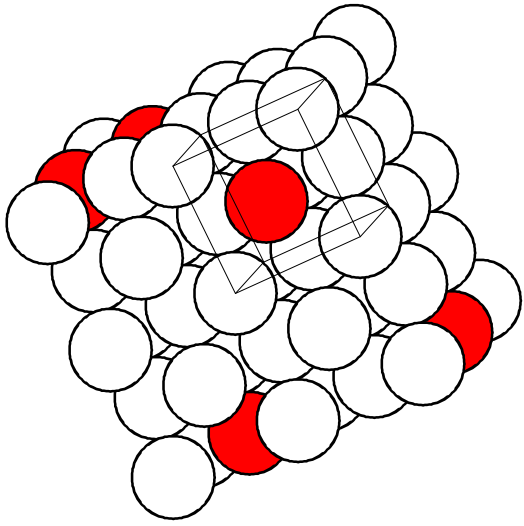


The vapour-solid approach towards controlled synthesis of intermetallic nanoparticles

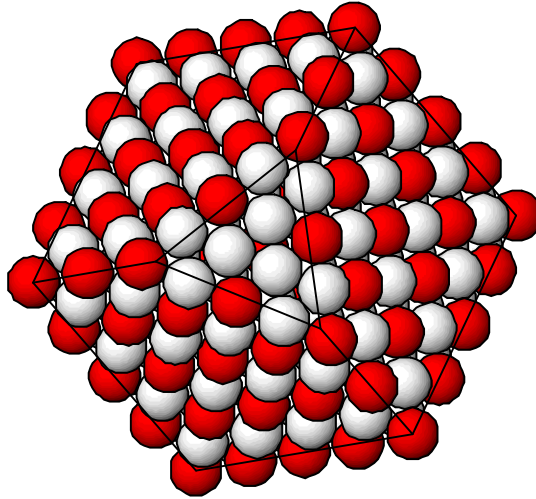
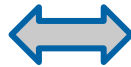
Klaus W. Richter , TOFA 2026, Bled, Slovenia



Why intermetallic nanoparticles?



Solid Solutions



Intermetallics

fundamental as well as application-related
interest for intermetallic nanoparticles

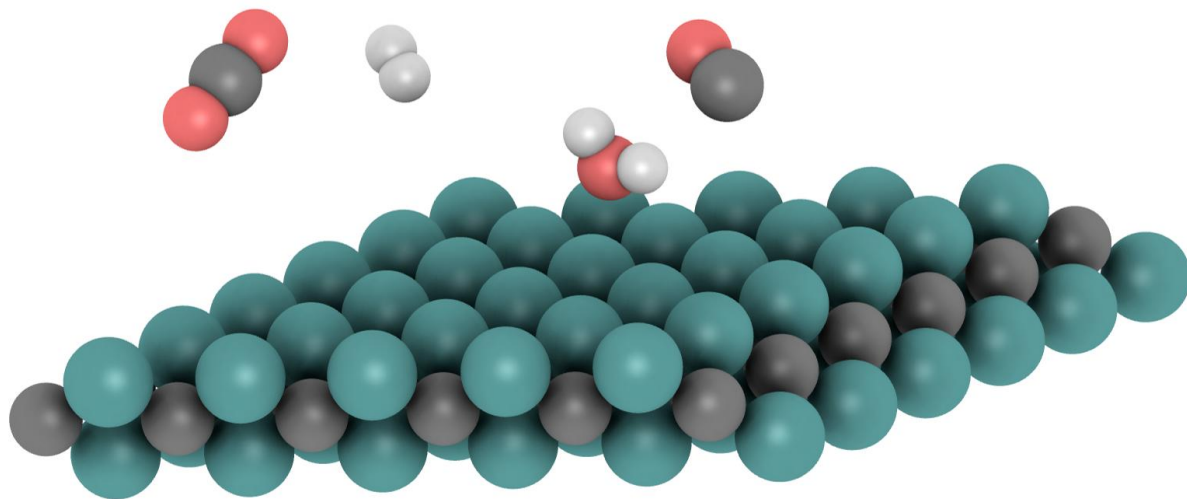


heterogeneous catalysis
as major topic

Important requirements for catalysts

- high catalytic activity
- high selectivity for the reaction
- low cost
- high stability under reaction conditions

Intermetallics in catalysis



Major strategies for catalyst improvement

- geometric effect (site isolation)
- ligand effect (electronic structure)
- support effect (triple phase boundary)
- conductivity (electrocatalysis)



> 30000 Intermetallics with > 1500 different structure types offer a large playground

Synthesis of intermetallic nanoparticles – a challenge

Synthetic goals:

- Controlled size & size distribution
- Controlled composition & crystal structure
- Clean and Scalable
- Controlled shape



Challenge:

Established routes for monometallic or randomly alloyed NPs are solution based and kinetically controlled.

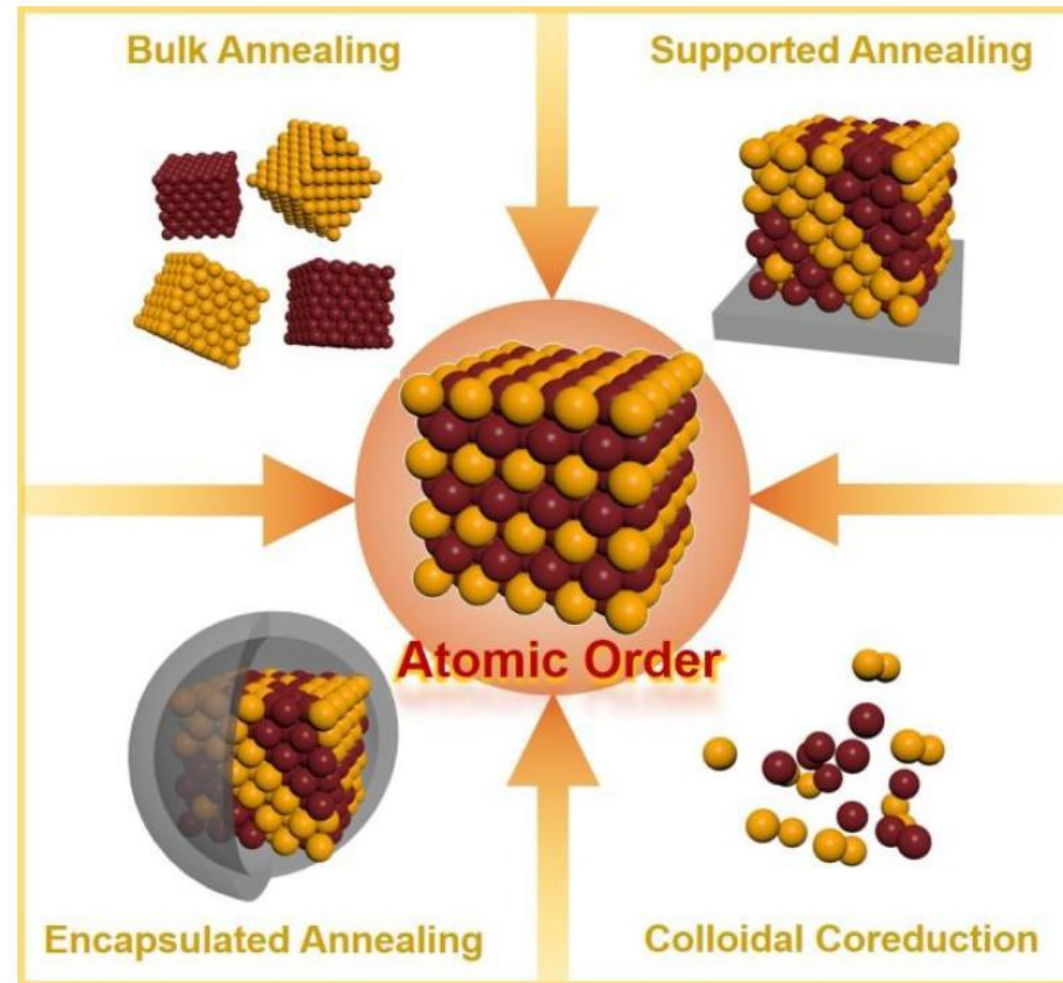
Intermetallic NPs usually need annealing

Much room for new synthetic concepts

Synthetic concepts: an overview

- + plain & easy
- + composition control
- surface area
- shape control

- + stable surrounding
- + shape control
- scalability
- difficult to realize

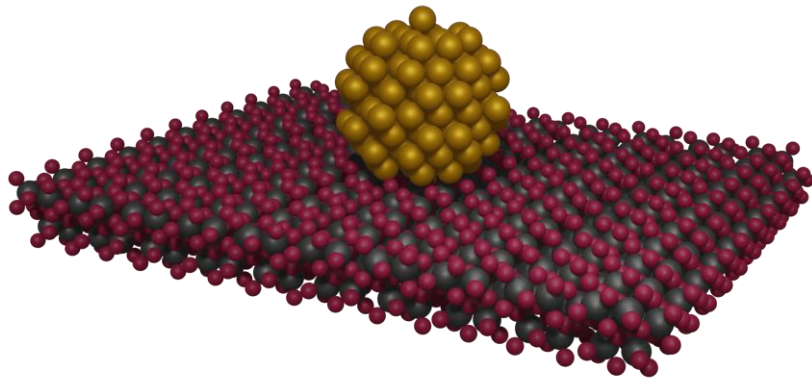


- + clean
- + size control
- + scalable
- shape control

- + broadly applicable
- + shape control
- surface contamination
- composition control

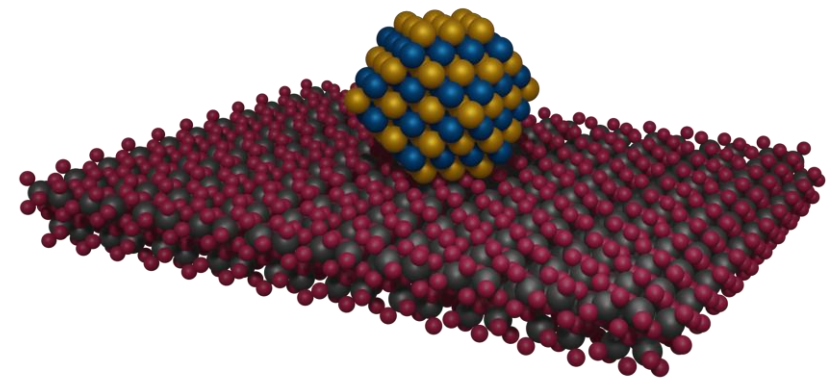
A new approach: the vapour-solid synthesis

- Direct interaction of supported, metallic nanoparticles with the vapour of a more volatile element
- Clean: no additives needed, simplest possible chemistry
- Plain process, (near) equilibrium
- High composition control & size control



monometallic supported nanoparticle

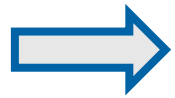
Vapour of the second
element



intermetallic supported nanoparticle

A first attempt in Di Salvo's group

- Unsupported and supported Pt-nanoparticles reacted with Zn vapor to PtZn
- Zn(g)/Ar flow over crucible / 500°C

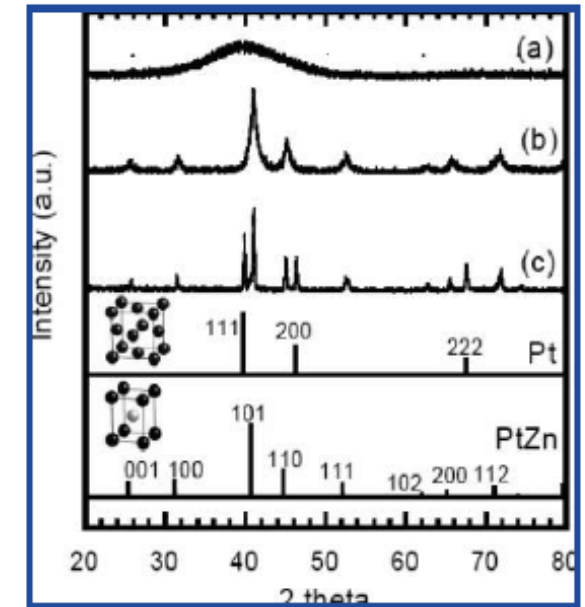
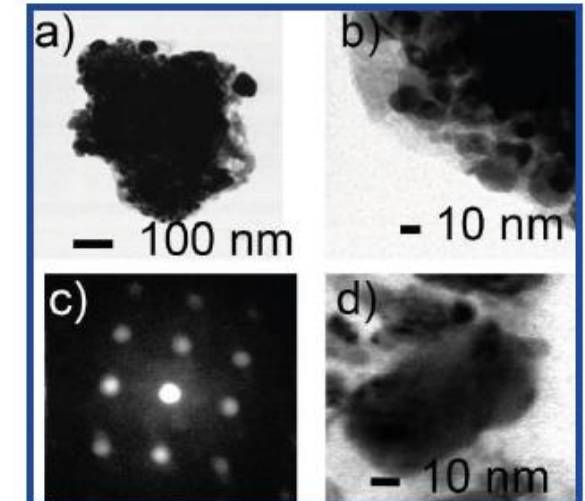


Conversion reached,
but sintering and limited composition control
No follow-up study

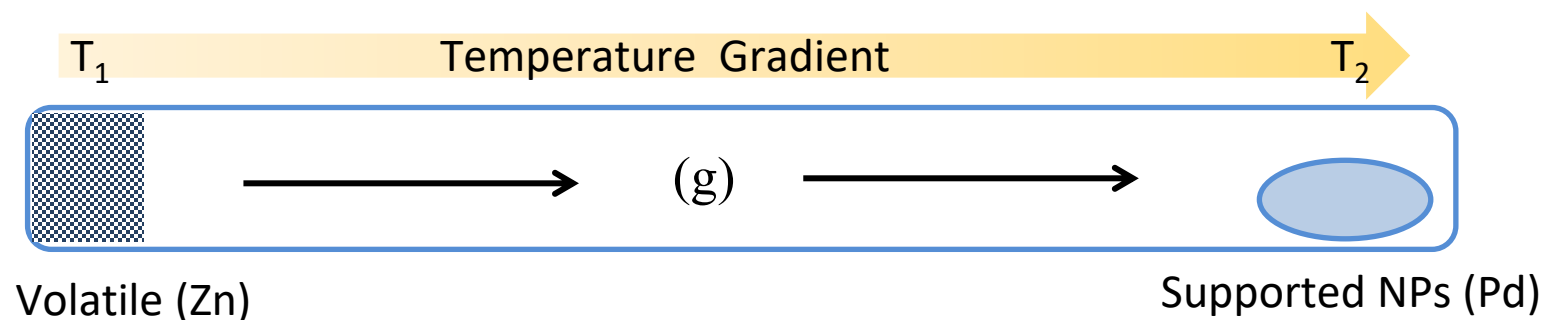
Project to improve the method for supported NPs:

initial cleaning step * closed reaction setup

use of temperature gradient * optimize steering of process



Why using a temperature gradient?



Steering of the reaction

Thermodynamics

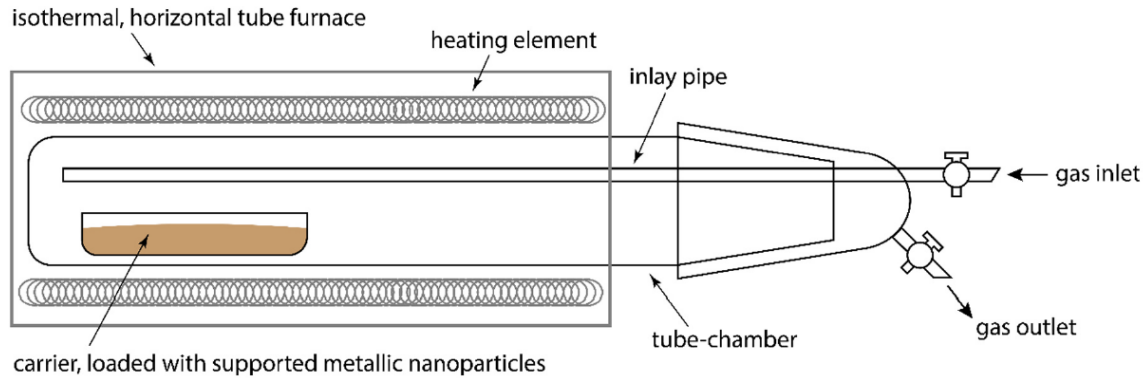
equilibration
surplus of volatile (reservoir)
gradient fixed
needs thermodynamic data

$$a_{\text{Zn}}(T_2) = p_{\text{Zn}}(T_2)/p_{\text{Zn}}^0(T_2) = p_{\text{Zn}}^0(T_1)/p_{\text{Zn}}^0(T_2)$$

Stoichiometry

mass balance
controlled amount of volatile
gradient flexible
control of reaction speed

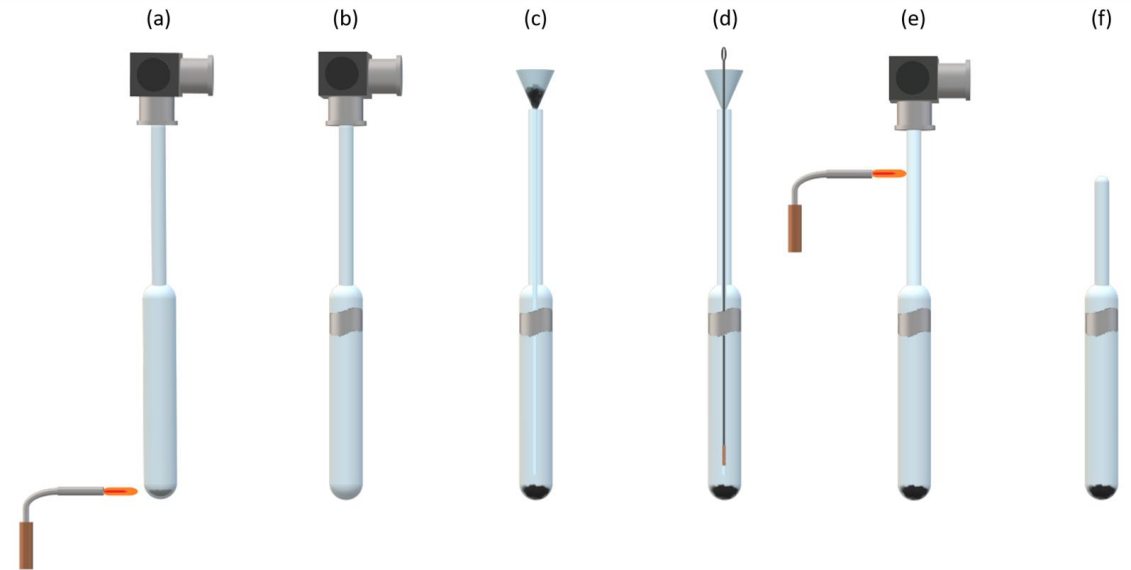
Vapour-solid approach: pre-treatment



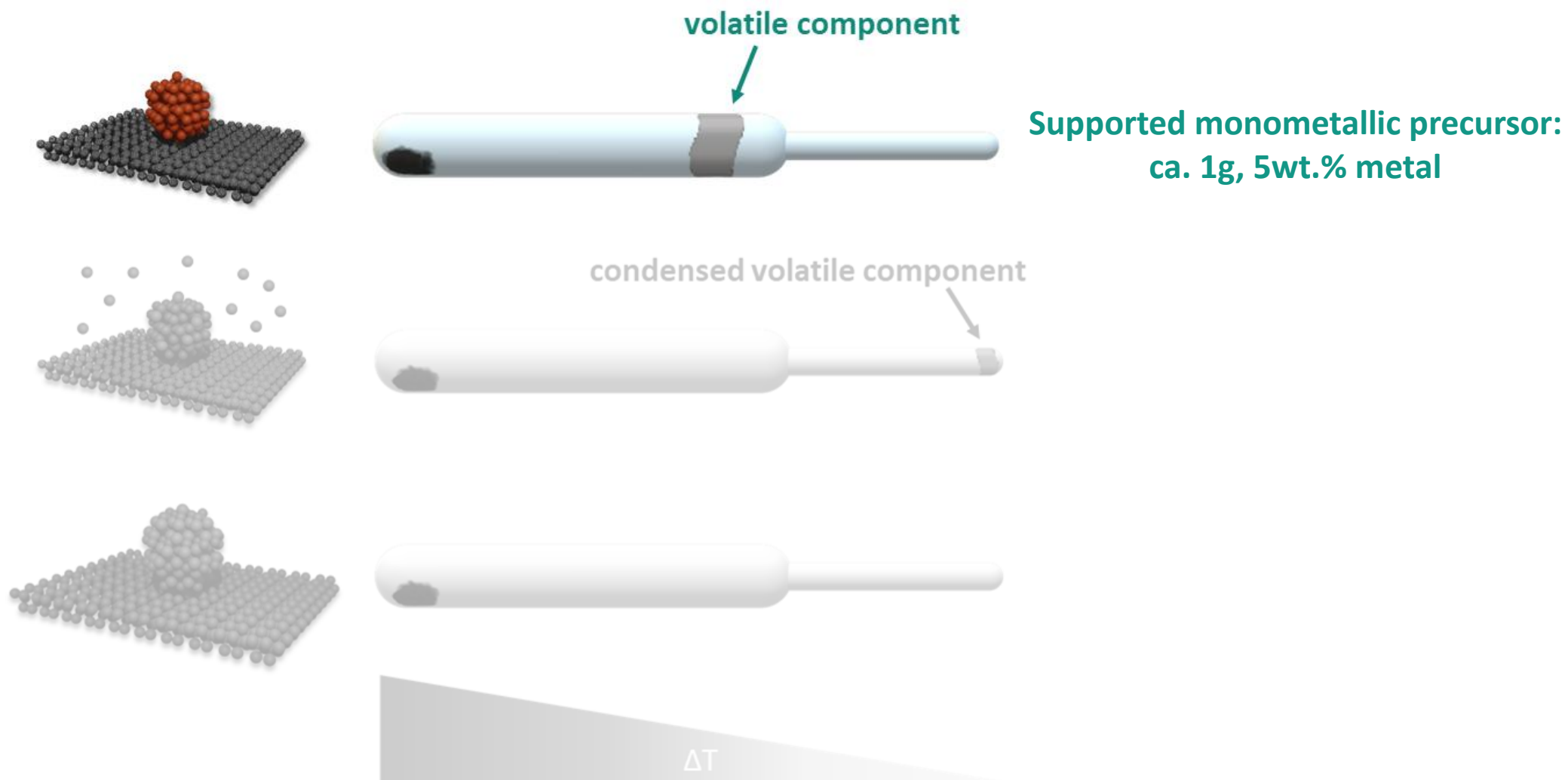
1. Reduction with Ar/5
2. Evacuation and de-ga
3. Storage and handling in a Glove-Box



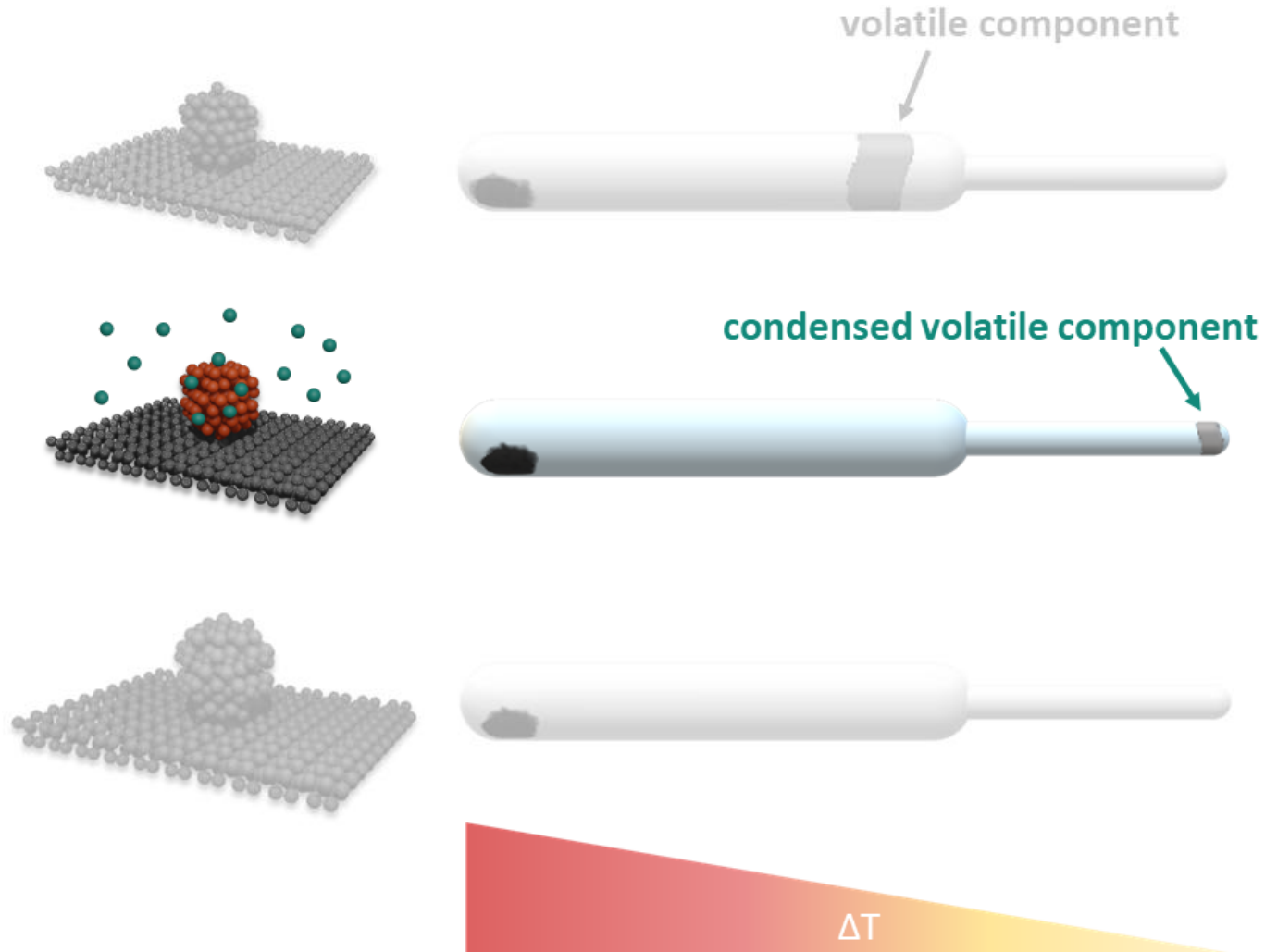
- a) Evaporation of the volatile component under vacuum
- b) Condensation of a mirror
- c) Addition of supported NPs (Glovebox)
- d) Cleaning of funnel
- e) Sealing of quartz glass container



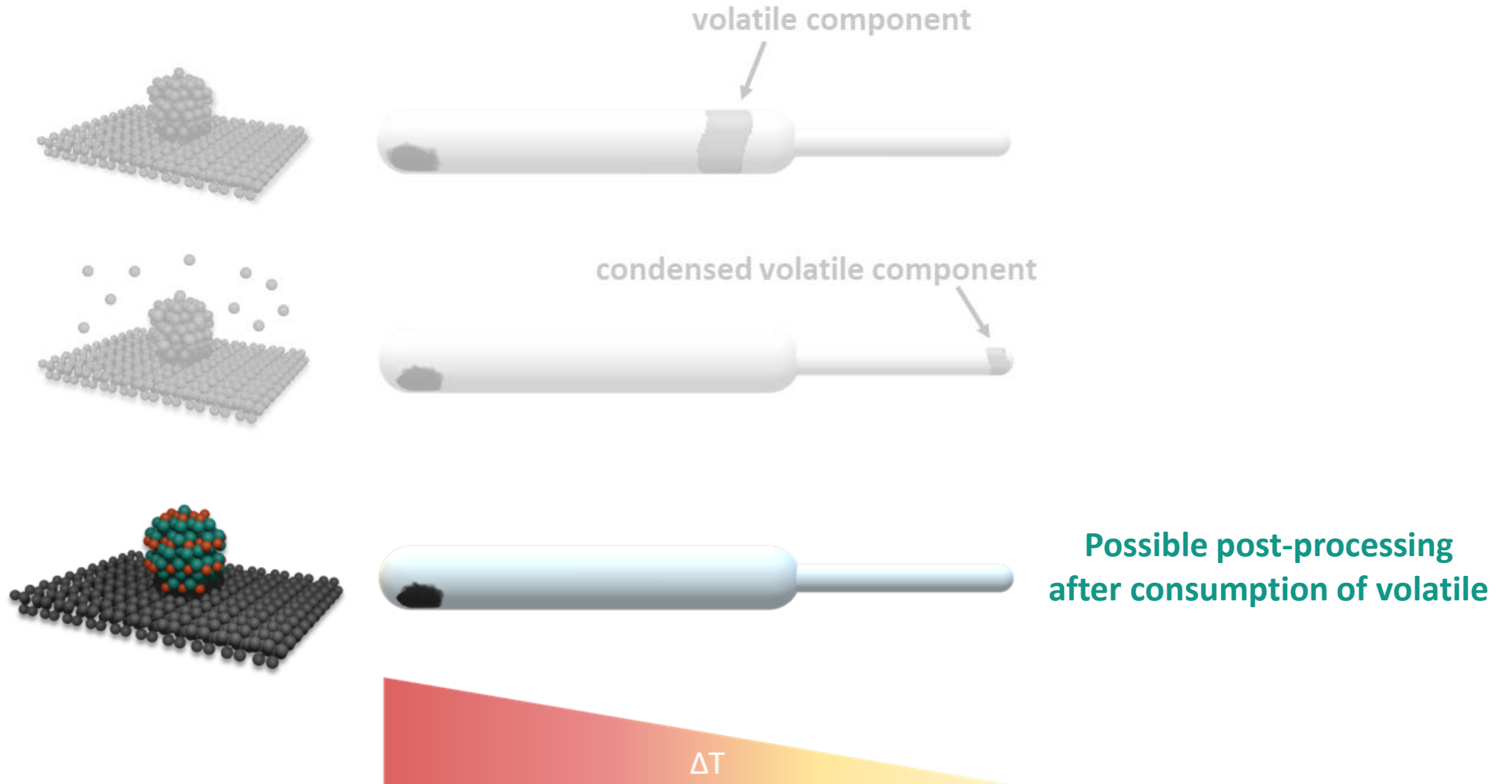
Vapour-solid approach – synthesis steps



Vapour-solid approach – synthesis steps



Vapour-solid approach – synthesis steps



Characterization & testing

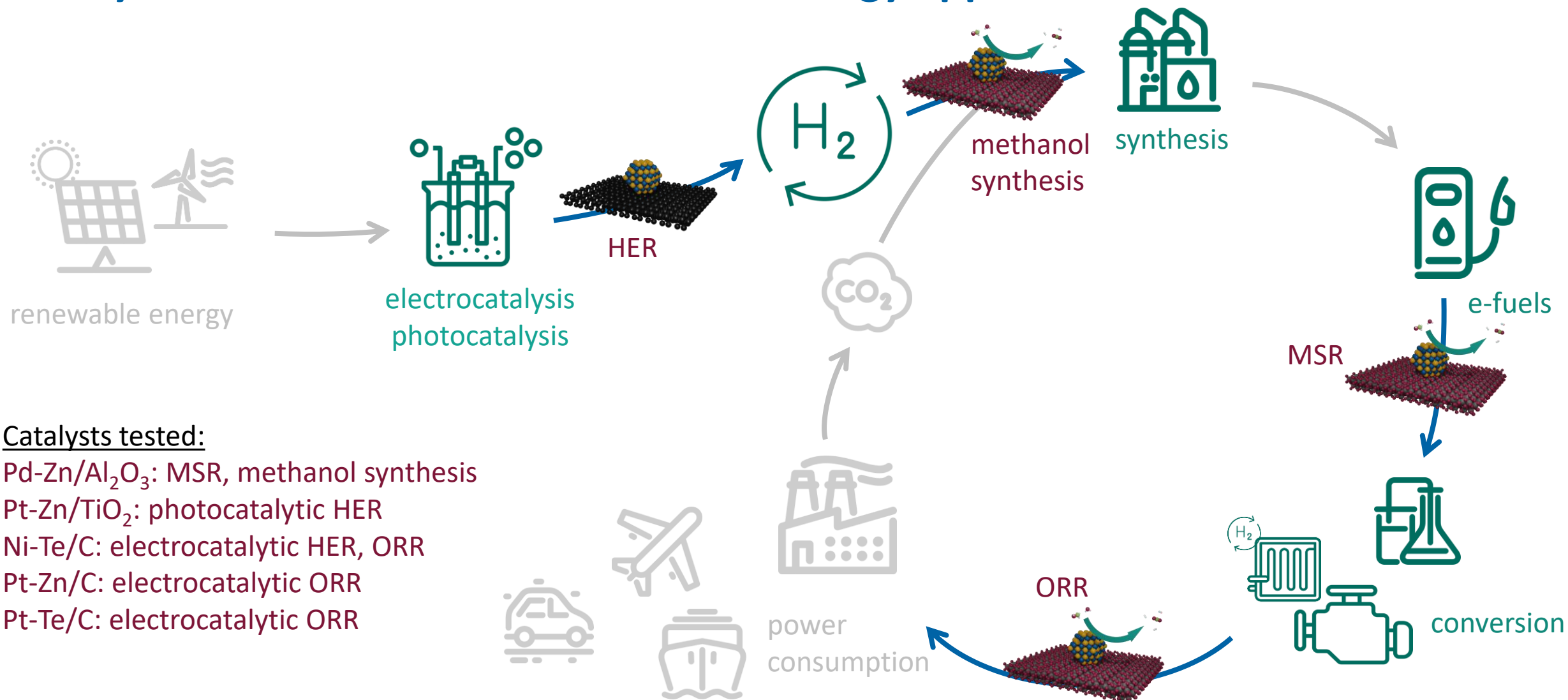
Characterization:

- Composition: ICP/OES, TXRF
- Crystal Structure: Powder XRD
- Particle Size, microstructure: TEM, PXRD
- Surface Structure: XPS, Auger
- Porosity/Support: Physisorption
- Local coordination XAS
- Catalytic tests: gas-flow, photocatalysis, electrocatalysis

Systems:

- Pd-Zn/ Al_2O_3
- Pt-Zn/ TiO_2
- Ni-P/ Al_2O_3
- Ni-Te/C
- Pt-Zn/C
- Pd-Zn/C
- Pt-Te/C

Catalytic reactions tested: sustainable energy applications



Catalysts tested:

Pd-Zn/ Al_2O_3 : MSR, methanol synthesis

Pt-Zn/ TiO_2 : photocatalytic HER

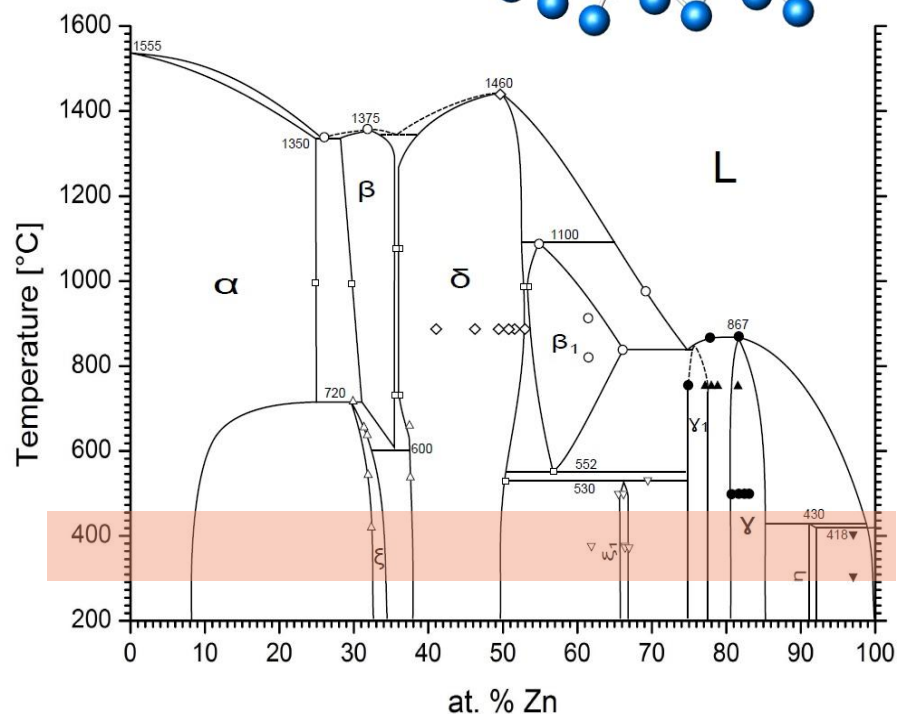
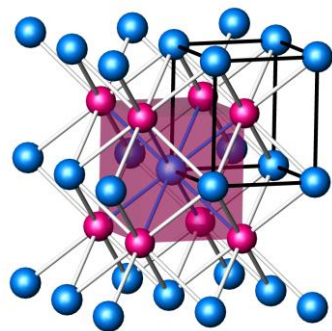
Ni-Te/C: electrocatalytic HER, ORR

Pt-Zn/C: electrocatalytic ORR

Pt-Te/C: electrocatalytic ORR

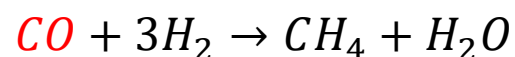
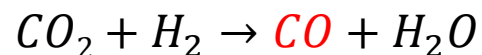
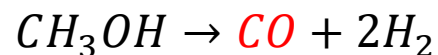
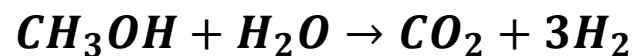
Pd-Zn/Al₂O₃: Methanol Steam Reforming

PdZn:
AuCu-type, P4/mmm
c/a = 1.16 at 1:1 ratio



Cooperation with Marc Armbrüster
TU Chemnitz / TU Darmstadt

PdZn as highly selective catalyst in MSR:



Methanol Steam Reforming

Methanol Decomposition

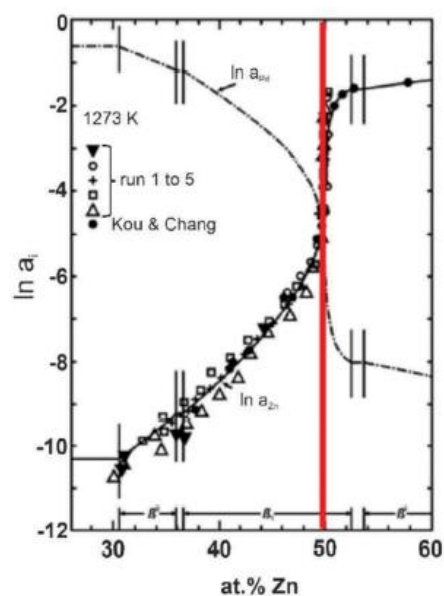
reverse Watergas Shift Reaction

Methanization

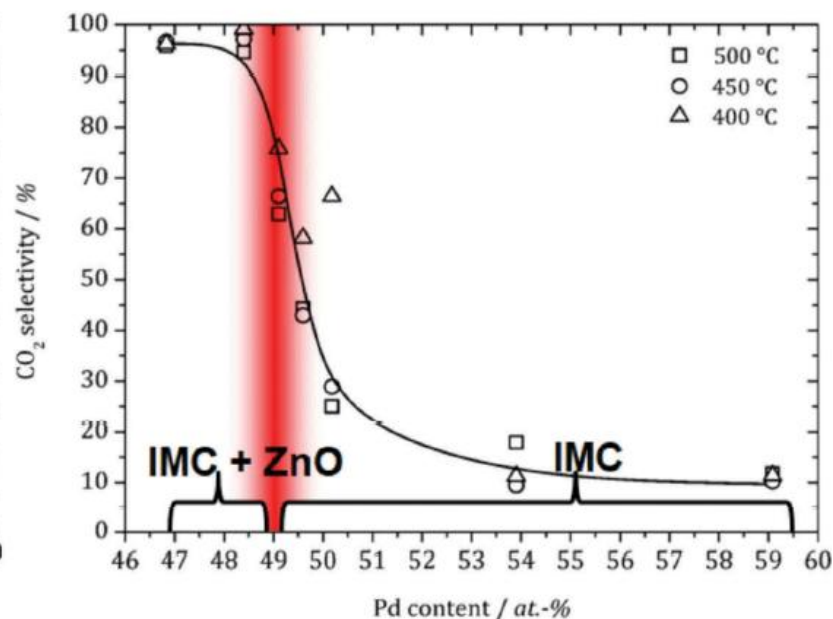


CO₂ / CO selectivity needed!

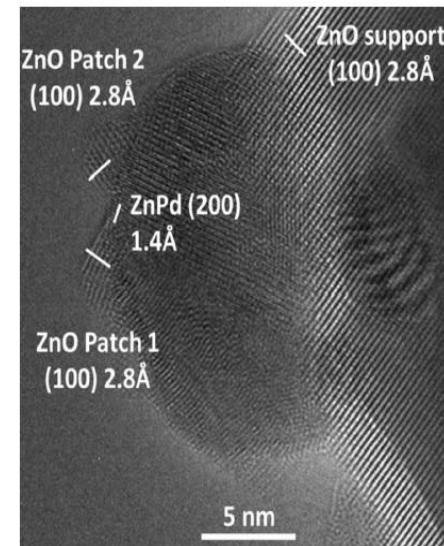
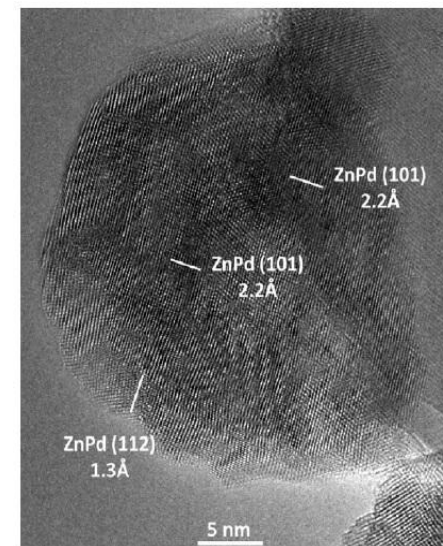
Pd-Zn/ Al_2O_3 : CO_2 -Selectivity and Composition



Thermodynamic activity of Zn in PdZn studied by isopiestic experiments



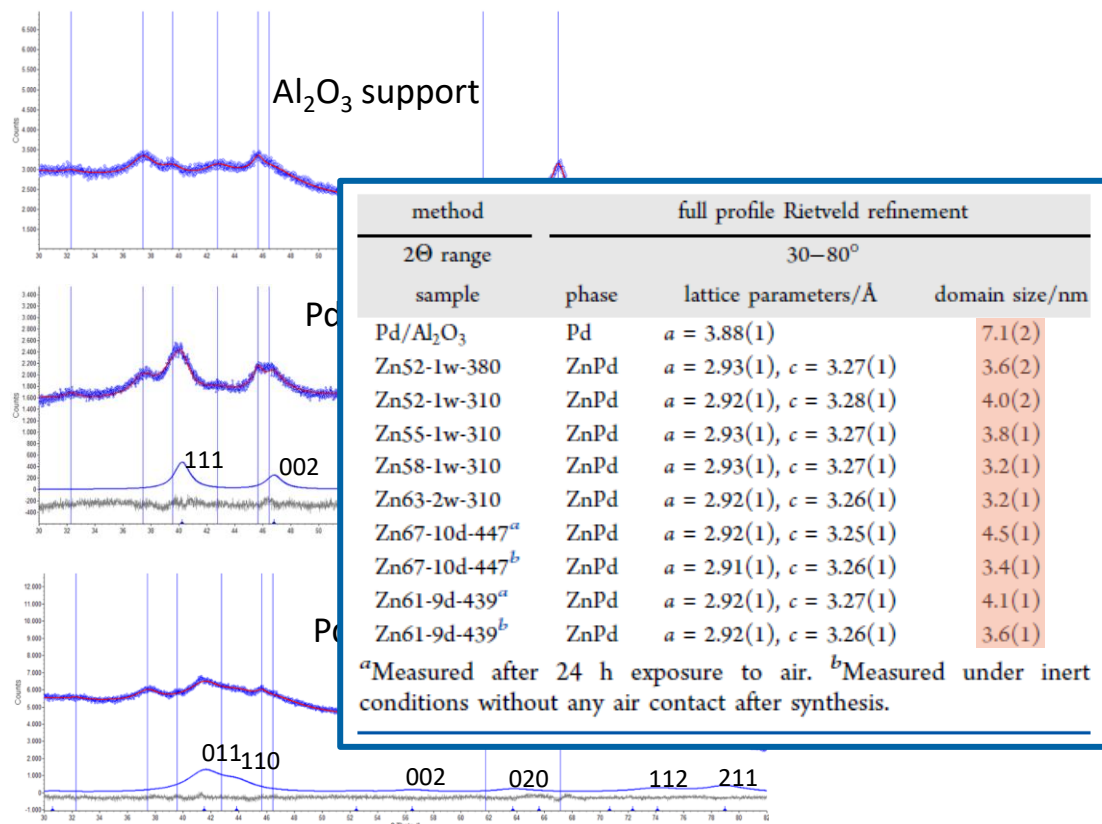
CO_2 selectivity studied from bulk-annealed samples



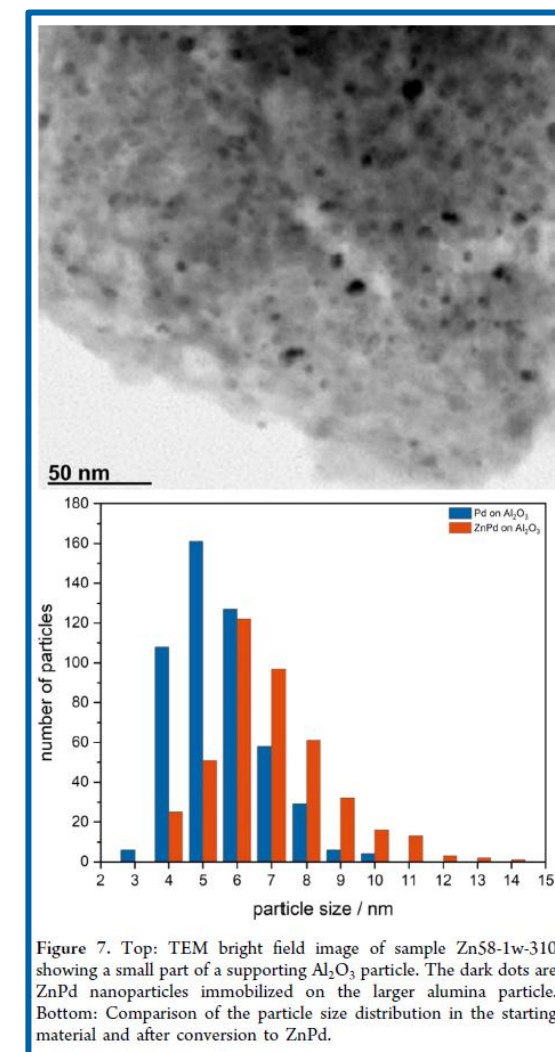
Formation of ZnO domains on PdZn nanoparticles under MSR conditions

Pd-Zn/Al₂O₃: synthesis, structure, composition

- > 20 samples prepared for testing synthesis conditions
- use of 5 wt.% Pd/Al₂O₃ (Sigma Aldrich)



- PdZn found in Samples up to 67 at% Zn
- No other crystalline Intermetallics visible
- PdZn₂-lines not detectable and/or different features of the nano-phase diagram
- PRXD suggests crystalline subdomains
- TEM confirms stable nanoparticle arrangement (no coagulation)

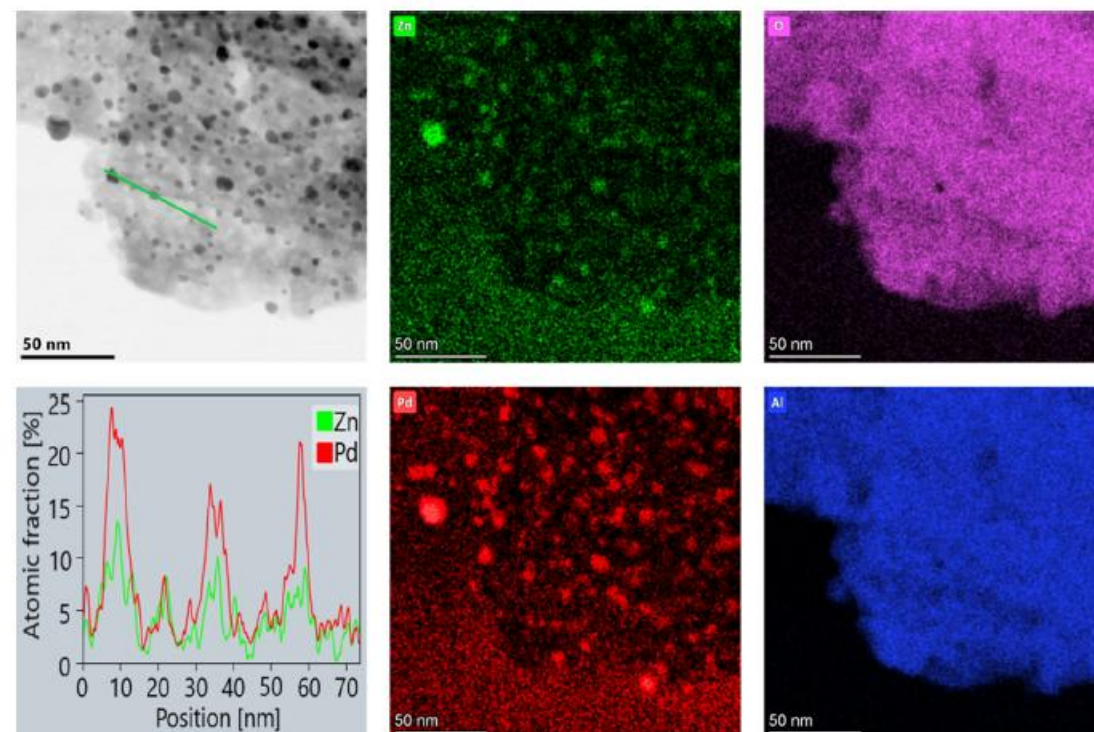


Pd-Zn/Al₂O₃: synthesis, structure, composition

- Chemical analysis confirms reasonable agreement with expected composition
- HAADF-STEM confirms (exclusive) reaction of Zn with Pd-nanoparticles

sample	expected composition		ICP-OES analysis	
	Pd	Zn	Pd	Zn
Pd/Al ₂ O ₃	5		4.8	
Zn53-4h-450 ^a	47	53	50.5	49.5
Zn64-8h-450 ^a	36	64	40.2	59.8
Zn53-18h-450	47	53	47.4	52.6
Zn52-1w-380	48	52	49.0	51.0
Zn52-1w-310	48	52	46.5	53.5
Zn55-1w-310 ^a	45	55	42.5	57.5
Zn58-1w-310	42	58	47.4	52.6
Zn63-2w-310	37	63	38.2	61.8
Zn59-2w-310	41	59	40.7	59.3

^aTraces of ZnO visible on the tube walls after the reaction.



Pd-Zn/ Al_2O_3 : Thermodynamics of supported nanoparticles

- Thermodynamic activity of Zn determined by re-condensation (dew point method)
- Successive lowering of sink temperature T1 until re-condensation of Zn is observed

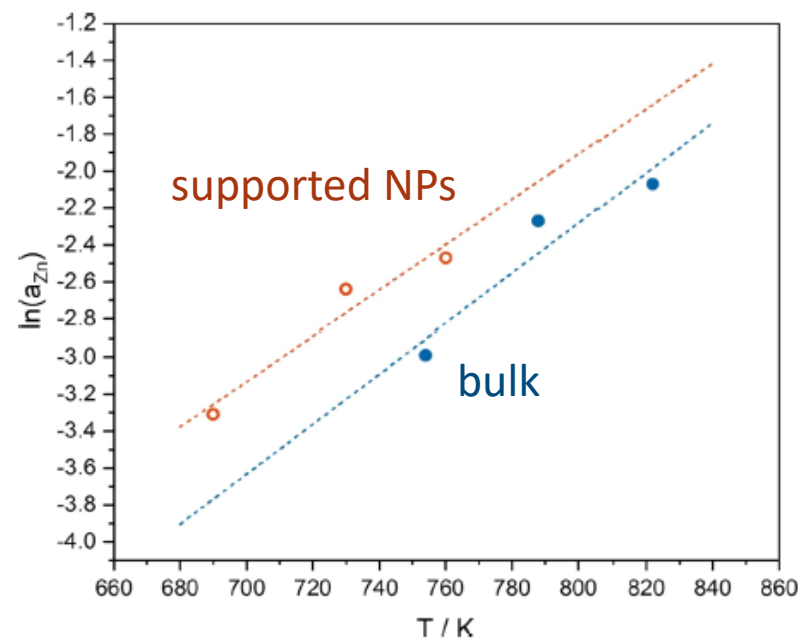
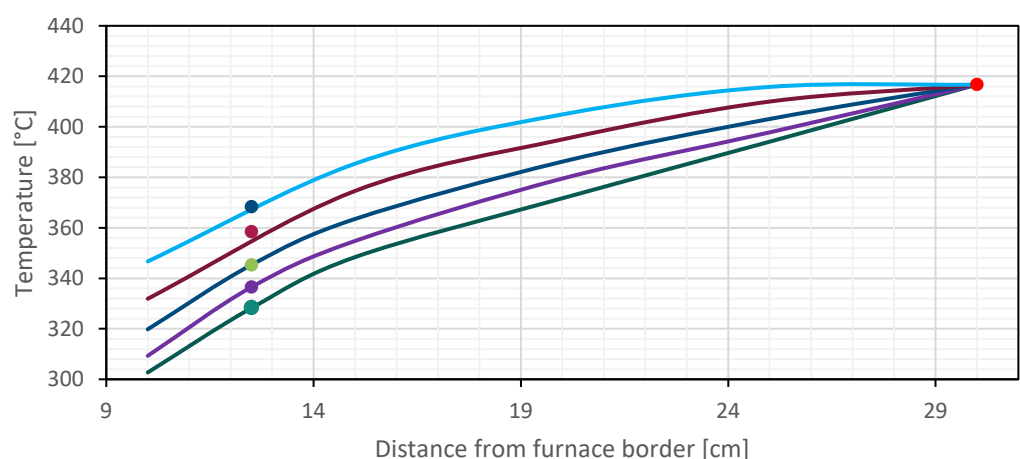
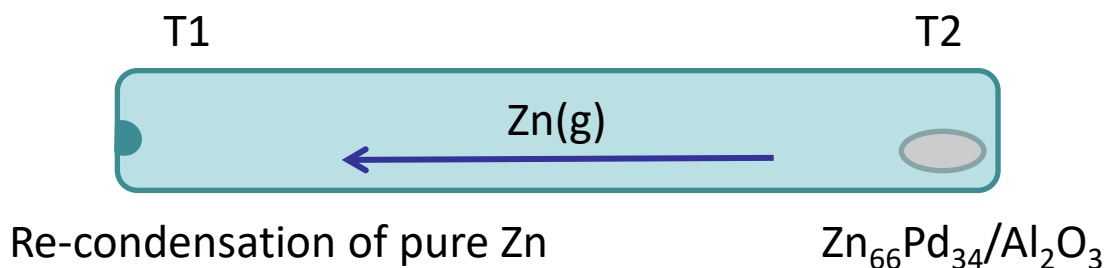
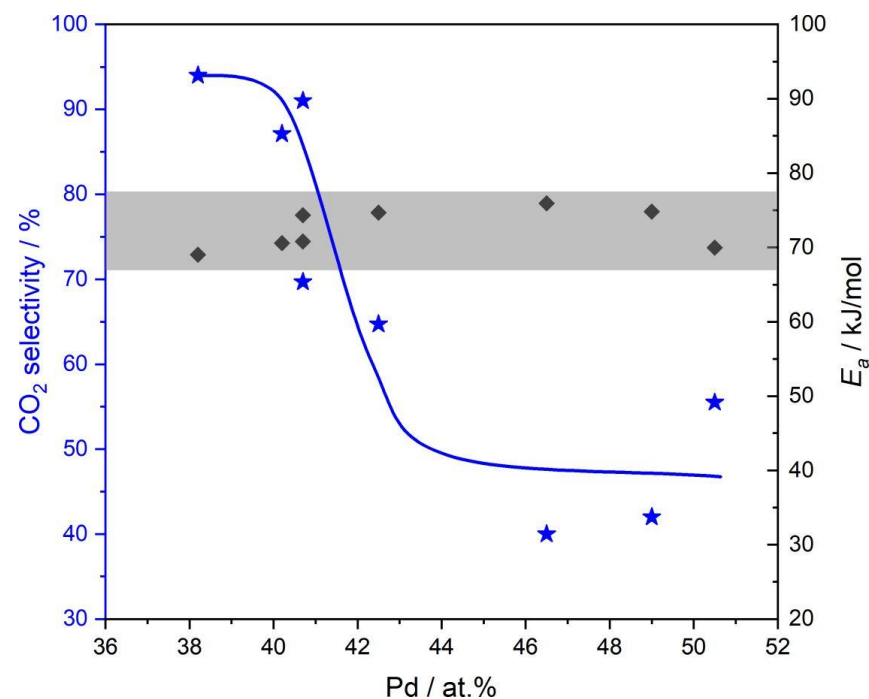


Figure 4. Zinc activity at the Zn-rich phase boundary of ZnPd for bulk alloys according to Chiang et al.²⁹ (blue full circles) and for ZnPd/ Al_2O_3 nanoparticles according to this work (orange open circles). Trendlines are a guide for the eye.

Pd-Zn/Al₂O₃ in MSR: catalytic performance

- Gas flow reactor, 150-300°C cycling, carrier gas He, GC for monitoring



Sample	Reference	Activity [mol (H ₂)/(mol (Pd) × h)]	CO ₂ selectivity [%]
Zn53-4h-450	this work	2880	55.5
Zn64-8h-450	this work	2766	87.1
Zn52-1w-380	this work	1046	42.0
Zn52-1w-310	this work	1327	40.0
Zn55-1w-310	this work	1632	64.7
Zn63-2w-310	this work	7202	94.0
Zn59-2w-310	this work	7352	91.0
Zn59-2w-418	this work	3517	69.7
Zn _{53.2} Pd _{46.8}	[33]	1.8	98
CuO/ZnO/Al ₂ O ₃	[35]	425	98
ZnPd/ZnO	[30]	310	96
5 wt.% Pd/Al ₂ O ₃	[34]	1850	2
ZnPd/ZnO aerogel	[34]	1540	96



High selectivity, unmatched activity

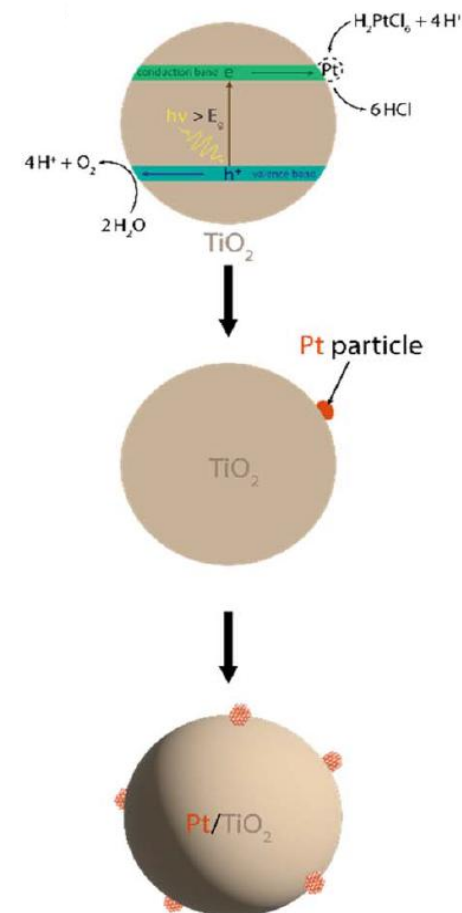
Pt-Zn/TiO₂: photocatalytic hydrogen evolution reaction

photocatalytic water splitting:

- direct use of solar energy under mild conditions
- suffers from poor efficiency & scalability
- use of ceramic materials in combination with co-catalysts

Cooperation with TU Wien, Alexej Cherevan:

Active site engineering of 1wt.% Pt/TiO₂ (prepared by in situ photoreduction) using vapour-solid synthesis with Zn as volatile component



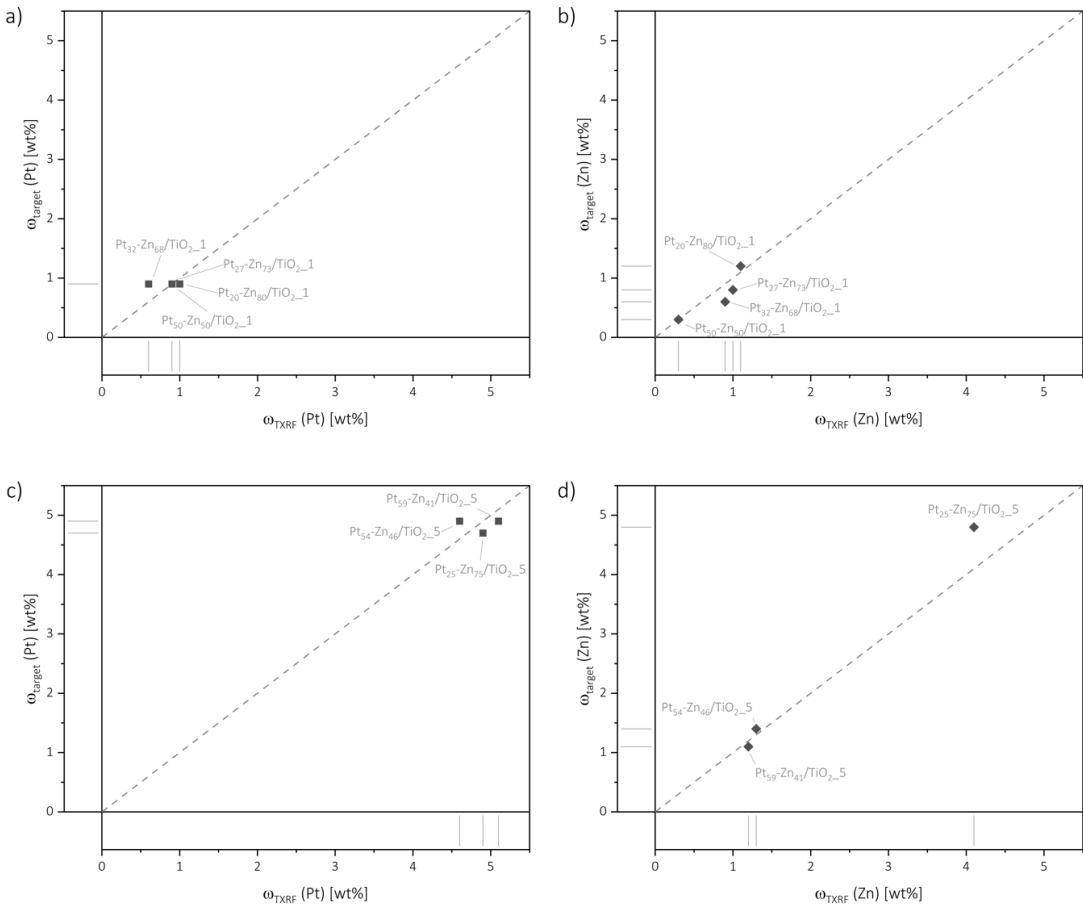
Pt-Zn/TiO₂: synthesis

1 wt.% Pt: catalytic testing

5 wt.% Pt: better analysis (PXRD, TXRF, etc)

Table 1 TXRF data based on the total catalyst mass

Sample	ω_{TXRF} (Pt) [wt%]	ω_{target} (Pt) [wt%]	ω_{TXRF} (Zn) [wt%]	ω_{target} (Zn) [wt%]
Pt/TiO ₂ _5	5.0	5.0	—	—
Pt ₅₉ -Zn ₄₁ /TiO ₂ _5	5.1	4.9	1.2	1.1
Pt ₅₄ -Zn ₄₆ /TiO ₂ _5	4.6	4.9	1.3	1.4
Pt ₂₅ -Zn ₇₅ /TiO ₂ _5	4.9	4.7	4.1	4.8
Pt/TiO ₂ _1	0.9	1.0	—	—
Pt ₅₀ -Zn ₅₀ /TiO ₂ _1	0.9	0.9	0.3	0.3
Pt ₃₂ -Zn ₆₈ /TiO ₂ _1	0.6	0.9	0.9	0.6
Pt ₂₇ -Zn ₇₃ /TiO ₂ _1	0.9	0.9	1.0	0.8
Pt ₂₀ -Zn ₈₀ /TiO ₂ _1	1.0	0.9	1.1	1.2

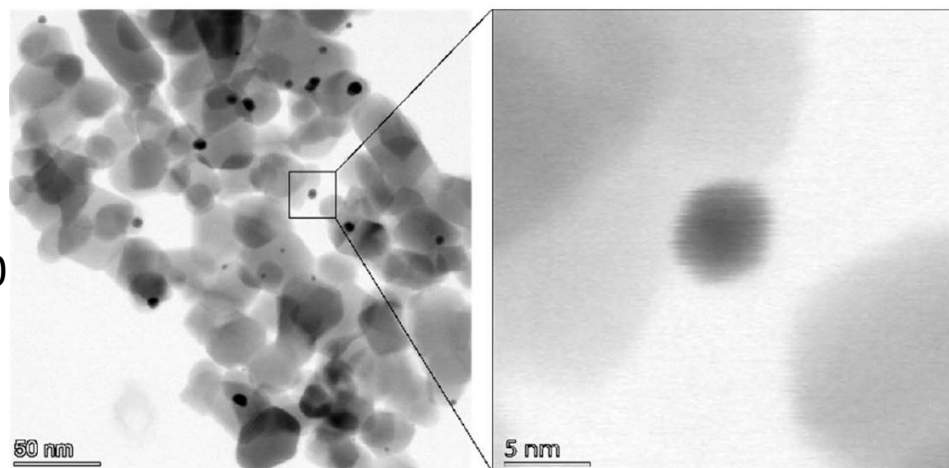


1wt.% Pt

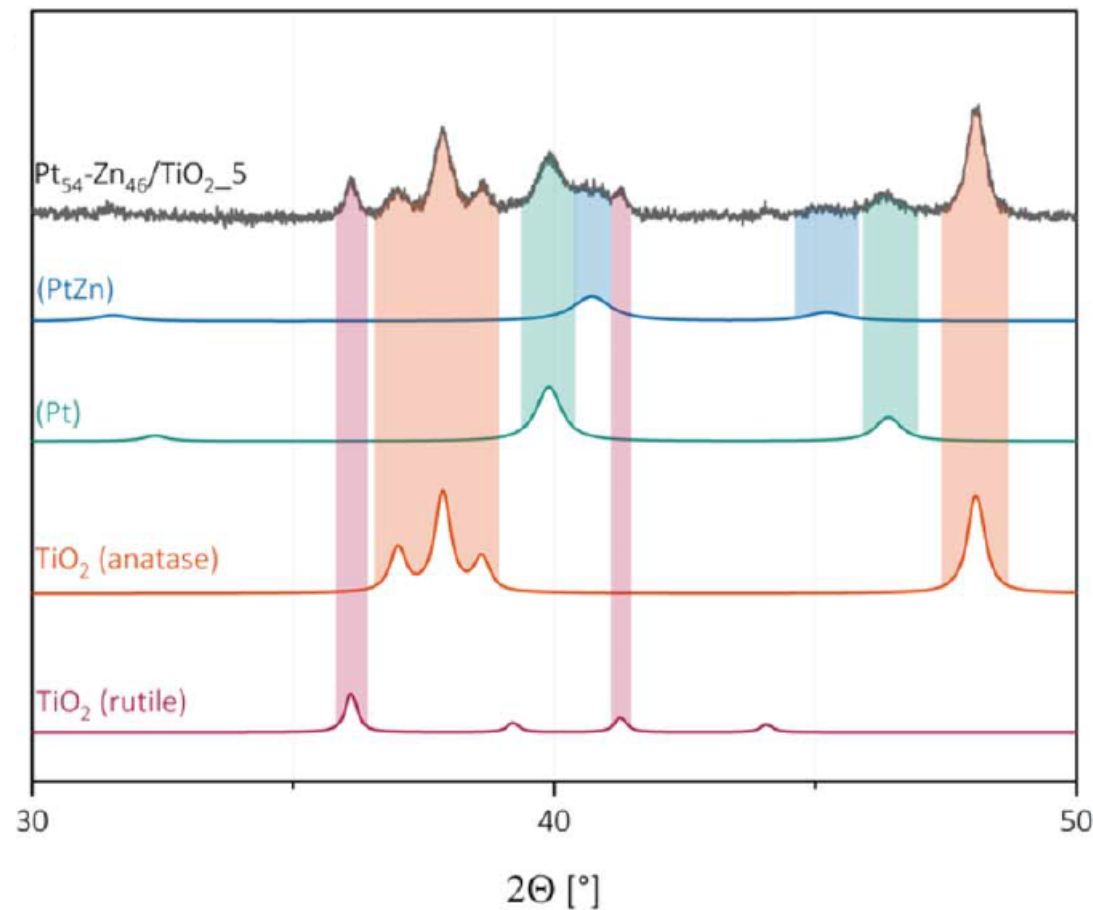
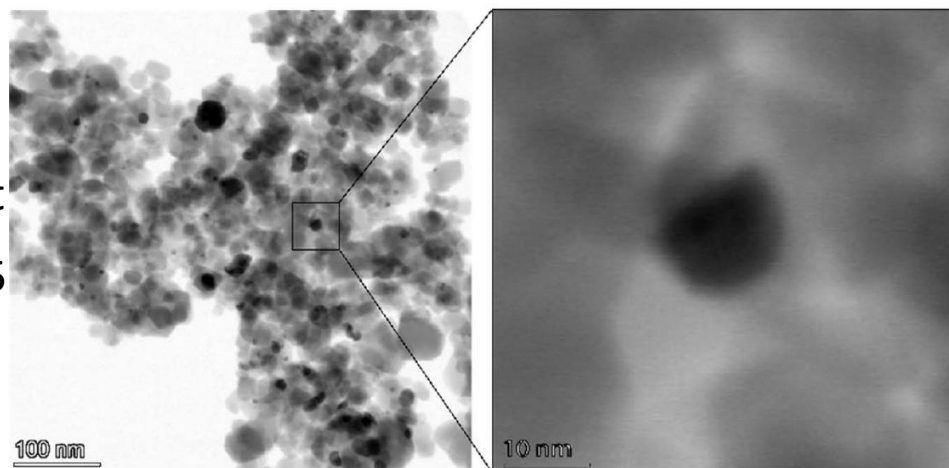
5 wt.% Pt

Pt-Zn/TiO₂: TEM/XRD

1wt.% Pt
Pt₅₀Zn₅₀



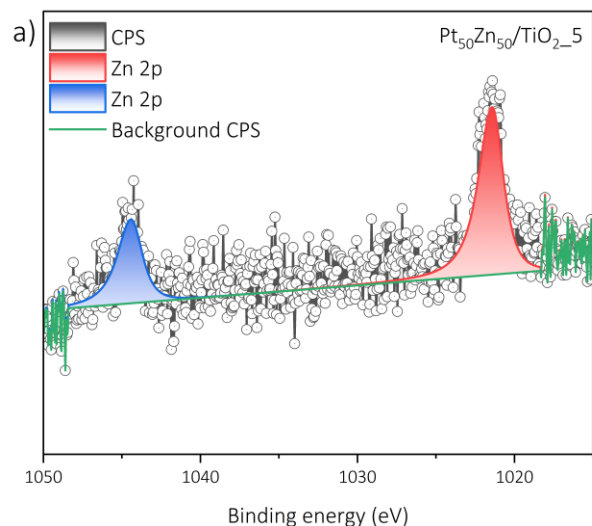
5 wt.% Pt
Pt₂₅Zn₇₅



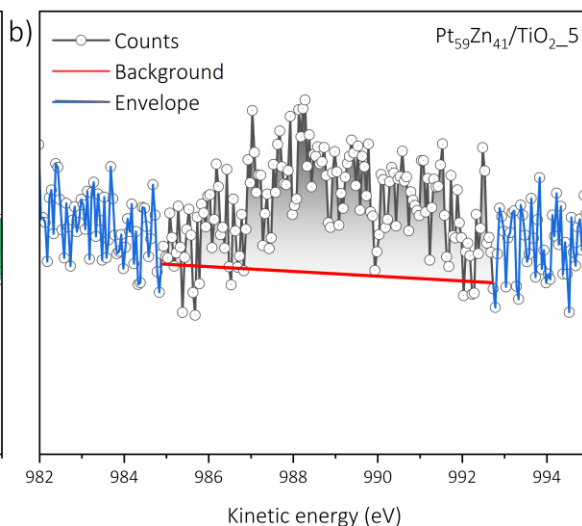
PXRD suggested a systematic underrepresentation of Zn-rich phases

Pt-Zn/TiO₂: reaction of Zn(g) with the TiO₂ support

XPS



Auger

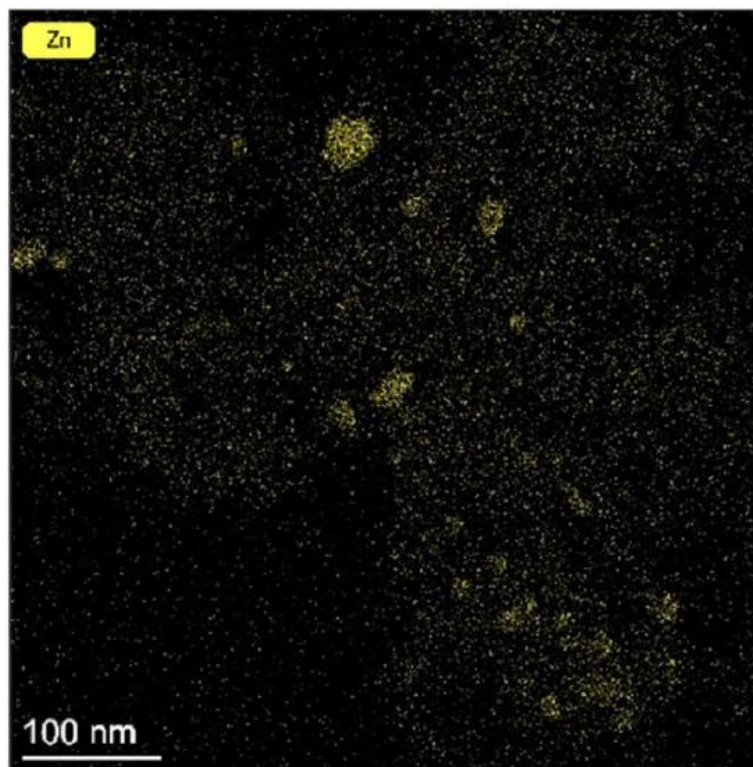
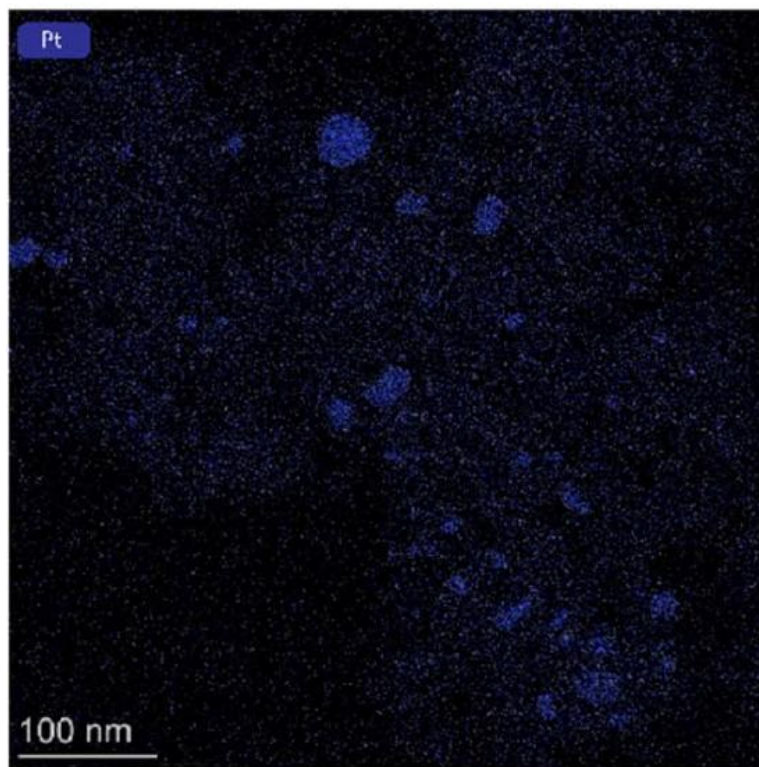


Colour change of TiO₂ support after treatment with Zn(g)

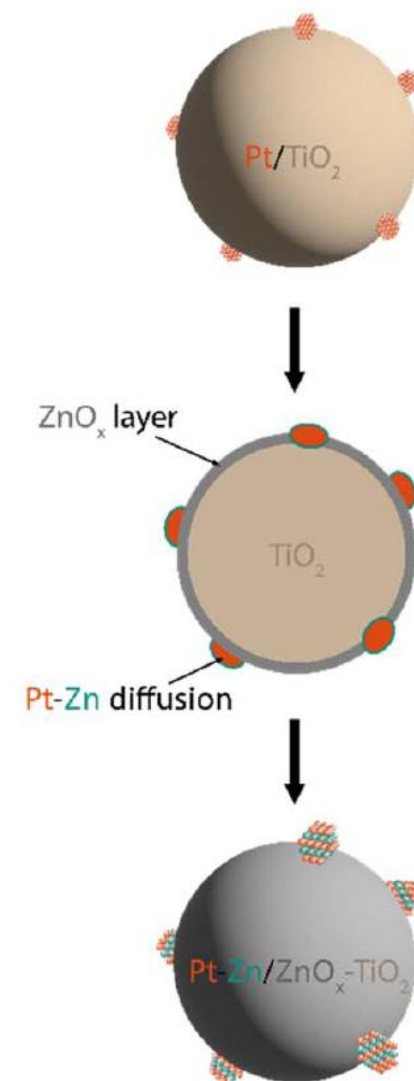


Formation of a thin layer containing Zn²⁺ on the surface of the P25 TiO₂ support

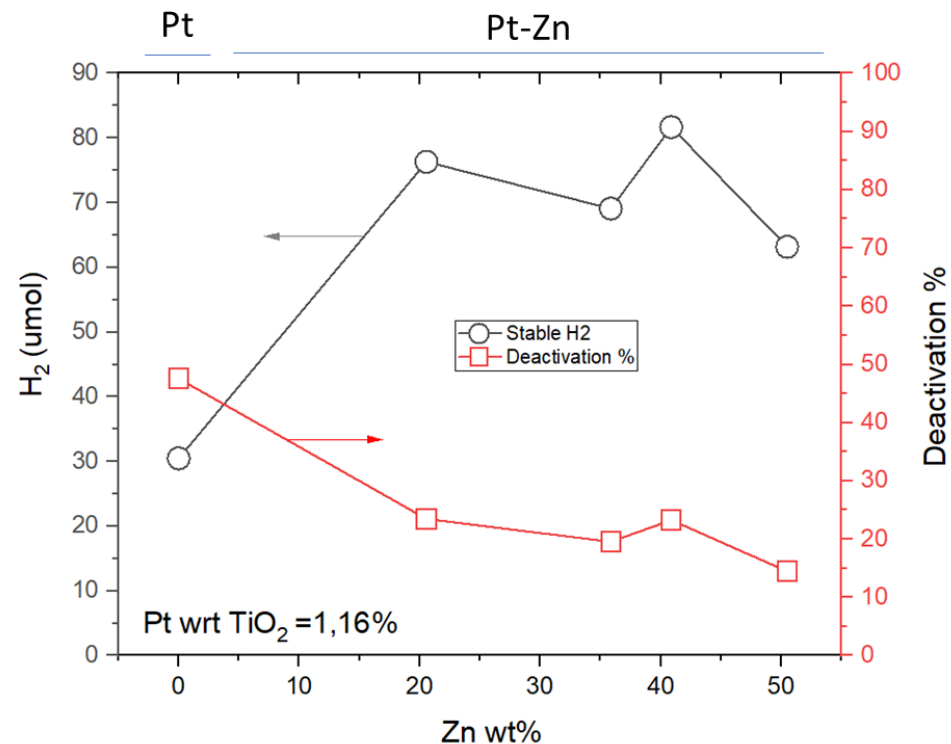
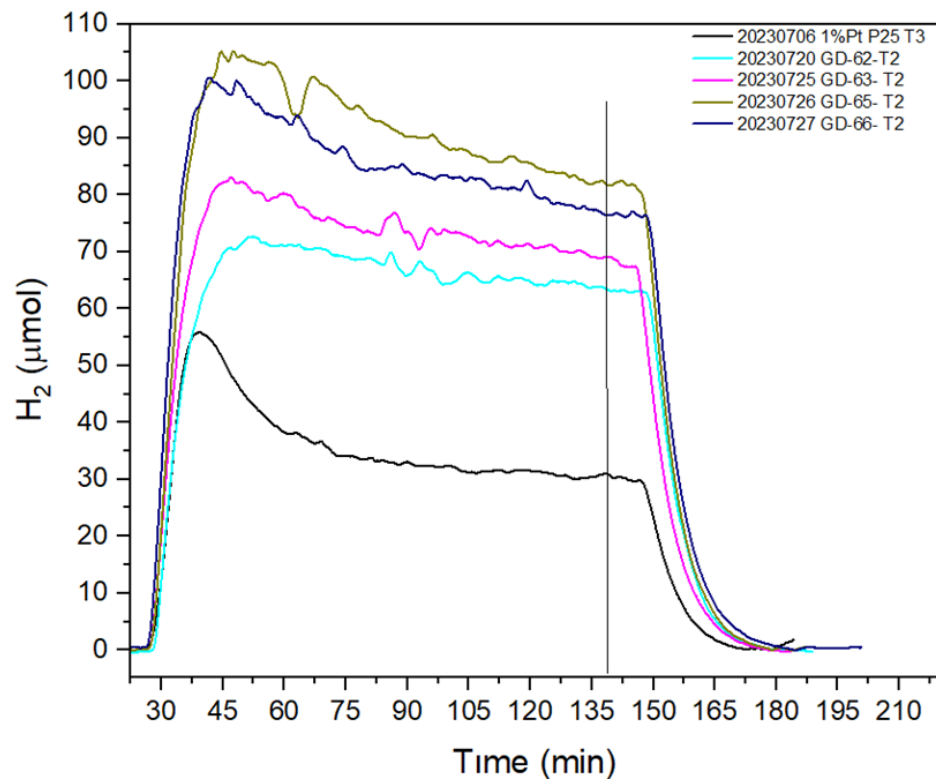
Pt-Zn/TiO₂: reaction with Zn(g)



EDX elemental mapping confirms strong overlap of Pt and Zn

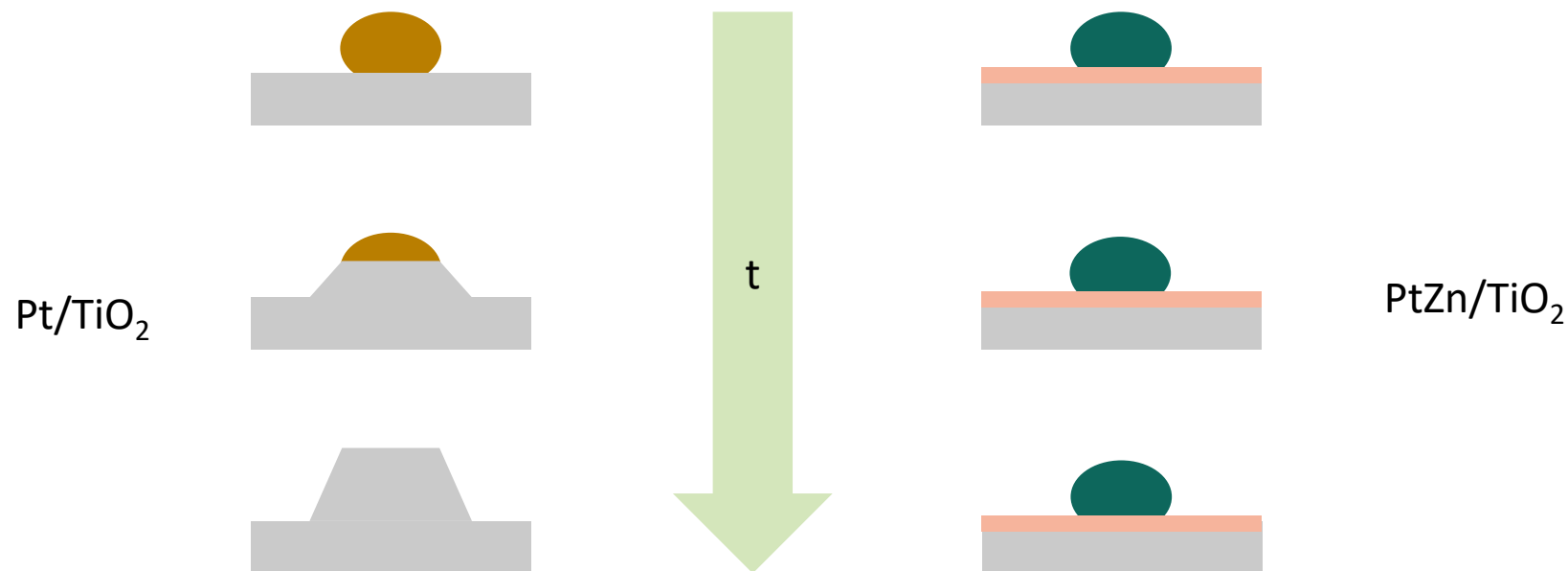


Pt-Zn/TiO₂: performance in photocatalytic HER



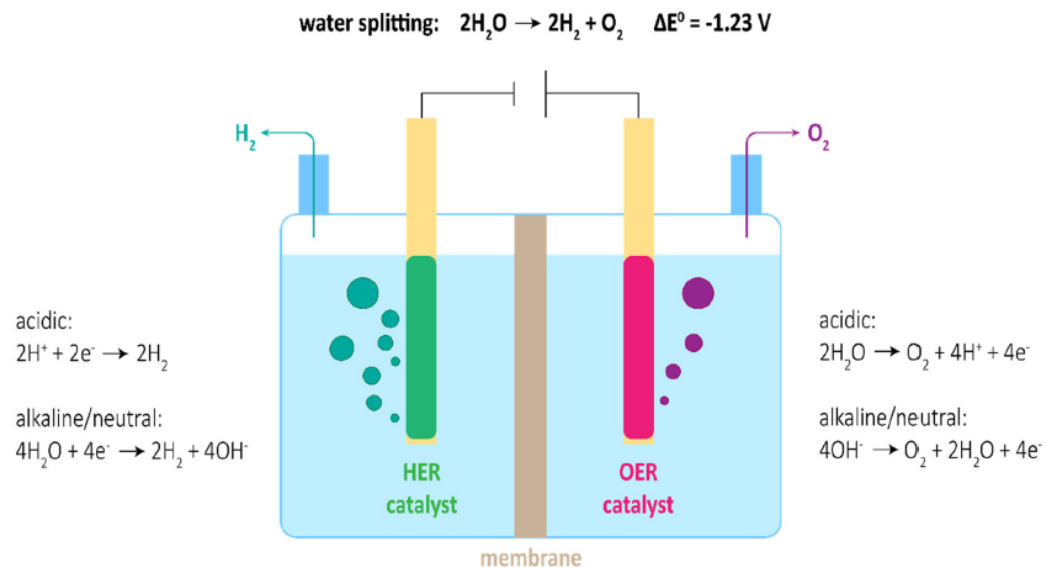
- PtZn-compounds significantly increase Hydrogen release (maximal effect for Zn-rich PtZn)
- Deactivation of catalyst with time is drastically reduced

Pt-Zn/TiO₂: proposed deactivation mechanism by vapour-solid synthesis

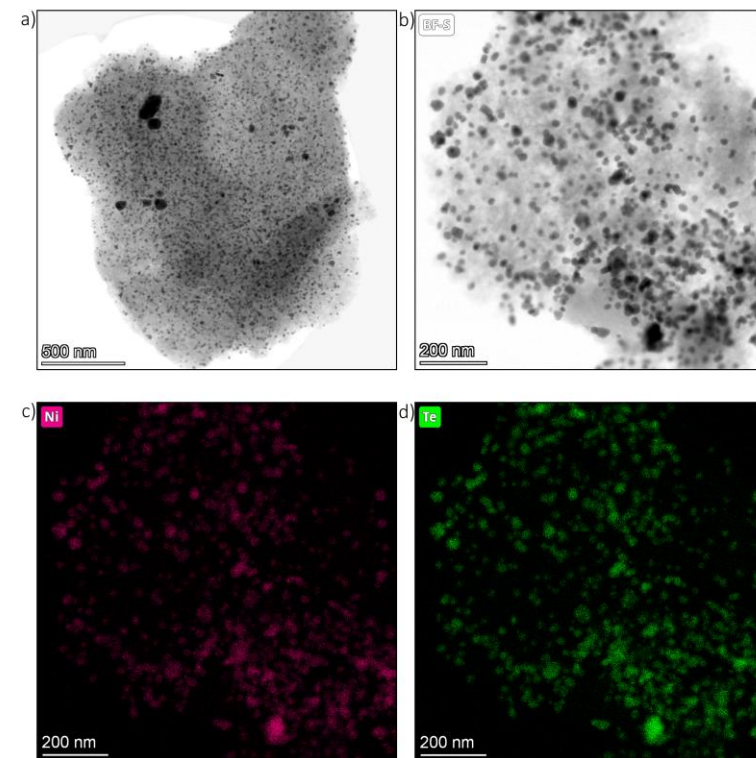


- Pt/TiO₂: Partial reduction under UV → TiO₂ grows over Pt nanoparticle
- PtZn/TiO₂: Zn(g) surface reaction stabilizes TiO₂ surface

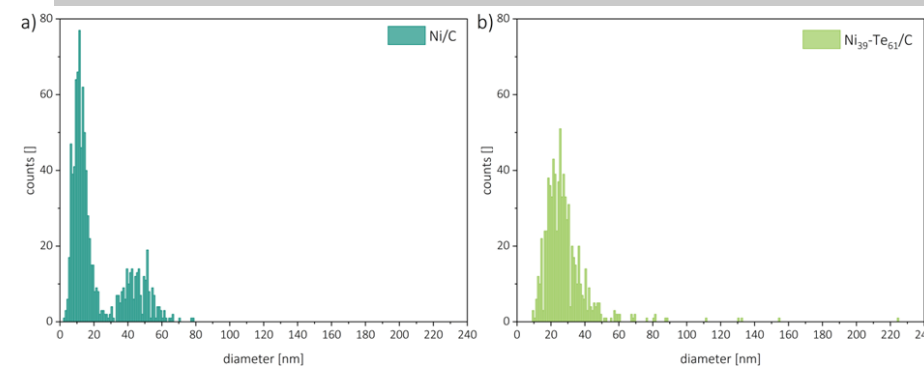
Ni-Te/C: electrocatalytic HER



- use of green electricity to produce H_2
- suffers from high overpotential
- use non-noble metal catalysts in alkaline media



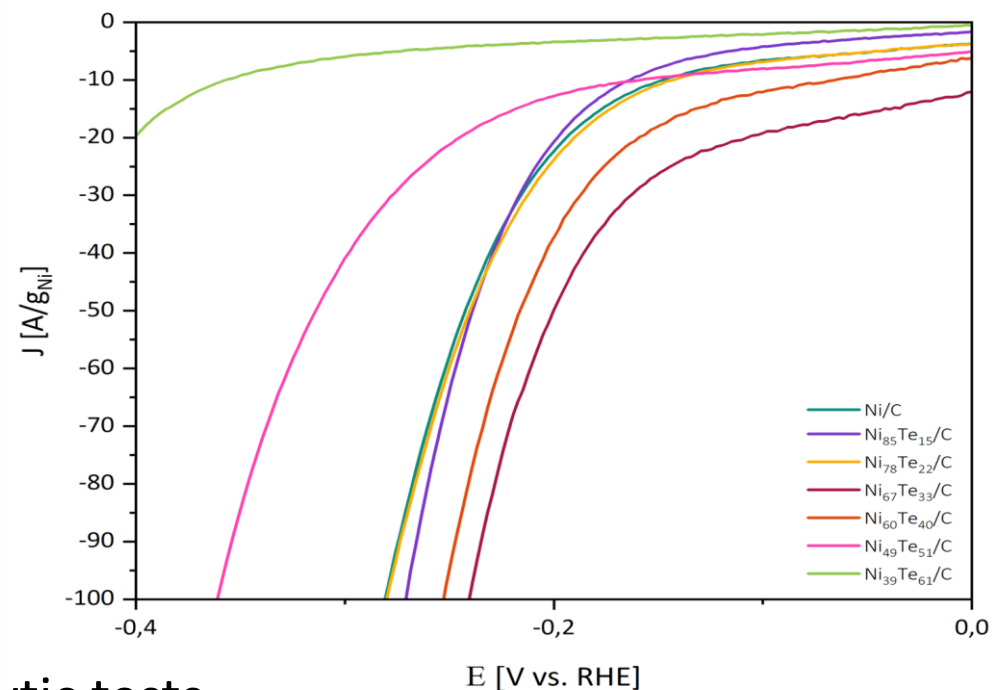
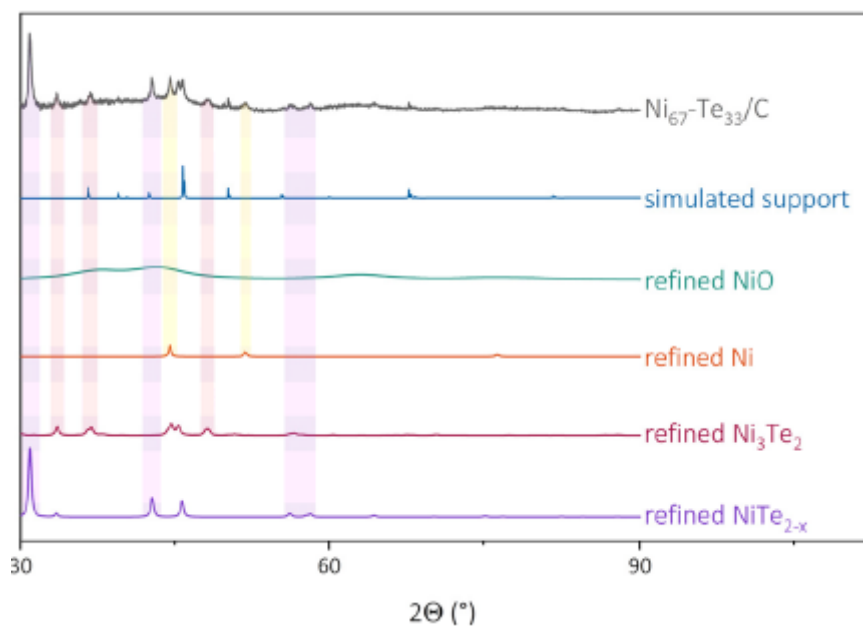
Bimodal particle size distribution



Ni-Te/C: electrocatalytic HER

PXRD results

- small amounts of NiO observed → Carbon support
- Some inhomogeneity from larger metal particles
- All Ni-Te phases were prepared & tested



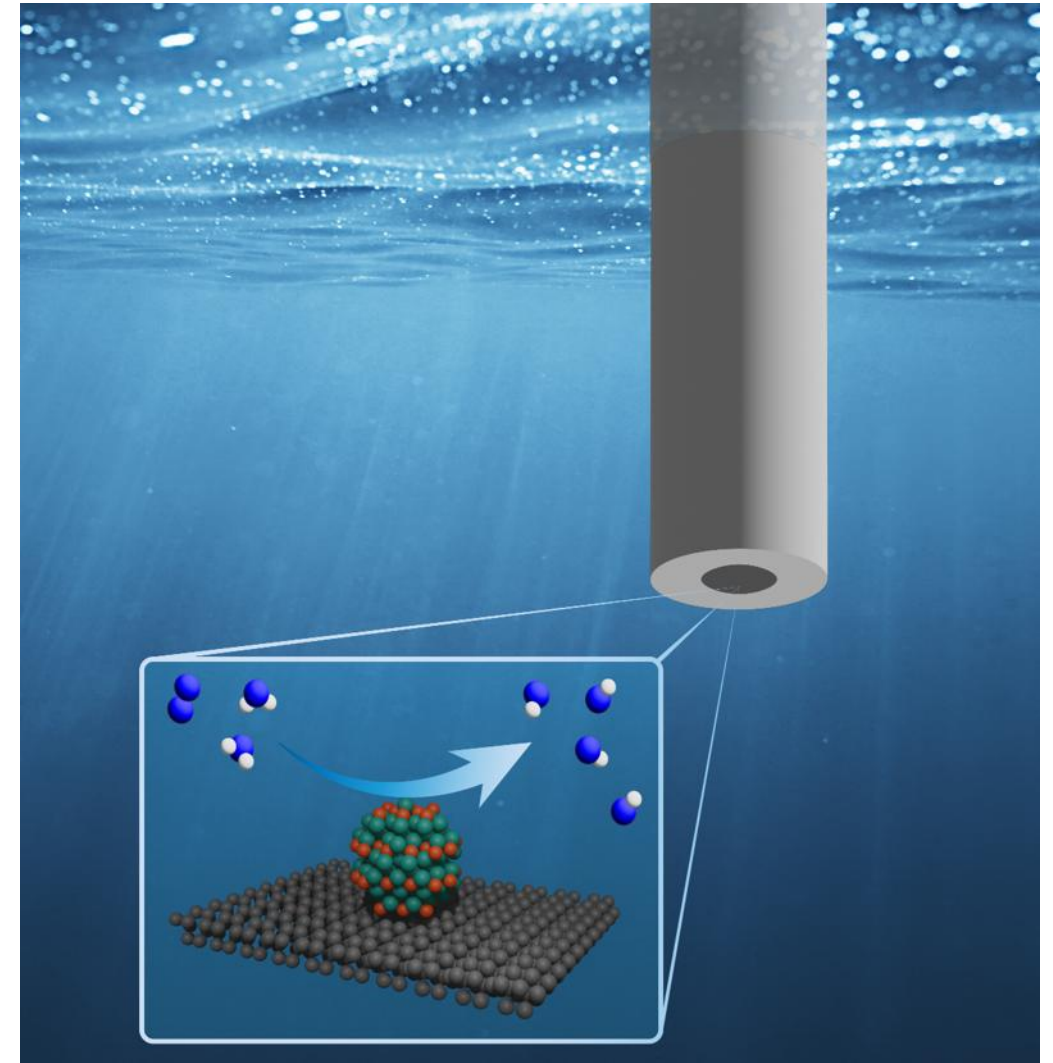
Electrocatalytic tests

- Linear sweep voltammetry
- Chronoamperometry

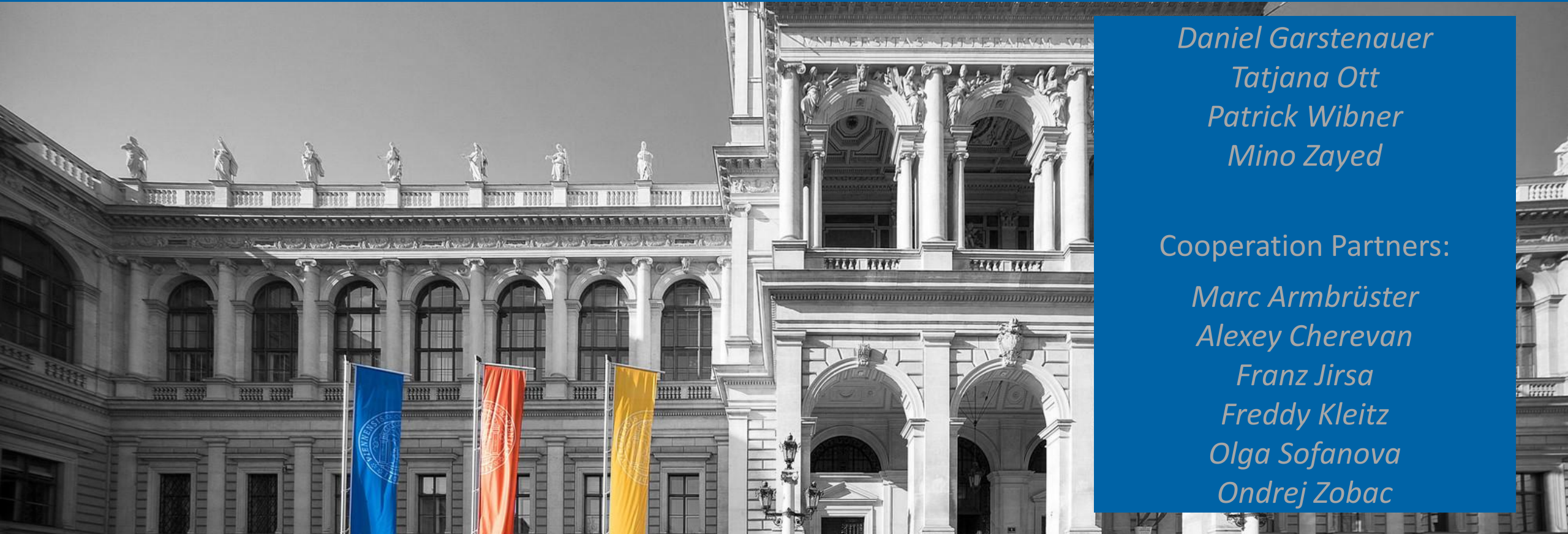
➤ Ranking of phases $\text{Ni}_3\text{Te}_2 > \text{NiTe} > \text{NiTe}_2$

Conclusions & Outlook

- The vapour-solid synthesis is a competitive method for intermetallic nanoparticles
 - Clean, plain and easy to perform
 - High control of particle composition & related crystal structures
 - Allows screening of all compounds in a binary system under identical synthesis conditions
-
- ❖ Vapour-support interaction: rationalization
 - ❖ Thermodynamic steering & upscaling
 - ❖ Broadening of elements basis



Many thanks to . . .



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Franz Jirsa
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Olga Sofanova
Ondrej Zobac*