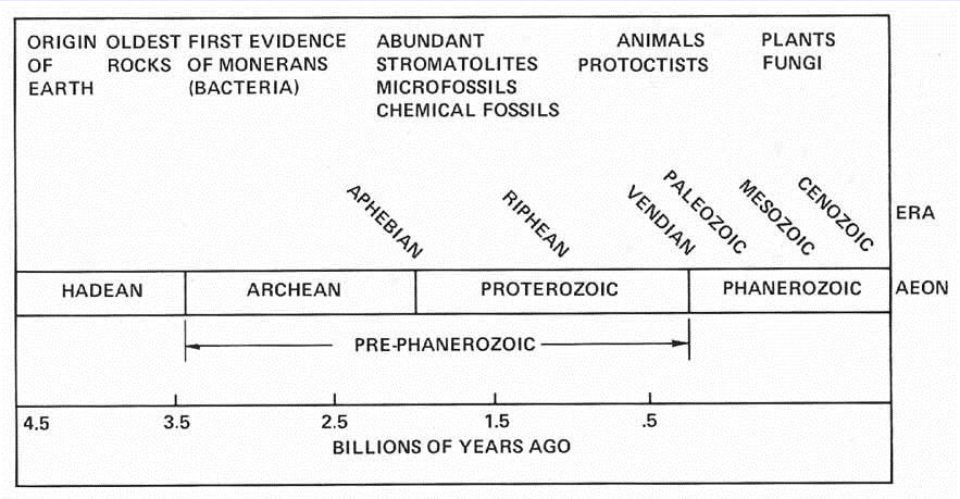
The beginning

Hadean Era

- metamorphosed quartz 4.4 Ga
- after 150 Ma: Earth, Ocean, continental crust
- an awful place: highly acidic, full of dissolved Fe, 20 bars pressure, presumably 200 ˚C, regular meteor impacts (500 km, see moon) evaporizing oceans, volcanos, high clouds

Hadean ≈ "hell-like"

- atmosphere: CH4, CO2, CO, NH3, H2O, H2S, HCN, (O2, O3)



Life, CO_2 chemistry ?

First evidence in Isua „supercrustal belt“, Greenland

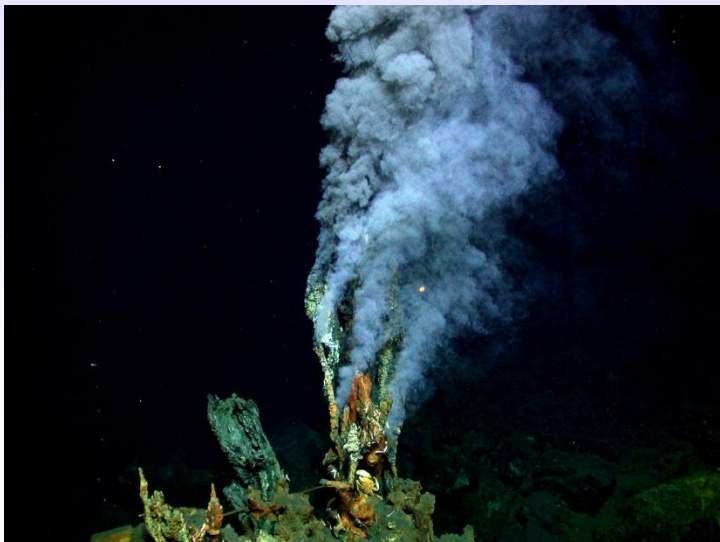
- Evidence of life ^{12}C /^{13}C-ratio
- biomass -20 – 30, natural -5.5, there -18
- CO_2-metabolization !
- 3.85 Ga old !!!
- First black shale: 3.2 Ga…

Molecular „fossils“, first polymers

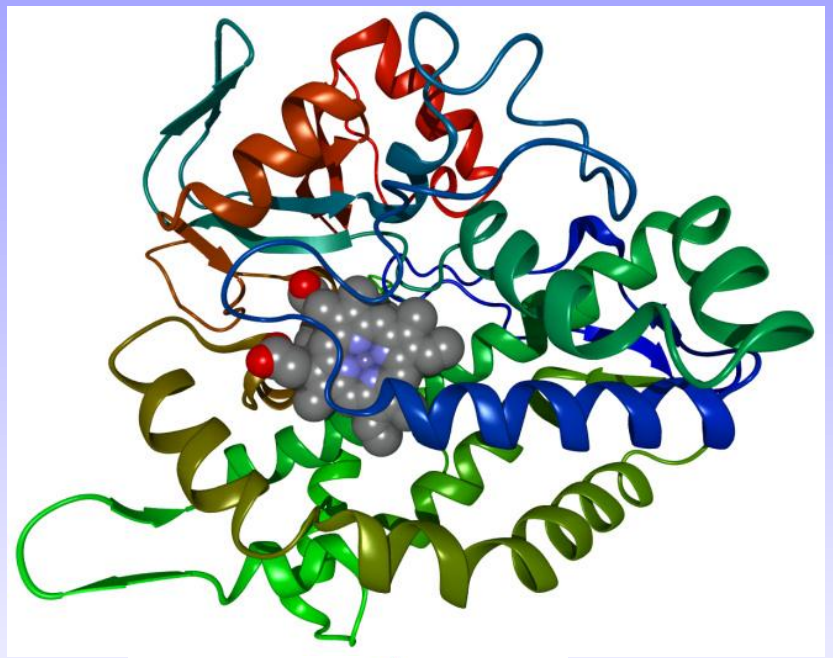
- Adenine
- Nucleobases
- Some enzymes (not too many)

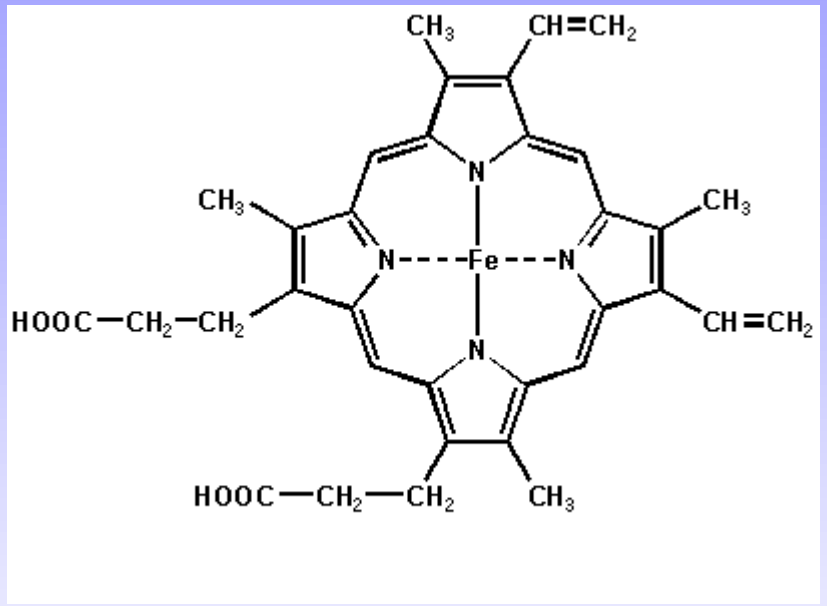
  (protein fabrication relies on ATP !!)
- 6 – 8 amino acids
- Fe/NiS clusters
- Sugars ??

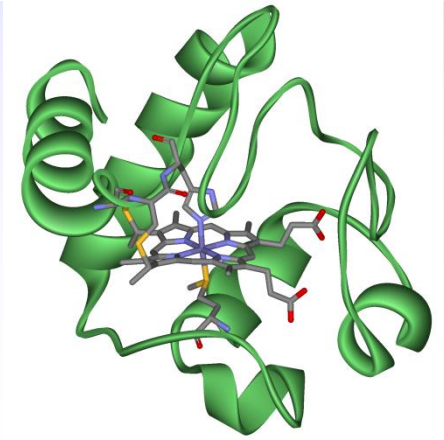
  (Murray meteorite CC contains simple sugar and sugar alcohol molecules), formose reaction
- Lipids ??



Artificial Photosynthesis, Polymeric Enzyme Mimicks

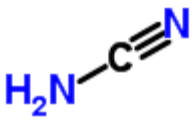


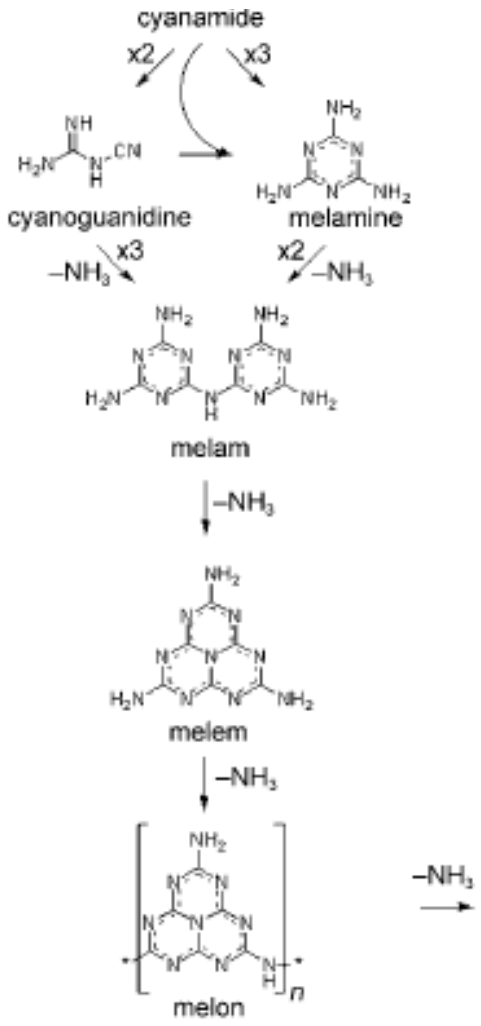


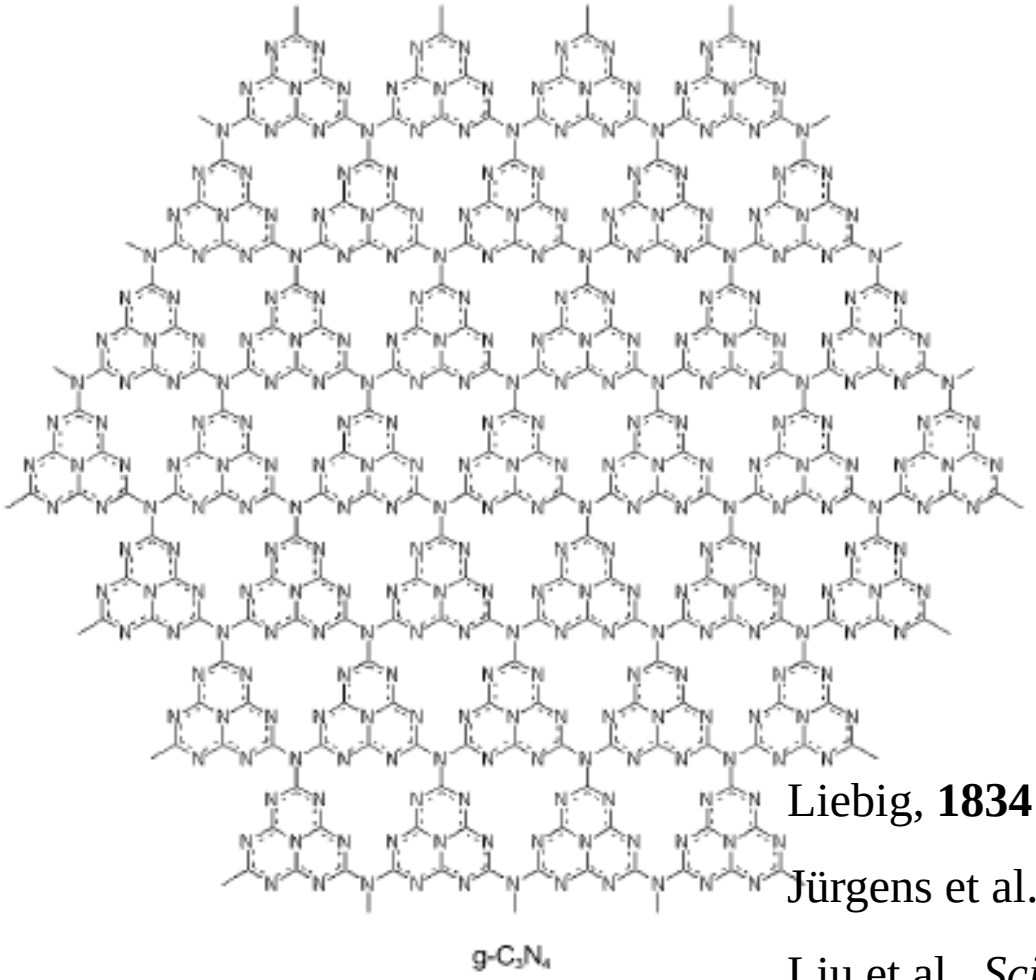


- Cytochrome C, Cytochrome P450
- But: mimick peribiotic solution ??

A hadean chemistry: towards melon and graphitic C_3N_4







Liebig, **1834**

Jürgens et al., *JACS* **2003**

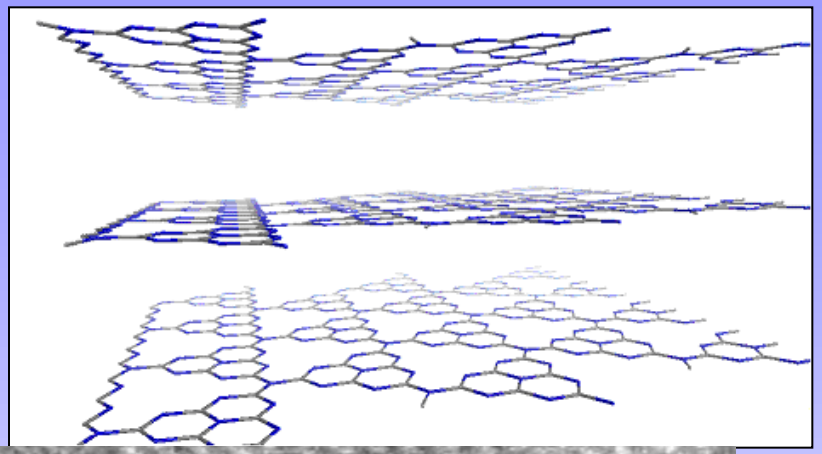
Liu et al., *Science* **1989**

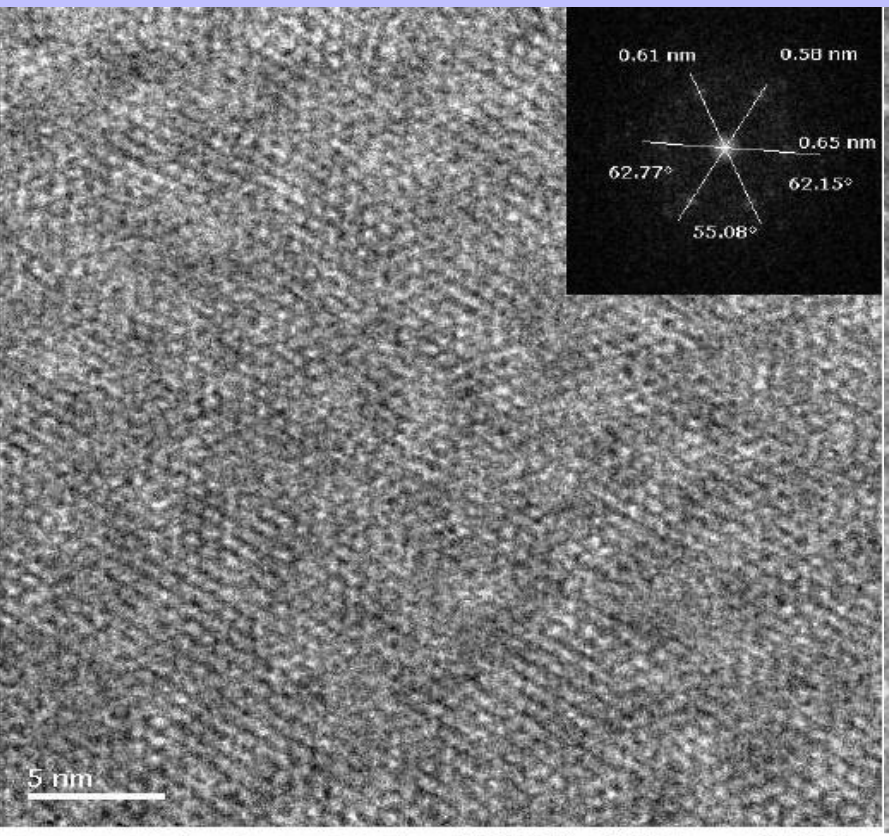
Results of HRTEM

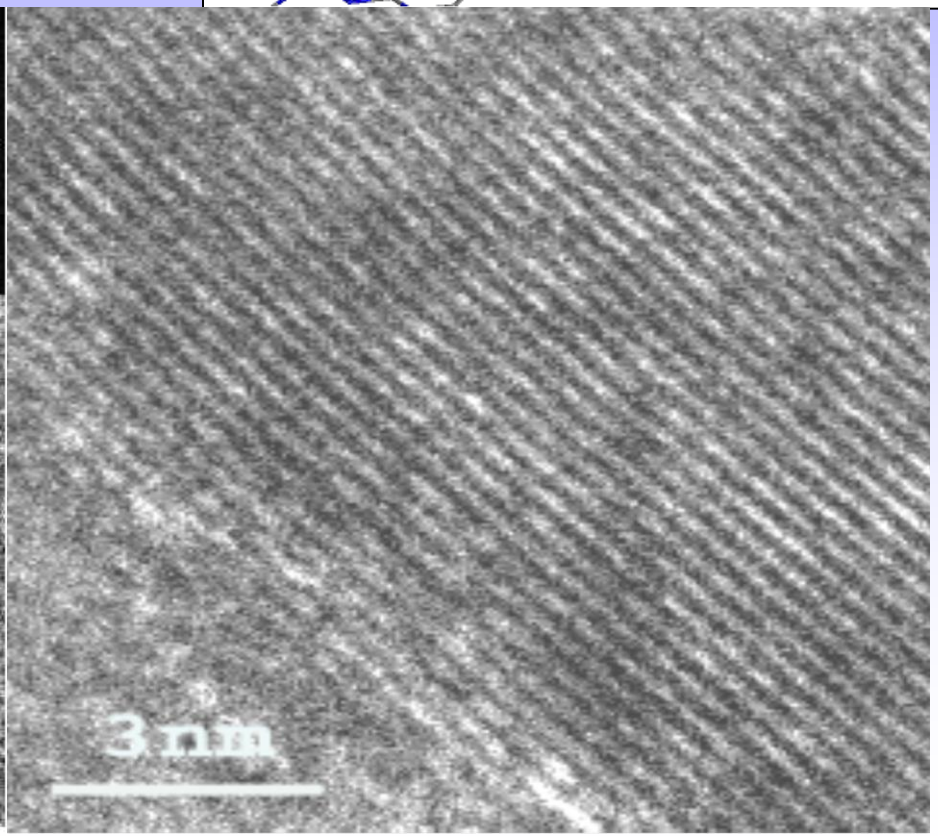
cooperation:

J.O. Müller

R. Schlögl







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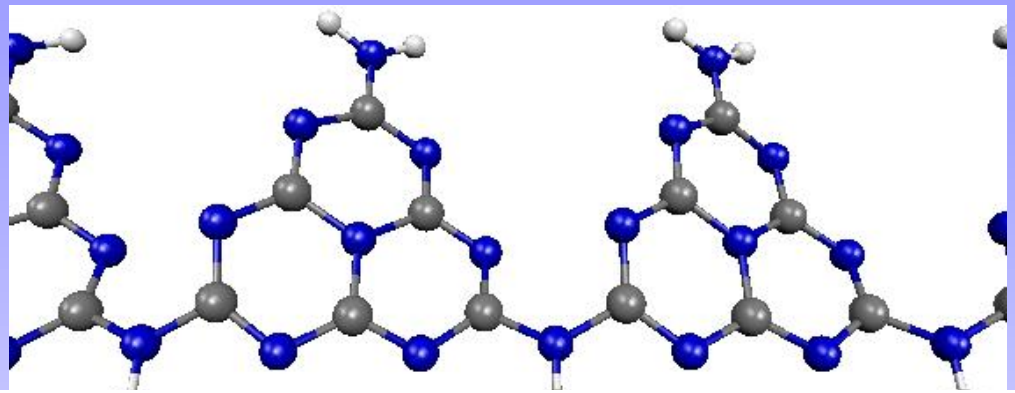
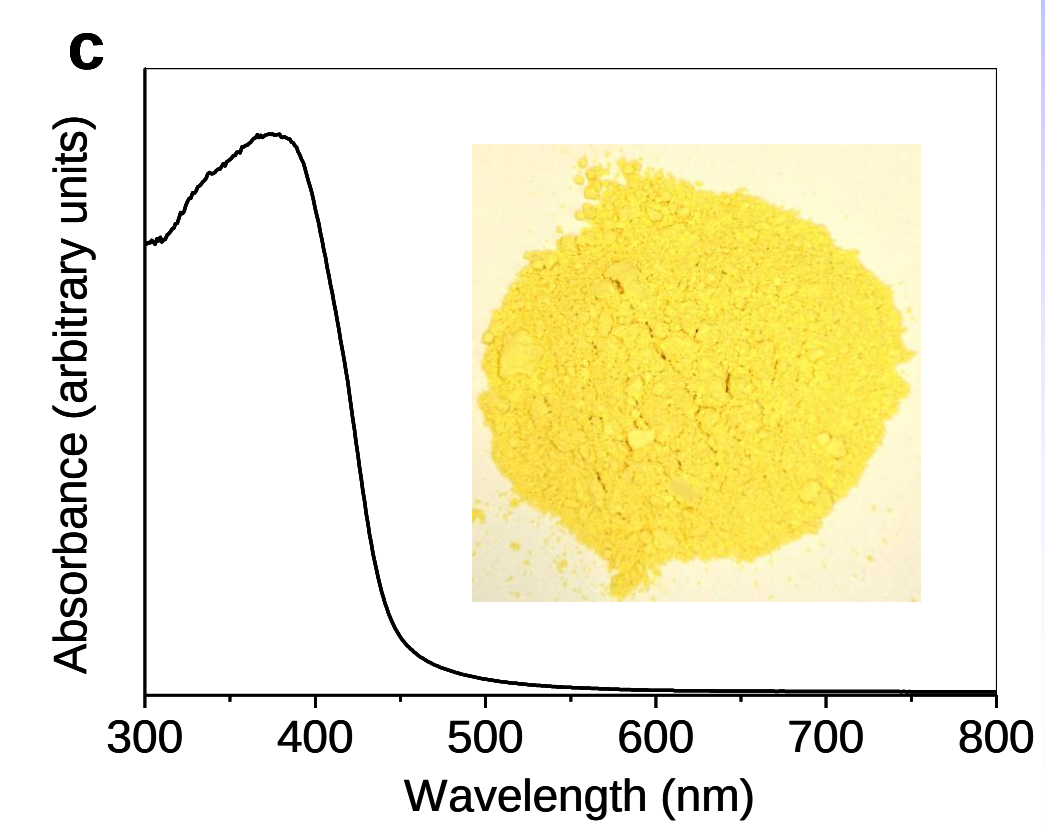
Melon (Poly-(heptazine)imine)

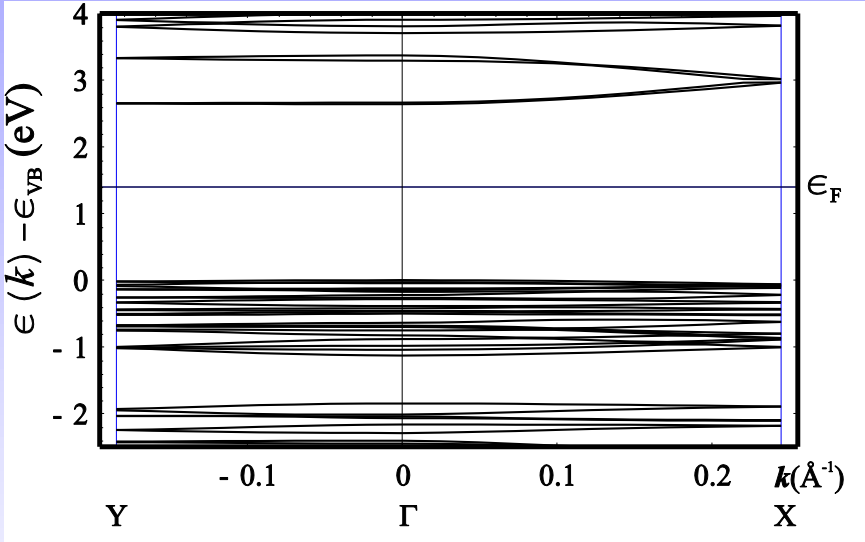


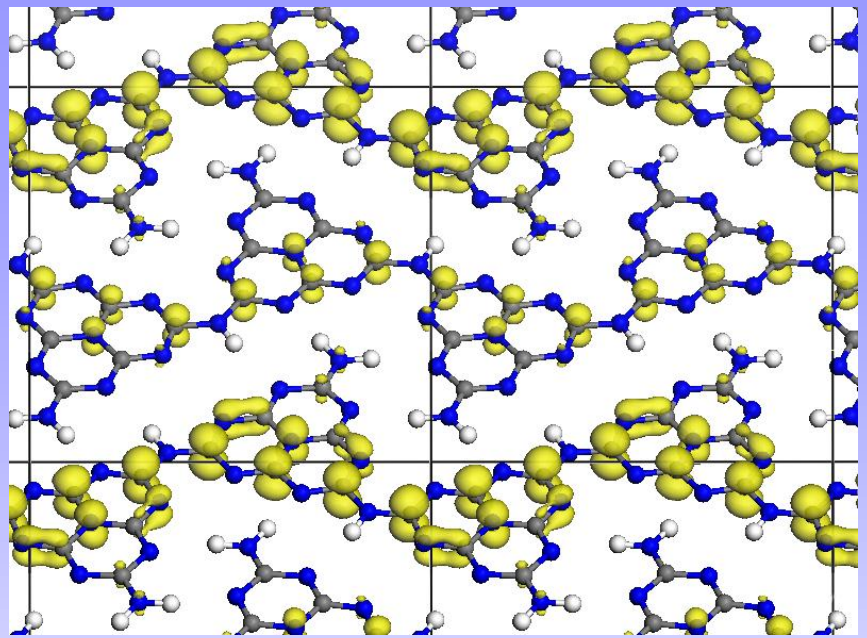


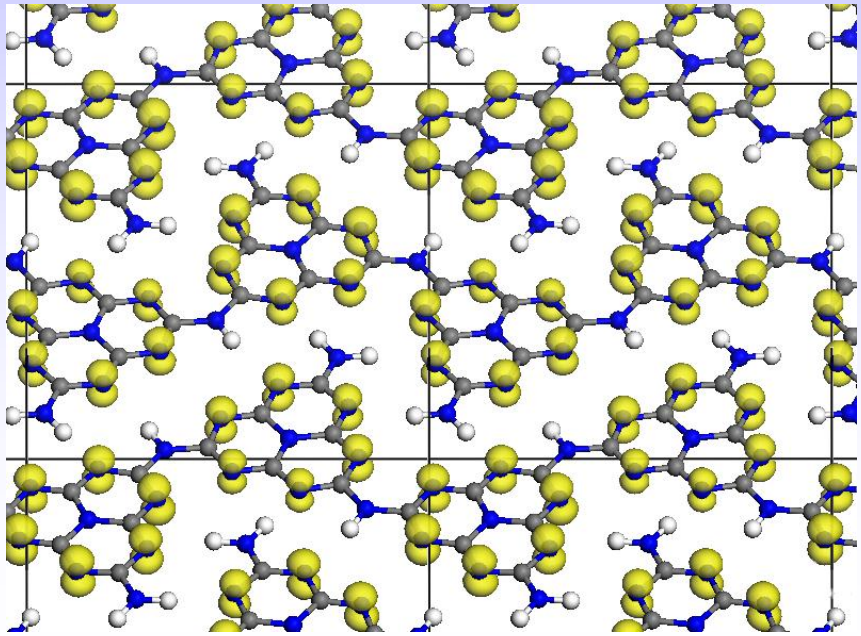
DFT- Calculations

by Dr. Johan Carlson

Fritz Haber Institute







E_{coh}= -5.5 eV / atom

E_f = 1.4 eV / unit

$E_g^{Direct\ (\Gamma)}$ = 3.2 eV

$E_g^{Indirect\ (\Gamma\text{-}X)}$= 2.3 eV

Artificial Photosynthesis:

„The conversion of light energy by a man-made machinery/system to create chemical energy storage molecules“
e.g. Hydrogen, Carbohydrates, Ammonia, Methane… from the artificial tree...

Target : 10 % efficiency
(300 t methanol /ha)

from: www.treehugger.com

Most „simple“ case: water splitting

Overall:

$$2\ H_2O + 4\ h\nu \rightarrow 2H_2 + O_2 \qquad (\Delta G^o = 4.92\ eV,\ n = 4)$$

Two half-reactions:

1) **Water oxidation:**

$$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^- \qquad (E^o = -1.23\ V)$$

2) **Water reduction:**

$$4\ H^+ + 4\ e^- \rightarrow 2\ H_2 \qquad (E^o = 0.00\ V)$$

The next option: CO_2-conversion

Overall:

$$2\ H_2O + CO_2 + 8\ h\nu \rightarrow CH_4 + 2O_2 \qquad (\Delta G^o = 10.3\ eV,\ n = 8)$$

Two half-reactions:

1) **Water oxidation:**

$$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^- \qquad (E^o = -1.23\ V)$$

2) **CO_2 reduction:**

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2\ H_2O \qquad (E^o = -0.22\ V)$$

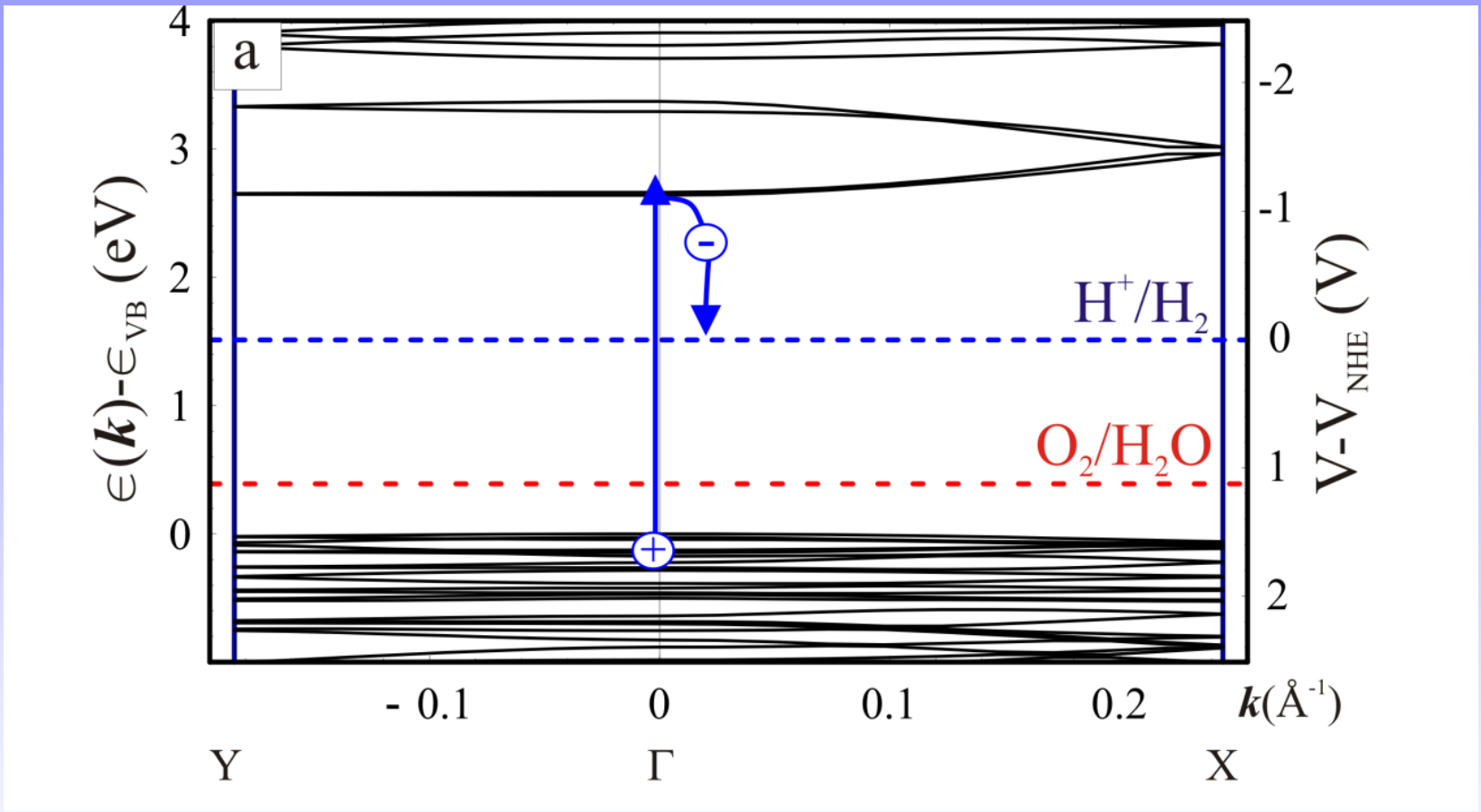
CO_2 Reduction:

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2\,H_2O \quad (E^o = -0.22\ V)$$

Four two-electron transfer reactions:

1) $CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$ (Formic Acid)
2) $HCOOH + 2H^+ + 2e^- \rightarrow H_2CO + H_2O$ (Formaldehyde)
3) $H_2CO + 2H^+ + 2e^- \rightarrow H_3COH$ (Methanol)
4) $H_3COH + 2H^+ + 2e^- \rightarrow CH_4 + H_2O$ (Methane)

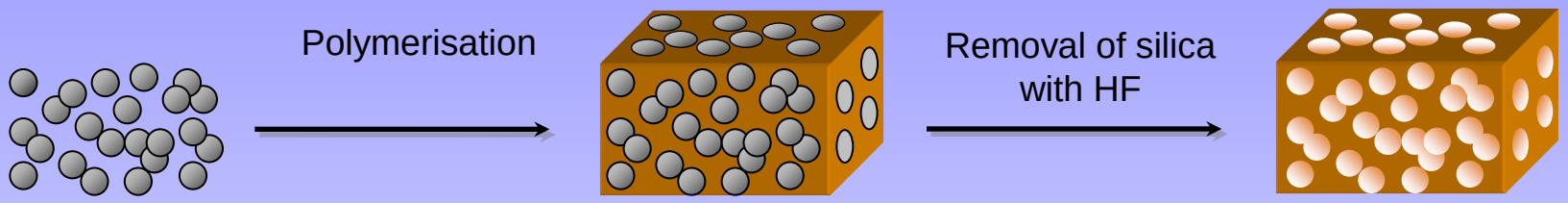
- Rates of reaction are slow
- Catalyst is needed to increase rate
- No good catalyst is currently known

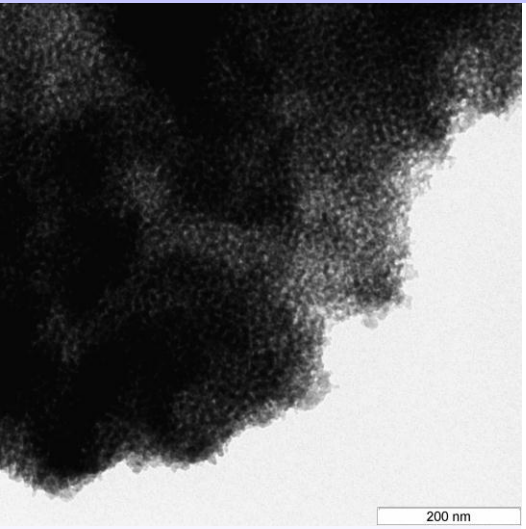


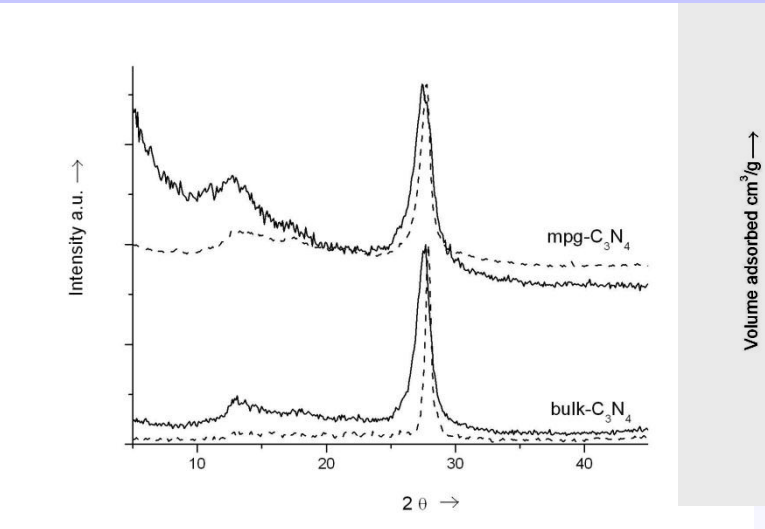
Band Positions: good for photochemical water splitting

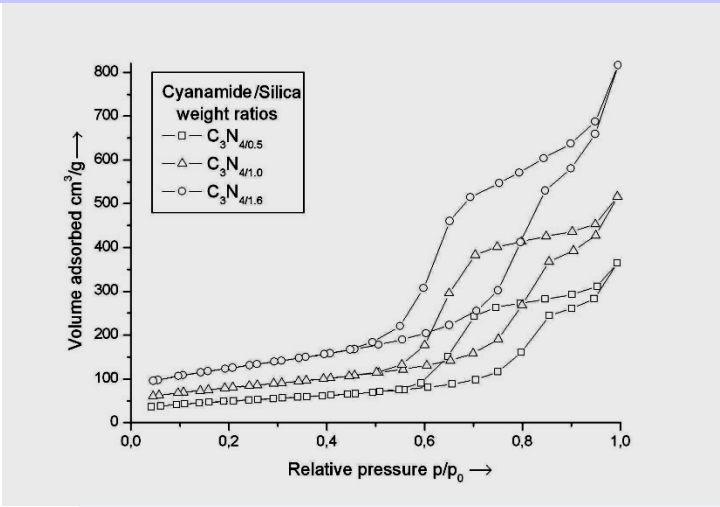
Mesoporous CN-materials for catalysis

Synthesis via hard templates, i.e. Silica NP dispersed in the monomer





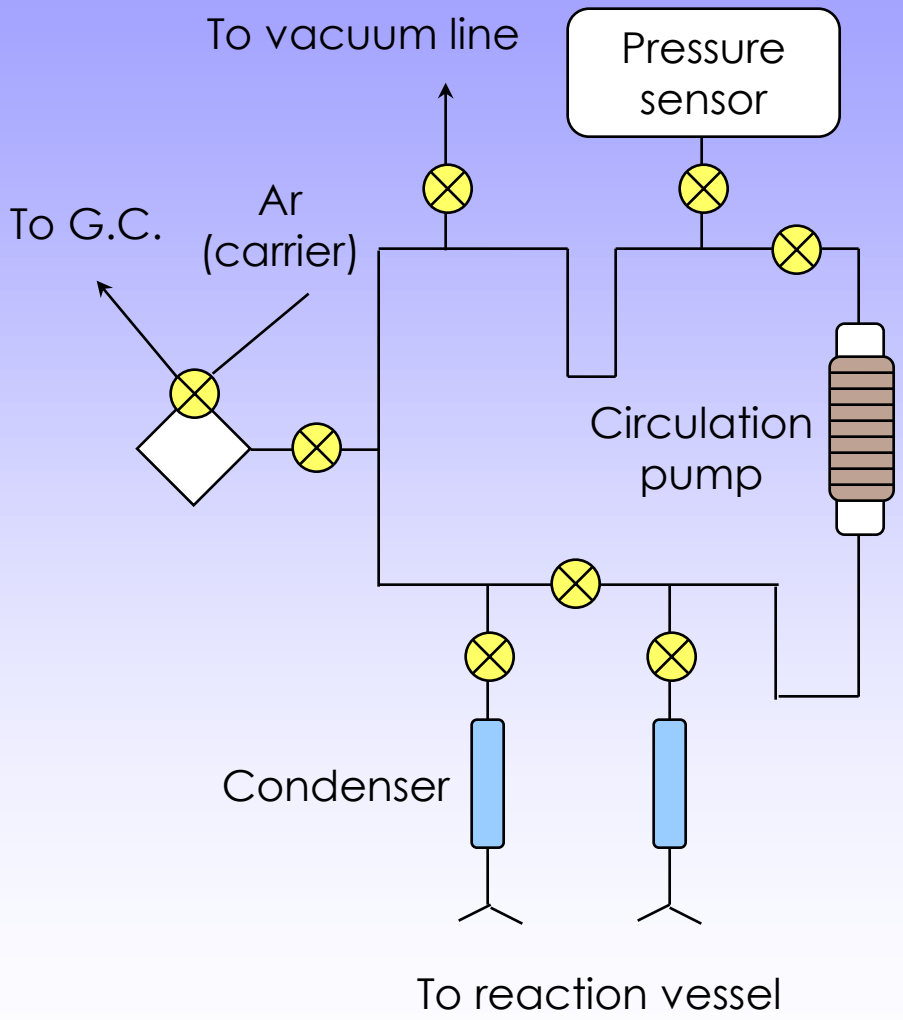




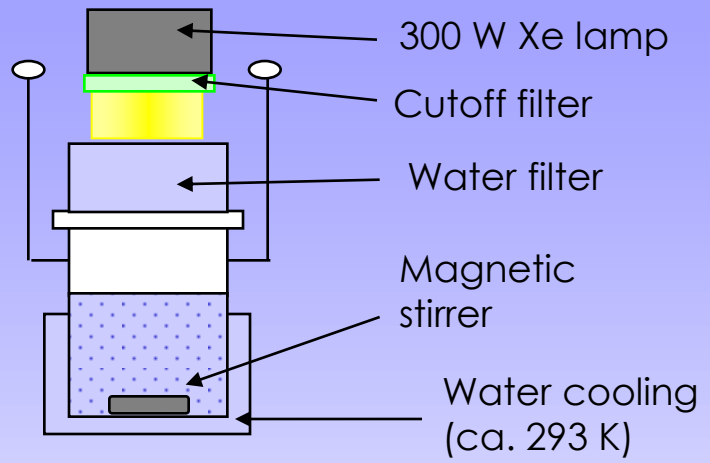
- the carbon nitride structure is preserved.
- porosity can be adjusted (90 to 400 m²/g)

F. Goettmann, A. Fischer, M. Antonietti, A. Thomas *Angew. Chem. Int. Ed.* **2006**, 4467

Photocatalytic reaction condition



Closed-gas circulation system

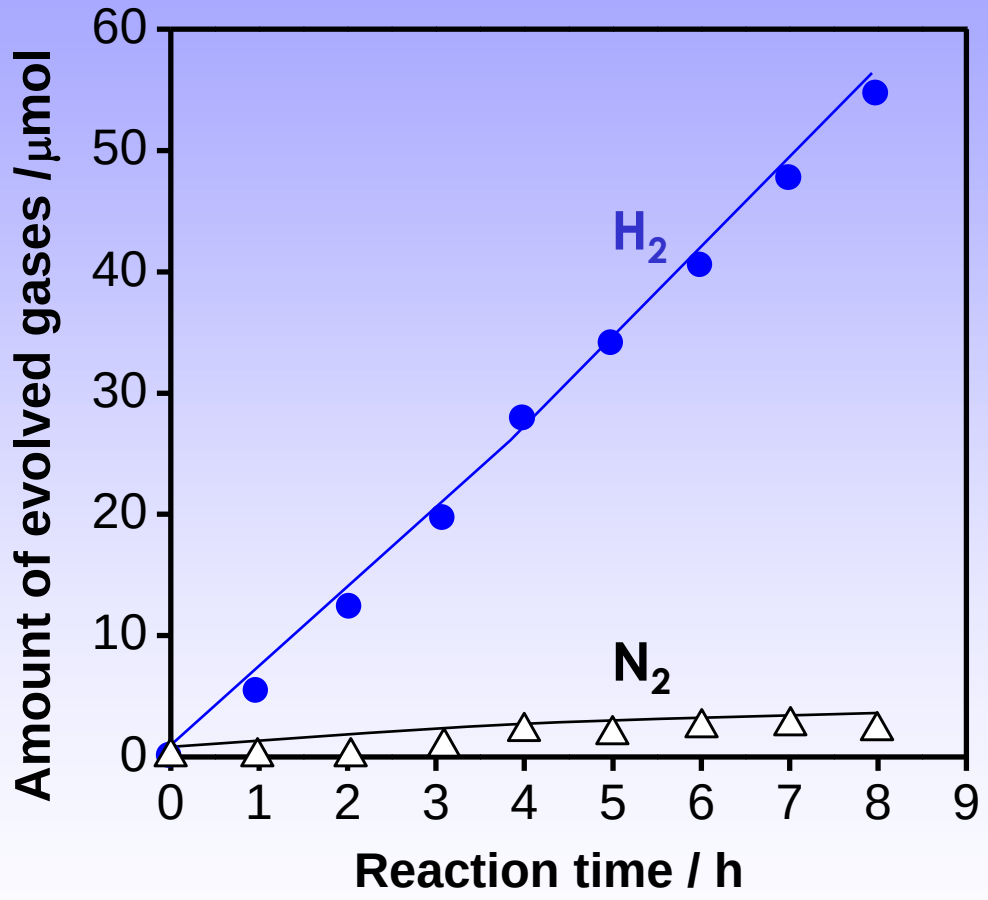


Top-irradiation type vessel

Catalyst: 0.1 g
Cocatalyst: 0.5 wt% Pt (loaded by in-situ photodeposition)
Gas analysis: GC with TCD (Ar carrier)

with Prof. Domen /Japan

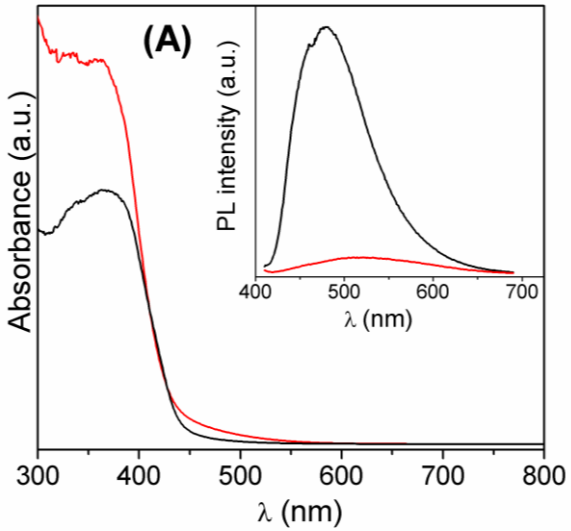
H_2 evolution on Pt (0.5 wt%)-loaded C_3N_4

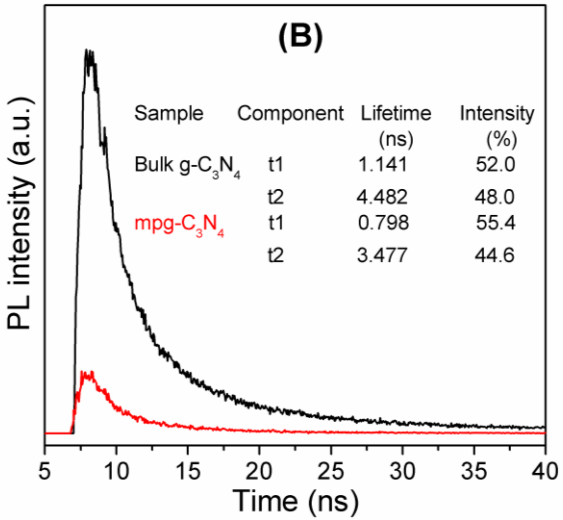


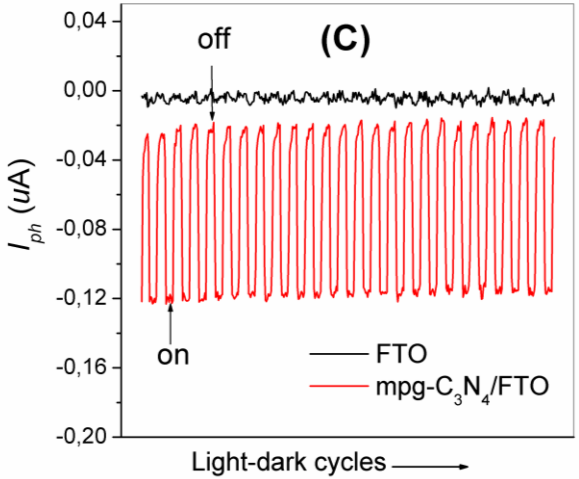
λ > 420 nm

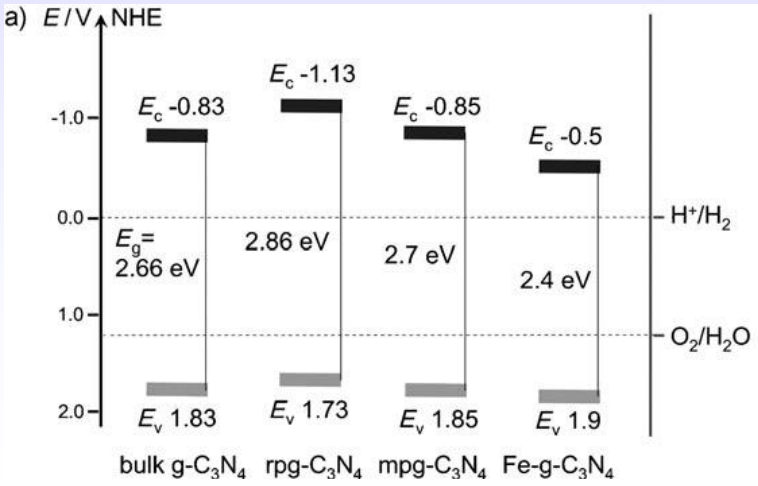
Catalyst, 0.1 g, Reactant solution, aqueous triethanolamine solution 100 mL 10 vol.%; Reaction vessel, Pyrex top irradiation-type; Light source, xenon lamp (300 W) attached with a cutoff filter

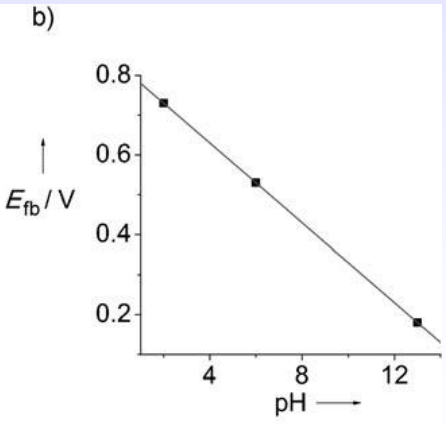
Additional characterizations



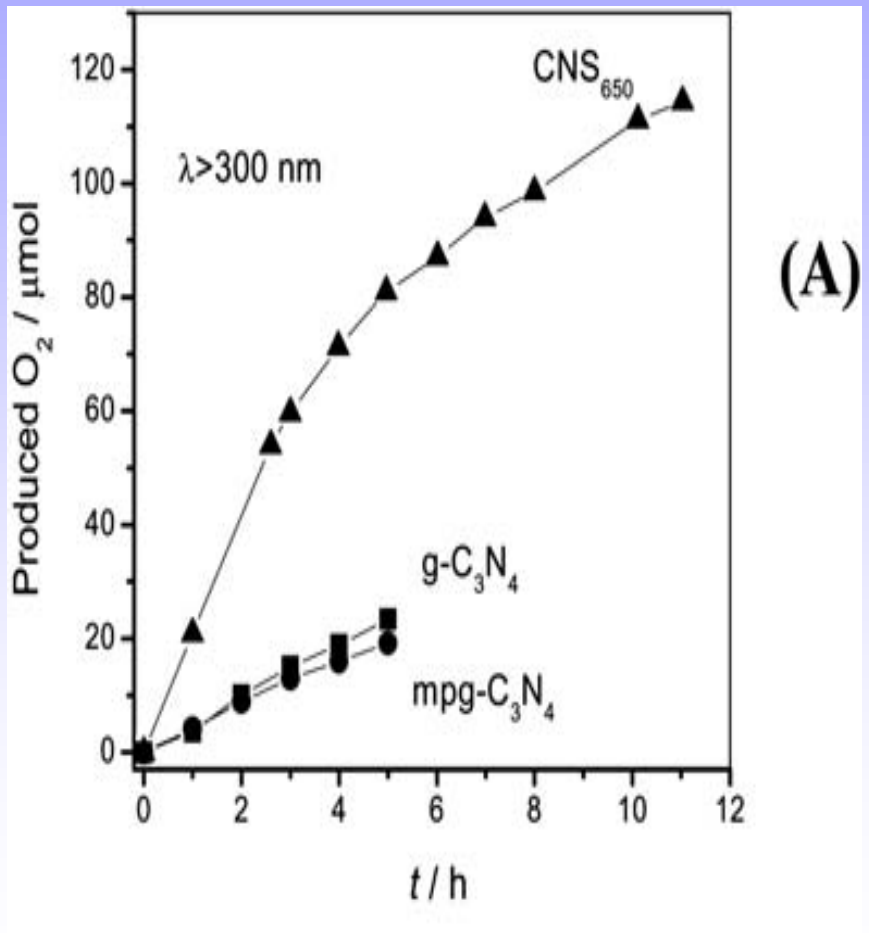


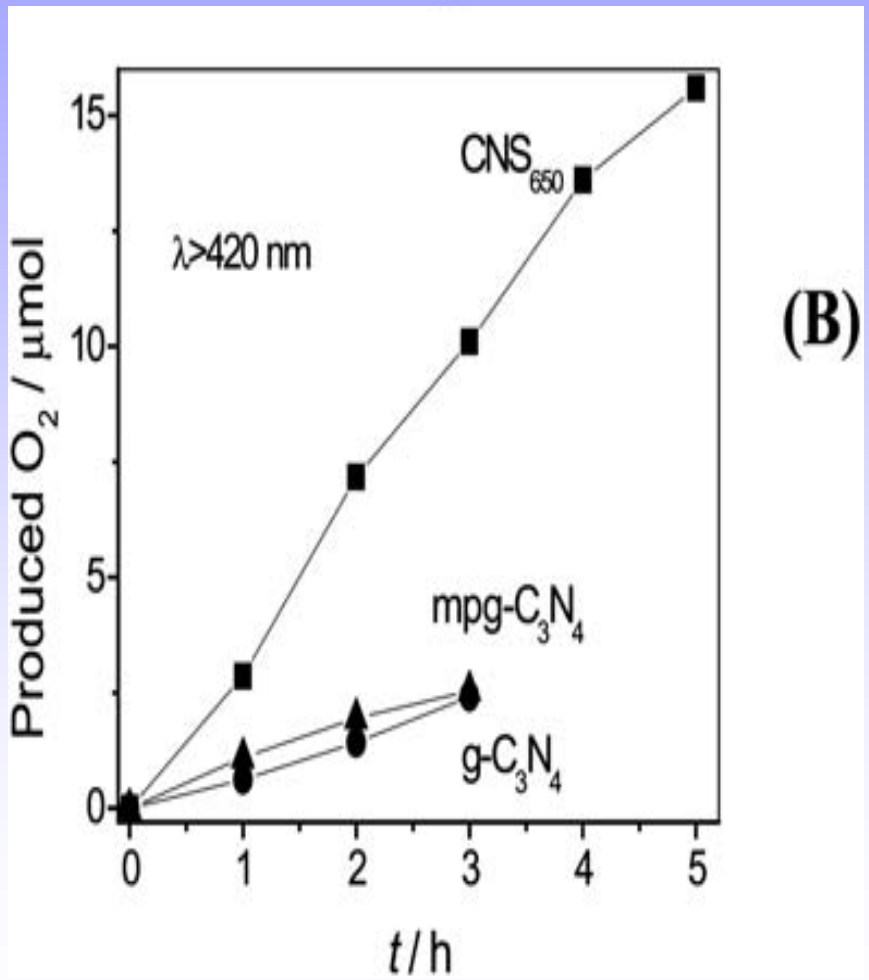




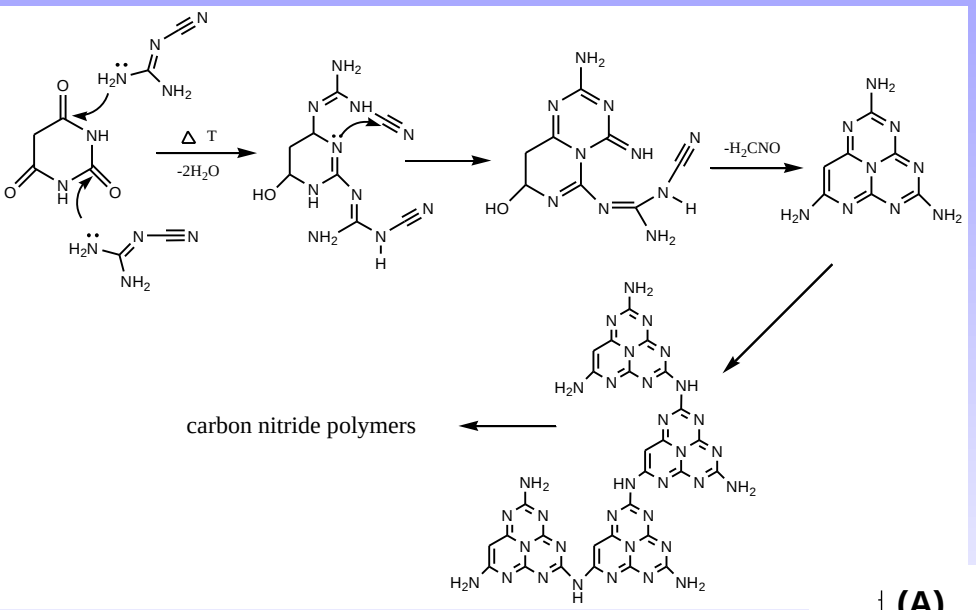


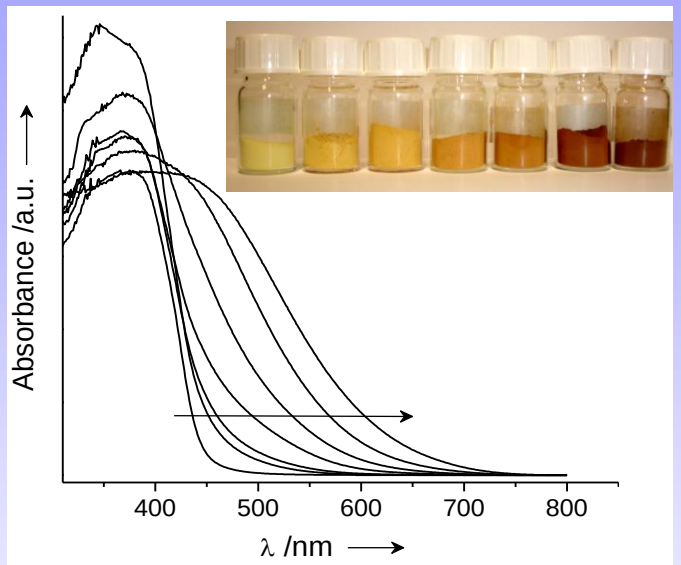
Oxygen Liberation (the more complicated side)

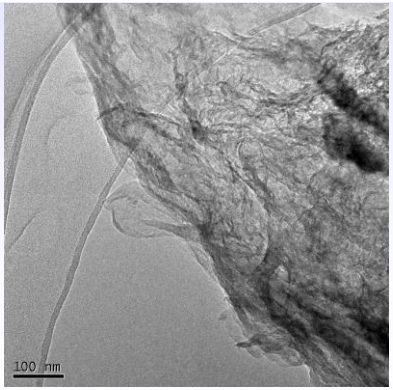


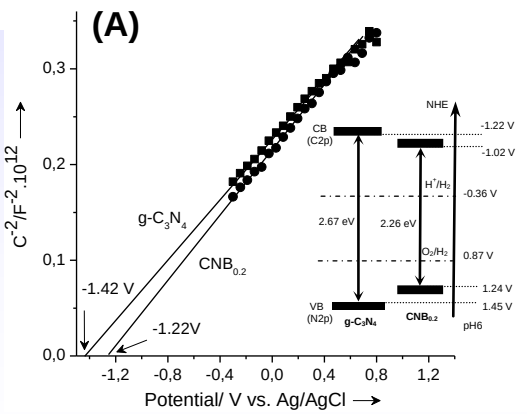


Extension of the 2d-polymerization principle: copolymerization

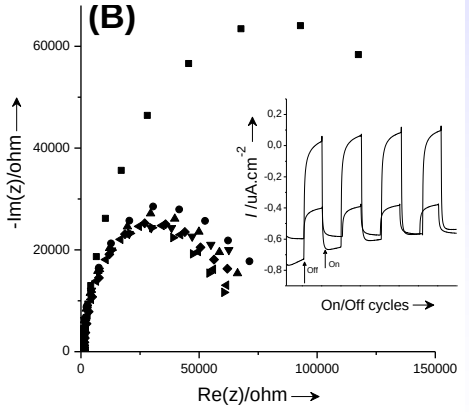








Mott-Schottky plot



Nynquist plot

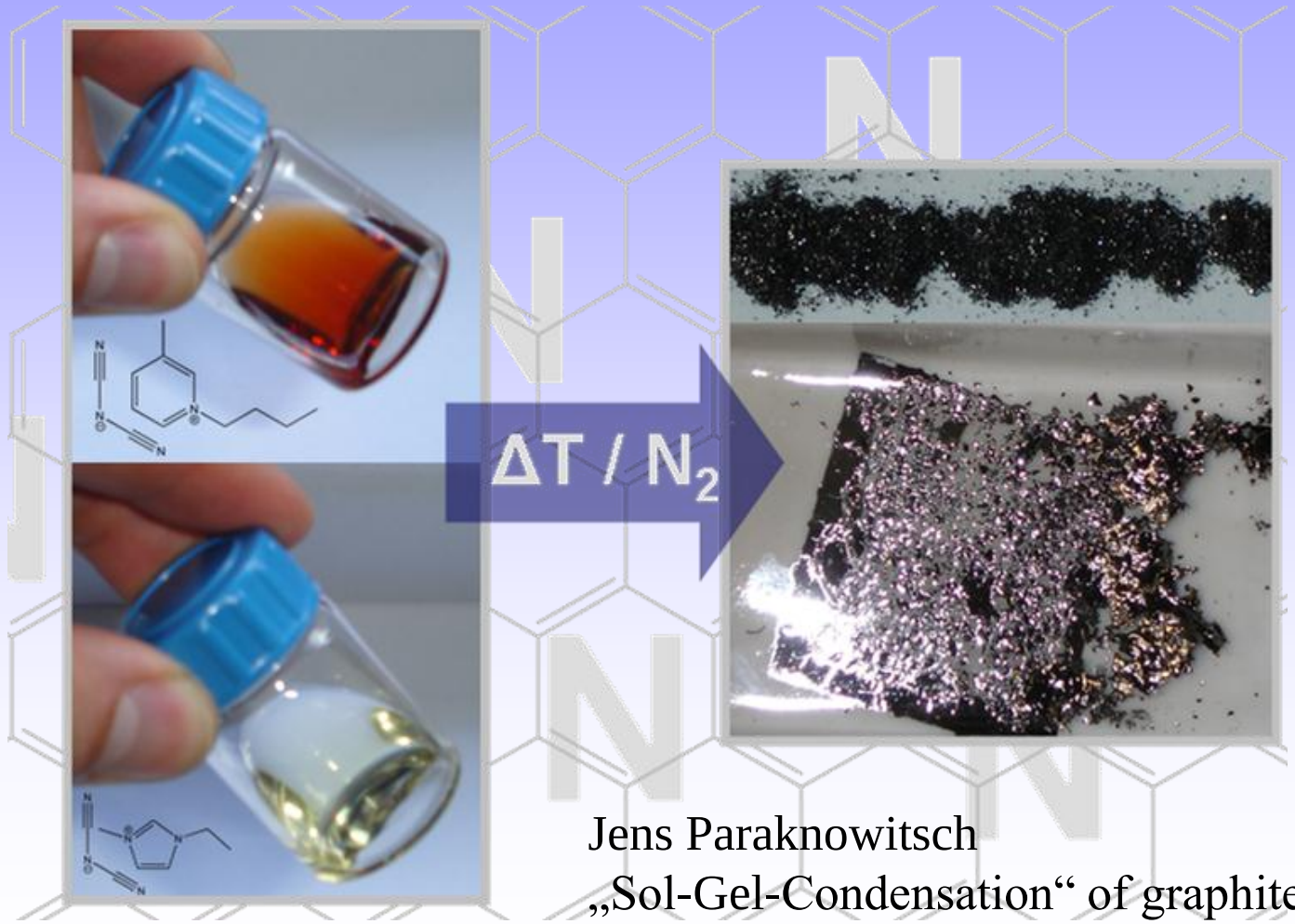
Hydrogen Productivity: remarkably improved by copolymerization

	catalyst	surface area [m^2/g]	C/N molar ratio	band gap [eV]	H_2 evolution rate [mmol/h]	
					λ>300 nm	λ>420 nm
1	g-C_3N_4	10	0.73	2.67	148.2	6.5
2	$CNB_{0.05}$	22	0.74	2.57	253.1	29.4
3	$CNB_{0.1}$	19	0.75	2.45	218.8	16.4
4	$CNB_{0.2}$	14	0.76	2.26	175.7	12.7
5	$CNB_{0.5}$	12	0.80	1.86	115.3	8.9
6	$CNB_{1.0}$	11	0.88	1.68	53.9	5.1
7	$CNB_{2.0}$	12	0.96	1.58	8.5	1.6

The artificial tree…

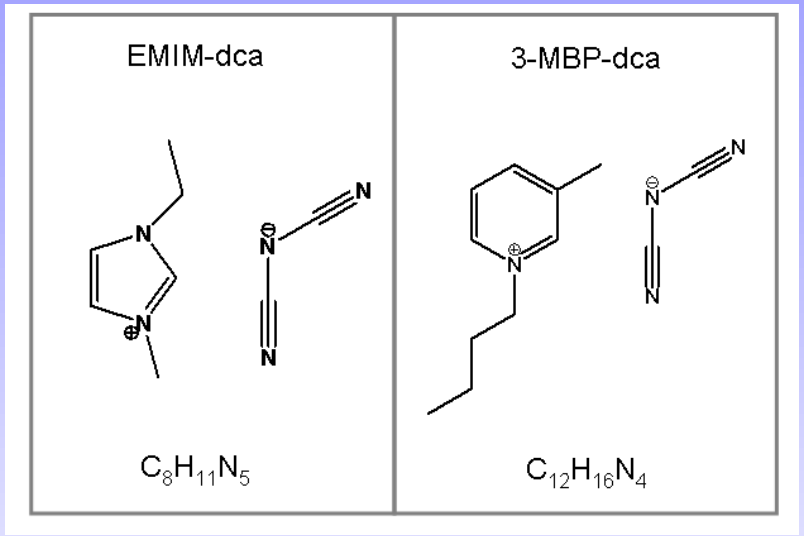

solar cells surface
unit
400cm
300cm
20cm

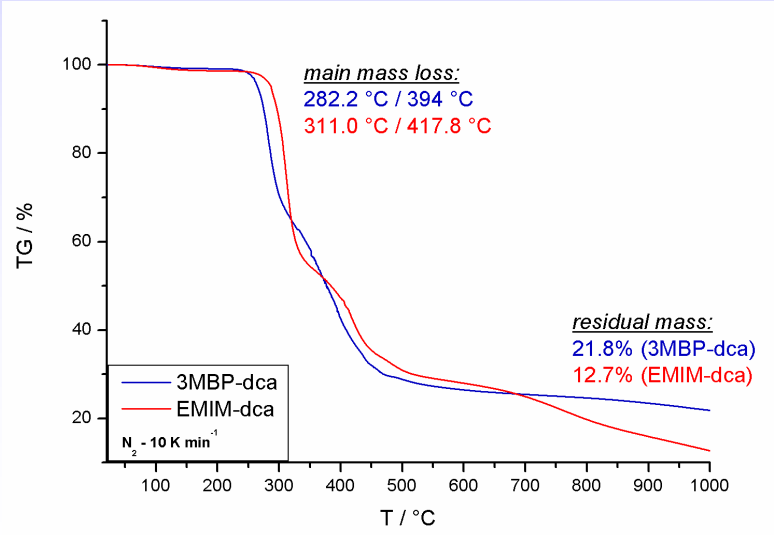
Version 2: „Noble“ Carbons / N-doped Carbon

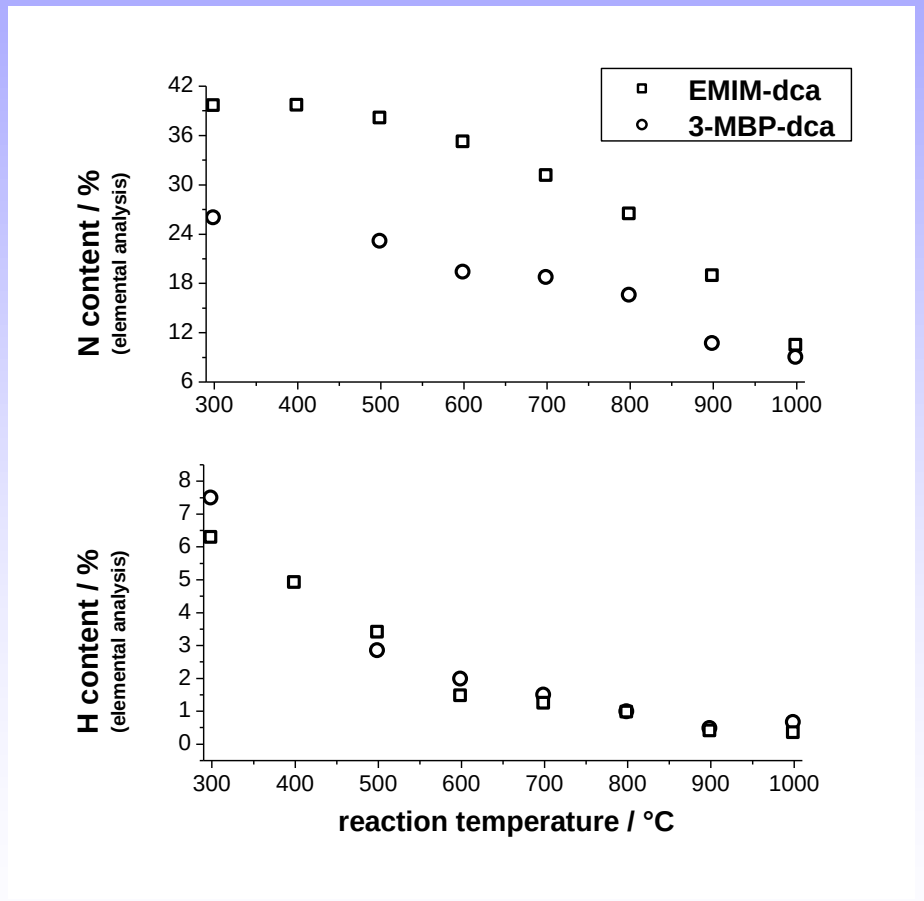


Jens Paraknowitsch
„Sol-Gel-Condensation“ of graphite

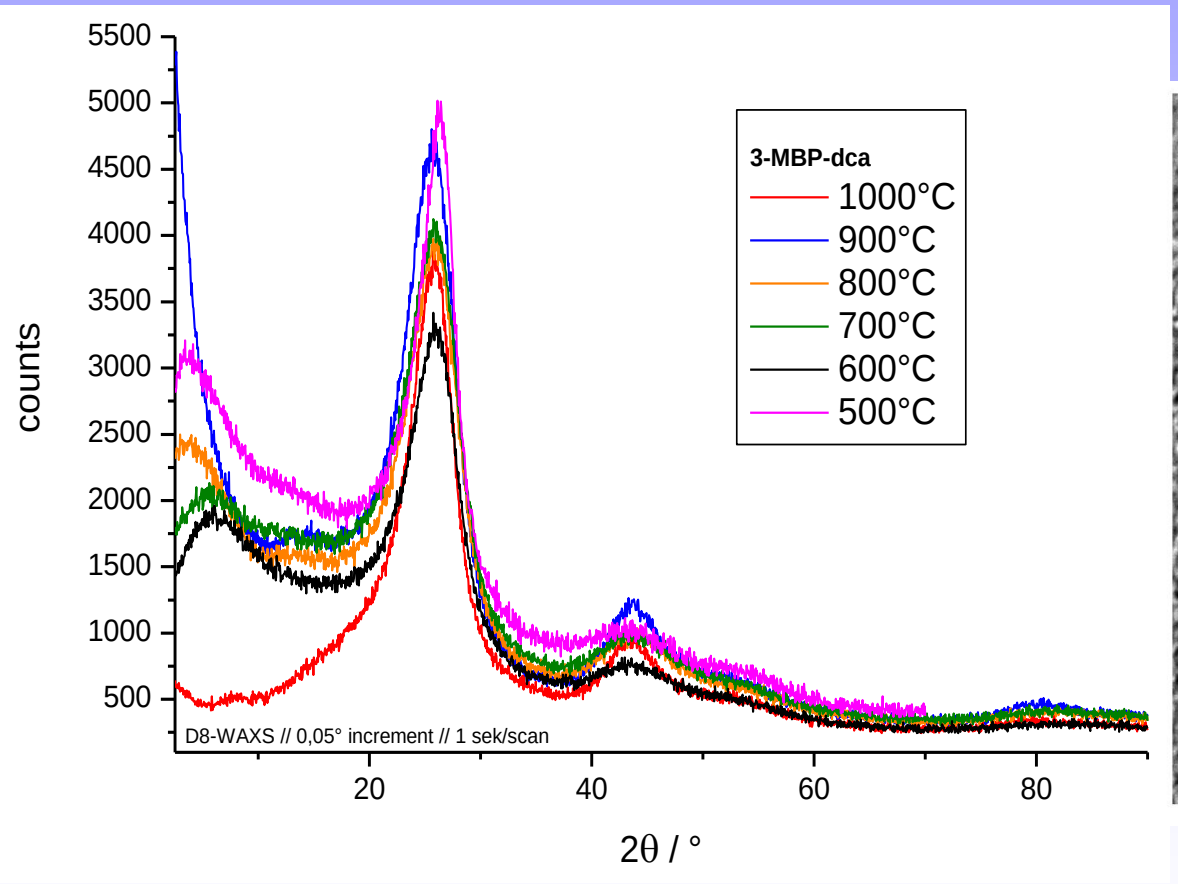
Ionic Liquids as „Sol-Gel“ Precursors for N-containing Graphitic Materials

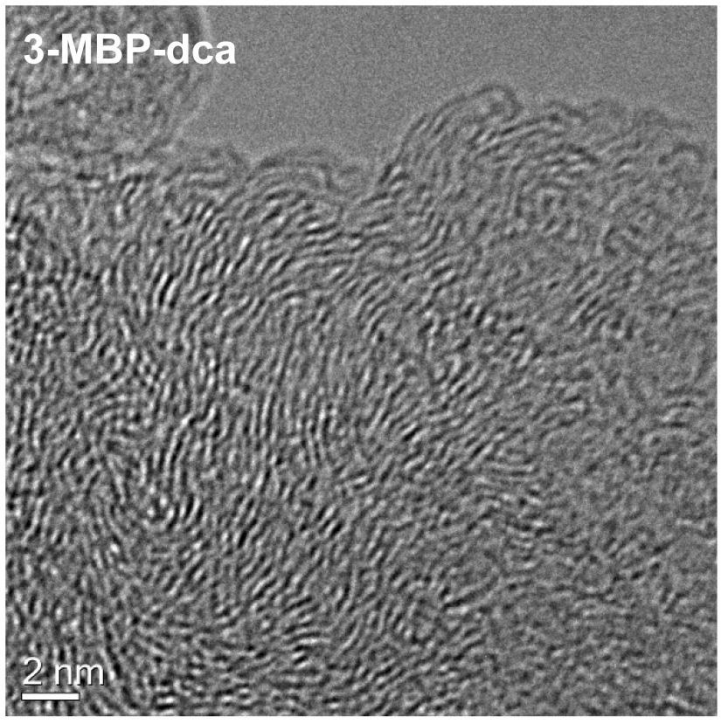




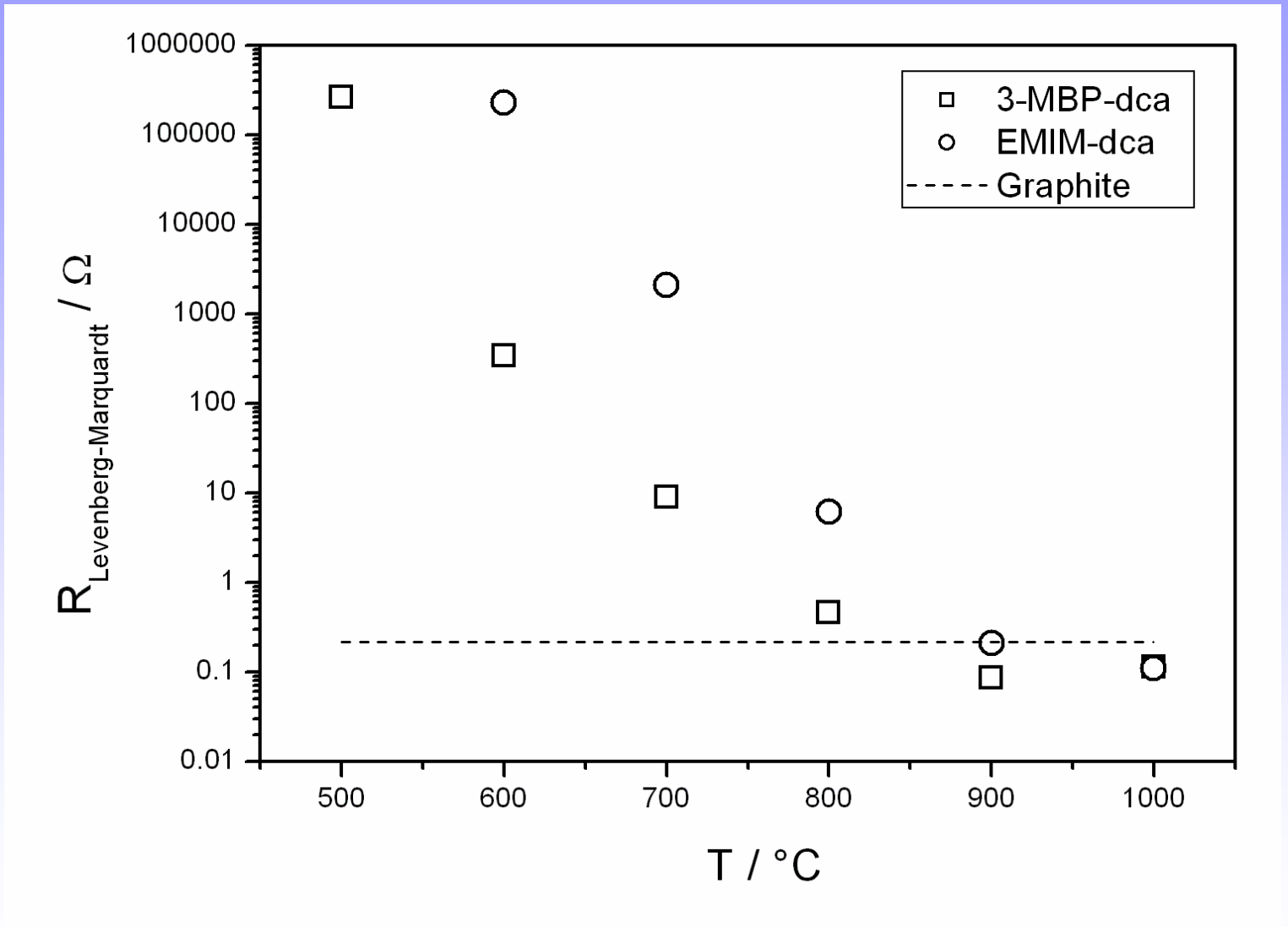


Structure of N-doped carbons „C_9N“





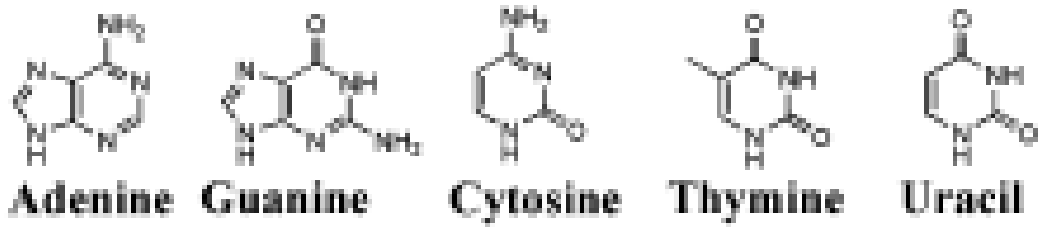
Surprise: the electric conductivity

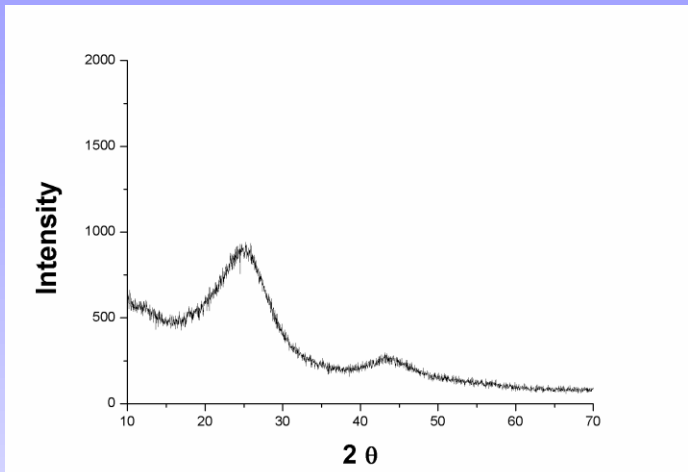


plus: the materials are noble !

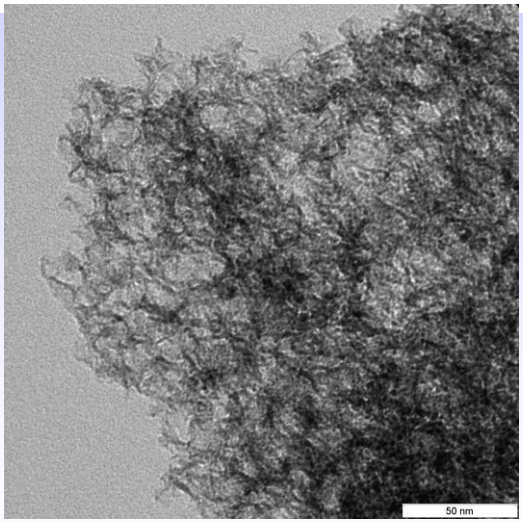
ORR: “Metal Free” O_2-Activation by Ordered Porous carbon materials

Highly conductive, highly noble, basic:
an electrocatalyst !



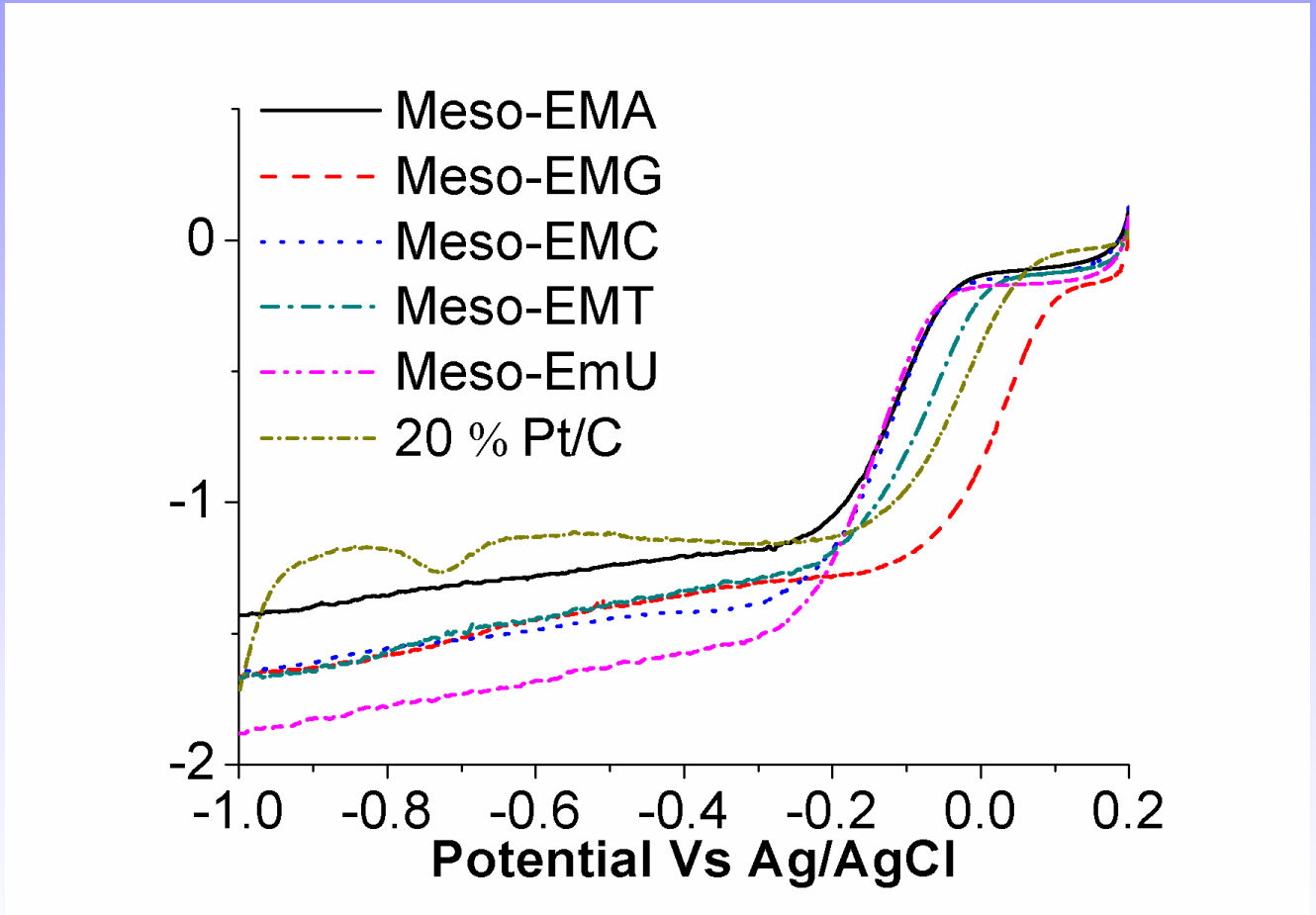


Hybridisation with nucleobases
dissolve in ILs
Increase of N-conent to 15 wt%



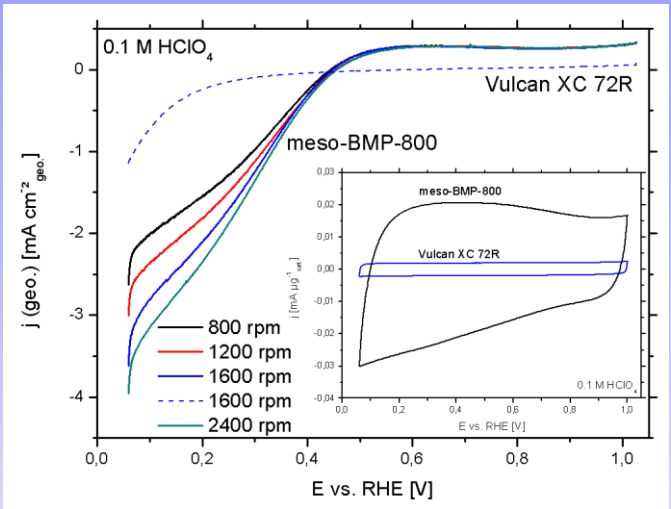
all data: Dr. Wen Yang, Tim Fellinger, Nina Fechtler
JACS 2011

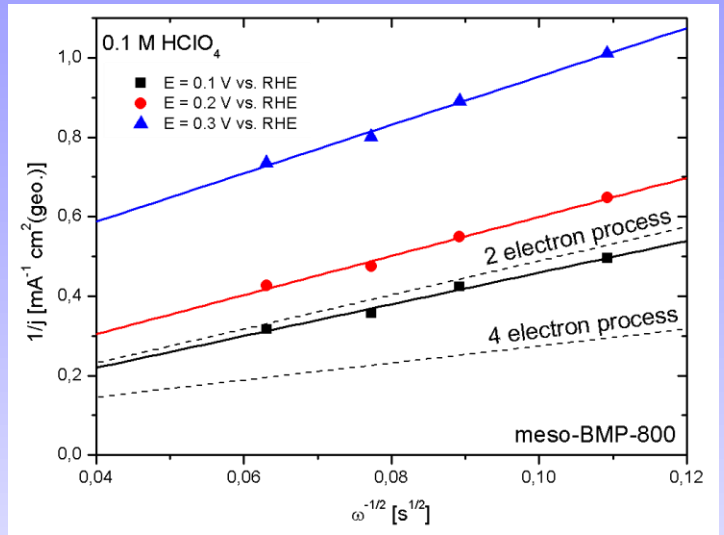
Electrochemistry- ORR

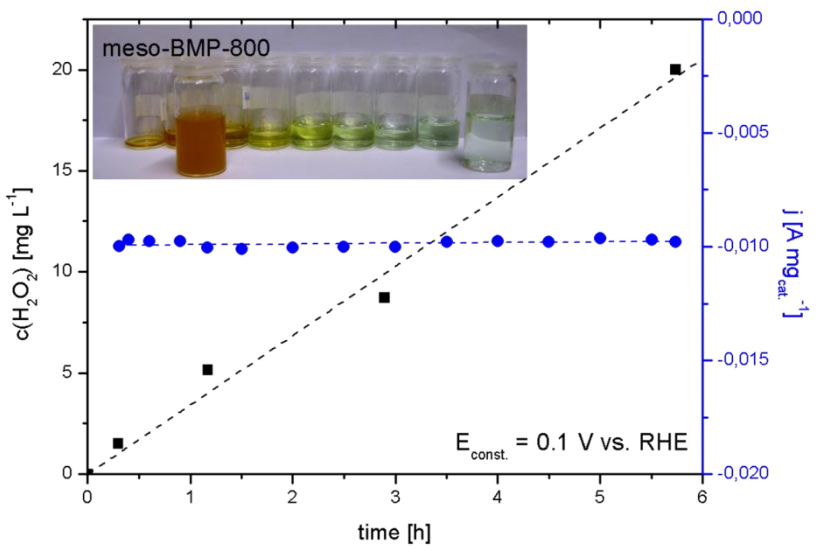


Rotating-disk voltammograms recorded for Meso-Em/nuclebase and 20 wt % Pt-C in O2-saturated 0.1 M KOH.

Electrochemical Synthesis of H2O2





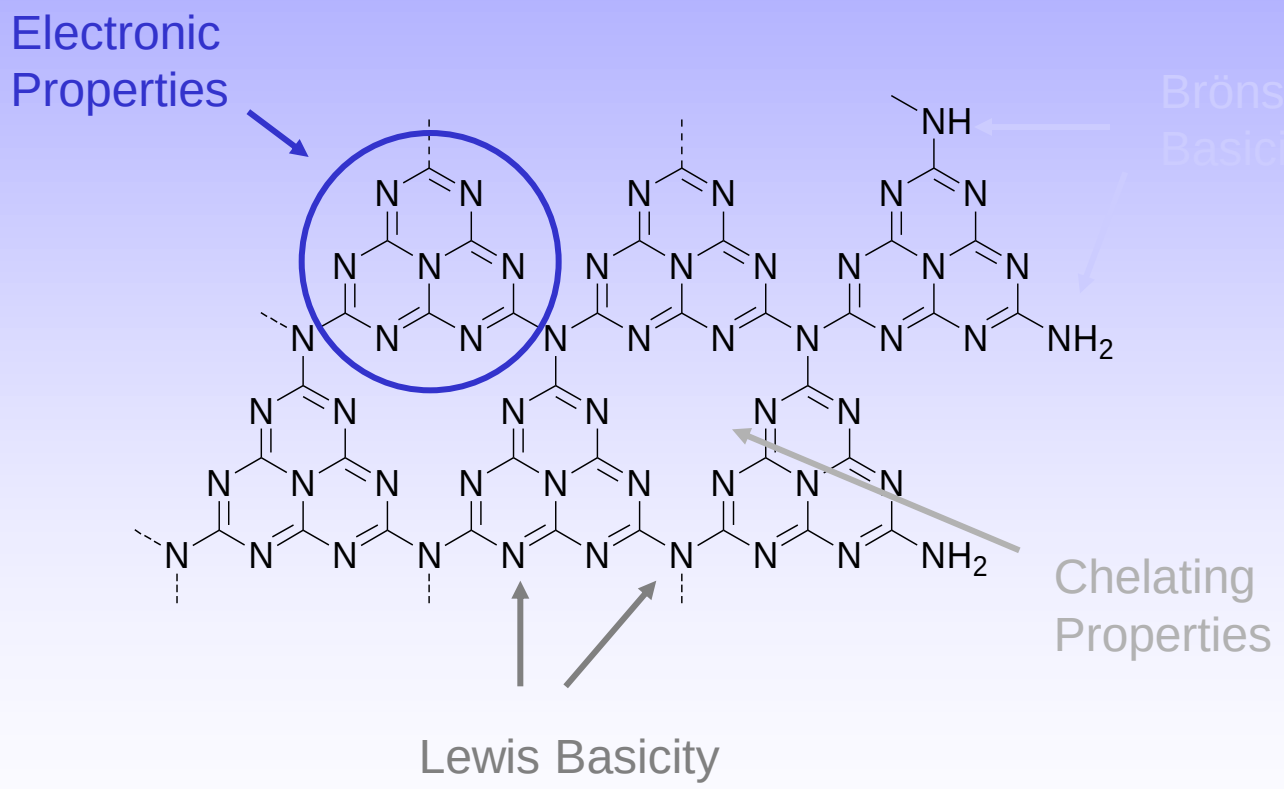


Price: 2.4 cents kg^{-1} H_2O_2

at 10 cents per kWh^{-1} !

With Tim Fellinger, Peter Strasser, Frédéric Hasché

Now: Catalytic application of mesoporous g-C_3N_4.



Catalytic features of mpg-C_3N_4

Oxidation catalysts by Copolymerization with B

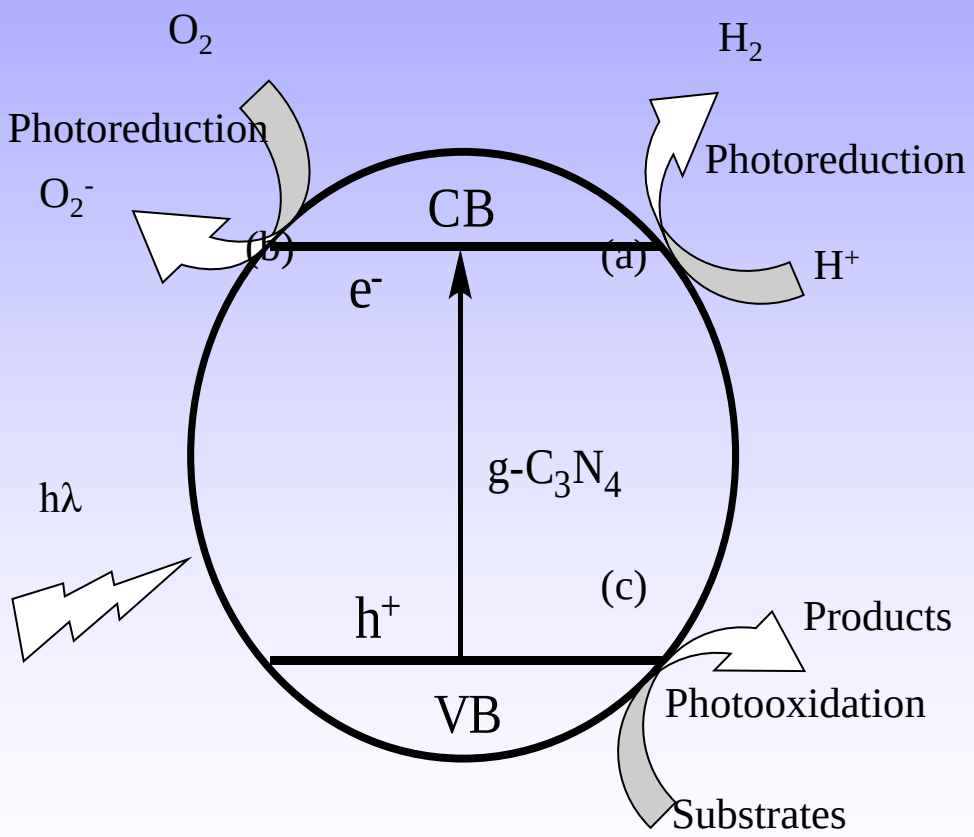
Table 1. Conversion and selectivity of cyclohexane oxidation over CNBF catalysts.[a]

Catalyst	Total conv. [%]	Selectivity [%] one	one/ol[b]	Selectivity (%) H_2O_2
CNBF-0.3	7.8	91	10.1	43
CNBF-0.5	7.5	89	8.4	33
CNBF-1.0	5.3	100	-	36

[a] Reaction conditions: cyclohexane 0.8ml, H_2O_2 (30% in water solution) 0.51ml, catalyst 50mg, temperature 150°C, time 4h. [b]cyclohexanone = one, cyclohexanol = ol.

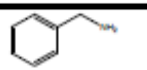
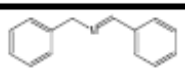
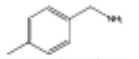
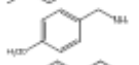
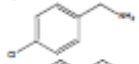
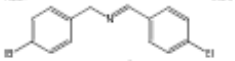
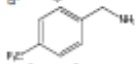
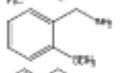
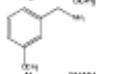
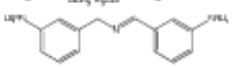
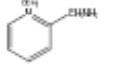
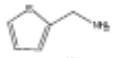
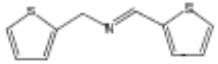
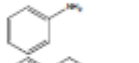
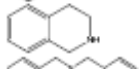
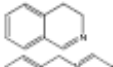
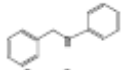
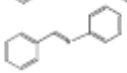
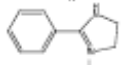
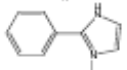
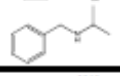
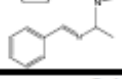
A „real“ cytochrome P450 reaction, but … without Fe !

Back to photochemistry, but …without H_2O !



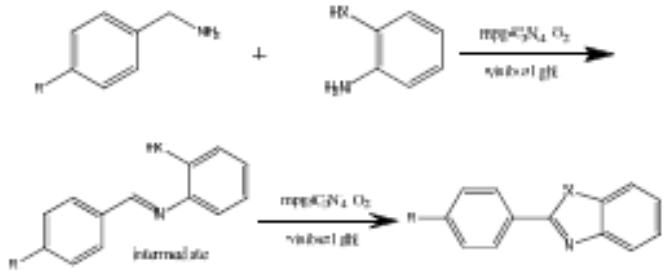
Oxidative Photo-dehydrogenation of Amines:

Table 2. Oxidation of various amines with mpg-C_3N_4

	Substrate	Product	t [h]	Con [%]	Sel [%]
1–4			3.5	>99	99
5			2.5	95	98
6			2	95	98
7			4	91	90
8			5	95	96
9			2	69	99
10			2	72	99
11			1	95	96
12			2	>99	98
13			2	<1	-
14			2	>99	91
15			2	70	80
16			3	46	92
17[a]			4.5	90	91
18			5	46	98
19			4.5	88	97
20			3	82	87

Reaction condition: 50mg mpg-C_3N_4, 1 mmol substrate, 10ml CH_3CN, 80 °C, 0.5 MPa O_2; [a] 0.6 mmol substrate, 100 °C

Table 3. Aerobic oxidative coupling synthesis of benzoxazoles, benzimidazoles and benzothiazoles



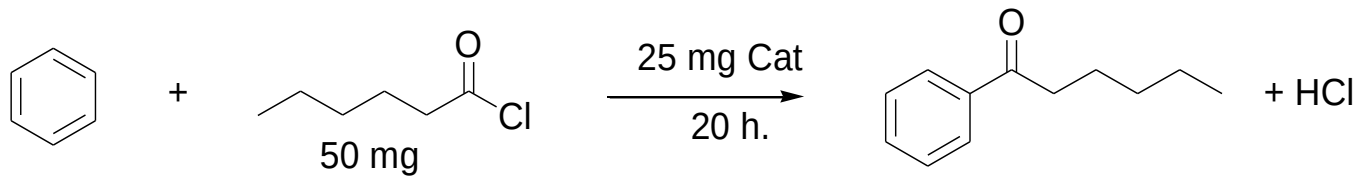
R	X	t (h)	Con. (%)	Sel. (%)
CH_3	O	5	>99	69
H	O	5	>99	75[a]
H	O	5	>99[b]	24[c]
Cl	O	5	70	74
CH_3	NCH_3	4	97	92
H	NCH_3	5	99	98
Cl	NCH_3	5.5	98	91
OCH_3	S	4	96	97
H	S	5	91	92
Cl	S	5.5	97	93

Reaction conditions: 50 mg mpg-C_3N_4, 1 mmol substituted benzylamine, 3 mmol 2-aminophenol (2-aminothiophenol, *o*-phenylenediamine), 10ml CH_3CN, 100 °C, 0.5 MPa O_2. [a] aldehyde. [b]: 80 °C. [c] 2-hydroxy-bezoimine

with Siegfried Blechert /TU Berlin

Catalytic application of mesoporous g-C_3N_4.

Friedel-Crafts acylation using acyl chlorides:

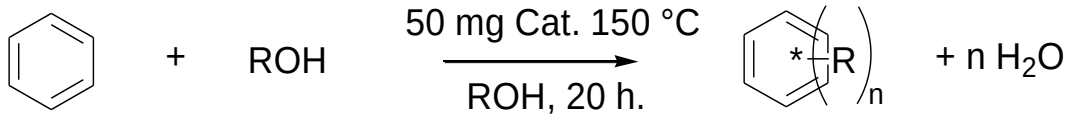


Solvent	Benzene	Heptane	Anisole
Temperature (° C)	80	90	150
Conversion rate (%)	16	80	60

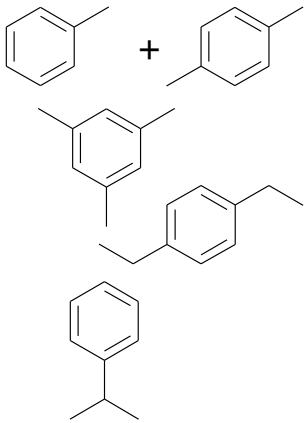
F. Goettmann, A. Fischer, M. Antonietti, A. Thomas *Angew. Chem. Int. Ed.* **2006,** *45*, 4467

Catalytic application of mesoporous g-C_3N_4.

Alkylations using less reactive electrophiles: Alkohols



Electrophile	Conversion rate (%)	Products
Methanol*	10	Toluene (20 %) p-Xylene (80 %)
Methanol	20	Mesitylene (100 %)
Ethanol	18	p-Diethylbenzene (100 %)
Isopropanol	13	Cumene (100 %)

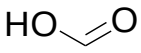
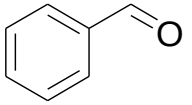
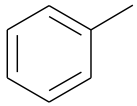
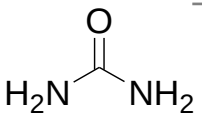
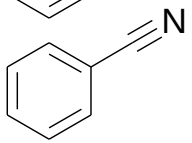


* Reaction in benzene

F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, *Chem. Commun.* **2006**

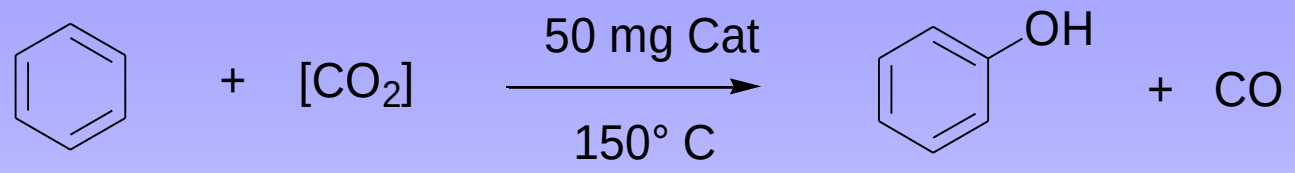
Catalytic application of mesoporous g-C_3N_4.

Unusual reactions (because of tolerance of functionalities:

	Electrophile	Conversion rate (%)	Products	
	Formic acid	100	Benzaldehyde (100 %)	
	Tetramethylammonium bromide	100	Toluene (100 %)	
	Urea	20	Benzonitrile (100 %)	

All reactions were carried out in benzene at 150°C for 20 h.

Kohlendioxid als Reaktionspartner

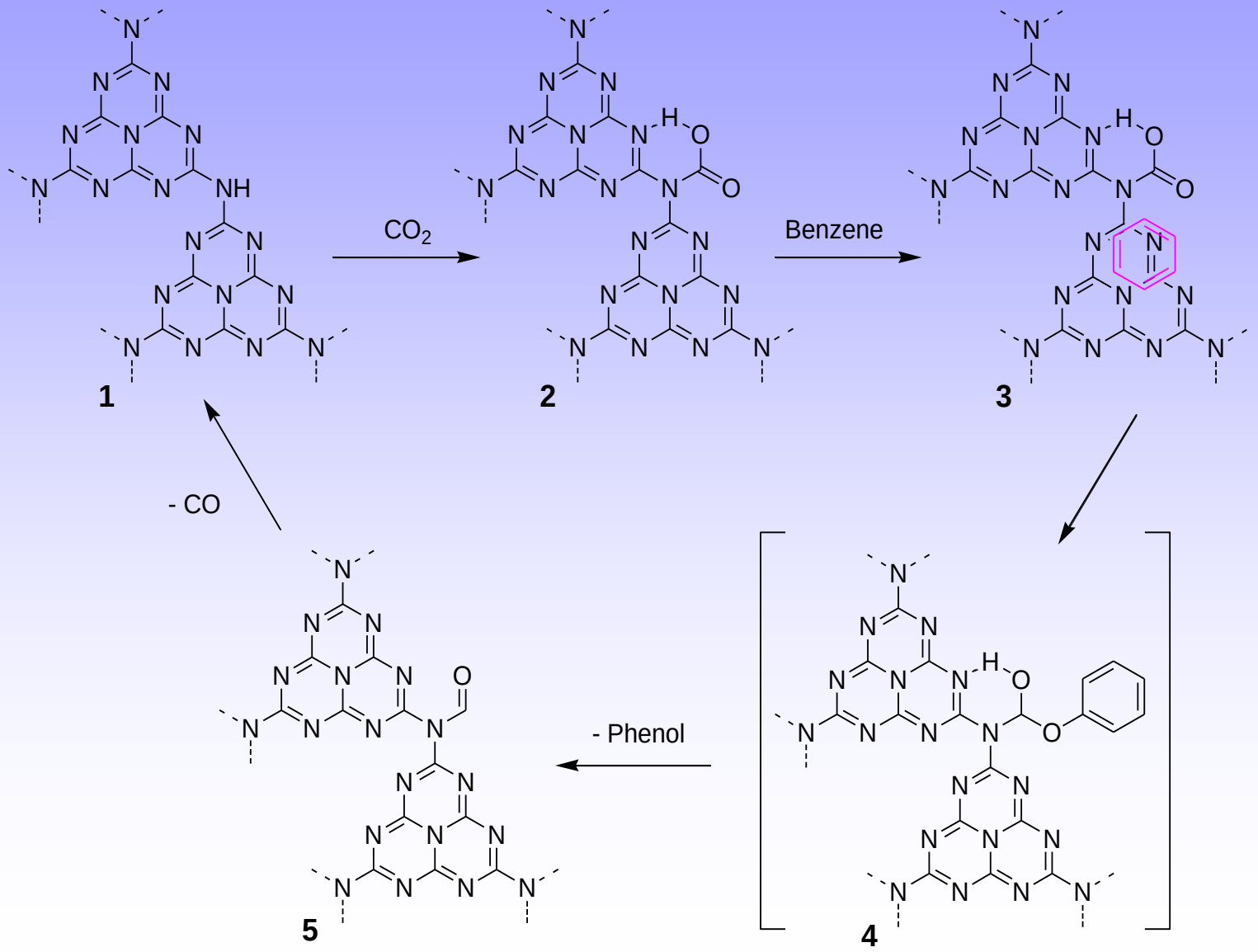


CO_2 Quelle	Lösemittel	Base	Reaktionszeit (h)	Umsatz (%)
$NaHCO_3$ (400mg)	Heptane	/	20	100
CO_2 (10 bars)	Benzene	Triéthylamine	12	20*

* Sowie 30% Biphenyl als Folgeprodukt

Catalytic application of mesoporous g-C_3N_4.

Metal-free activation of CO_2: proposed mechanism

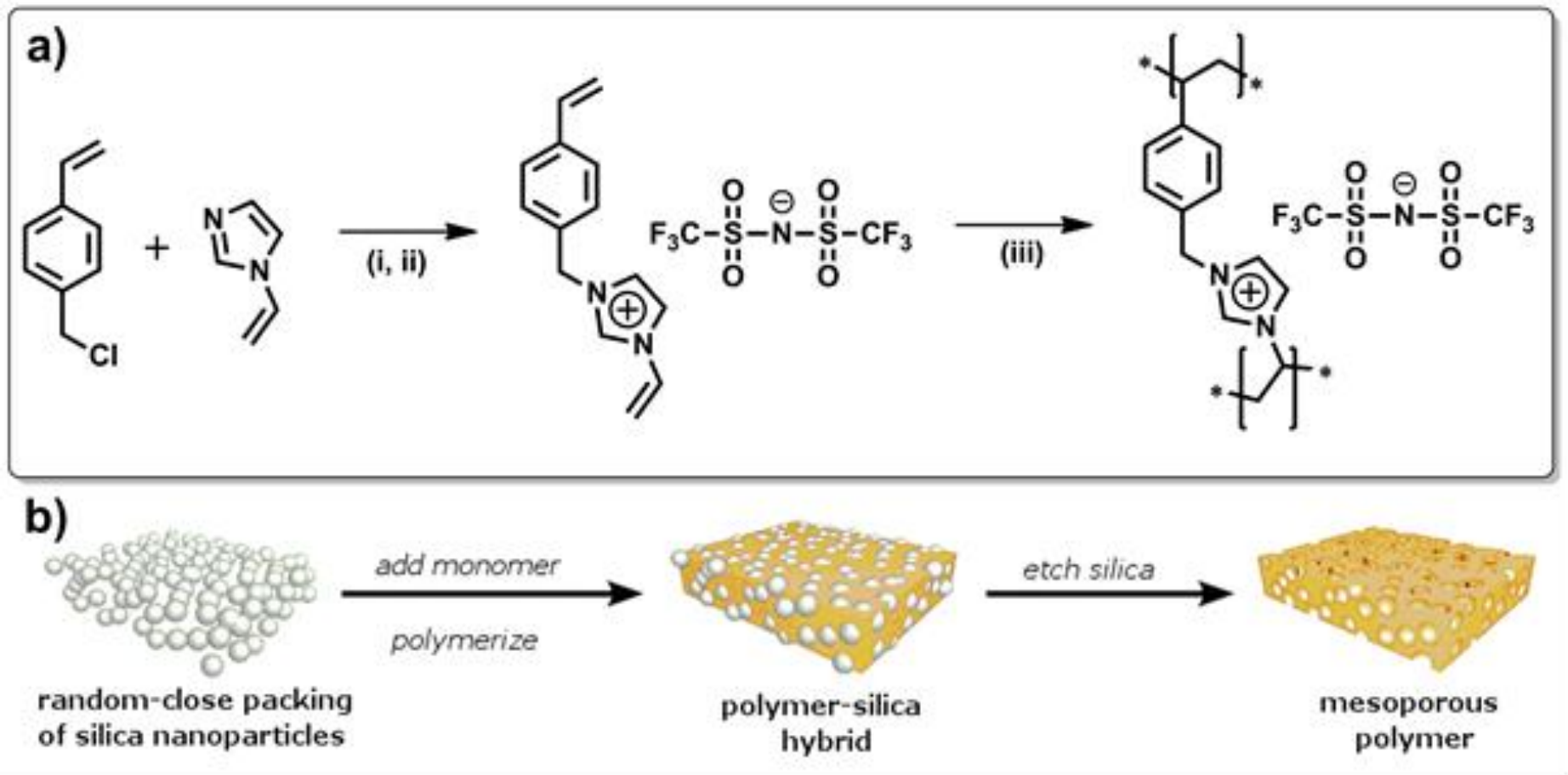


Catalytic application of mesoporous g-C_3N_4.

But:

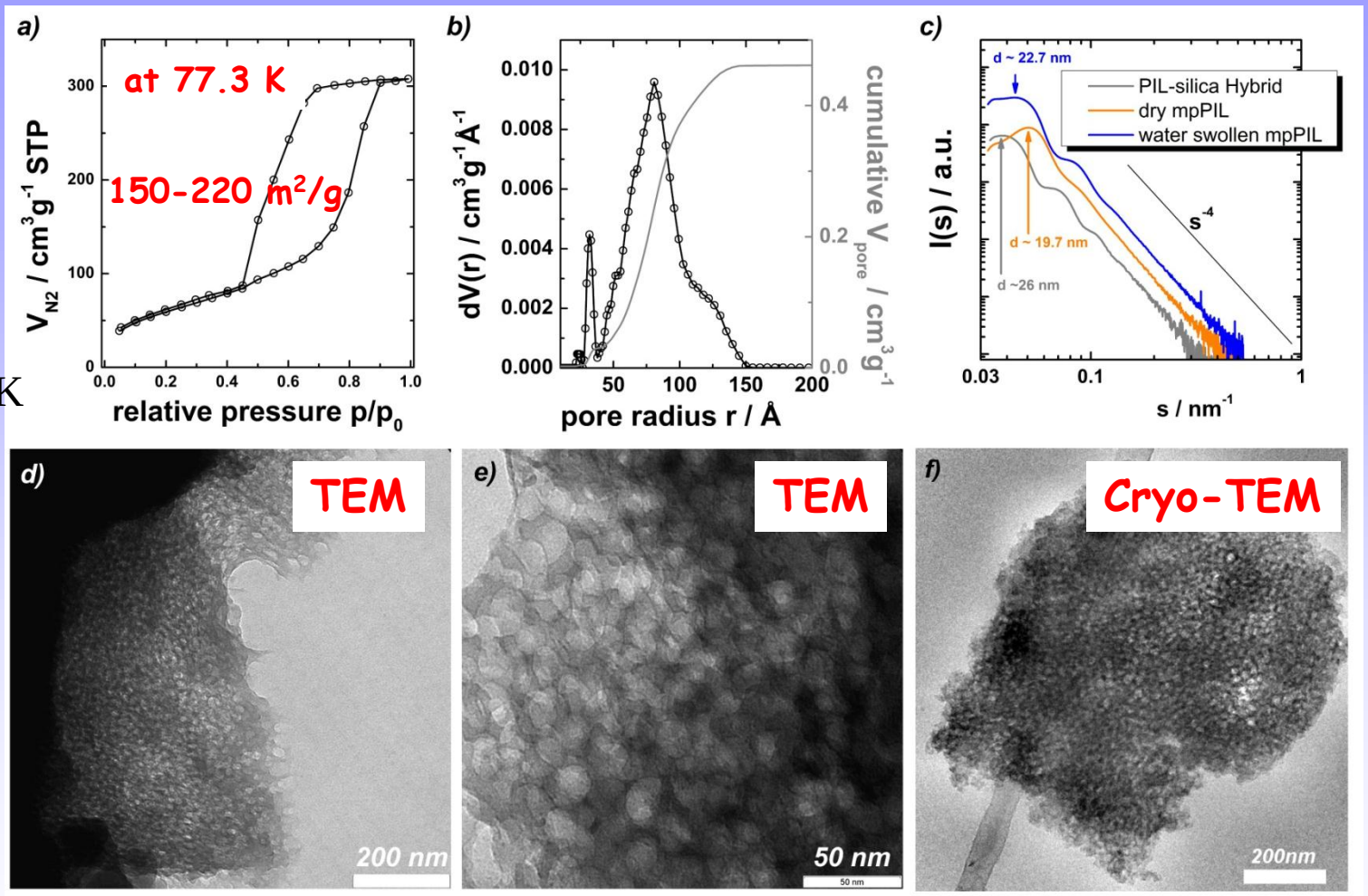
- **reaction rates very slow, low CO2 concentrations at reaction site**
- **All catalyst optimizations lead to more and more biphenyl, less phenol**
- **This in the very end is rather activated formamide decomposition**

Ordered mesoporous PILs



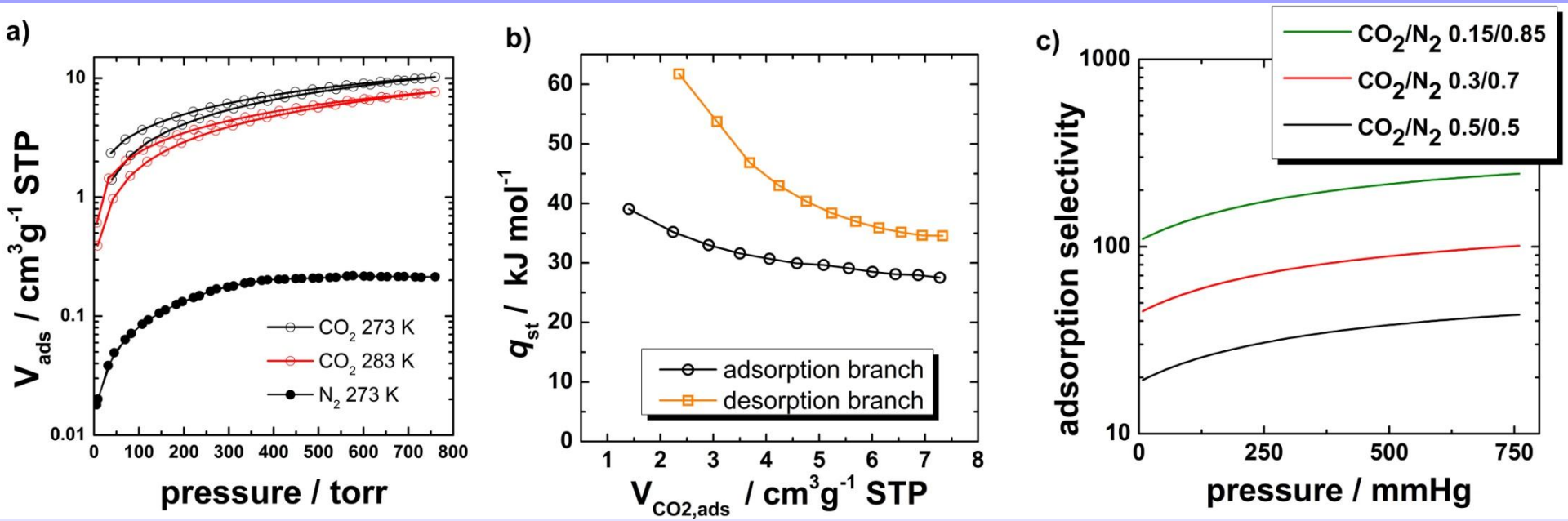
Mesopore structures

at 77.3 K



a) N_2 adsorption/desorption isotherm of mpPIL measured at 77.3 K; b) pore size distribution (black circles) and cumulative pore volume (grey line) of mp-PIL calculated by QSDFT methodology using a spherical pore model (adsorption branch); c) SAXS patterns of the PIL-silica hybrid (grey), the dry mp-PIL (orange) and water swollen mpPIL (blue); d) TEM micrograph of mpPIL, scale bar: 200 nm; e) TEM micrograph of mpPIL, scale bar: 50 nm; f) Cryo-TEM of mpPIL, scale bar: 200 nm, image obtained after background subtraction

High CO_2/N_2 selectivity



a) CO_2 (open circles) and N_2 (closed circles) adsorption/desorption isotherms measured at 273K and 283 K respectively; b) isosteric heats of sorption calculated from the adsorption branch (black circles) and desorption branch (orange circles) of the CO_2 isotherms obtained at 273 and 283 K; c) IAST prediction of the CO_2 over N_2 selectivity for different gas compositions.

ca 2 - 5% of the heat of formation !!!

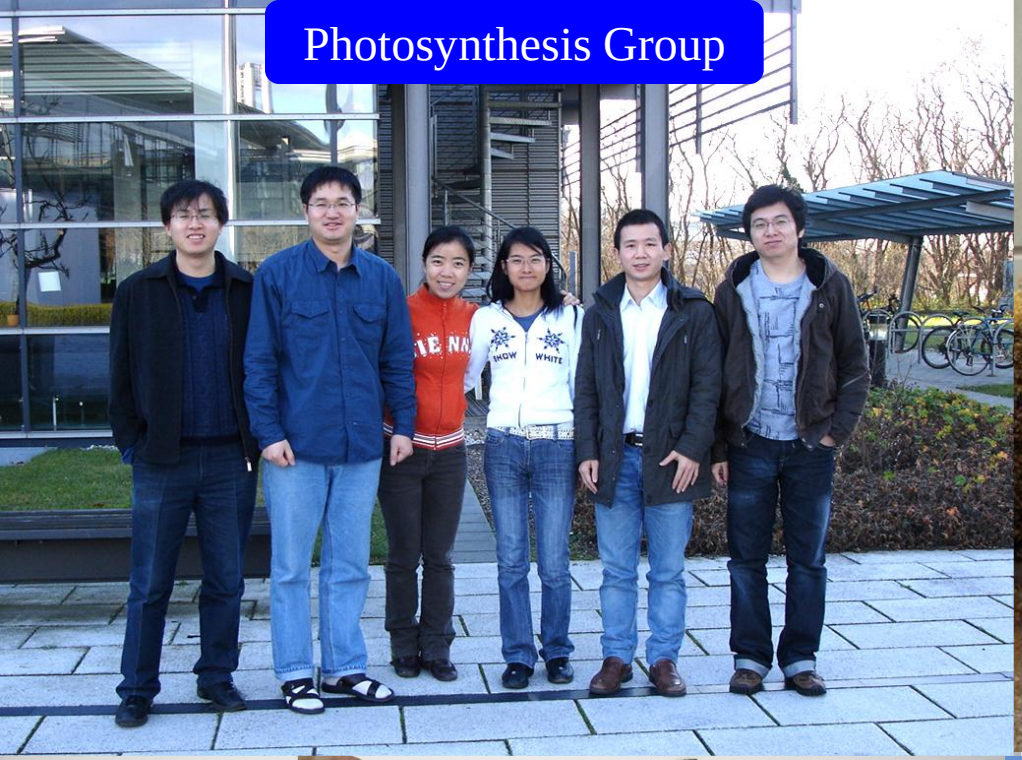
Next step: bind and convert !!

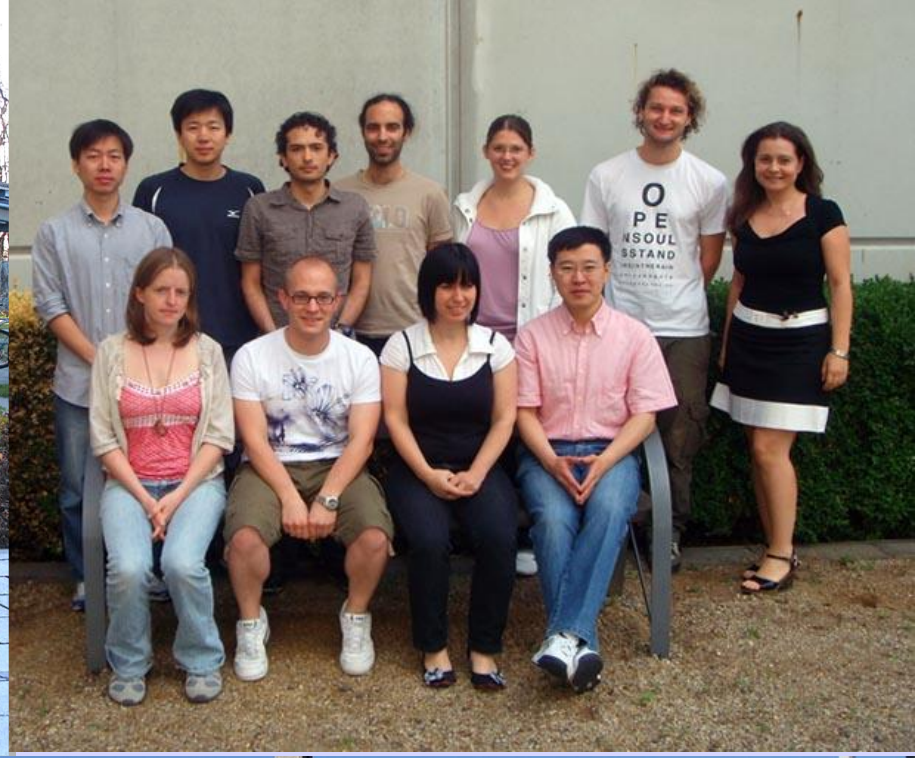
- CO_2 – reduction
- photochemistry
- electrochemistry….

Conclusion

- o going to biological phenomena/ events allows to identify interesting questions for polymer science → BMS
- o two-dimensional C/N polymers are active catalysts, even without metal
- o noble carbons, carbon catalysis: good perspective for electrochemistry, O_2, H_2O_2, CO_2
- o ionic liquids as monomers, PILS, and scaffolds: chemical binding of CO2, partial activation

Photosynthesis Group





“Die Bilanzierung von Energie und Entsorgung – eine unliebsame Meinung ”

Markus Antonietti
Max Planck Institute of Colloids and Interfaces
Research Campus Golm, D-14424 Potsdam

Das "CO_2-Problem" aus der Sicht des Chemiker

- Welt Öl Produktion 4 km^3
- jetziger Wert 1.7 Trillion US $ / 1.3 Billionen Euro
- Verbrennung von Öl erzeugt 15 GT CO_2 pro Jahr,
  insgesamt ca. 30 GT CO2 -- > Klimawandel
- 385 ppm + 2 ppm/Jahr
- in 2020: 20% der dann erzeugten Energie regenerativ
- Anstieg nicht gebremst, bestenfalls 2. Ableitung kleiner

→ Wir brauchen eine CO_2- Minderungstechnologie (nicht CCS)

→ Kosten ca. 130 Milliarden Euro

“CO_2-capture” Thermodynamik ?

$$\Delta G = \Delta H - RT \ln (c_1 / c_2)$$

c_1 = 0. 0105 % c_2 = 40% n RT ΔS = 6.1 x 10^{18} J !!

d.h. selbst bei idealer Fahrweise ca. 40% des Energieverbrauchs der BRD, nur für das Sammeln ??

Kosten: 169 Milliarden Euro bei 10 ct/KWh; eff = 1

5.6 Euro /Tonne CO_2

Lösung: natürliche Kreisläufe

Pflanzen: $\Delta G = \Delta H - RT \ln (c_1 / c_2)$

Welt-Biomasseproduktion" 60 GT Kohlenstoff /Jahr

$$n_{bio}\, RT\, \Delta S = \quad 45 \times 10^{18}\ J$$

$$\Delta H_{bio} = \ 200 \times 10^{18}\ J$$

davon 7 GT bereits "landwirtschaftliche Seitenprodukte"

1 Tonne pro Mensch

→ Biomasse niemals die Lösung der Energieprobleme,

wohl aber eine mögliche Lösung des CO2-Problems …

Chemisch-Technische Aufgabe:

„fixiere C aus Biomasse in eine biologisch nicht mehr abbaubare Form, erhalte P und N für den Kreislauf“

aus 7 GT C-Äquivalent landwirtschaftliche Reststoffe

1 Tonne pro Mensch

vorzugsweise hochgradig dezentral !

Biomasse- Verkohlung

www.biochar-international.org

www.enertech.com

Carbon Solutions
/Kleinmachnow

Hydrothermale Carbonisierung?

Eine Technik, pflanzliche Biomasse

- in Monomere
- in Polymere
- in Schwarzboden / Torf / Braunkohle / Kohlenstoffprodukte

  zu verwandeln
- alles in Wasser…
- Kohlenstoffeffizienz nahe 1

Friedrich Bergius beschrieb schon 1913 die Elementarschritte der HTC

HTC II

Läuft via durch Wasserabspaltung aus Kohlehydraten

- bei 180 °C – 200 °C
- für 1.5 – 16 h´s
- $C_6H_{12}O_6$ _ → $C_6H_6O_3 + 3\ H_2O$ → $C_6H_2O + 5\ H_2O$
- billig (70 € /t Bioabfall)
- Führt zu nützlichen Nanostrukturen
- Mit nützlicher Oberflächenchemie

Hydrothermale Carbonisierung : ein exothermer Prozess mit CE = 1

$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2$

3230 KJ/mol

40°C, 5 d

2720 kJ

$C_6H_{12}O_6 \longrightarrow 3\ CH_4 + 3\ CO_2$ 2680 kJ

40°C, 21 d

HTC

$C_6H_{12}O_6 \longrightarrow$ „C_6H_2O“ + $5\ H_2O$

200°C, 2 -12 h

ca. 2700-3000 kJ