Multifunktionale Elektrodenmaterialien von Hydrothermalem Kohlenstoff

AKK-Fachausschuss „Neue Kohlenstoff-Formen“

Selb, 6. November 2014

Sylvia Reiche

Outline

I. Background & Mission

II. Tuning Carbon by HTC-Process Parameters

III. Tuning Carbon by N-functionalization

MPI for Chemical Energy Conversion

Heterogeneous Reactions

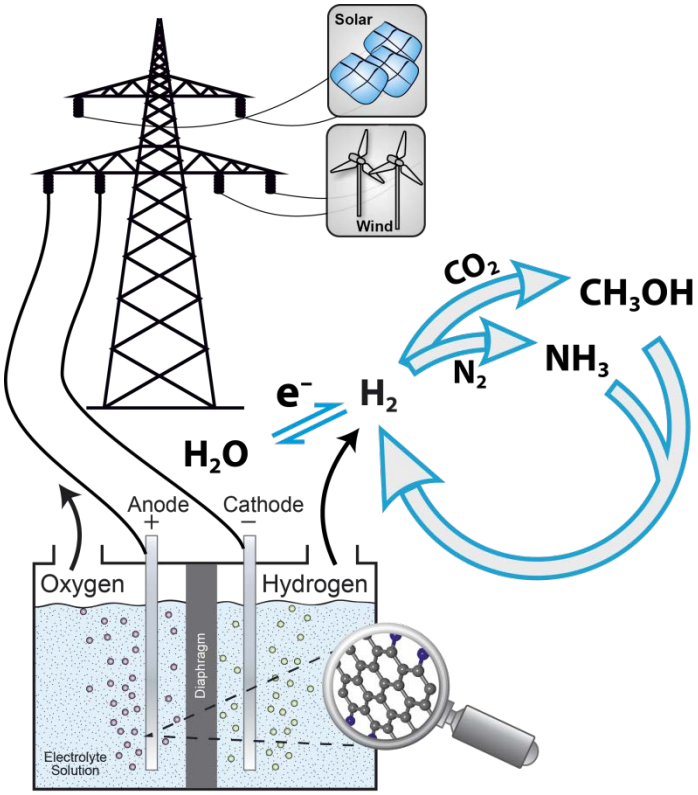
Prof. Dr. Robert Schlögl

Biophysical Chemistry

Prof. Dr. Dr. h. c. Wolfgang Lubitz

Molecular Theory and Spectroscopy

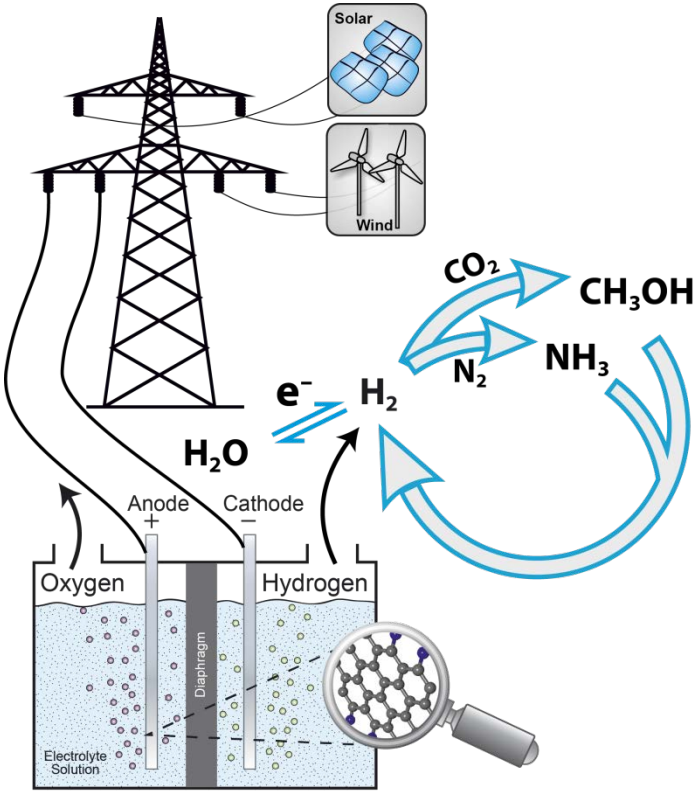
Prof. Dr. Frank Neese



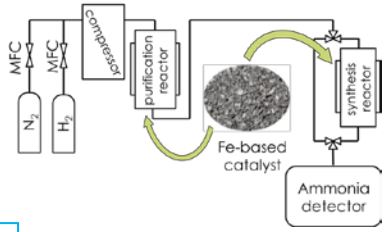
Department Heterogeneous Reactions

Heterogeneous Reactions

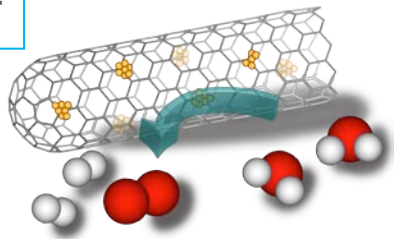
Prof. Dr. Robert Schlögl



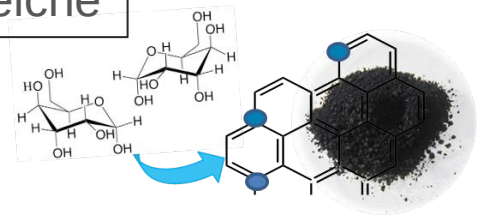
M. Bukhtiyarova



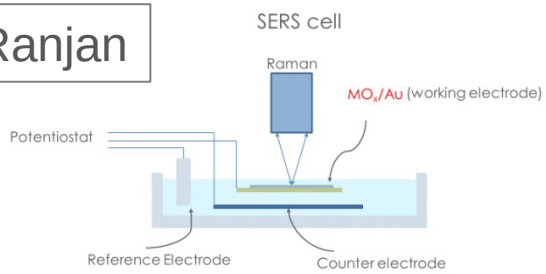
S. Buller



S. Reiche



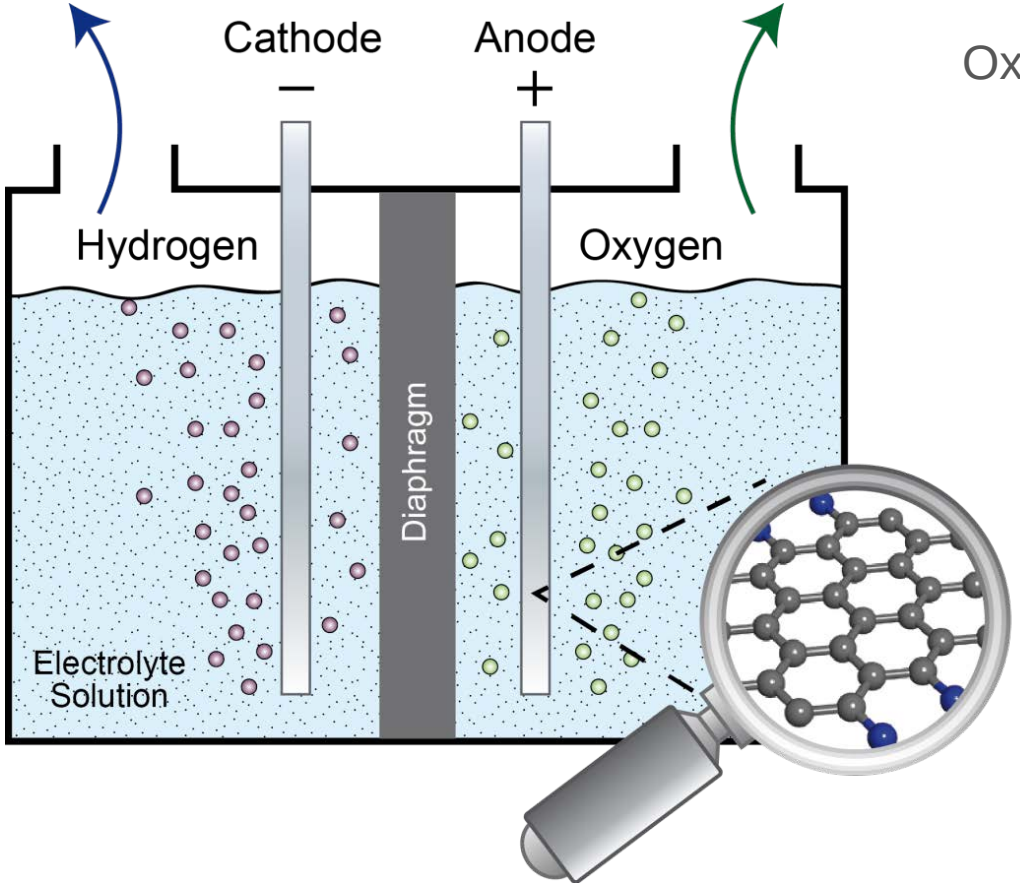
C. Ranjan



Electrode for water electrolysis

$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

Hydrogen Evolution Reaction (HER)



Oxygen Evolution Reaction (OER)

Electrode for water electrolysis

$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

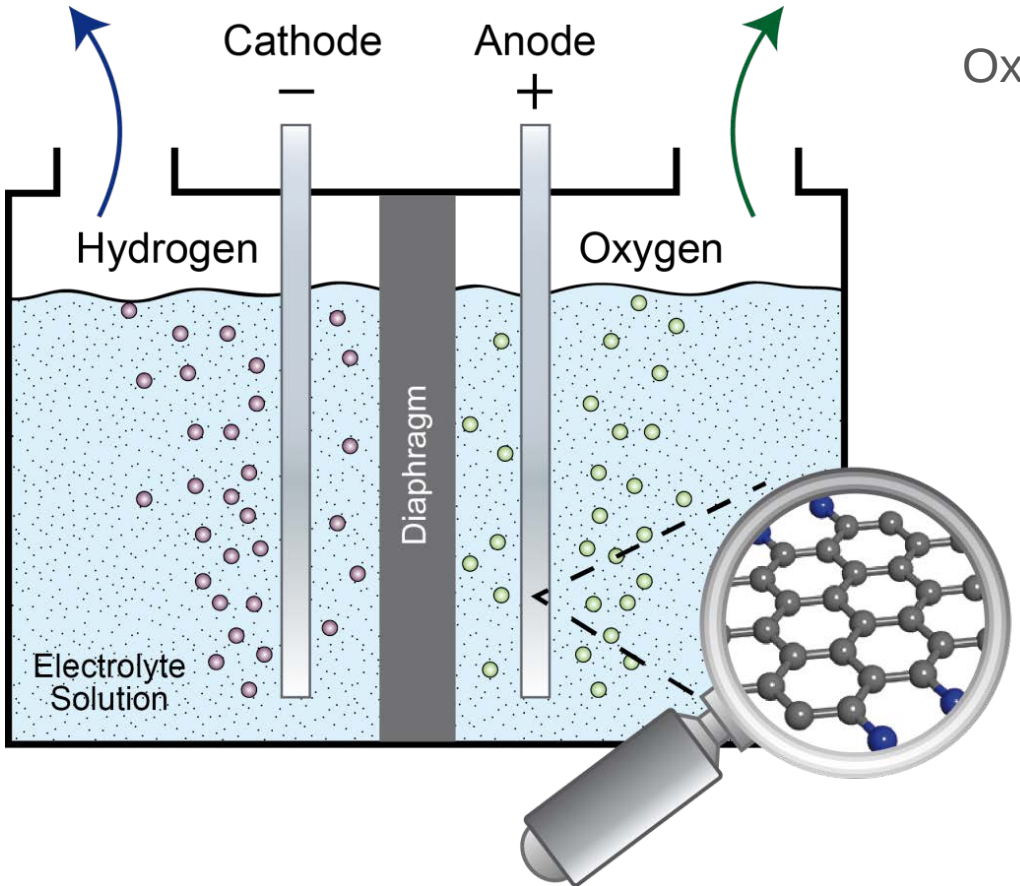
Acidic: $4\ H^+ + 4\ e^- \rightarrow 2\ H_2$

Basic: $4\ H_2O + 4\ e^- \rightarrow 2\ H_2 + 4\ OH^-$

Acidic: $2\ H_2O \rightarrow 4\ H^+ + O_2 + 4\ e^-$

Basic: $4\ OH^- \rightarrow O_2 + 2\ H_2O + 4\ e^-$

Hydrogen Evolution Reaction (HER)



Oxygen Evolution Reaction (OER)

Electrode for water electrolysis

$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

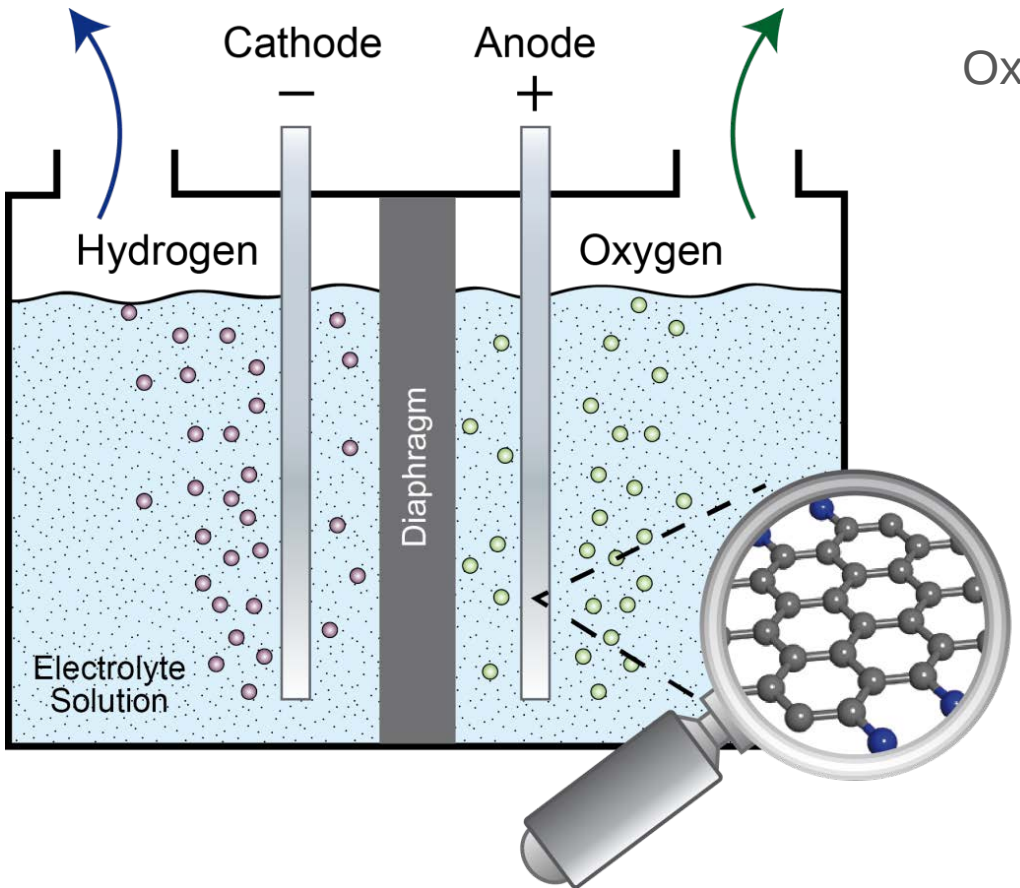
Acidic: $4\ H^+ + \mathbf{4\ e^-} \rightarrow 2\ H_2$

Basic: $4\ H_2O + \mathbf{4\ e^-} \rightarrow 2\ H_2 + 4\ OH^-$

Acidic: $2\ H_2O \rightarrow 4\ H^+ + O_2 + \mathbf{4\ e^-}$

Basic: $4\ OH^- \rightarrow O_2 + 2\ H_2O + \mathbf{4\ e^-}$

Hydrogen Evolution Reaction (HER)

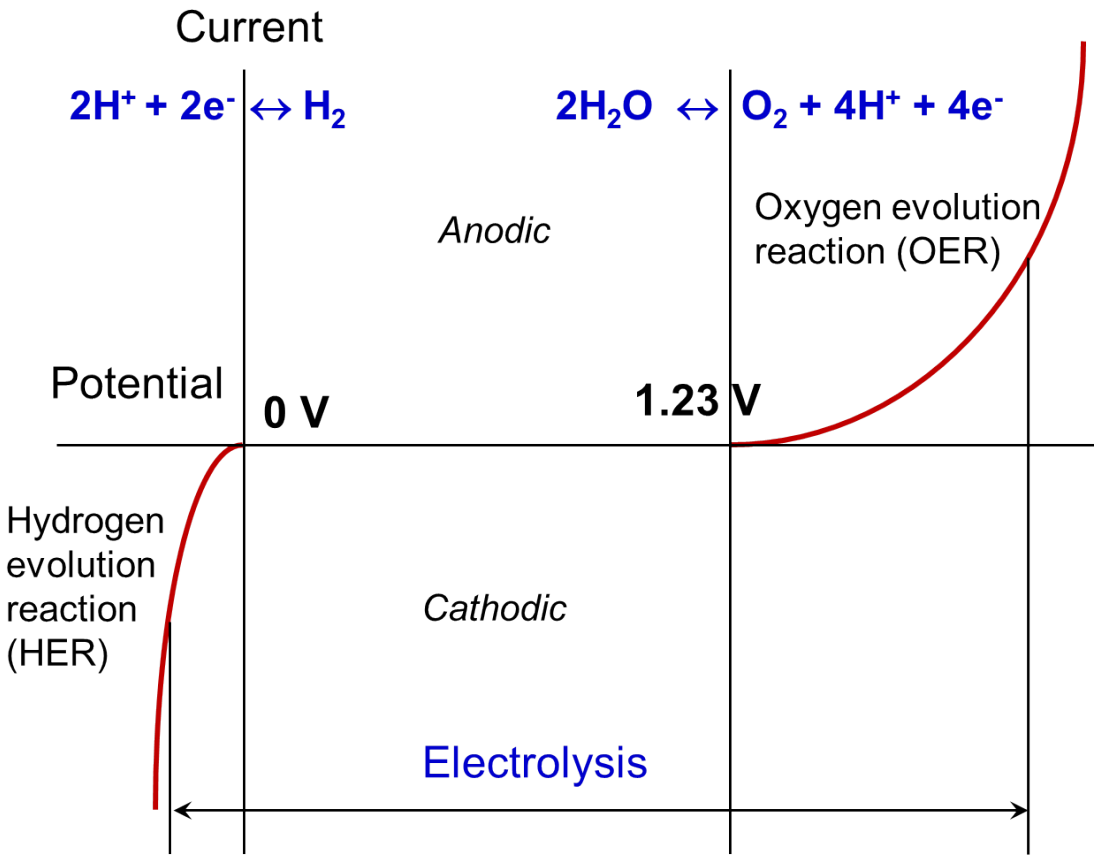


Oxygen Evolution Reaction (OER)

4 e⁻ transfer

Focus on OER because…

…most challenging



- 1.23 V above standard potentials of almost all the solid elements
- complex reaction pathways
- high activation energy
- high energetic intermediates

Electrode requirements

1. Conductivity

2. Performance

High number of sites for:

- H_2O adsorption
- H-O dissociation
- 4 e^- transfer
- O_2 desorption

3. Stability

1.23 V + η

high energetic intermediates

Traditional Catalysts for OER

1. Conductivity

2. Performance

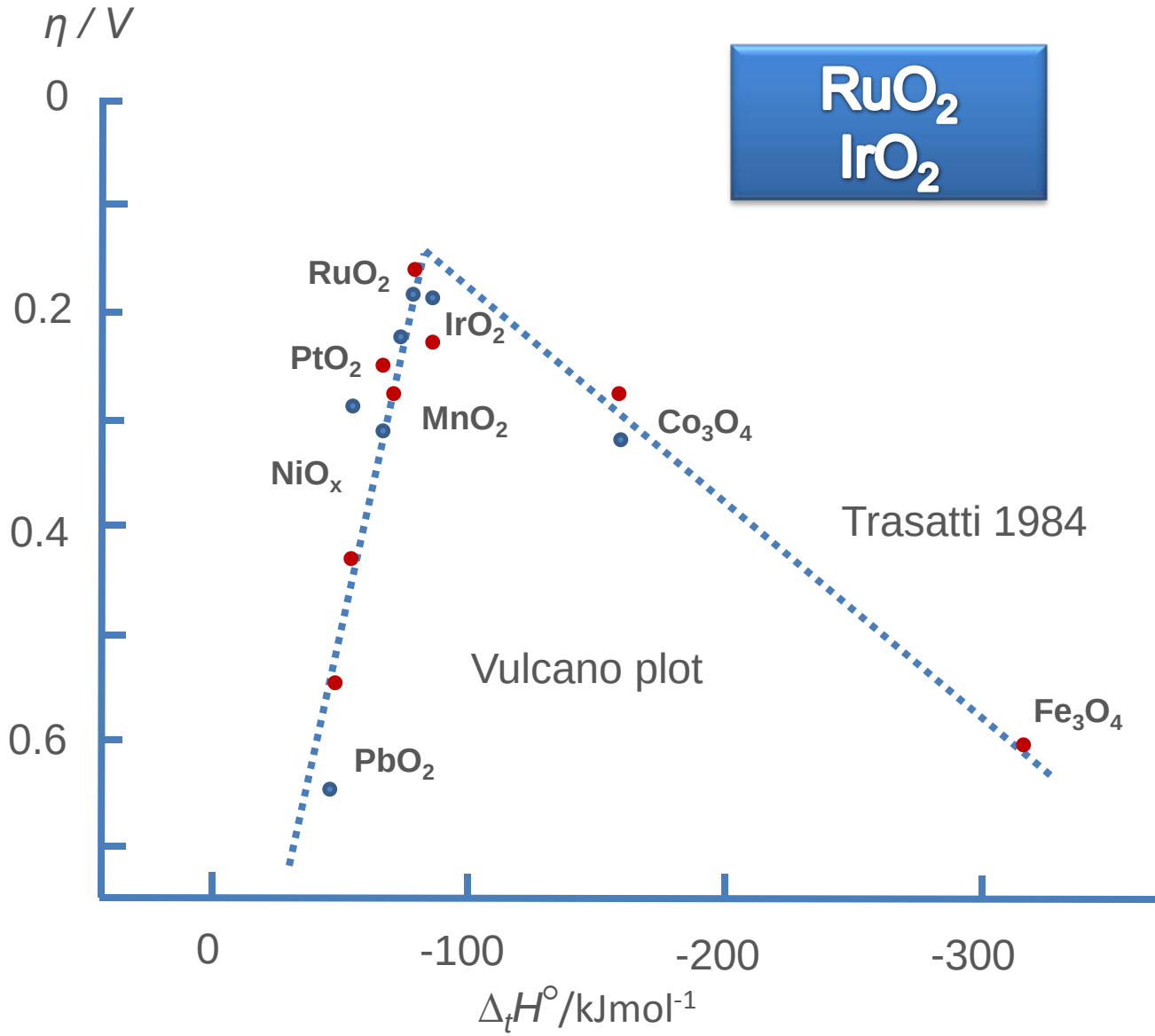
High number of sites for:

- ➢H_2O adsorption
- ➢H-O dissociation
- ➢4 e^- transfer
- ➢O_2 desorption

3. Stability

1.23 V + η

high energetic intermediates



RuO_2
IrO_2

Traditional Catalysts for OER

1. Conductivity

- ✓ **RuO_2: 2.0 x10^6 S/m**
- ✓ **IrO_2: 1.7 x 10^6 S/m**

2. Performance

High number of sites for:

- ✓ H_2O adsorption
- ✓ H-O dissociation
- ✓ 4 e^- transfer
- ✓ O_2 desorption

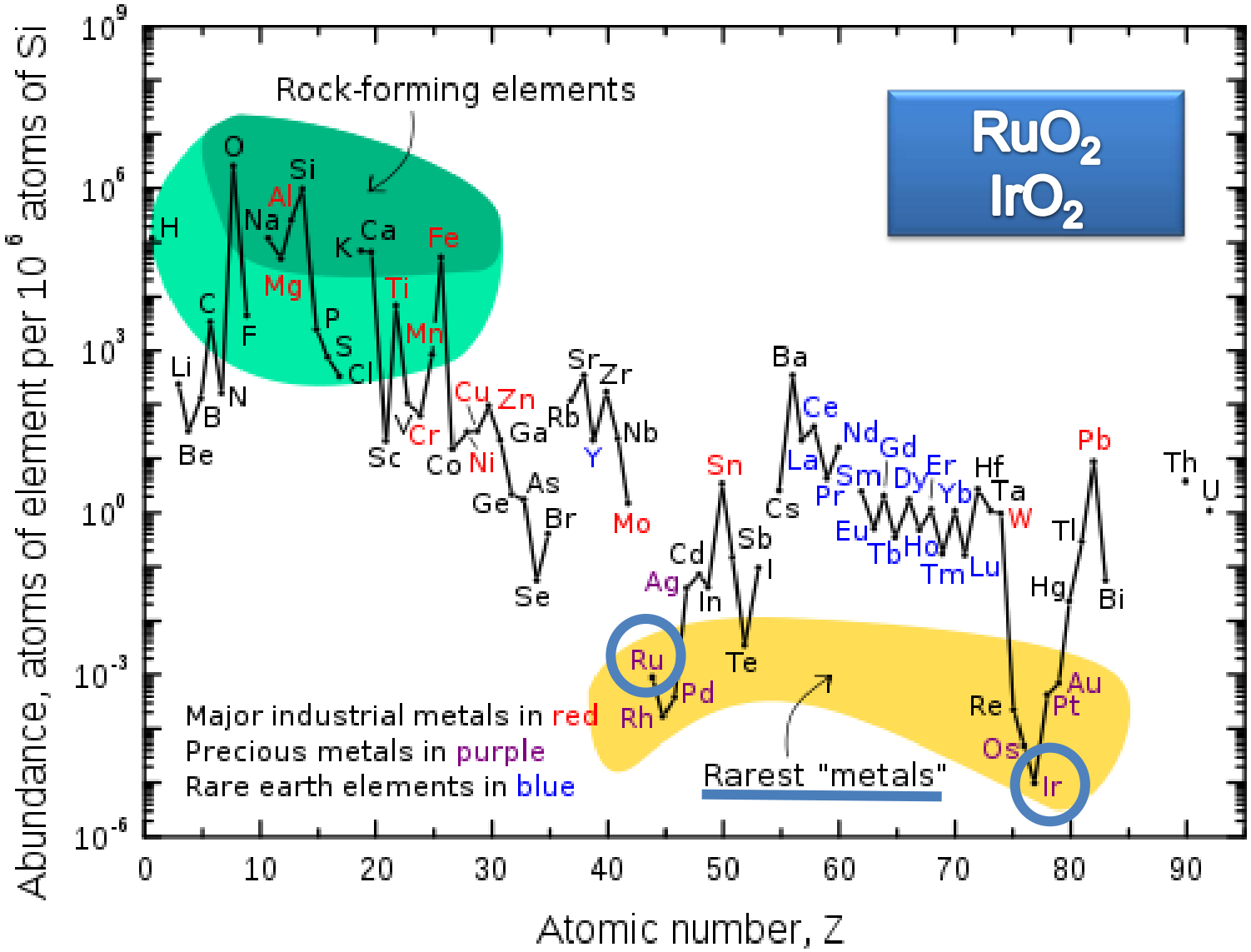
3. Stability

- ✓ 1.23 V + η

  high energetic intermediates

RuO_2
IrO_2

Traditional Catalysts for OER



Electrode requirements

1. Conductivity

2. Performance

3. Stability

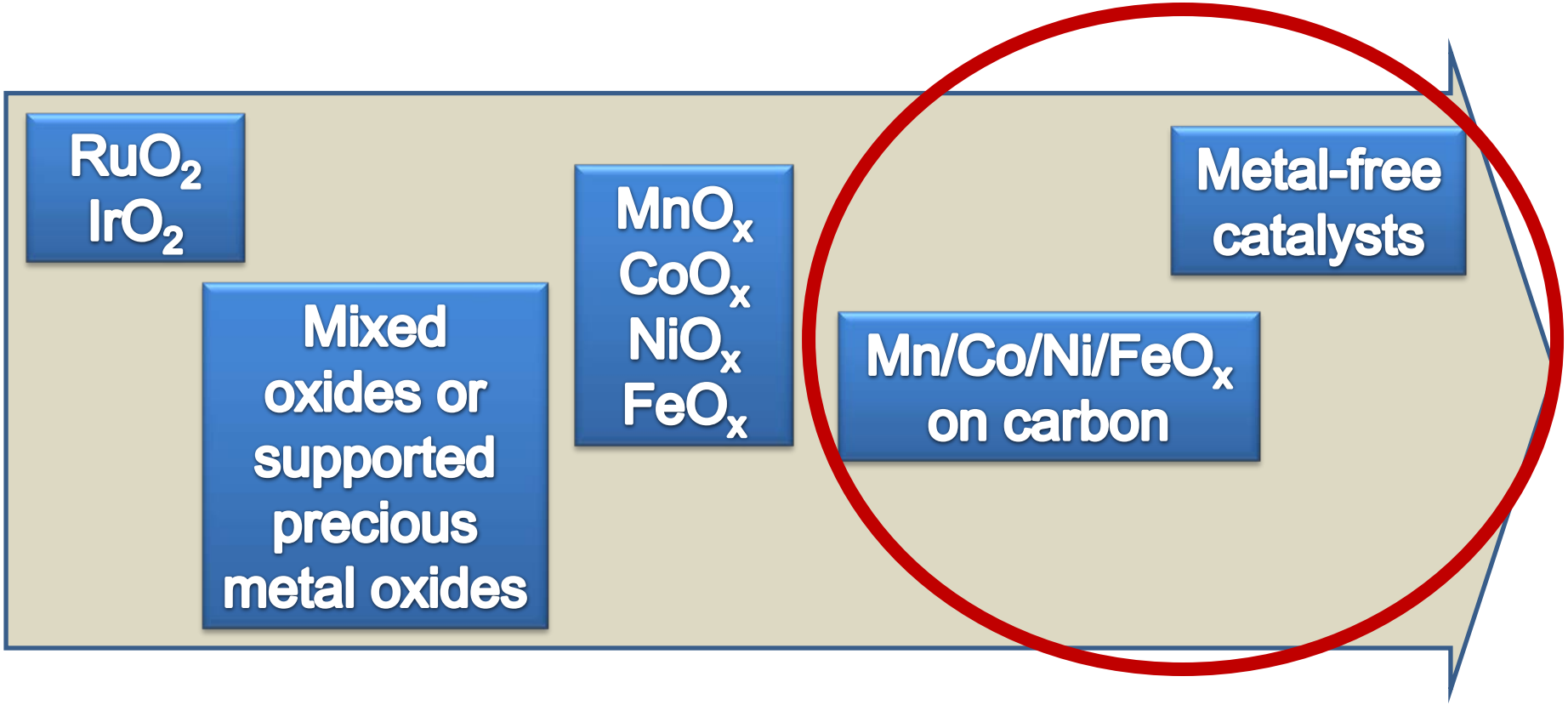
4. Sustainability

- Based on abundant, renewable resources
- Non-toxic to human health and environment

by Alex Falco
www.toonpool.com/cartoons/balance_106256

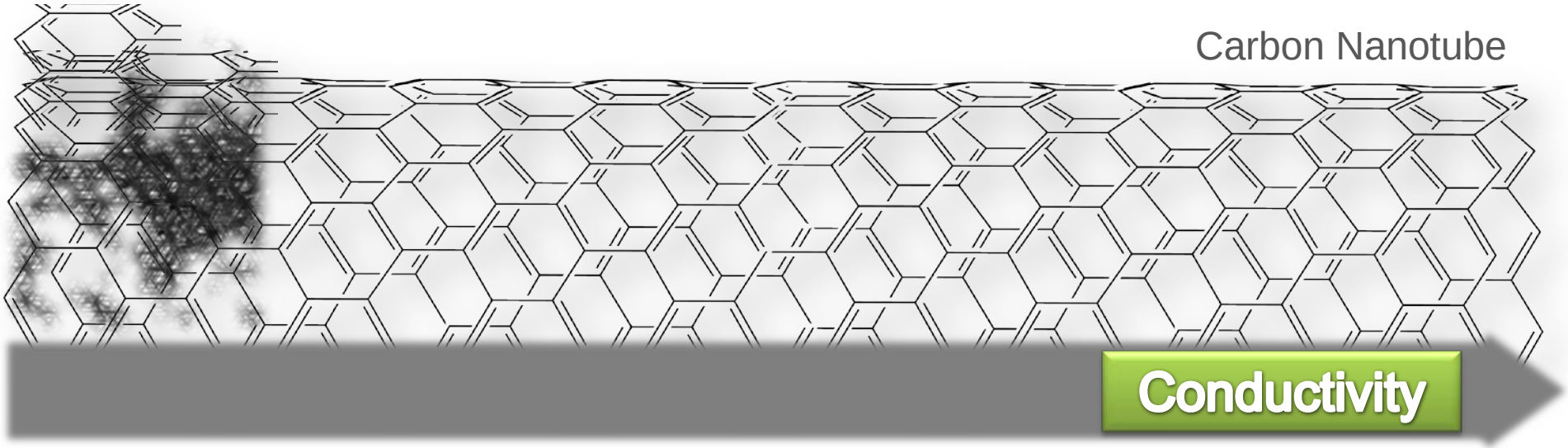
Catalyst Design

1. Conductivity
2. Performance
3. Stability
4. Sustainability



Catalyst Design

Mn/Co/Ni/FeO_x on carbon

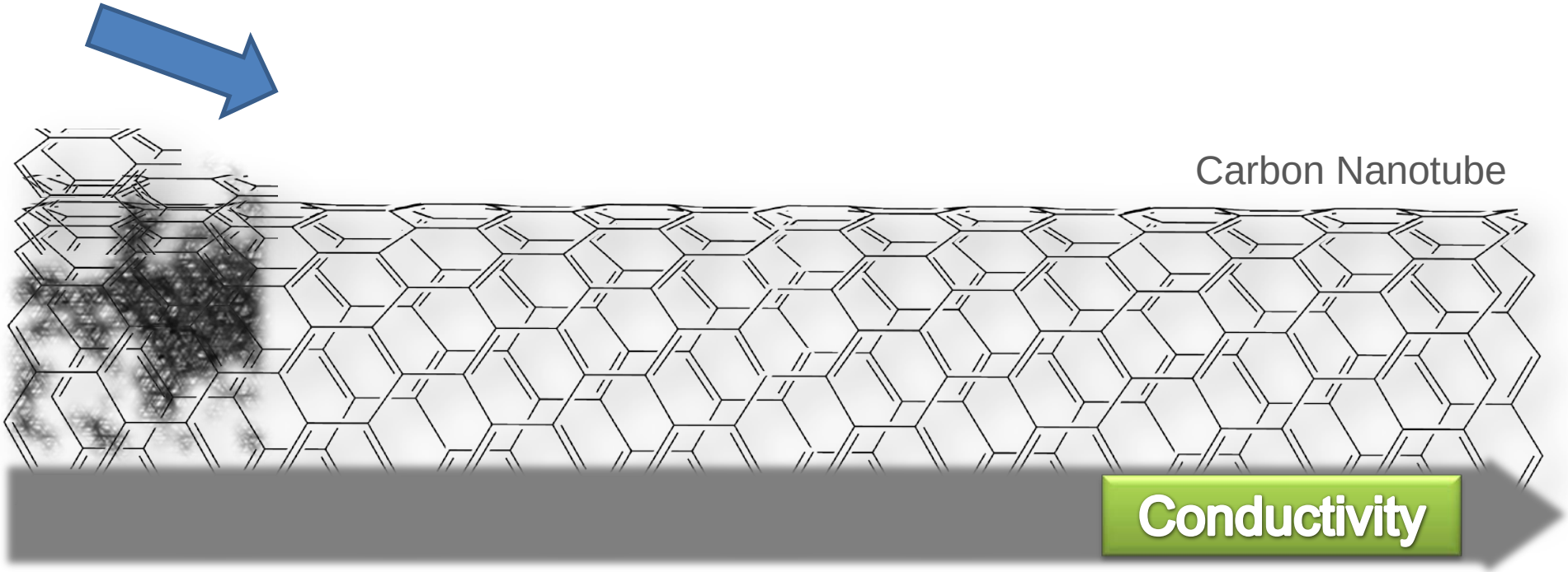


Catalyst Design

Mn/Co/Ni/FeO_x on carbon

Purification

Ref.
Ali Rinaldi
Klaus Friedel



Catalyst Design

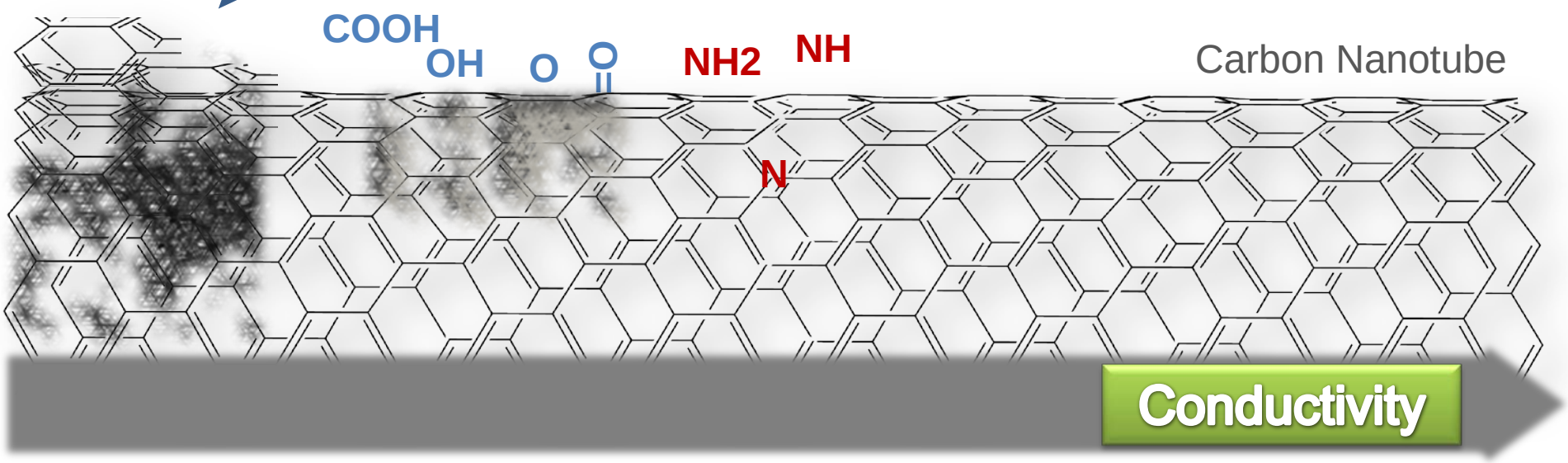
Mn/Co/Ni/FeO_x on carbon

Purification

Ref.
Ali Rinaldi
Klaus Friedel

Oxidation by HNO_3
O- or N-sputtering
Chemical grafting

Ref.
Rosita Arrigo
Henan Li
Olivier Majoulet
JP Tessonnier
Klaus Friedel



Catalyst Design

Mn/Co/Ni/FeO_x on carbon

Purification

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Oxidation by HNO_3
O- or N-sputtering
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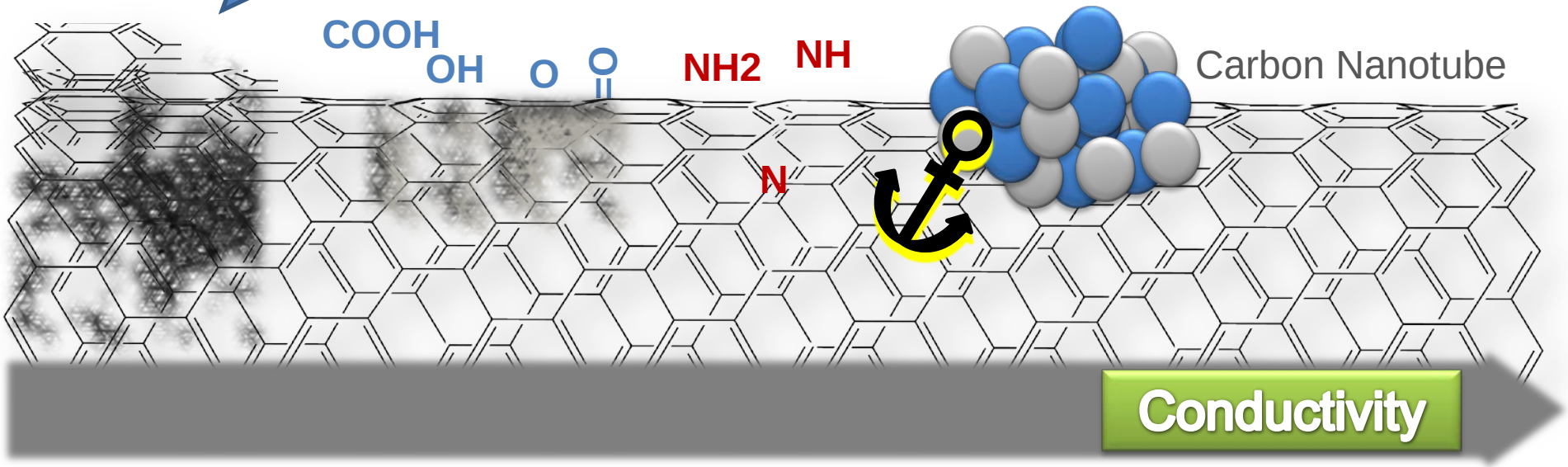
Rosita Arrigo
Henan Li
Olivier Majoulet
JP Tessonnier
Klaus Friedel

Particle deposition by impregnation or precipitation

Ref.
JP Tessonnier
Alberto Villa
Dangsheng Su, Jiang Zhang
Lidong Shao
Katharina Mette, Malte Behrens



Catalyst Design

Mn/Co/Ni/FeO_x on carbon

Purification

Ref.
Ali Rinaldi
Klaus Friedel

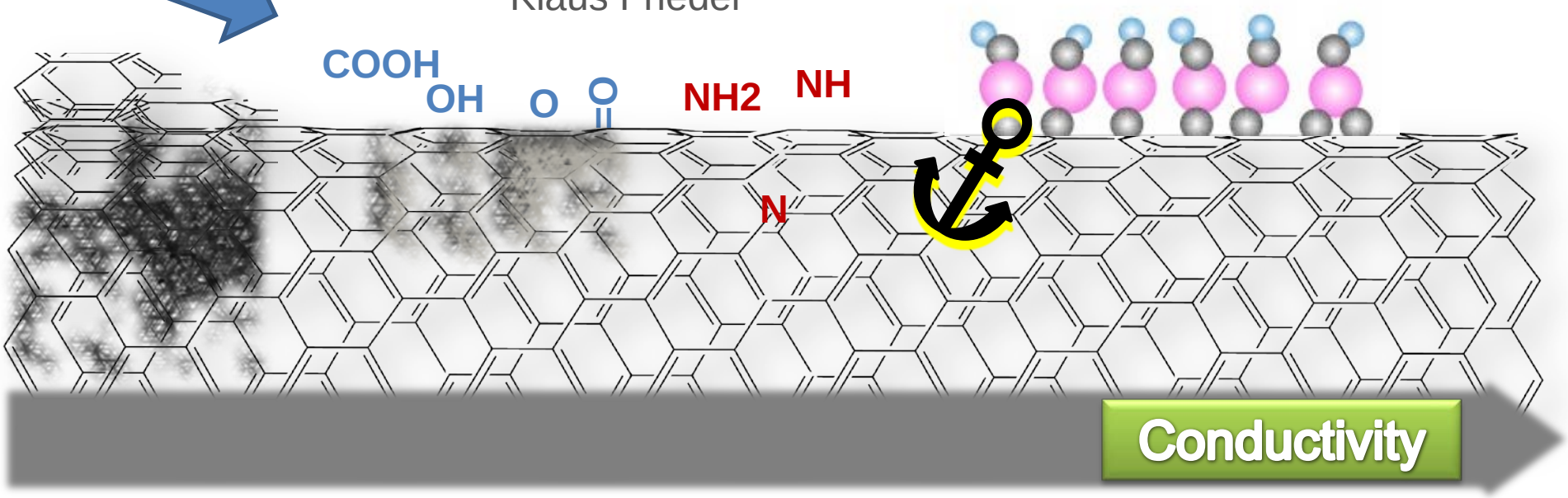
Oxidation by HNO_3
O- or N-sputtering
Chemical grafting

Ref.
Rosita Arrigo
Henan Li
Olivier Majoulet
JP Tessonnier
Klaus Friedel

Atomic layer deposition (ALD)

Saskia Buller
MPI-CEC

S. Buller



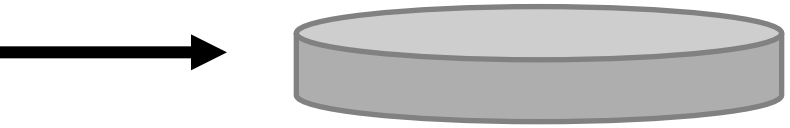
Electrode requirements

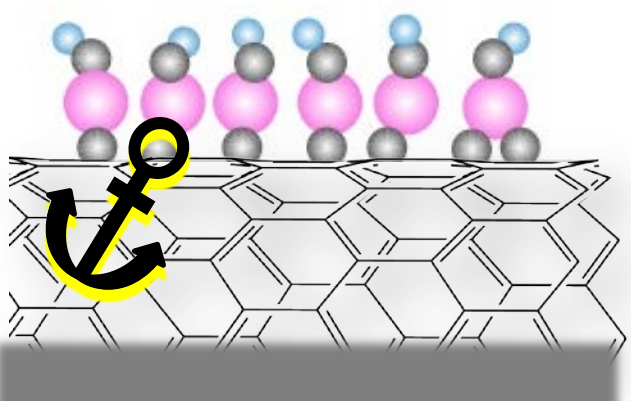
Powder
+
Binder
+
Processing

or

Powder
+
Binder
+
Glassy carbon disk

Bulk electrode





→ Prevention of unknown site effects by binder

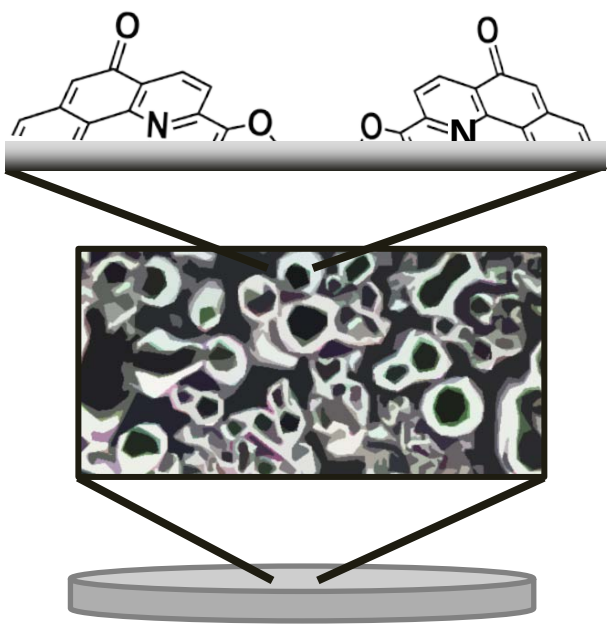
Electrode requirements

1. Conductivity

2. Performance

3. Stability

4. Sustainability

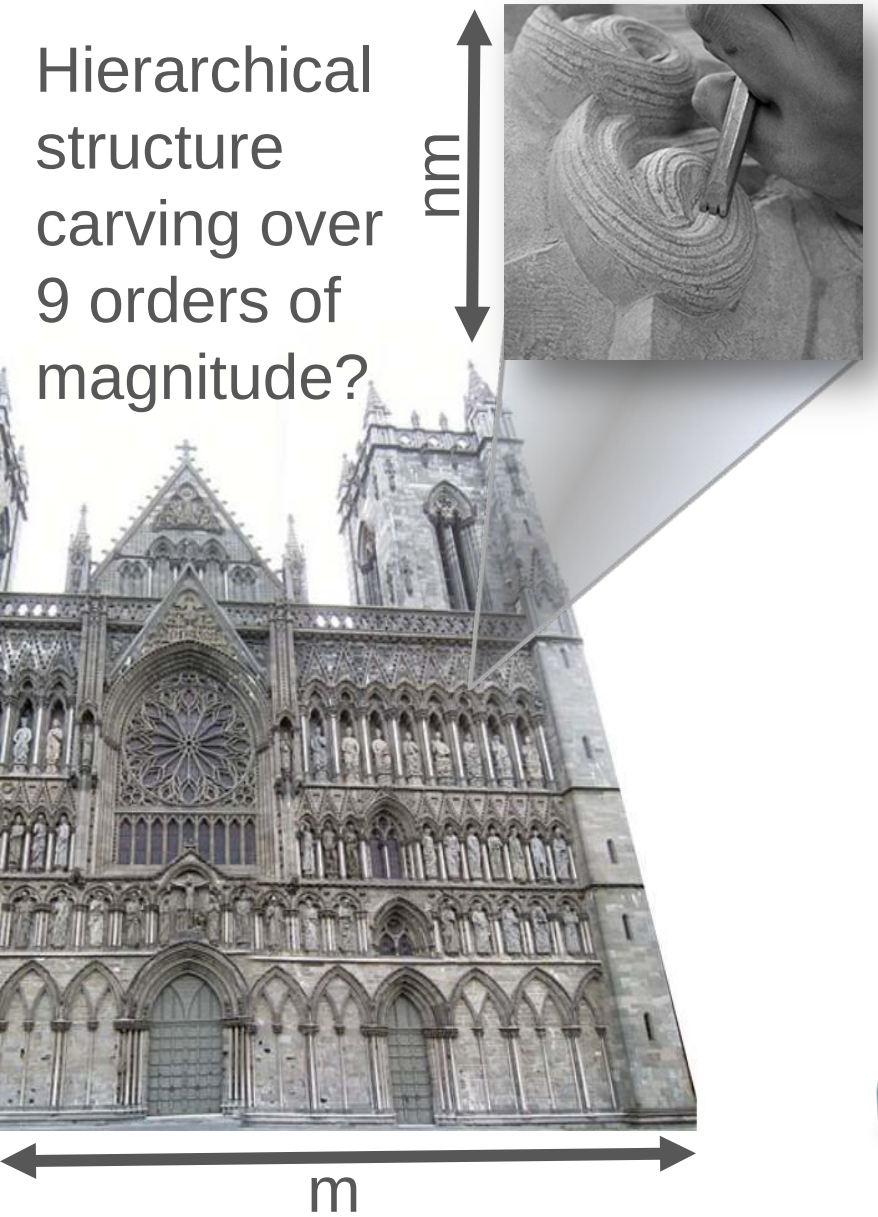


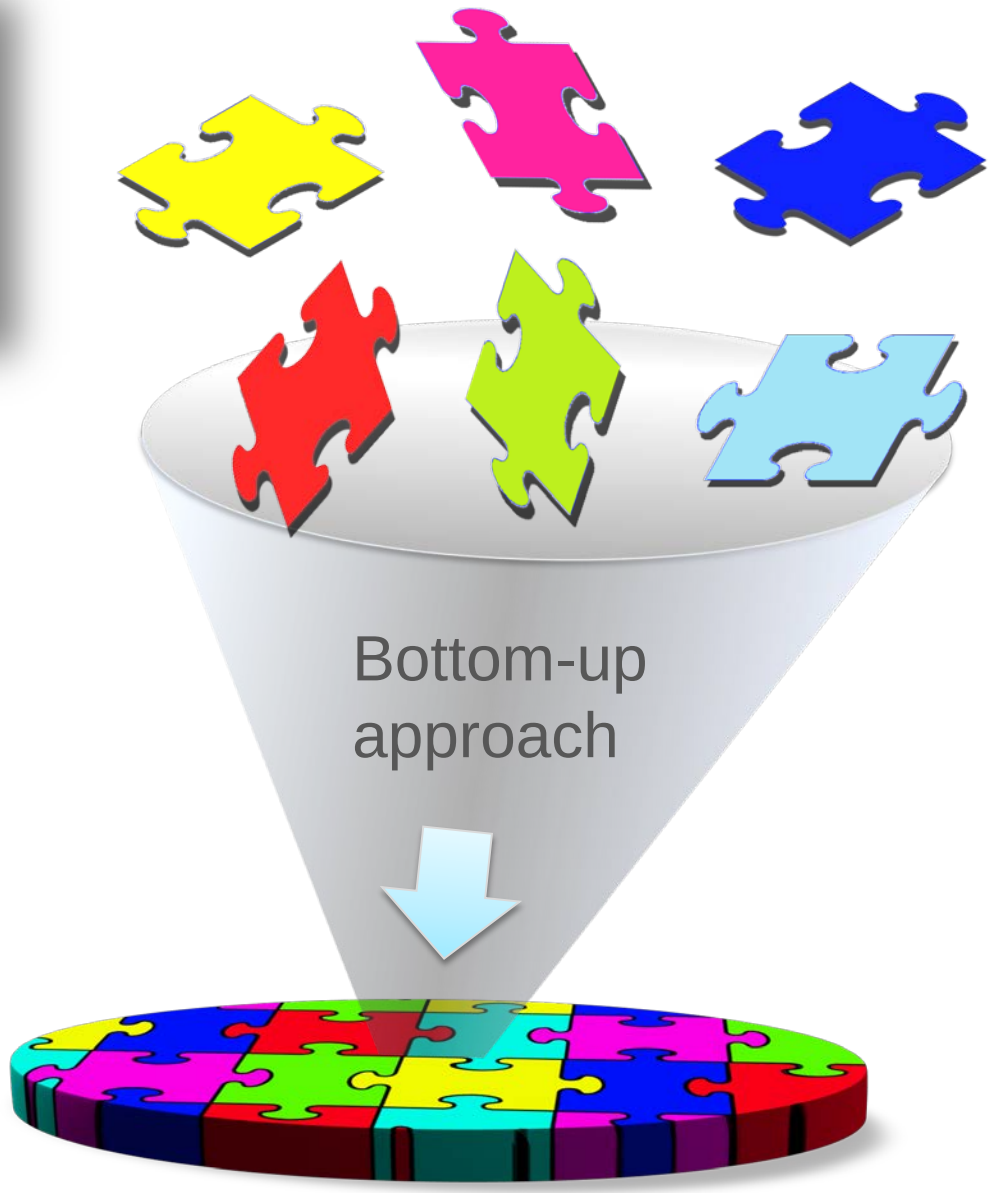
5. Shaping feasibility

- Bulk shape of specific hierarchical structure
- Possibility of quantitative analysis before and after test reaction
- Prevention of unknown site effects by binder and post-processing

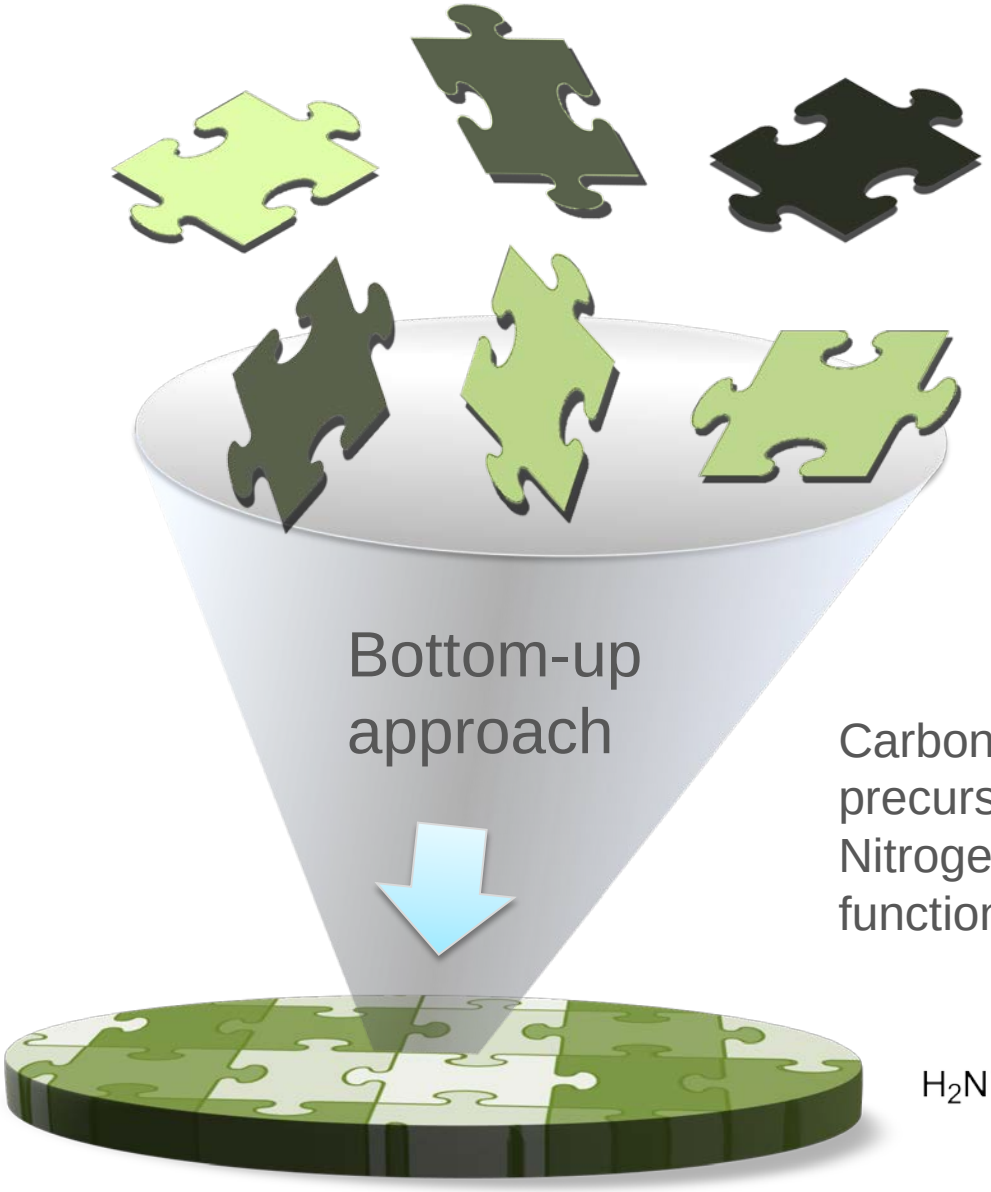
Concept

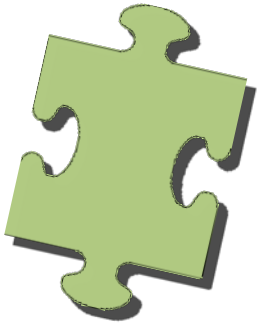
Hierarchical structure carving over 9 orders of magnitude?



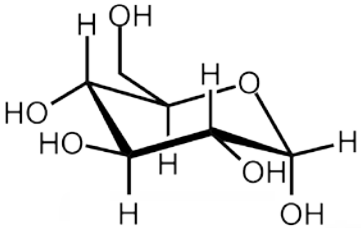


Concept



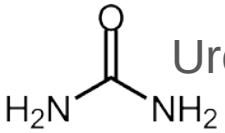


Carbon precursor
Oxygen functionalized

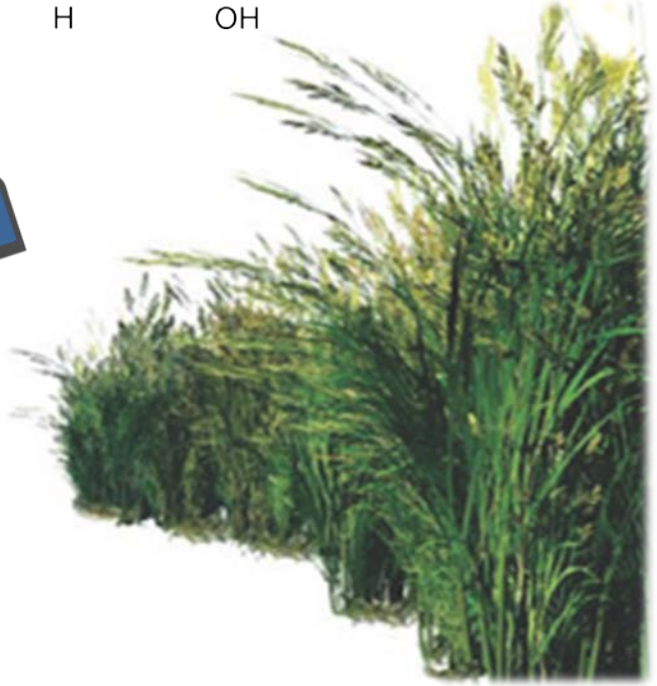


Glucose
Cellulose
Biomass

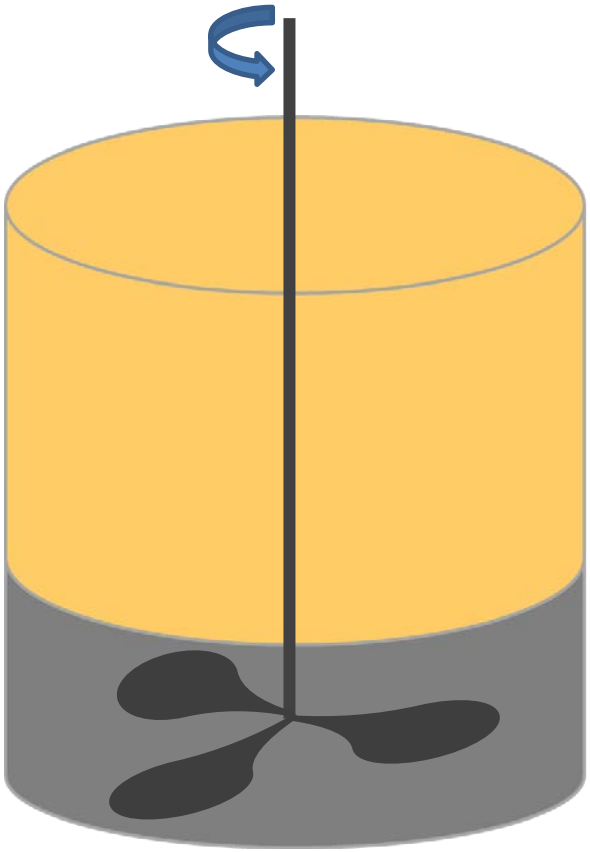
Carbon
precursor
Nitrogen
functionalized



Urea



Hydrothermal carbonization



Reaction vessel = autoclave

5-20 wt% glucose solution

180-220°C

2-20 h

Supernatant

Carbonaceous Product

Hydrothermal carbonization

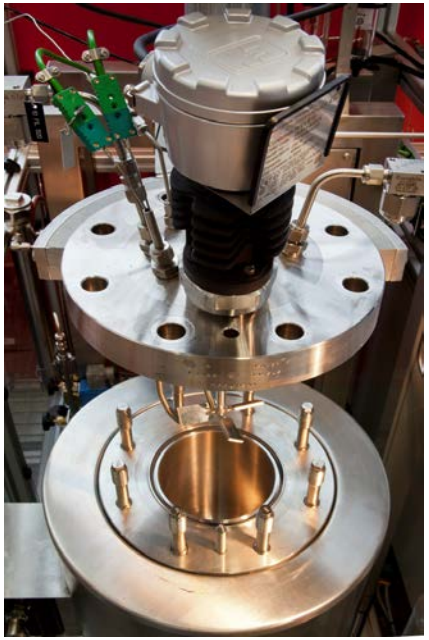
12 x 50 ml
12 x 3 g product

2 x 300 ml
2 x 20 g

2000 ml
80-100 g

Electrode requirements

1. Conductivity
2. Performance
3. Stability
4. Sustainability
5. Shaping feasibility



6. Scalability

Sufficient material for thorough testing and analytics

Electrode preparation

20 wt% glucose solution in H_2O

220°C
6 h

HTC

Hydro**T**hermal **C**arbon

Pressing:
10 t
2 min

d = 13 mm
m_0= 50 or 100 mg

T = 900°C
6 h
250 ml/min

d = 10 mm
m = ½ m_0

Electrode preparation

20 wt% glucose solution in H_2O

220°C
6 h

HTC

Pressing:
10 t
2 min

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T = 900°C
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250 ml/min

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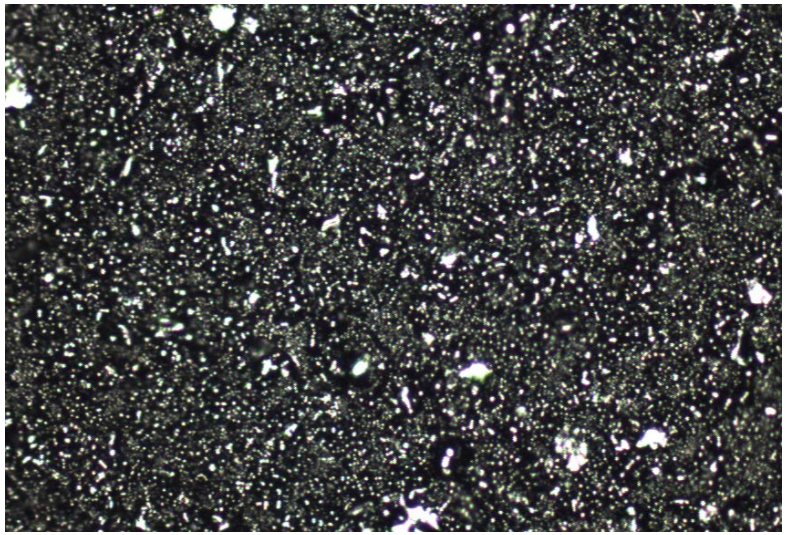
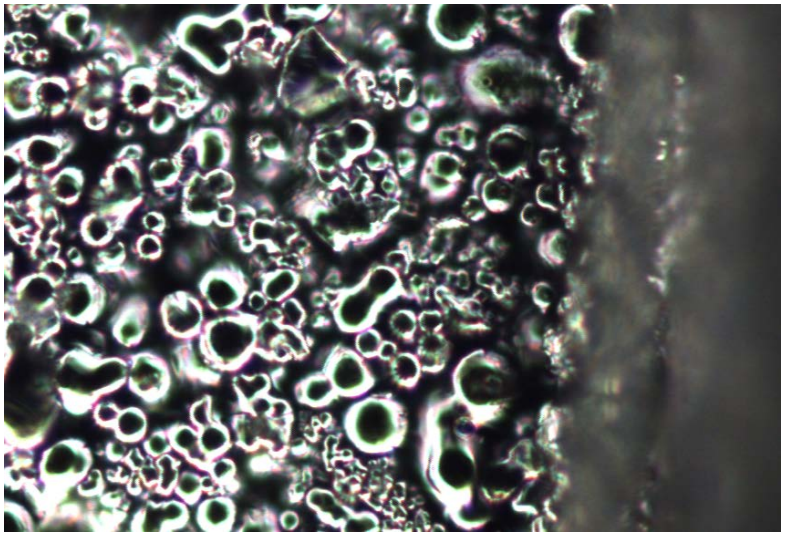


Light microscopy (10x)

1 mm



Light microscopy (50x)
Darkfield

200 µm

Electrode Preparation

20 wt% glucose solution in H_2O

220°C
6 h

HTC

Pressing:
10 t
2 min

d = 13 mm
m_0= 50 or 100 mg

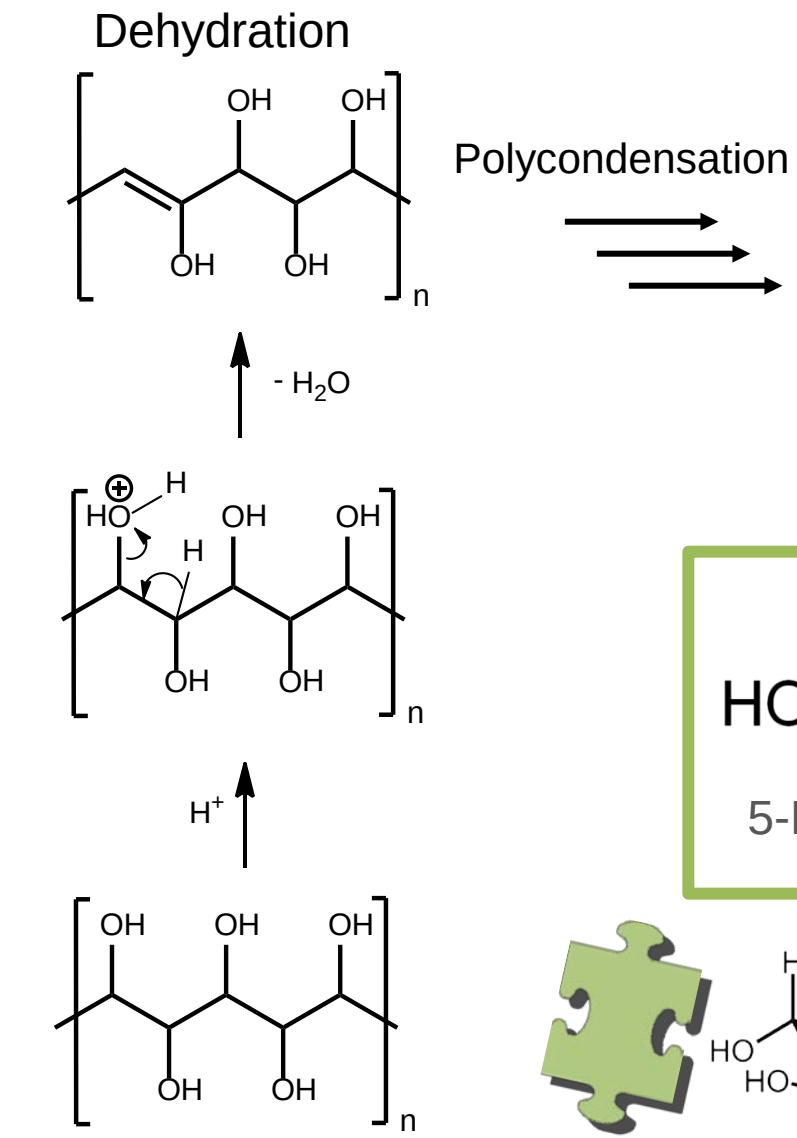
T = 900°C
6 h
250 ml/min

d = 10 mm
m = ½ m_0

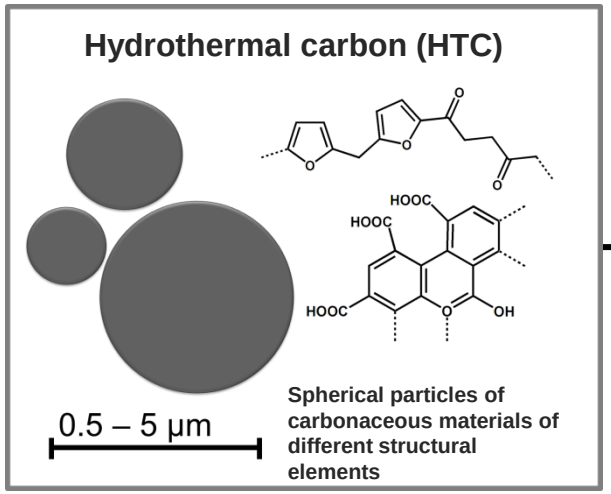
Focus of Research

Properties of final electrode determined by hydrothermal synthesis process

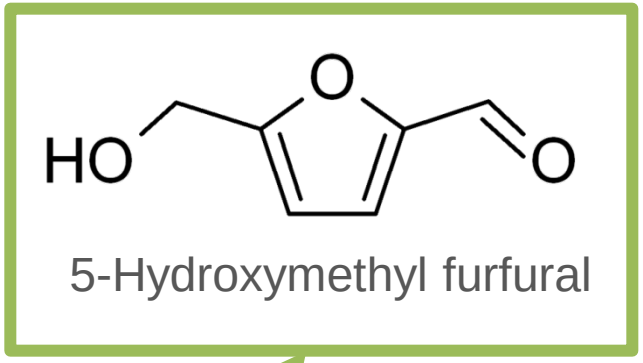
Hydrothermal carbonization - principle

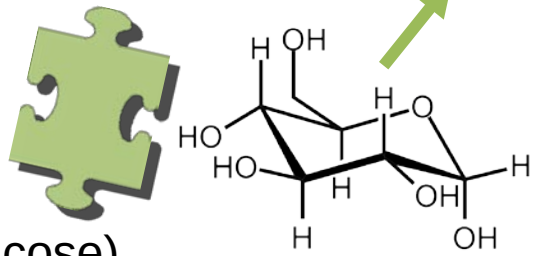


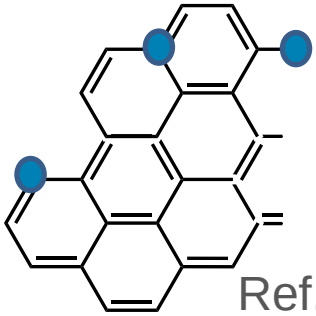
Polycondensation



Δ T



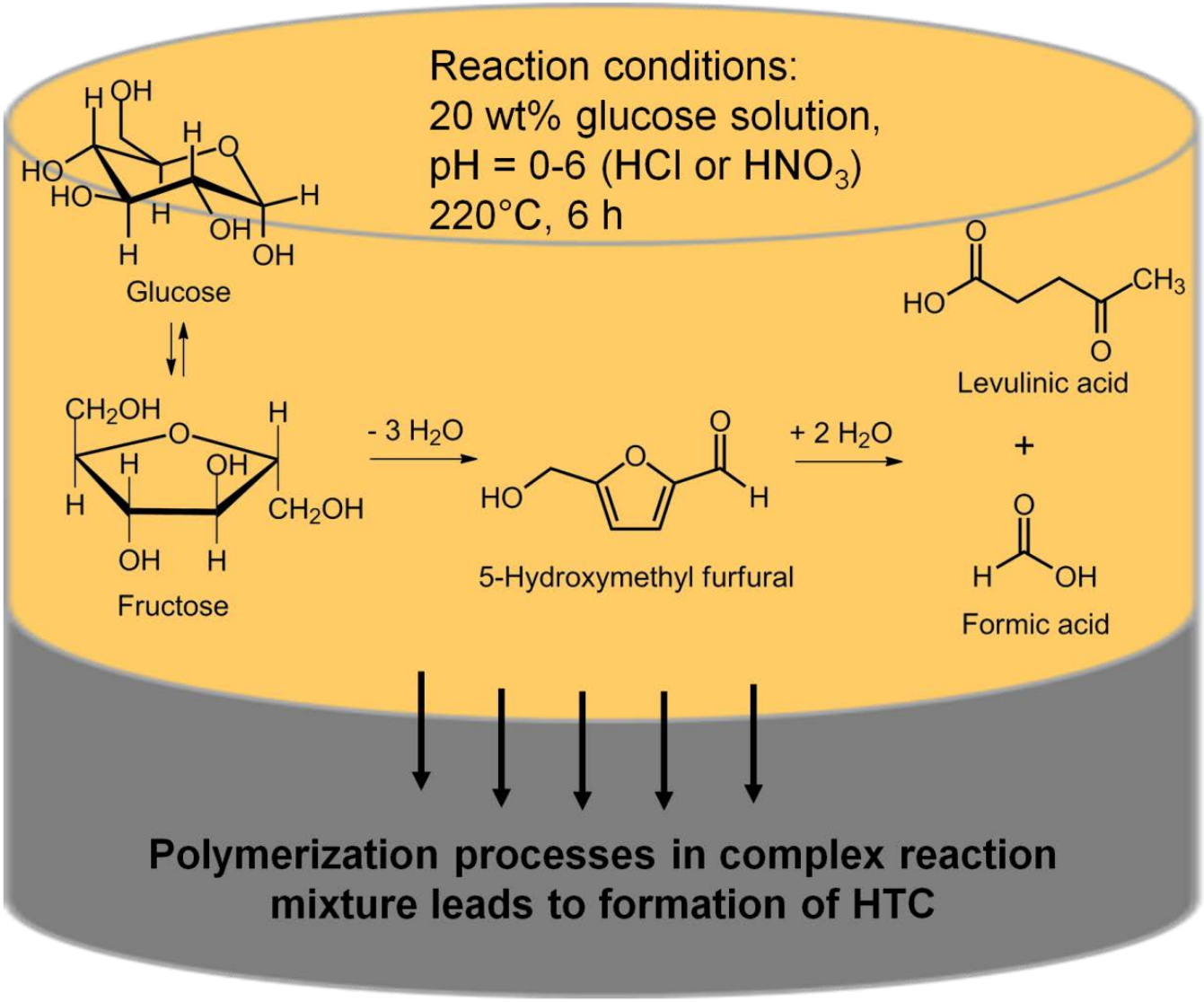




Polyol (e.g. cellulose, glucose)

Ref.:
J. Dumesic
N. Baccile, M.-M. Titirici,
M. Antonietti

Hydrothermal carbonization - principle



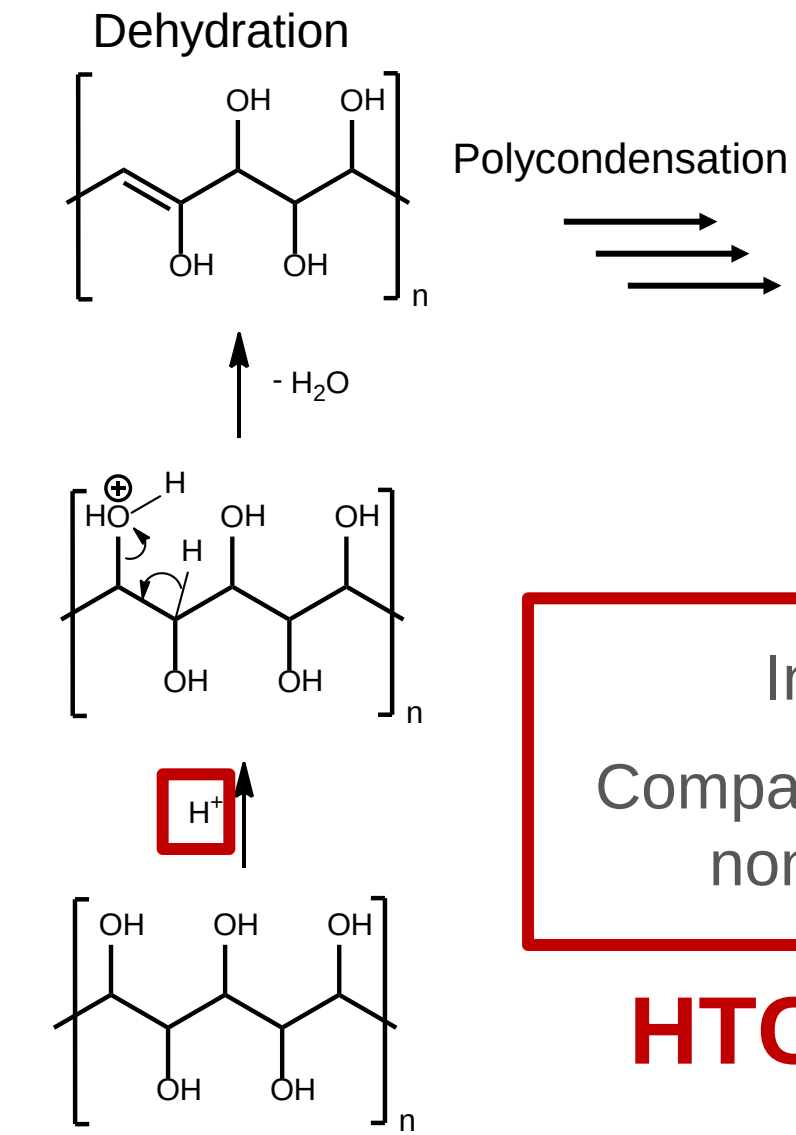
Hydrothermal Carbon

Tuning of carbon properties by reaction conditions

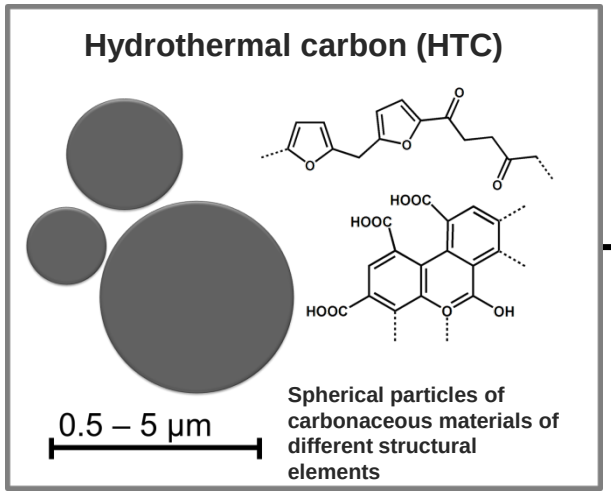
HTC

Hydro**T**hermal **C**arbon

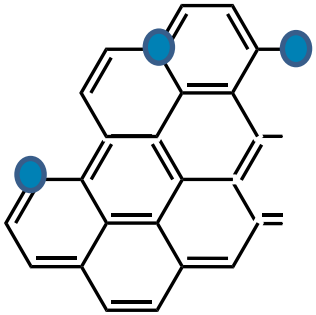
Hydrothermal carbonization - principle



Polycondensation



Δ T



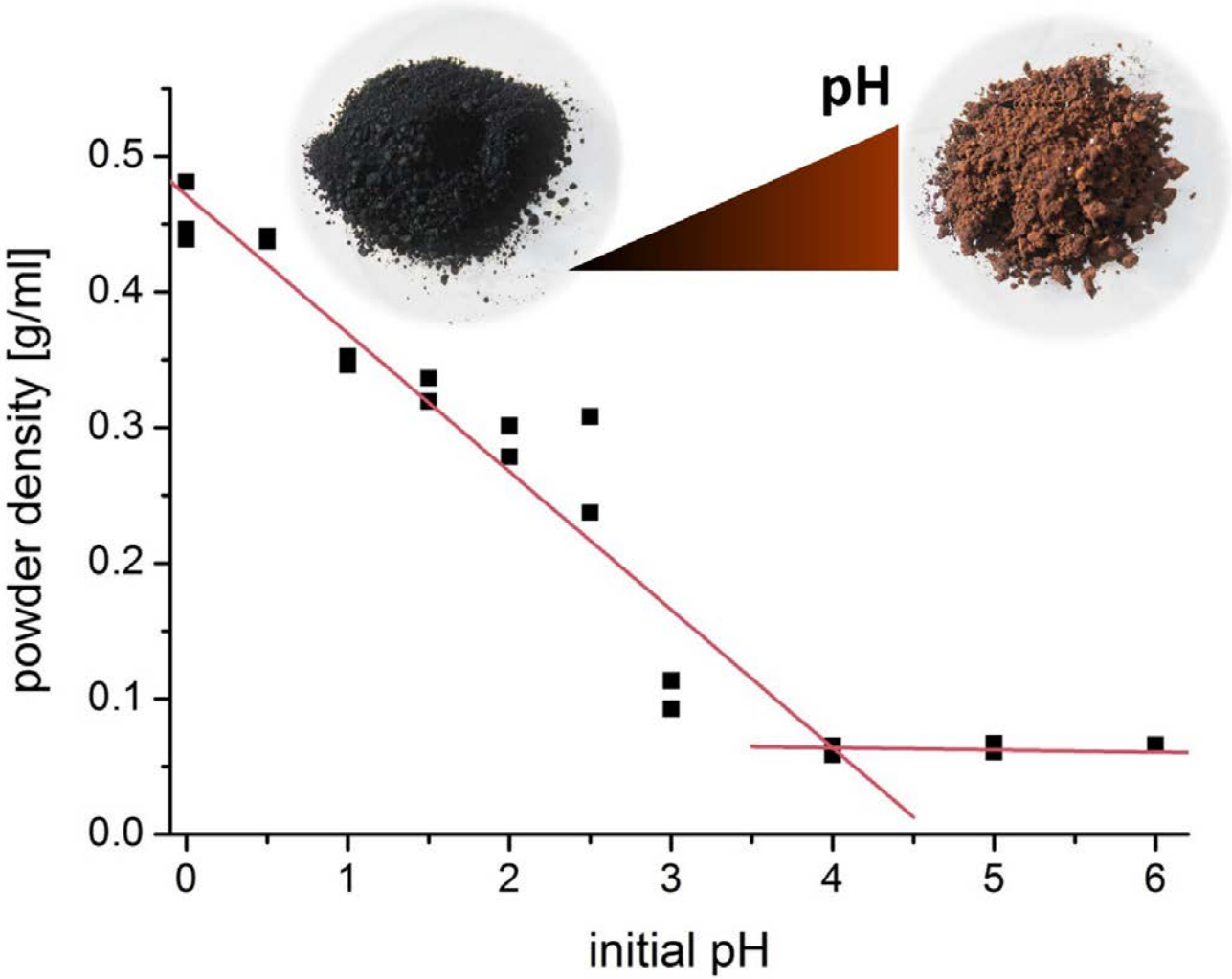
Influence of **pH**

Comparison of oxidizing an non-oxidizing acids

HTC_{HNO3} **HTC_{HCl}**

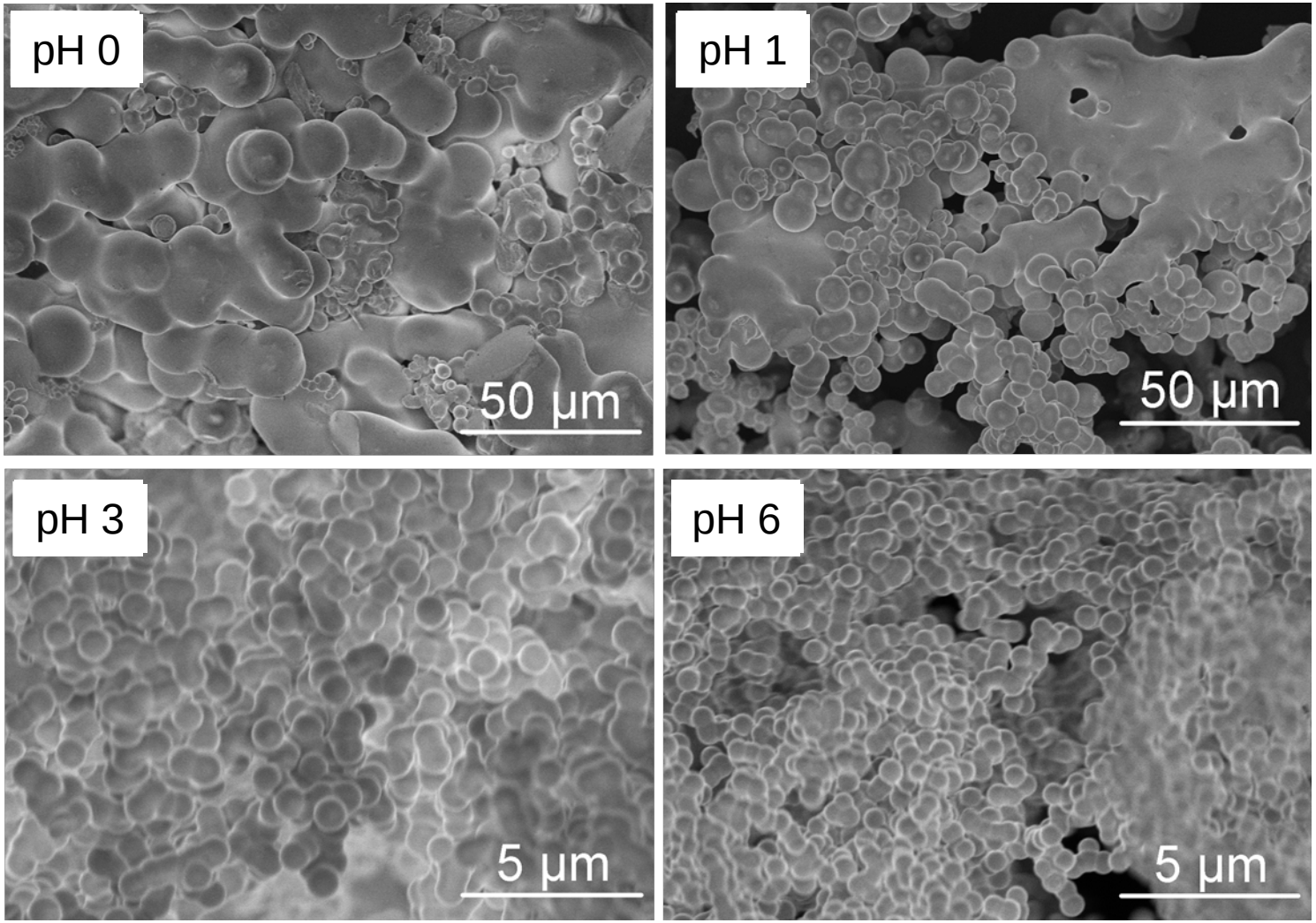
pH-dependence: powder density

Natalia Kowalew

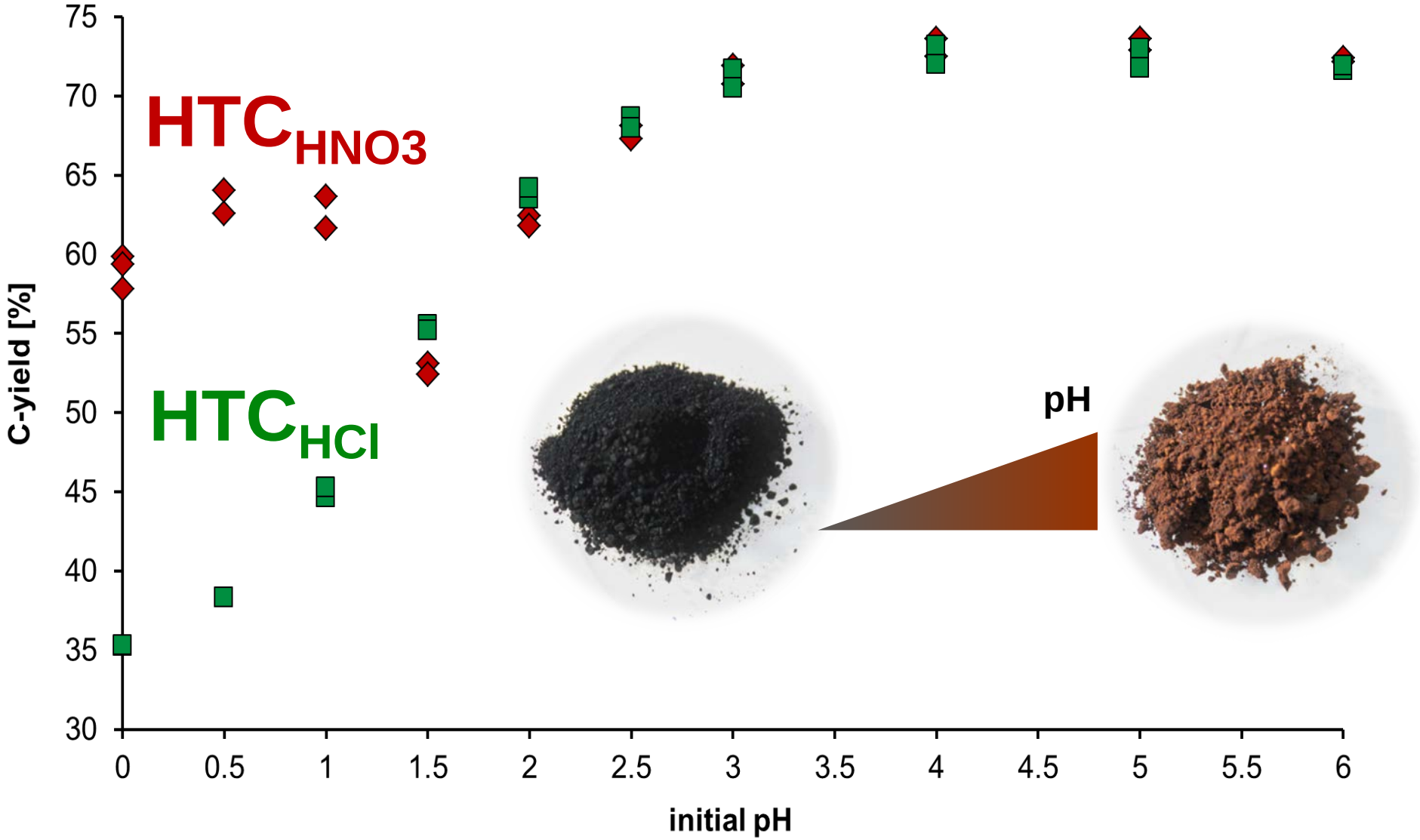


pH-dependence: SEM

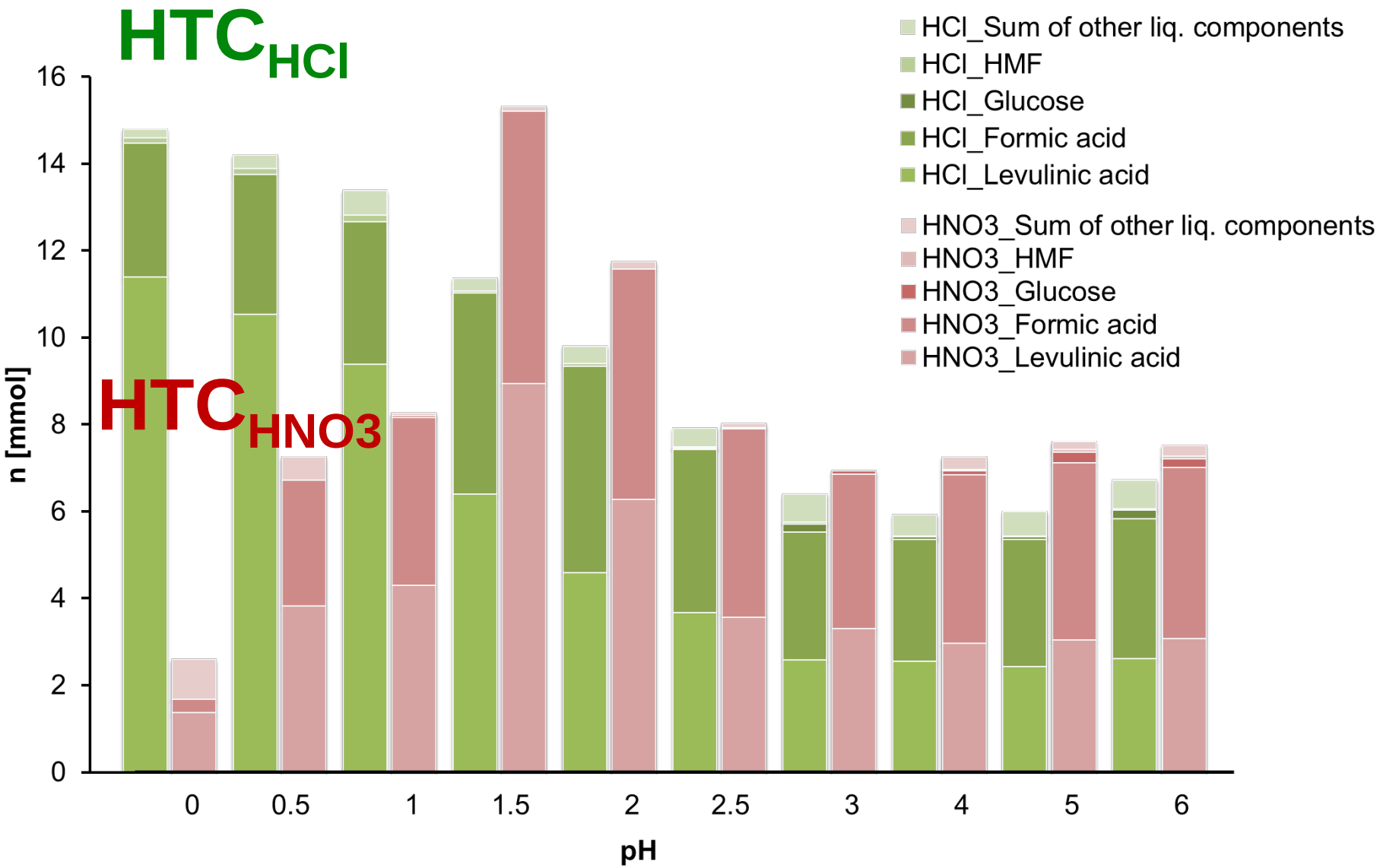
Wiebke Frandsen (FHI Berlin)



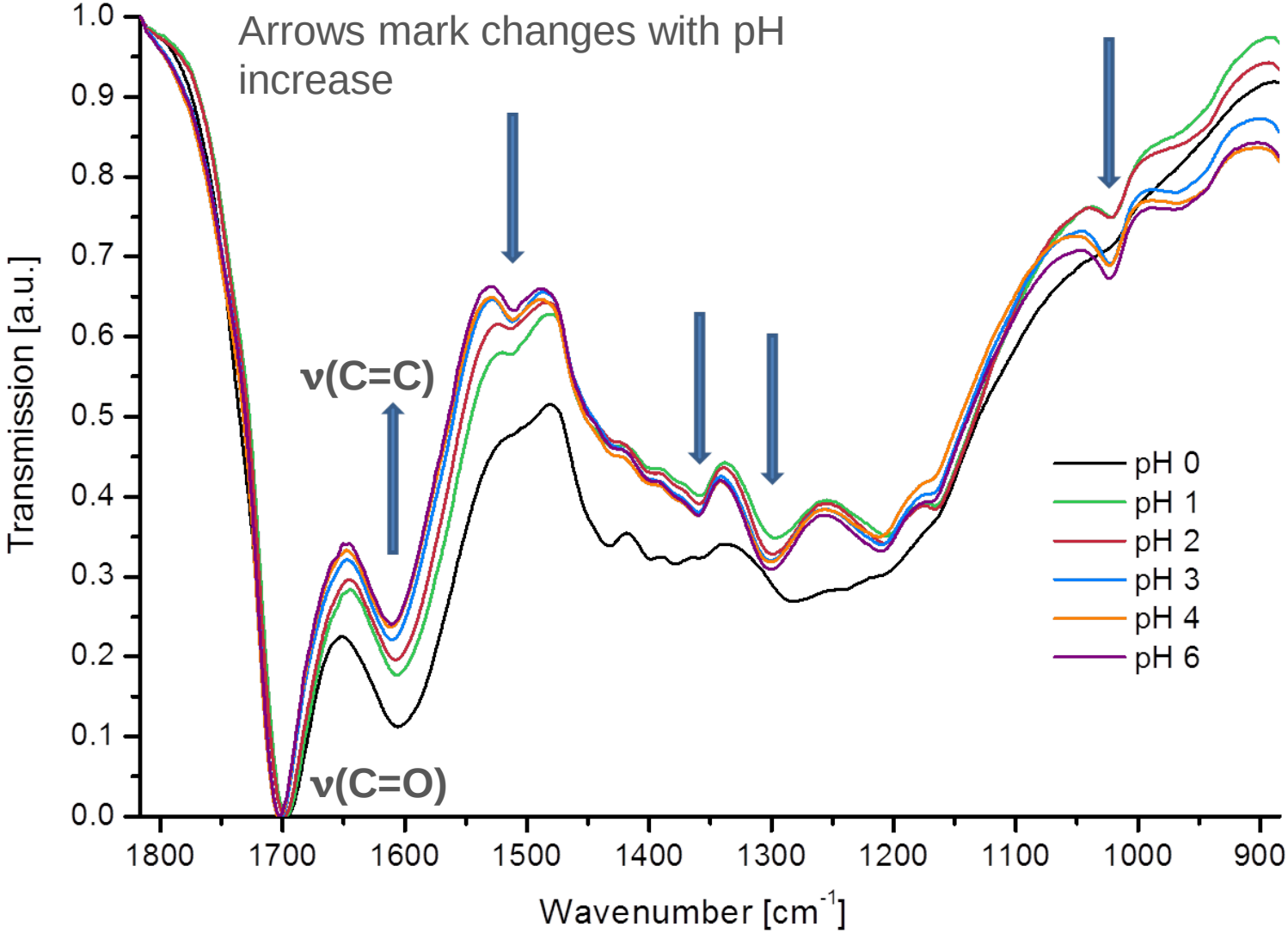
pH-dependence: carbon yield



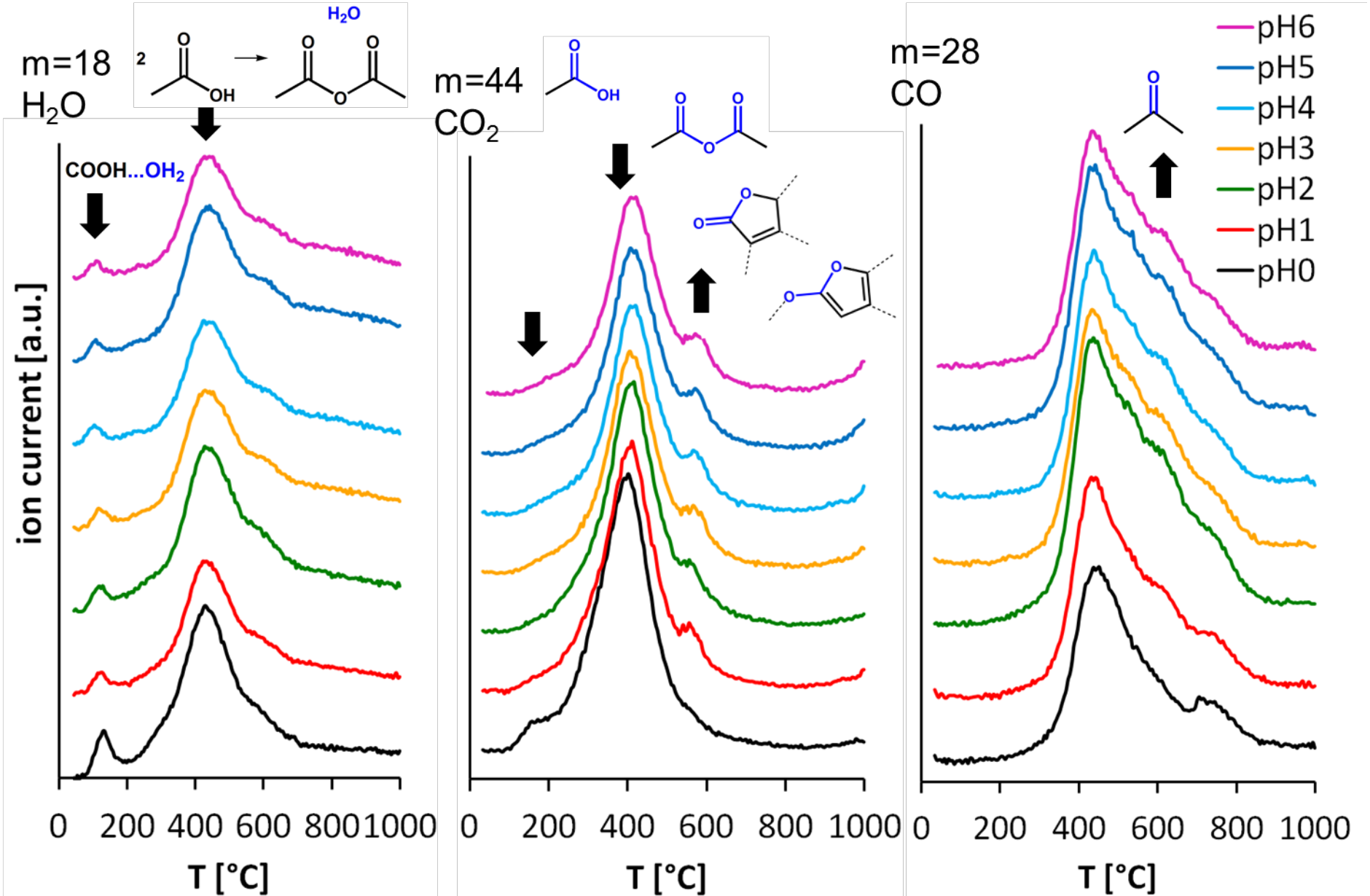
Critical process parameters: pH



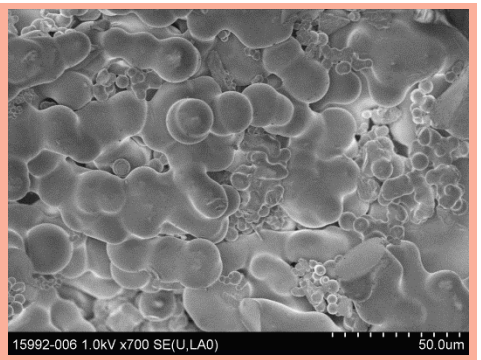
pH-dependence: FT-IR spectroscopy



pH-dependence: TG-MS

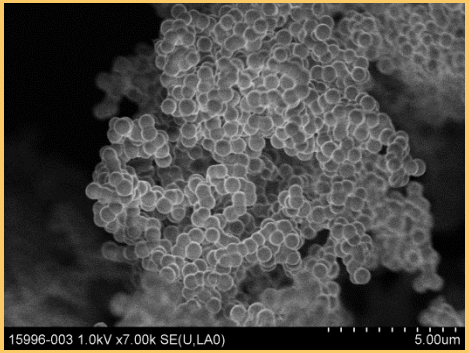


Influence of pH variation



50 µm

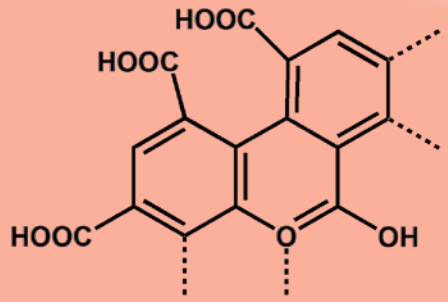
Structure of HTC



5 µm

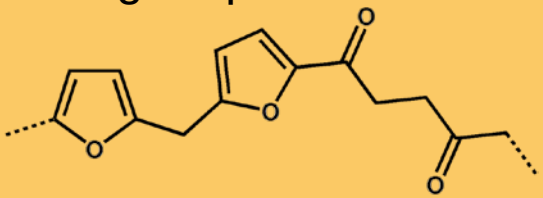
pH

Low pH



higher fraction of

Higher pH



higher fraction of

Electrode properties

20 wt% glucose solution in H_2O → 220°C 6 h

HTC

Hydro**T**hermal **C**arbon

Pressing: → T = 900°C →

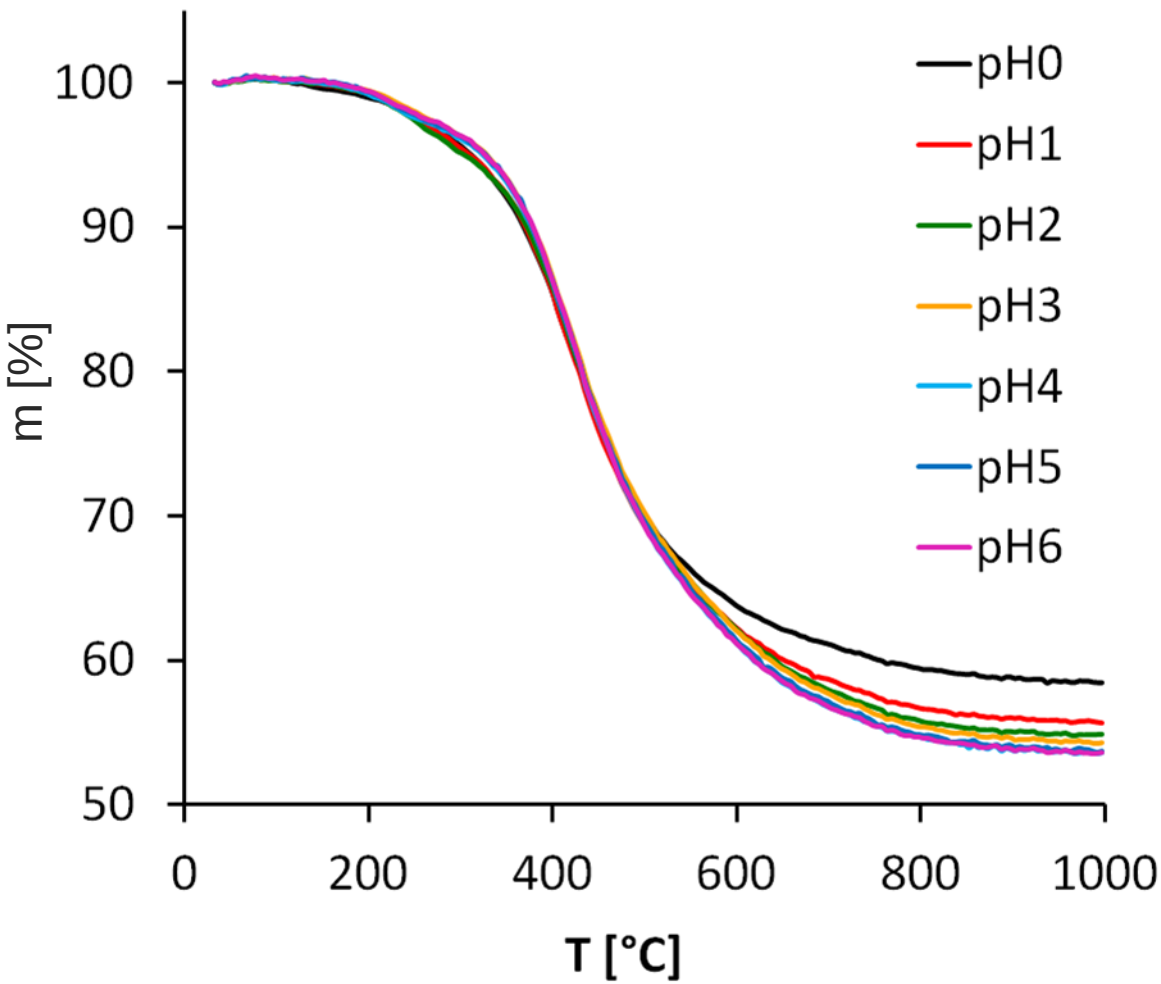
d = 13 mm
m_0= 100 or 250 mg

d = 10 mm
m = ½ m_0

pH	m_0 [g]	m_{T900} [g]	mass loss	geometric density [g/cm³]
0	0.256	0.146	43.0%	0.9
3	0.253	0.132	47.8%	0.7
6	0.255	0.133	47.8%	0.8

Thermogravimetry

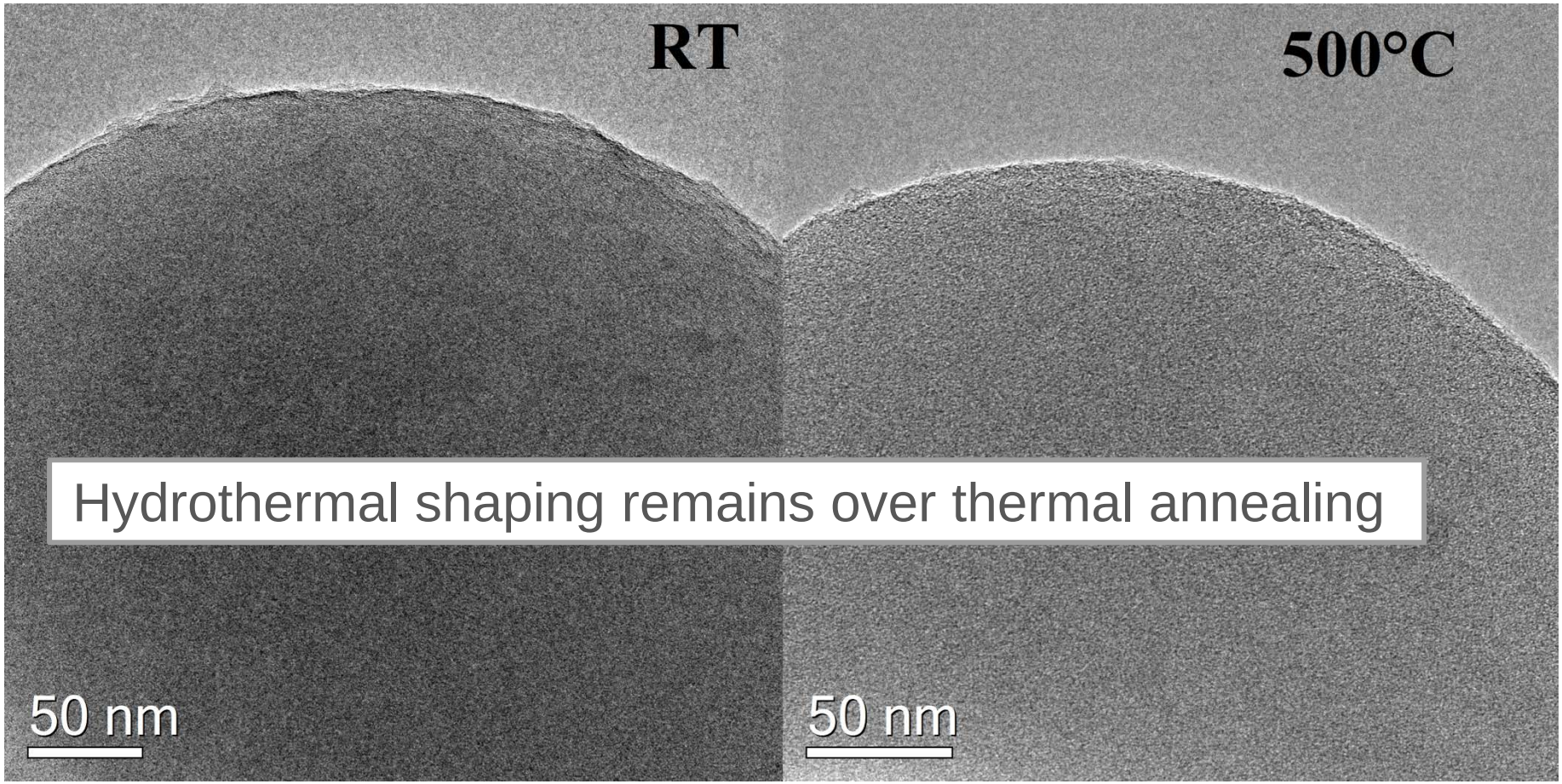
20 K/min, 50 ml/min Ar



pH	C [%]	Residual mass
0	70.2	58.5
1	69.6	55.7
2	68.9	54.9
3	68.6	54.3
4	67.7	53.6
5	68.1	53.6
6	67.7	53.6

TEM

by Marc Willinger
FHI Berlin

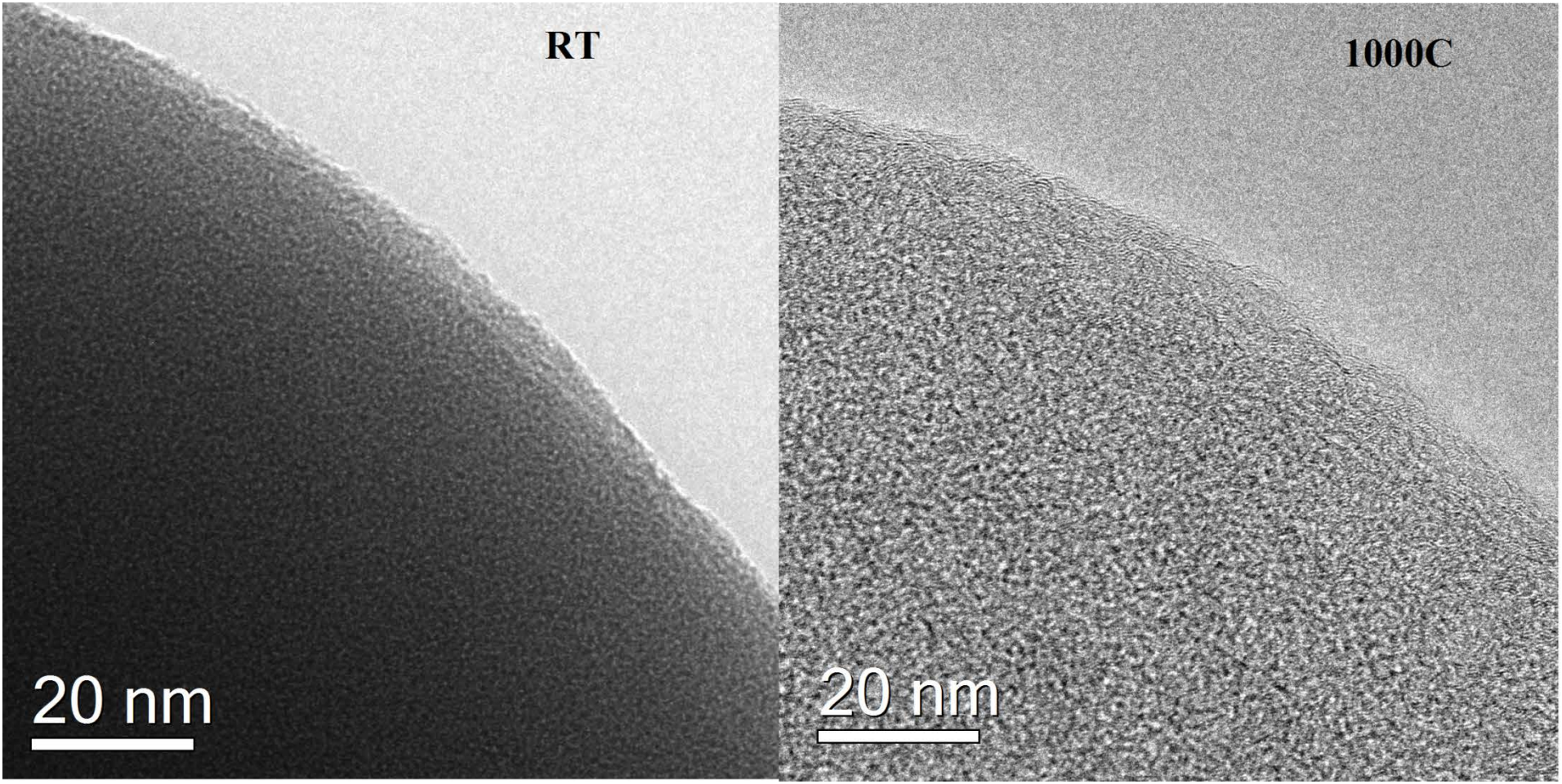


Hydrothermal shaping remains over thermal annealing

Contrast change →. mass-thickness contrast is reduced.
Volume (particle size) remains roughly constant

TEM

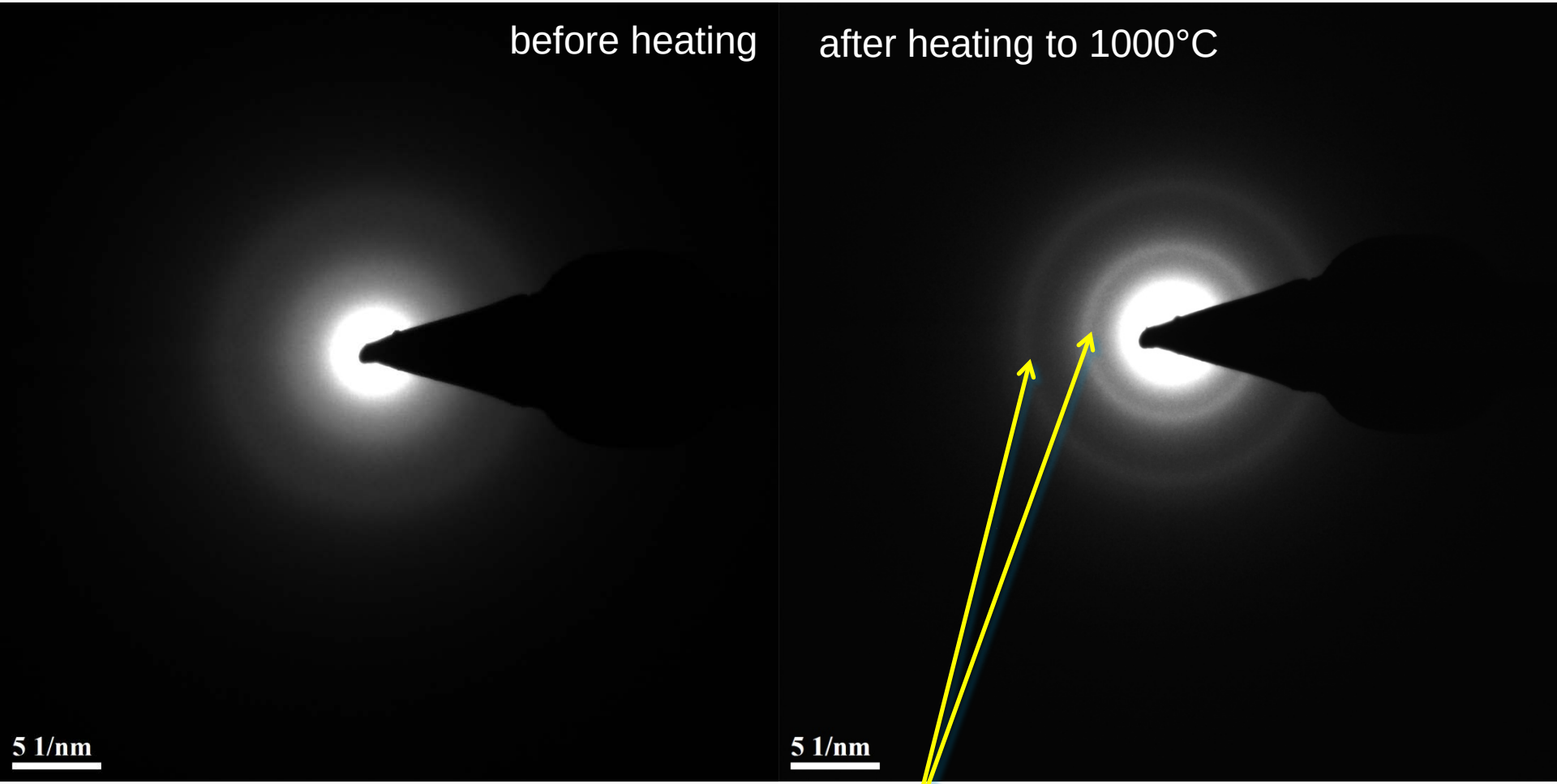
by Marc Willinger
FHI Berlin



not only has the contrast changed, also the structure of the carbon (in agreement with diffraction) has changed.

TEM

by Marc Willinger
FHI Berlin

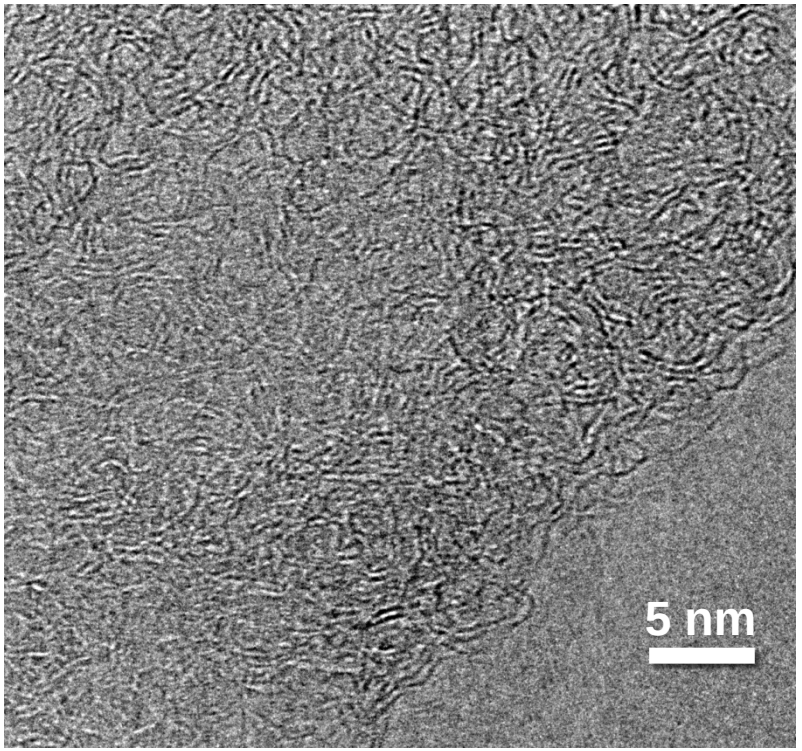


Diffraction pattern shows rings due to graphitic carbon…

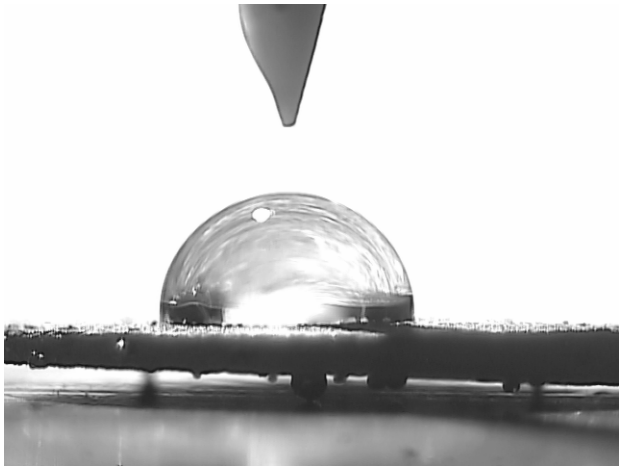
TEM

by Marc Willinger
FHI Berlin

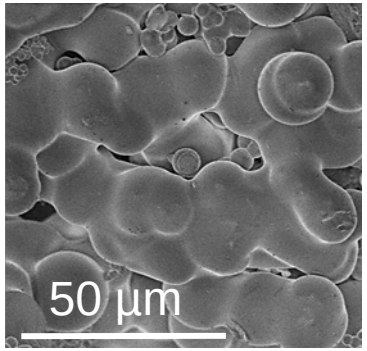
Carbon exhibits “Tagliatelle-like” structure similar to glassy carbon



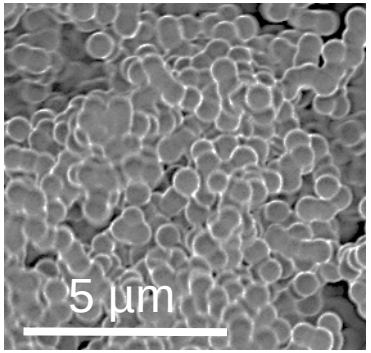
Electrode properties



319: pH 0
contact angle : 86°



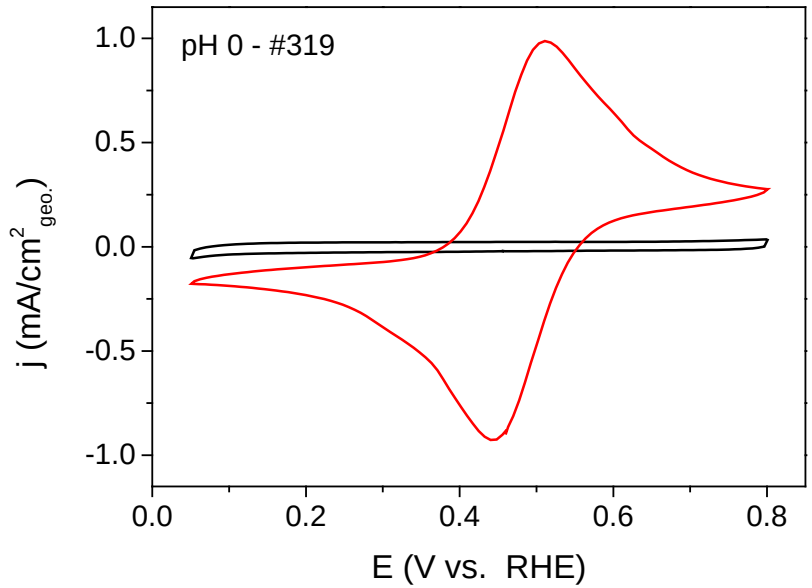
320: pH 6
contact angle : 21°



Equipment at Prof. Axel Rosenhahn (RUB)

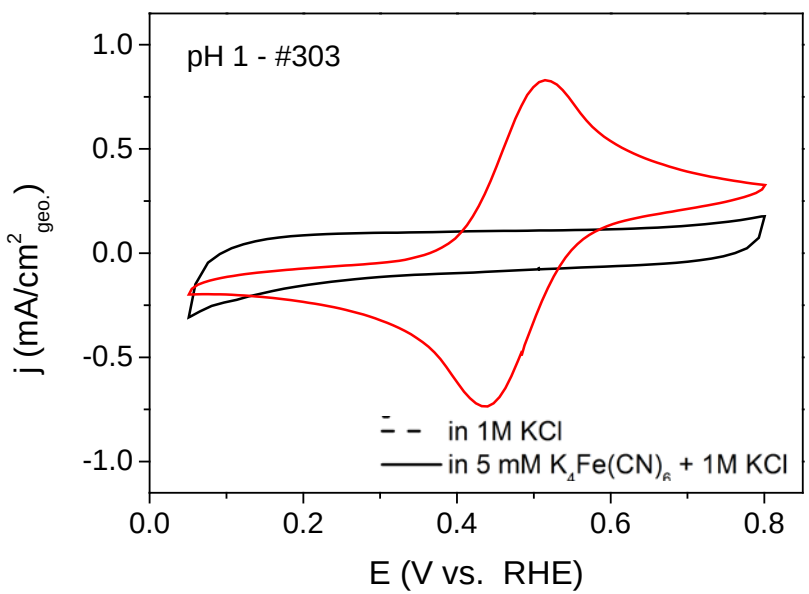
HTC_900°C				
pH	C [wt%]	H [wt%]	N [wt%]	O [wt%]
0	92.5	1.7	2.9	3.0
3	97.7	0.45	0.48	1.4
6	93.9	0.82	0.2	5.1

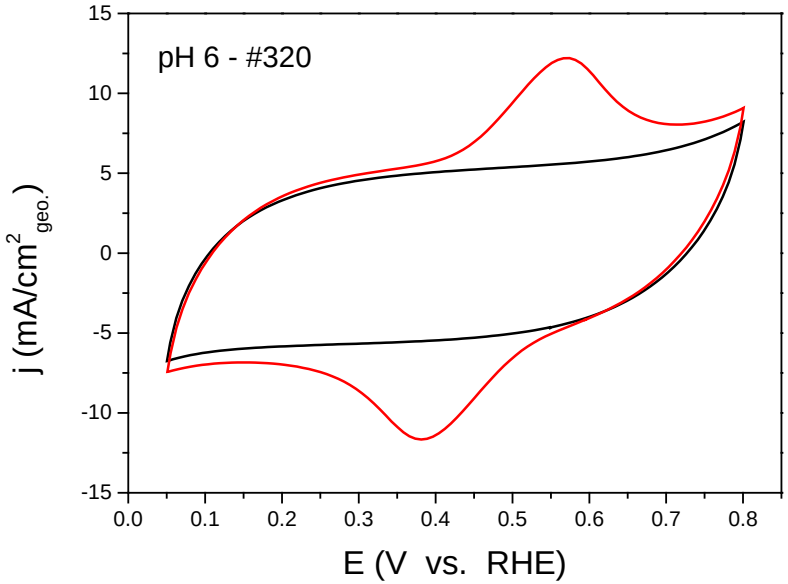
Electrode properties



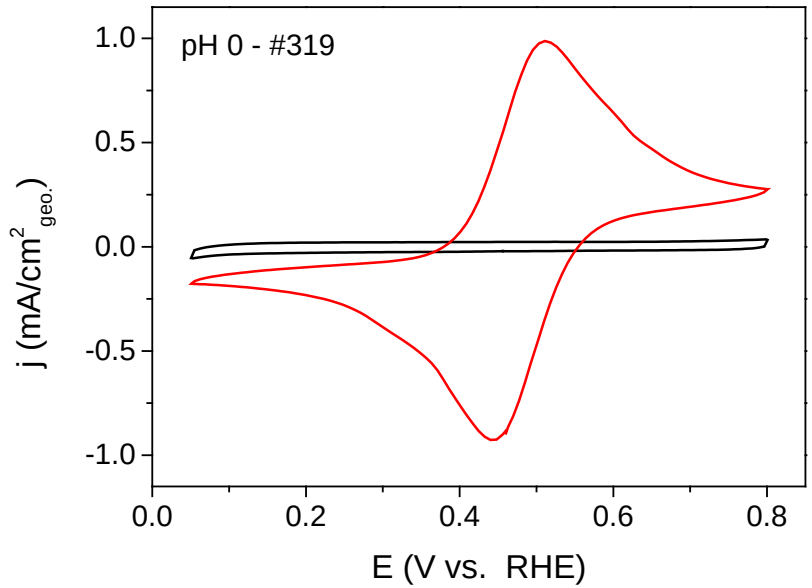
Resistance by 4 point probe

Sample	ρ_{Vol} [mΩ]
pH 0	10-30
pH 1	20-50
pH 3	40-80
pH 6	40-100

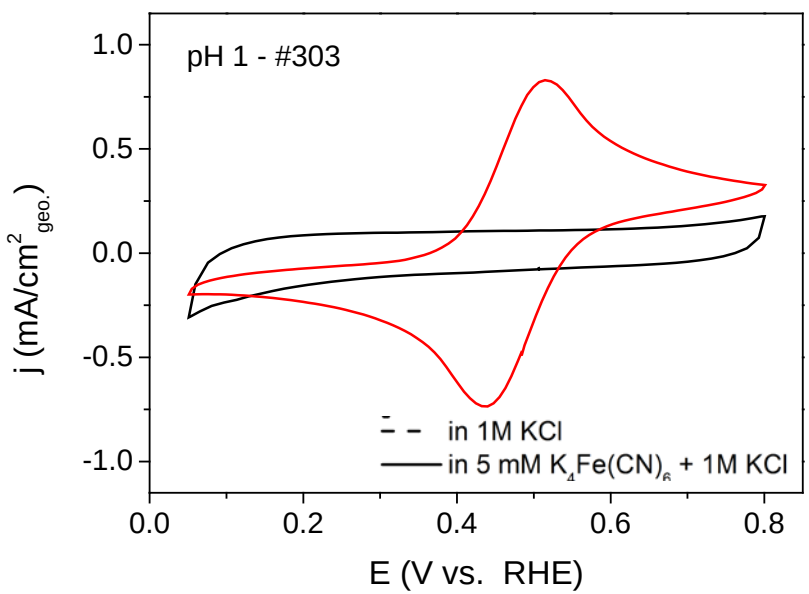


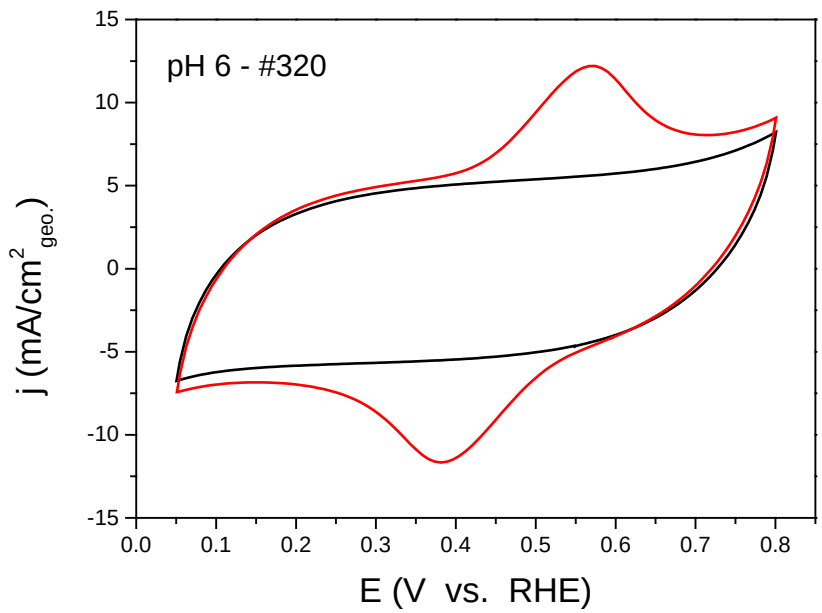


Electrode properties



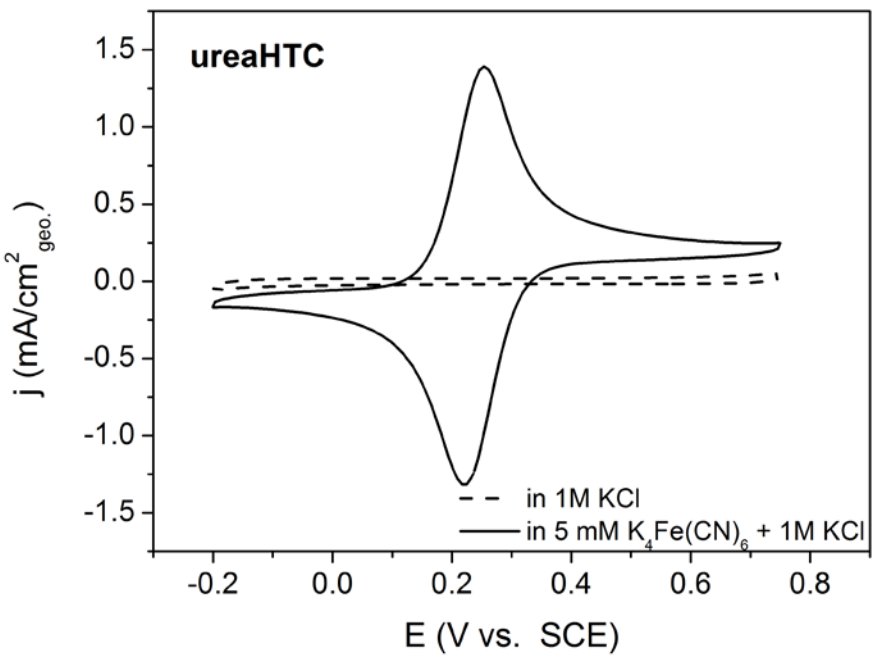
pH	ΔE_p (mV)	Capacitance (mF/cm^2)
0	63	0.09
1	75	0.42
6	179	95.7





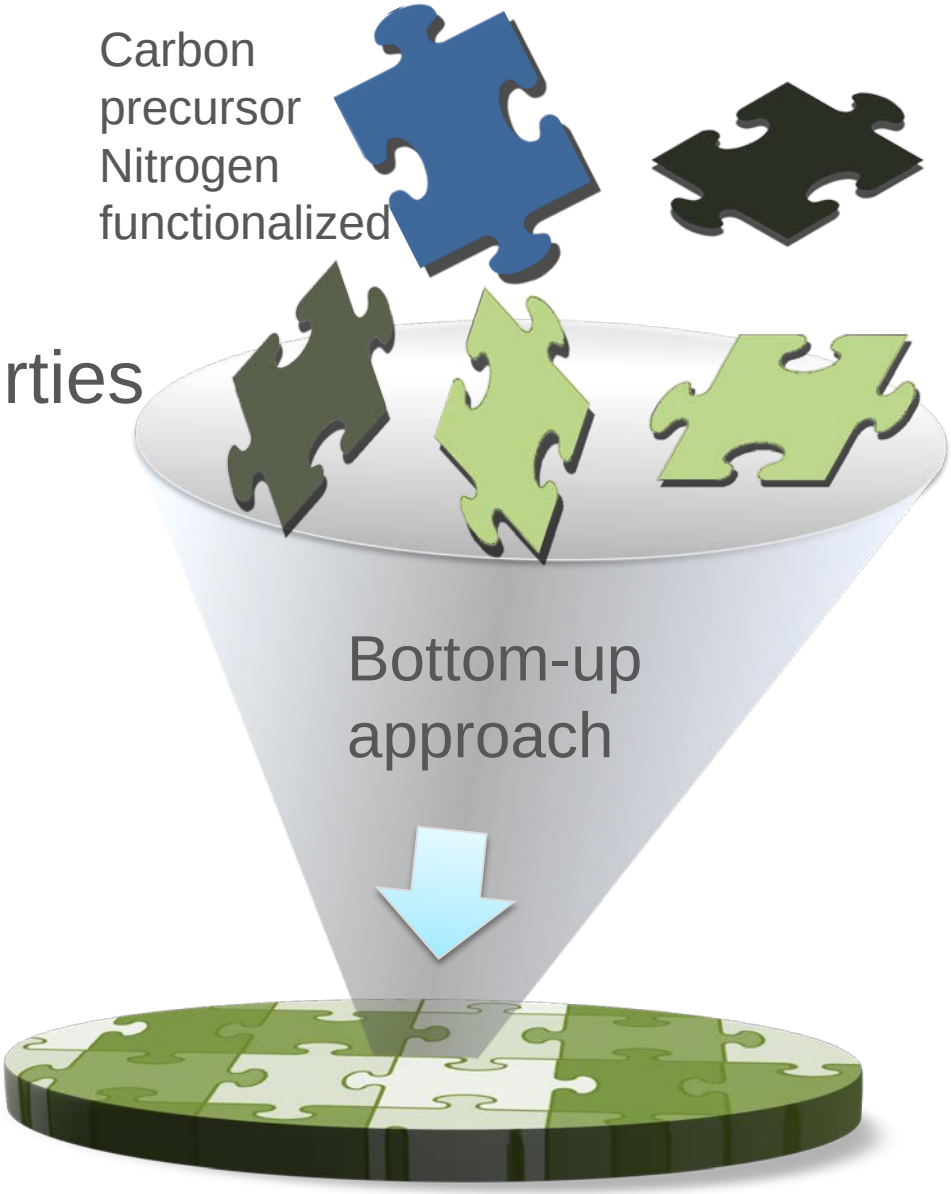
Electrode properties

Further improvement of electron transfer kinetics by N-functionalization



Hydrothermal Carbon

Tuning of electrode properties by N-functionalization

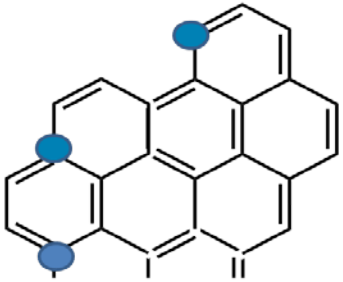


Introduction of N-functional groups

N-functionalization of hydrothermal carbon (HTC) by

Robert Rameker

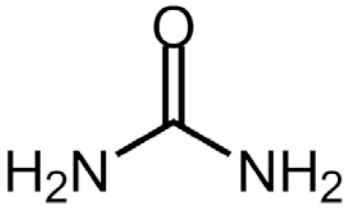
Jan Straten



Teresa Bartoldus

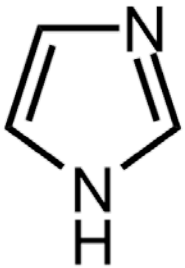
Precursor

Urea



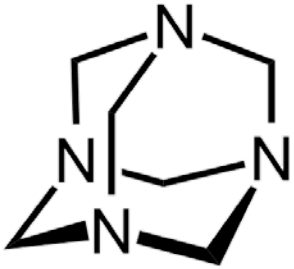
HTC_U

Imidazol



HTC_{IMI}

Urotropin



HTC_{URO}

Post-treatment

in liquid phase

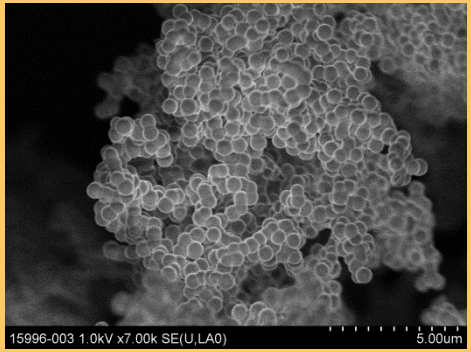
e.g. HNO_3

in gas phase

e.g. NH_3

Post-treatment of HTC synthesized at pH 3-6

pH **3** **4** **5** **6**

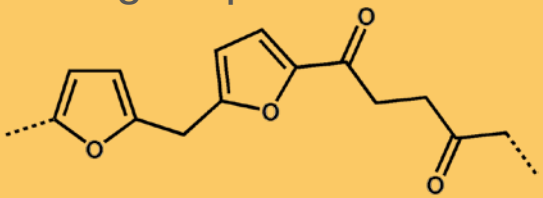


5 µm

2.5 g HTC (pH 3-6)
+ 1 mol/l HNO_3
220°C, 6 h

Sample	C [wt%]	H [wt%]	**N [wt%]**	Yield [%]
HTC (pH3)	66.5	4.0	**4.8**	65.2
HTC (pH4)	63.5	4.2	**5.3**	62.1
HTC (pH5)	62.3	4.4	**5.3**	61.6
HTC (pH6)	63.3	4.4	**5.5**	60.4

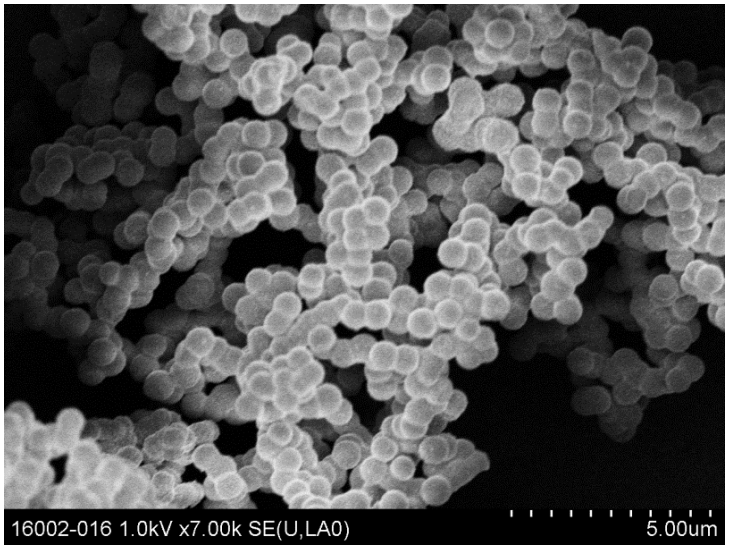
Higher pH

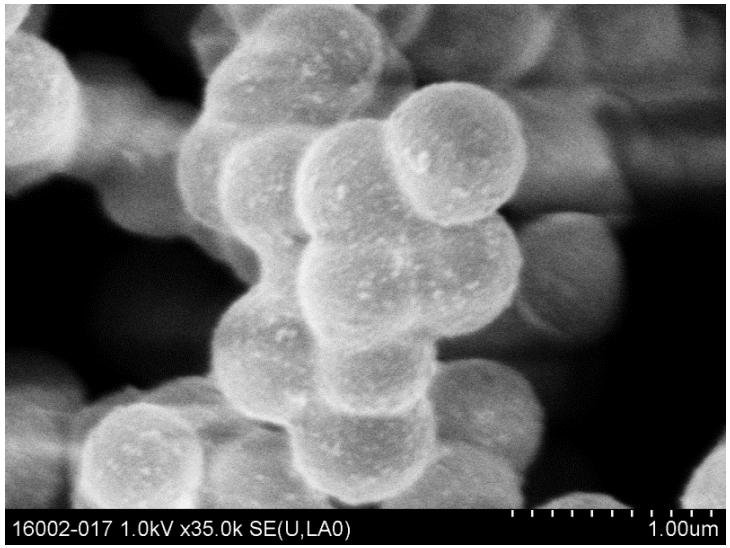


higher fraction of

Post-treatment of HTC synthesized at pH 3-6

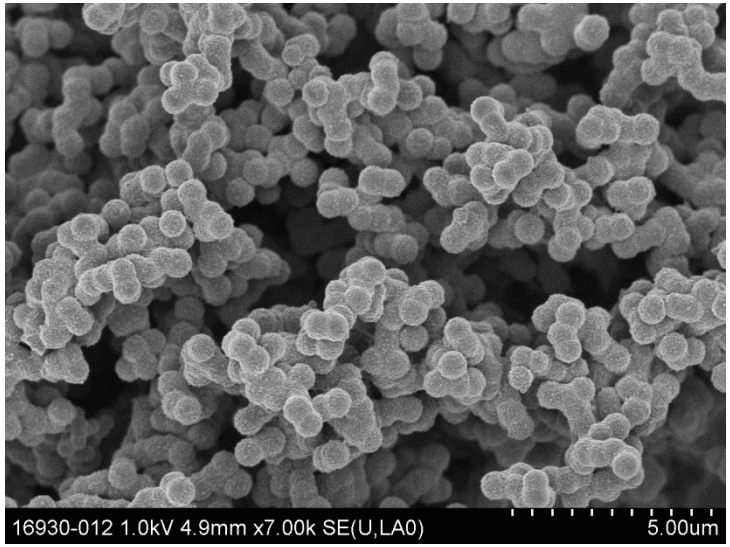
pH 3 + pH 0

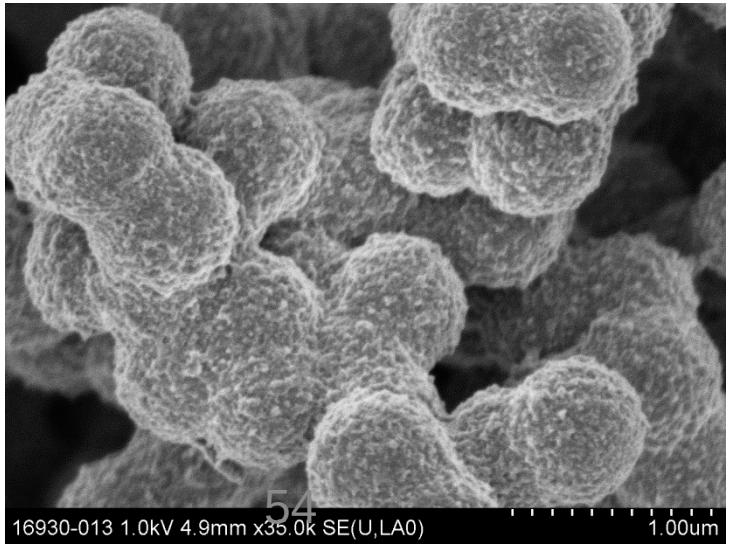




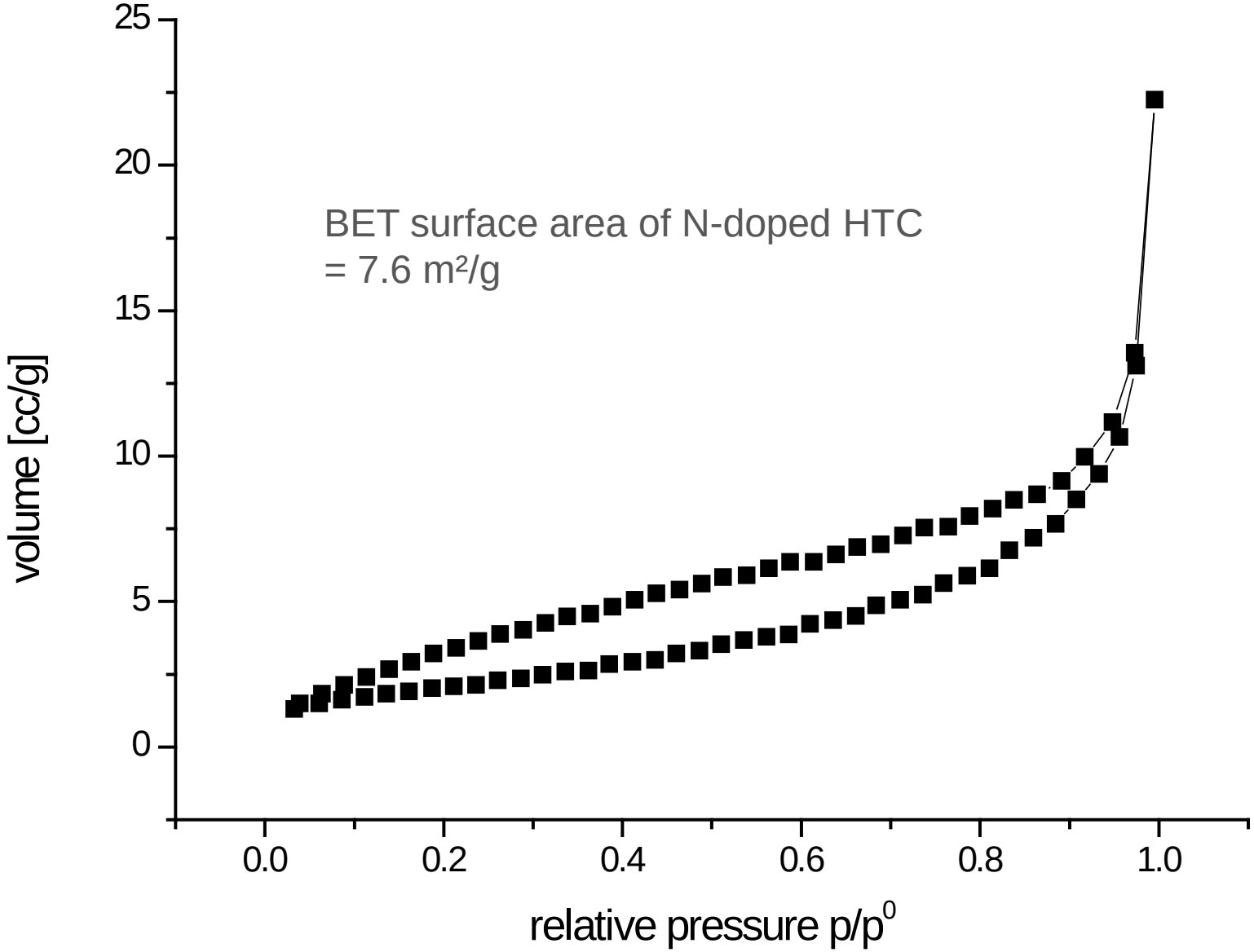
900°C
250 ml/min N_2
5 h

pH 3 + pH 0 + 900°C



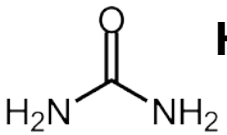


Post-treatment of HTC synthesized at pH 3-6

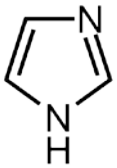


Addition of N-rich precursor

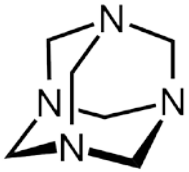
Precursor



HTC_U



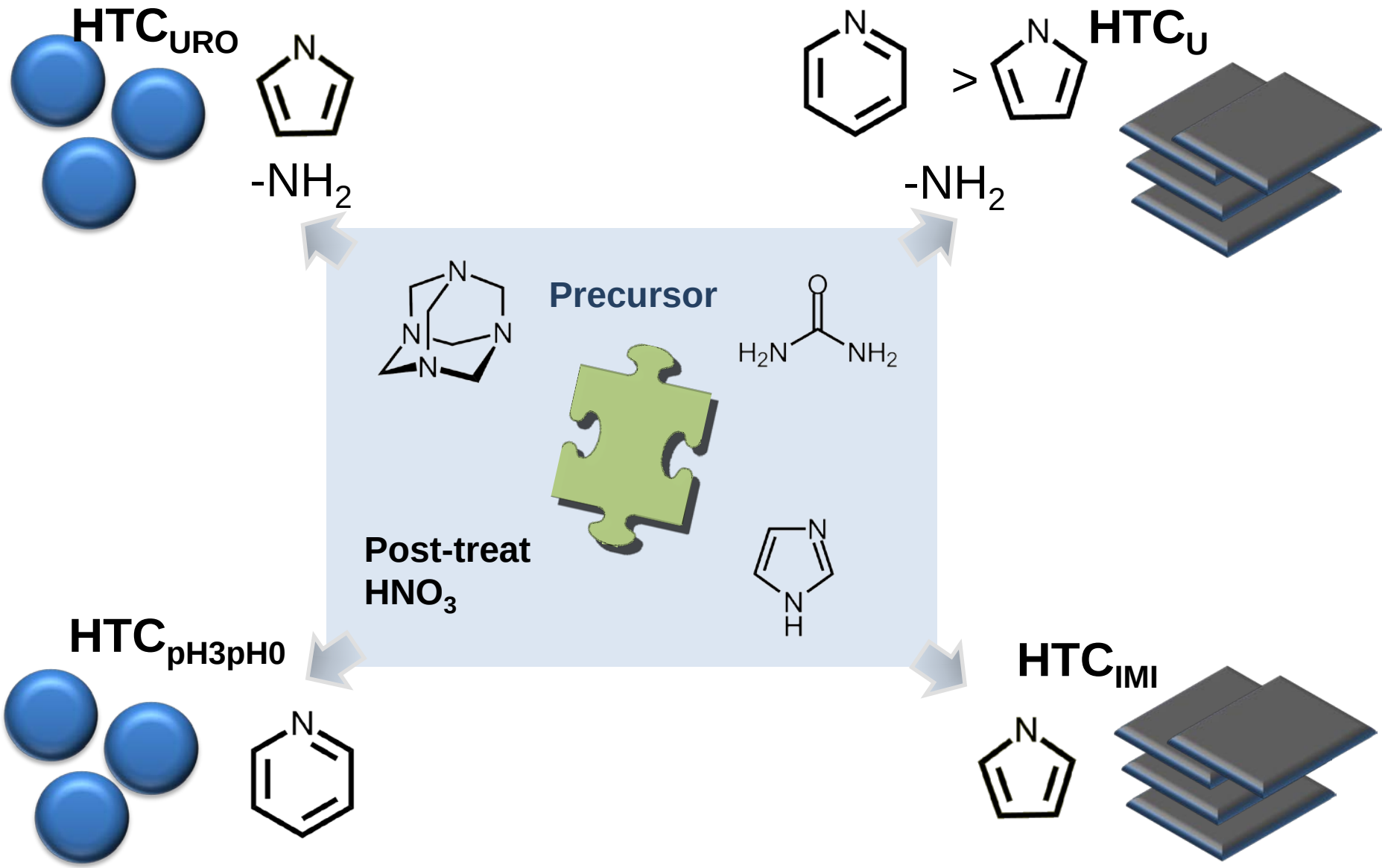
HTC_{IMI}



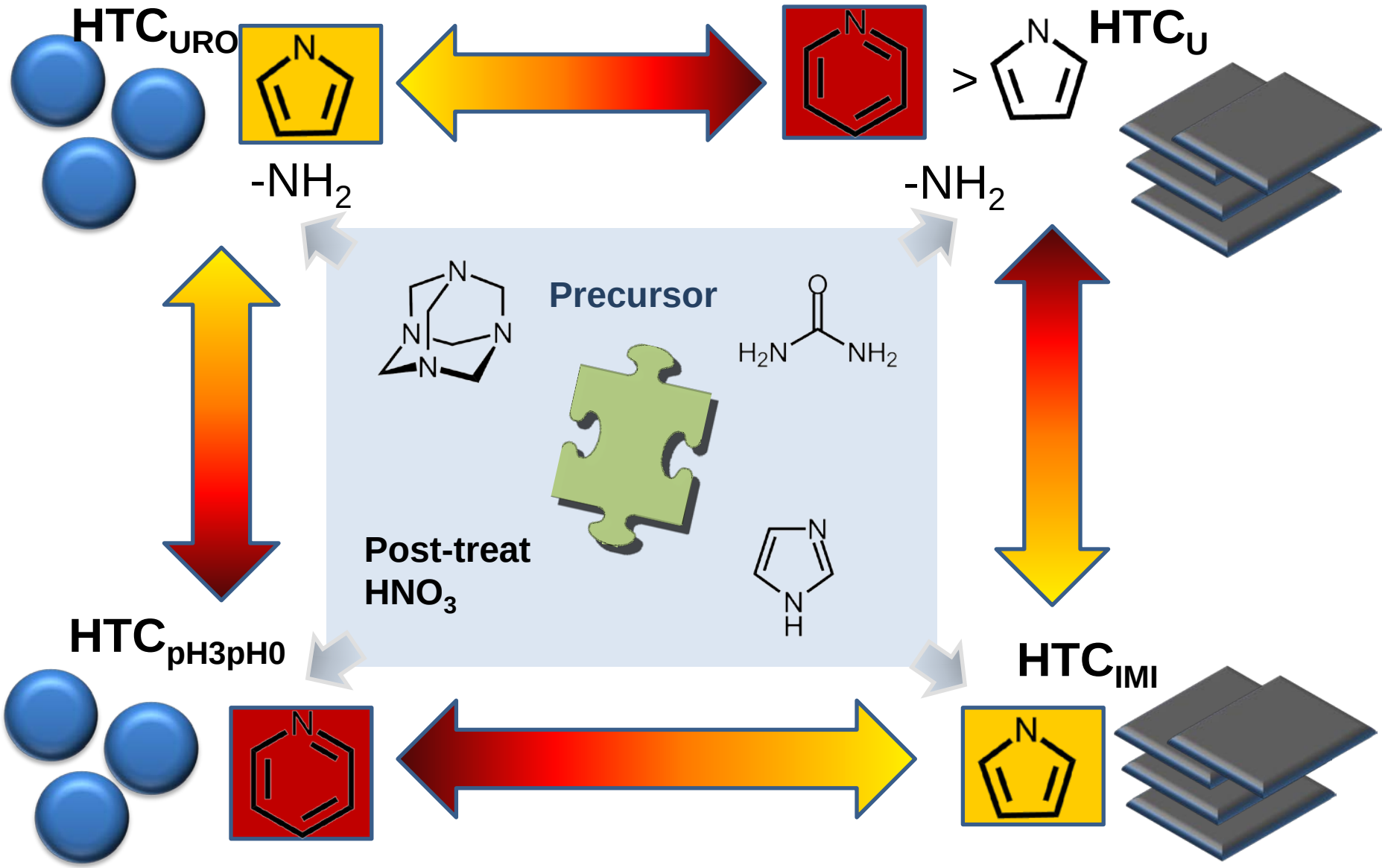
HTC_{URO}

G:U [mol]	C [wt%]	H [wt%]	**N [wt%]**	O [wt%]
HTC_U	65	5.6	**17**	13
HTC_{IMI}	70	5.6	**9.0**	16
HTC_{URO}	59	5.8	**16**	20
HTC_{pH3pH0}	67	4.0	**4.8**	24
HTC_{pH6}	68	6.3	**0**	26

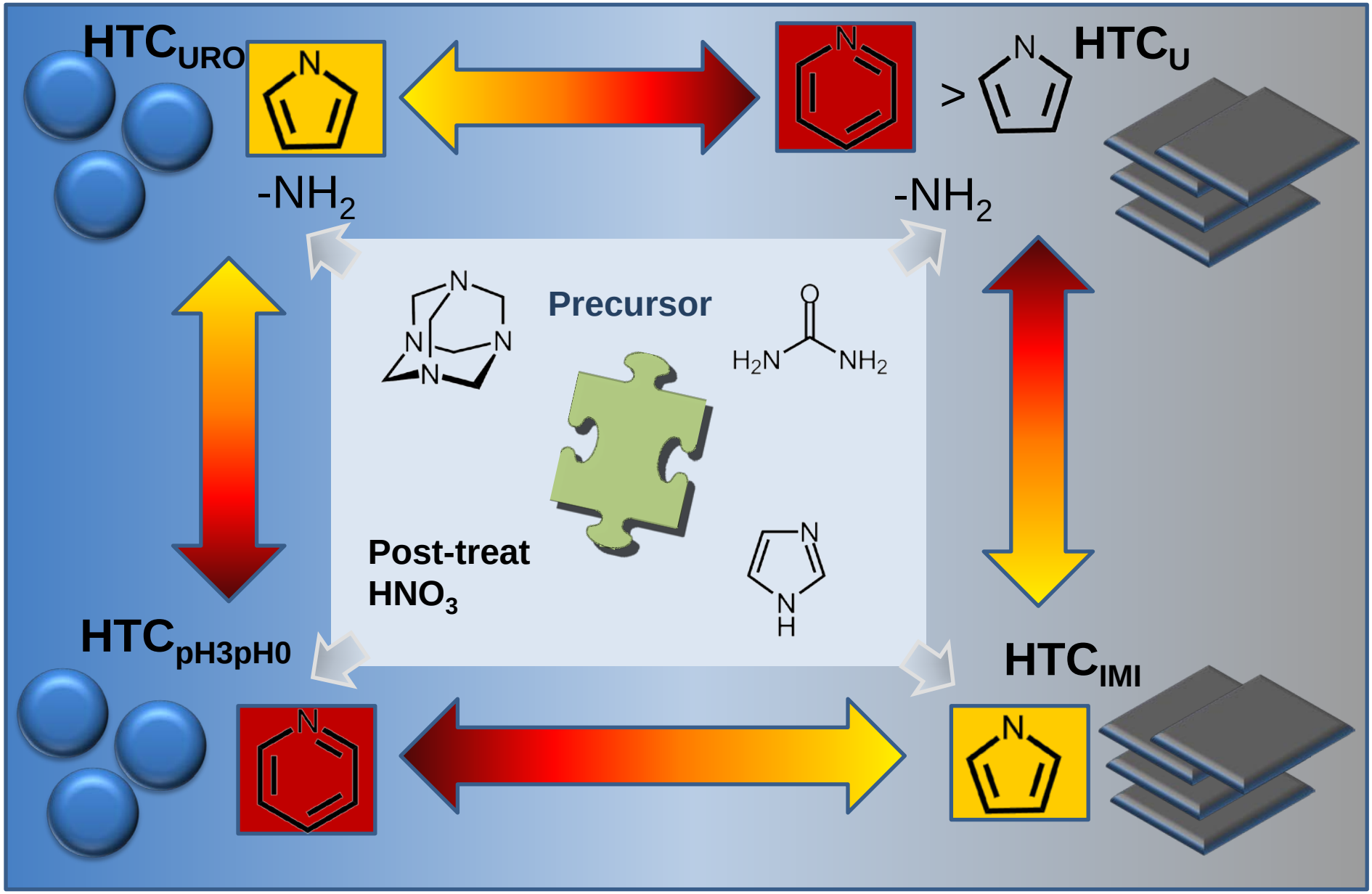
N-HTC Portfolio



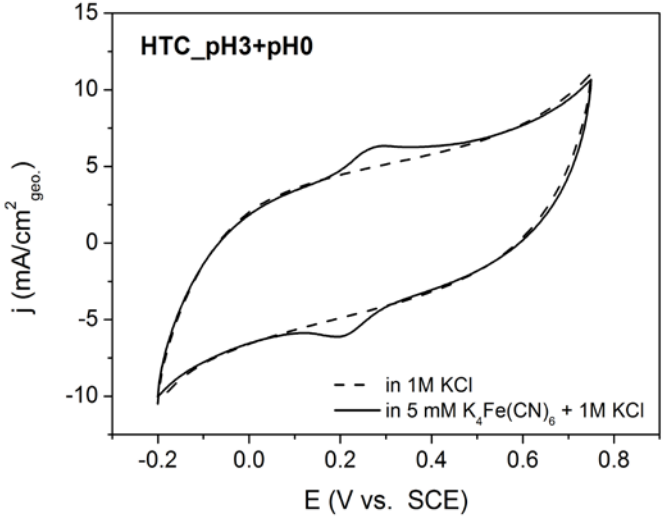
N-HTC Portfolio

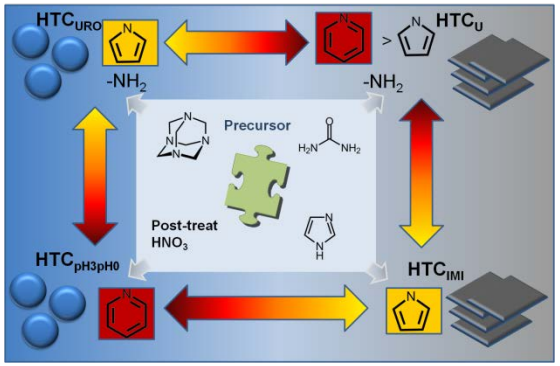


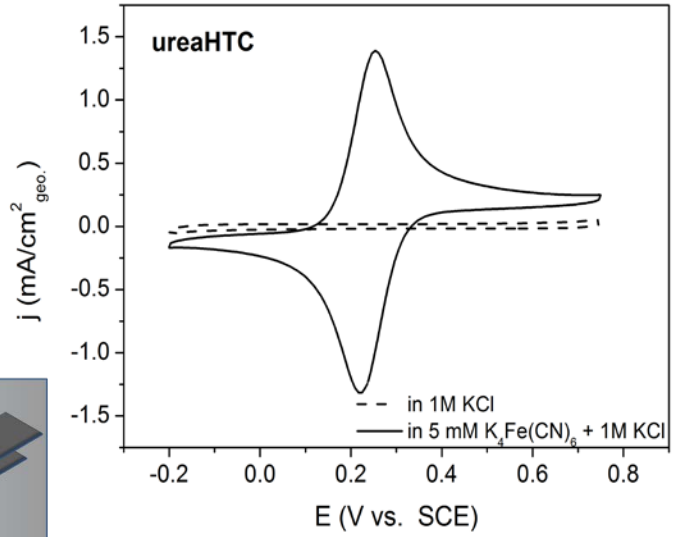
N-HTC Portfolio



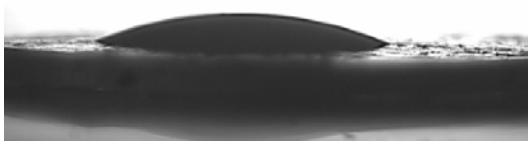
N-HTC Portfolio



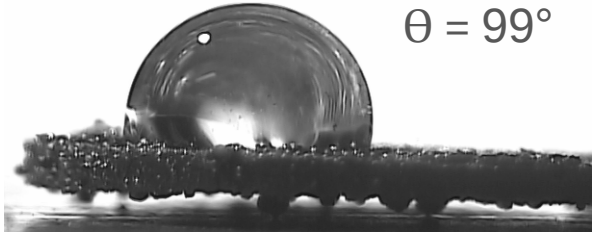




θ = 26°



θ = 99°



Conclusion

I. Background & Mission

→ 6 requirements for electrode (support) materials

II. Tuning Carbon by HTC-Process Parameters

→ Low pH-synthesis for high density and high electric conductivity

→ High pH-synthesis for small particles of higher content of –C=O for post-functionalization

III. Tuning Carbon by N-functionalization

→ improvement of electron transfer properties and conductivity

→ N-HTC portfolio for systematic study of structure reactivity relationship

Acknowledgment

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Marc Willinger FHI

Prof. Robert Schlögl

Max Planck Society

Max-Buchner-Forschungsstiftung

Thank you very much for your kind attention

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