

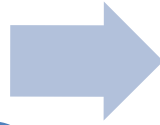
Observing nanochemical processes in real time

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Problem

- How to observe reactions in liquid inside an electron microscope?



Solution

- A chamber, transparent for electrons, that could be placed inside the microscope.

Transmission electron microscopy (TEM) allows to observe nanostructures with extremely high resolution (down to below 1 Å). But in order to analyse physical reactions in real time, a special technique is needed: Liquid Cell TEM.

The aim of the PhD is to perform a series of experiments using Liquid Cell TEM, to show its potential and its limits.

Liquid Cell Transmission Electron Microscopy (LC-TEM)

Poseidon Select system for liquid cells. The bottom plate of the

E-chip for electrochemical experiments. Scale bar: 300 μm .

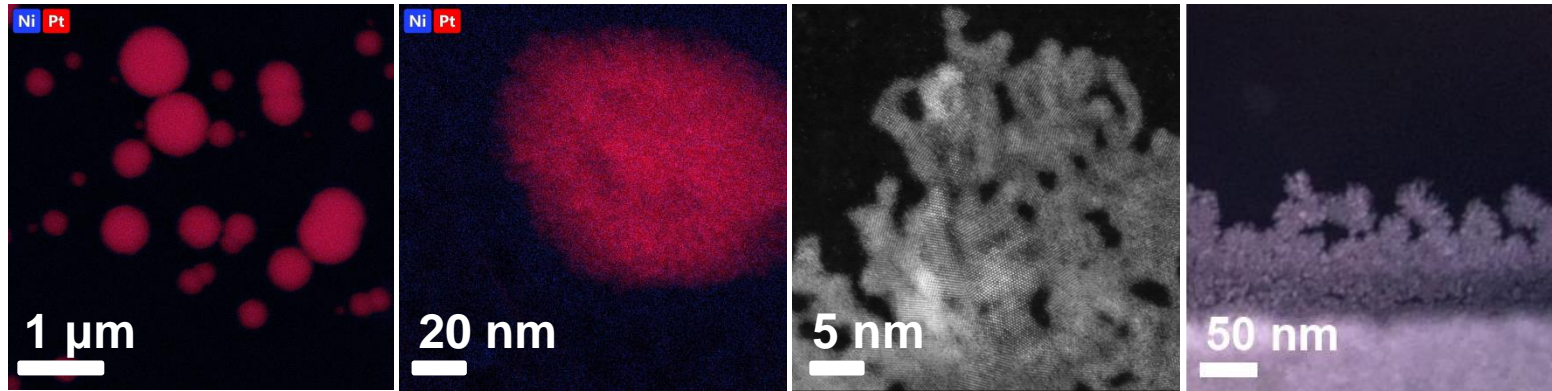
Cr and the top plate of the holder
Also there are 3
golden electrodes on the bottom
plate (Protochips)



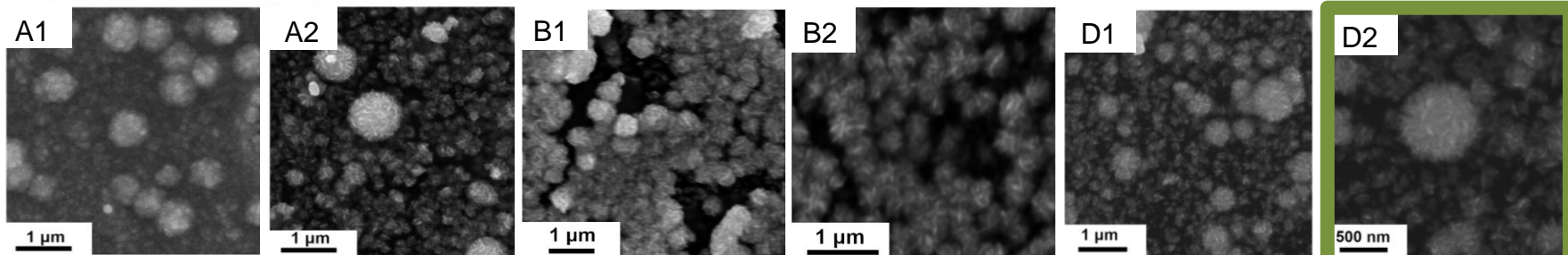
ELECTRODEPOSITION

Process

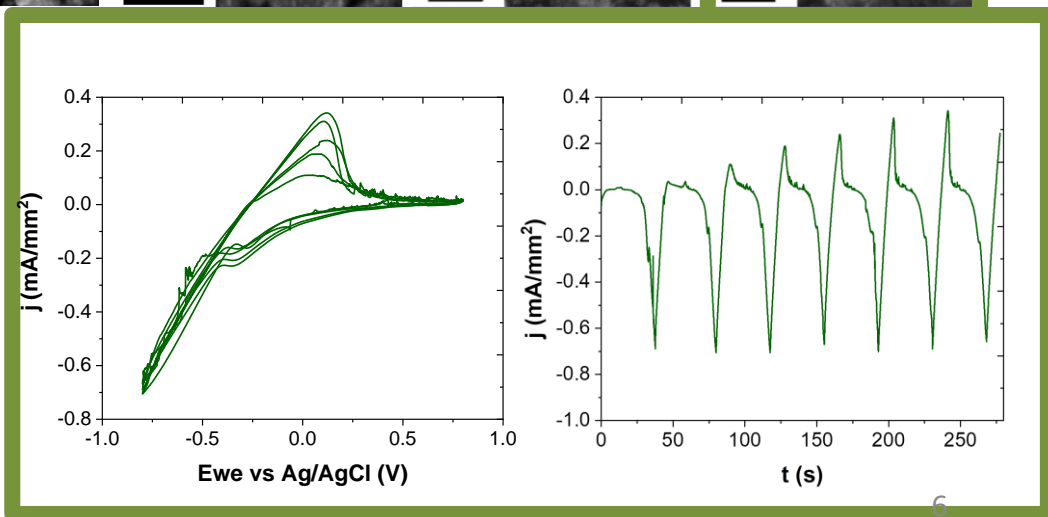
Real time observation of PtNi nanoparticle film growth via electrodeposition and understanding the growth mechanism.



Choice of electrodeposition parameters



Parameter	Sample series					
	A1	A2	B1	B2	D1	D2
E_1 [V]	1.2	1.2	1.2	1.2	1.2	0.8
E_2 [V]	-0.8	-0.8	-0.8	-0.8	-0.8	-0.8
dE/dt [mV/s]	100	100	85	85	85	80
n	15	10	7	7	7	7

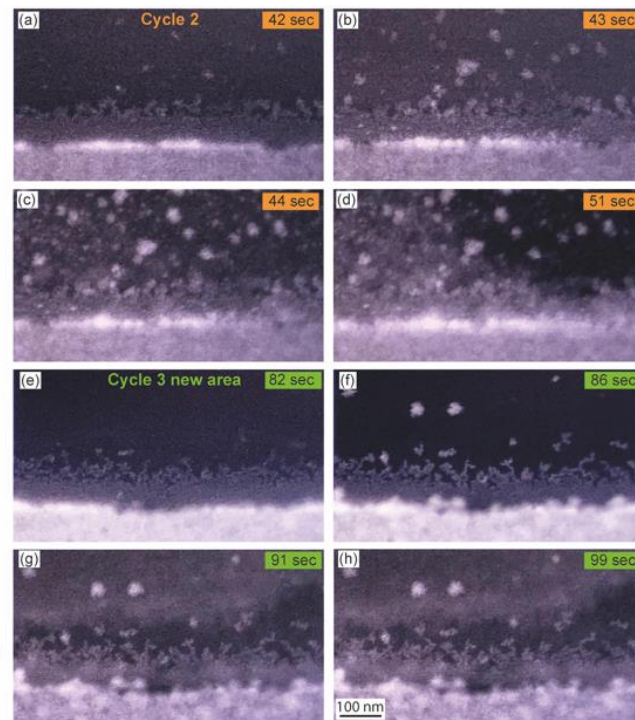
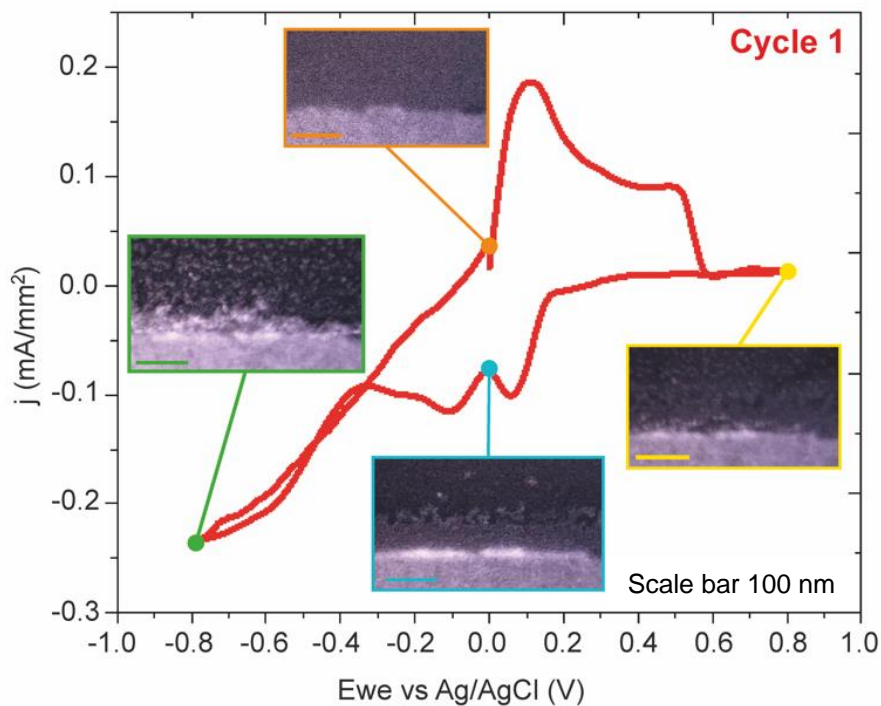


Cycle 1

10 mm

Electrodeposition *in situ* Parameters and Results

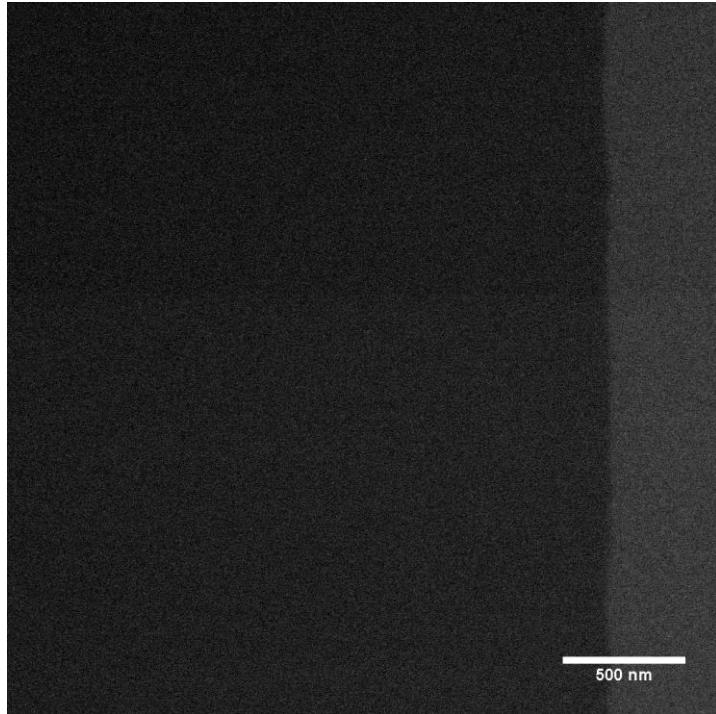
E_1 [V]	E_2 [V]	dE/dt [mV/s]	n	Electron Dose Rate [$e/\text{\AA}^2\text{s}$]	Pump rate [$\mu\text{l}/\text{min}$]
0.8	-0.8	80	7	0.04	3



Electrodeposition *in situ*

Higher scan rate

E_1 [V]	E_2 [V]	dE/dt [mV/s]	n	Electron Dose Rate [$e/\text{\AA}^2\text{s}$]	Pump rate [$\mu\text{l}/\text{min}$]
0.8	-0.8	10	7	0.04	3



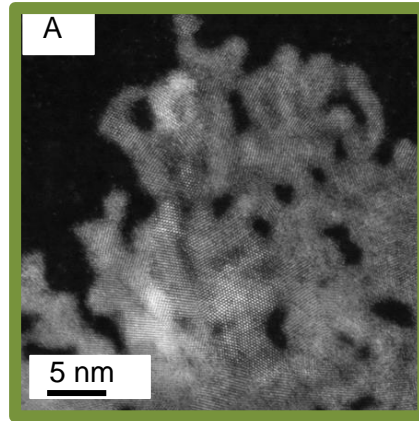
Another electrodeposition was performed for deeper investigation of the process. With lower scan rate and lower magnification, it becomes visible how the nanospheres nucleate and grow on the whole electrode and interconnect. After 2nd cycle, the stress inside the film is too high and the film detaches from the electrode.

Correlation between *ex situ* and *in situ* results

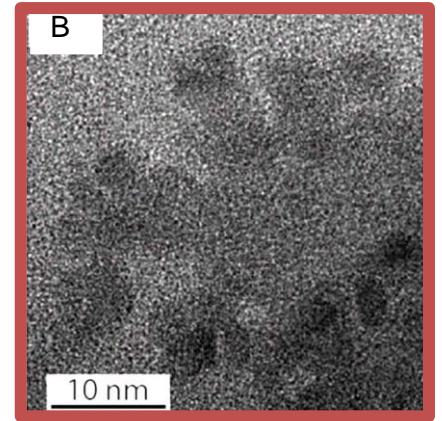
Post mortem analysis of the nanostructures was performed to compare the morphology and chemical composition of nanoparticles.

Fig.A: HR-STEM image of the surface of a single PtNi nanoparticle synthesised *ex situ*.
Fig.B: HR-TEM image of the PtNi surface synthesised in LC-TEM. Branched-like structure is visible in both cases.

EDS analysis confirms high consistency of results from both experiments.



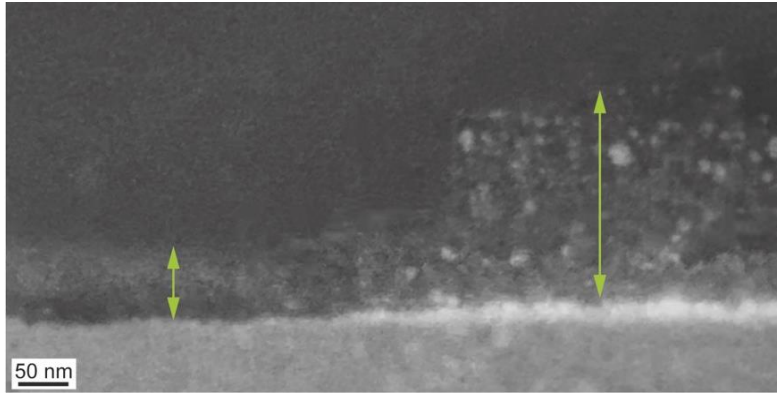
obraz HR-STEM warstwy otrzymanej w eksp. *ex situ*



obraz HRTEM warstwy otrzymanej w eksp. *in situ*

	Ex situ	In situ
Pt	85%	84%
Ni	15%	16%

Electron beam influence

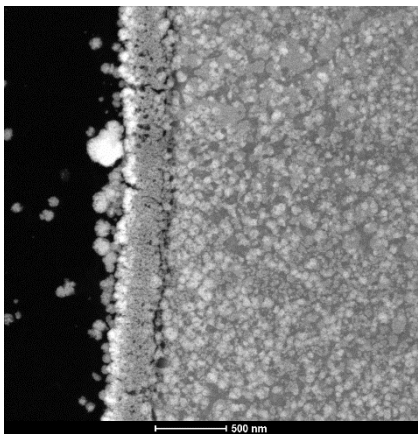


HAADF STEM image of the electrode edge with the electrodeposited PtNi nanograined film. Comparison between the structure stimulated (right arrow) and non-stimulated (left arrow) by the electron beam.

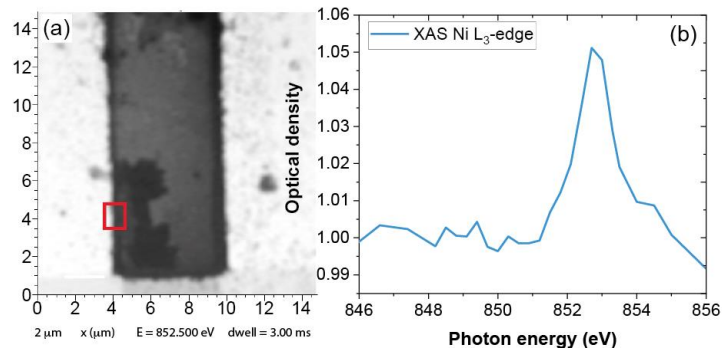


BF imaging of the PtNi nanoparticle during EDS scanning. The particle dissolves, under the focused electron beam.

In situ STXM at SOLARIS synchrotron centre



Post mortem SEM image of the working electrode's edge



(a) STXM absorption map on the working electrode after cycling, for the photon energy in the Ni absorption peak (852.5 eV). It can be seen, that certain areas of the electrode is darker, indicating the presence of NiO; (b) XANES spectra taken from the edge of the WE (red box).

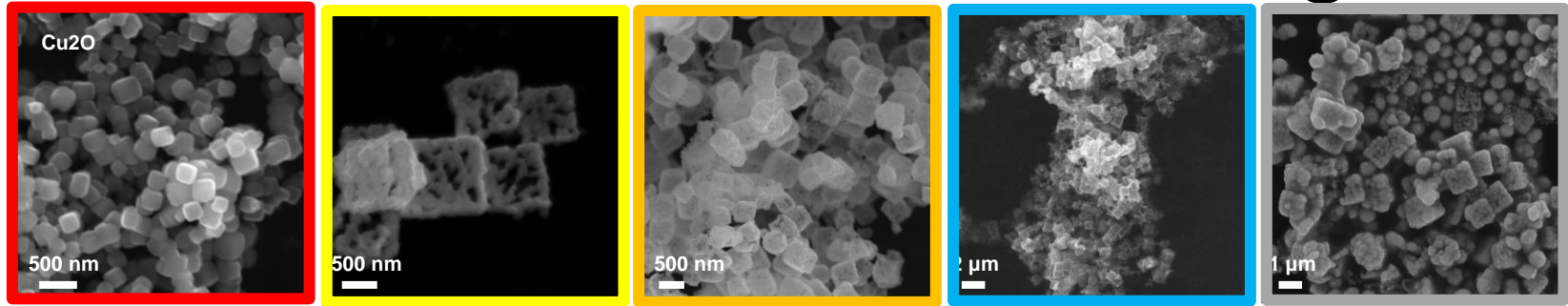
In situ electrodeposition was performed using STXM in order to analyse, what was the oxidation state of nickel in the nanoparticles. The working electrode edge was scanned after every voltammetric cycle to investigate time evolution of the 852.5 eV peak, which reportedly indicates the NiO $2p^63d^8 \rightarrow 2p^53d^9$ transition. This peak was visible throughout the synthesis process, which indicates, that the nickel oxide has been formed by electrodeposition and not by *post mortem* oxidation.

Electrodeposition: CONCLUSIONS

- ✓ The electrodeposition of PtNi alloyed nanoparticles film has been successfully transferred into the LC-TEM. It was confirmed by morphological (High Resolution TEM imaging) and chemical analysis (EDS mapping).
- ✓ The PtNi film starts to grow directly on the Working Electrode edge. Due to the electron beam stimulation, clusters appear also above the electrode and slowly attach to the film surface.
- ✓ Focusing the beam on the specific nanoparticle during EDS acquisition may be damaging for it, causing its degradation or dissolution.

CHEMICAL SYNTHESIS

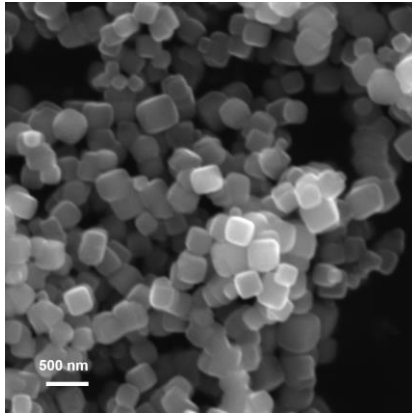
Cu₂O nanocubes synthesis and reaction with Au, Pt, Pd i Ag



Cu₂O nanocubes (NCs) were synthesised *via* wet chemistry methods *ex situ*. Next, galvanic replacement reaction with Au, Pt, Pd and Ag was performed, resulting in a structure, which looks like a hollow ‘nanobox’. The EDS mapping showed high concentration of the noble metal; TEM and STEM images suggest that the cubes are indeed hollow.

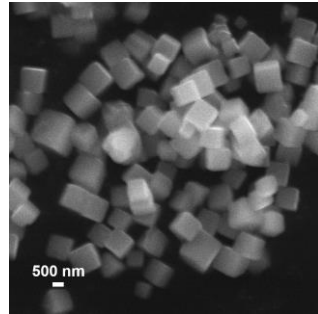
SEM images, from left: Cu₂O NCs synthesised *via* wet chemistry; hollow NCs replaced with Au; hollow NCs replaced with Pt; hollow NCs replaced with Pd; hollow NCs replaced with Ag.

Cu₂O nanocubes variations

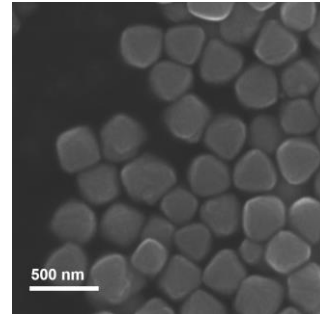


Cu₂O cubes with average size of ca. 200 nm.

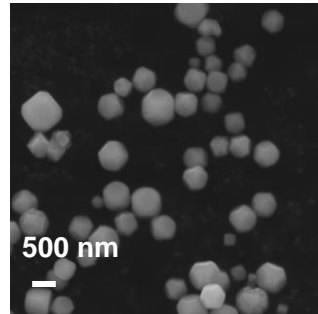
Precursor: CuSO₄
Stabiliser: sodium citrate
NaOH solution: 1.2 mol/dm³
Reducer: ascorbic acid,
Reducer/precursor ratio: 0.6
Temp.: room temperature
Time of reaction: 3 min



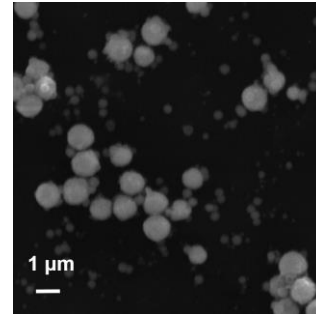
Time of reaction: 1 h



Stabiliser: PVP



Stabiliser: none
Reducer: glucose



stabiliser solution:
0.2 mol/dm³

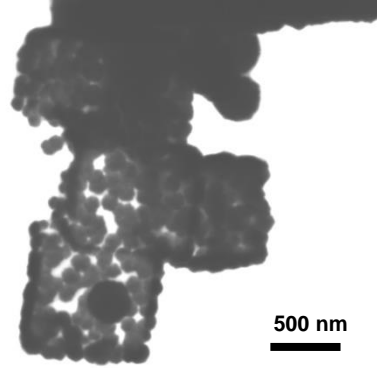
By varying different synthesis parameters, their influence on the crystallization has been investigated.

Stabiliser and reducer determine the shape of nanoparticles.

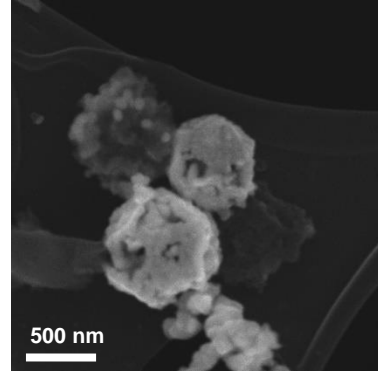
Hollow nanoparticles



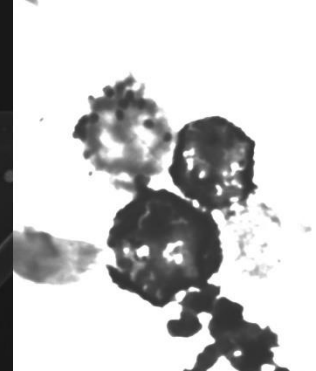
Au@Cu₂O HAADF image



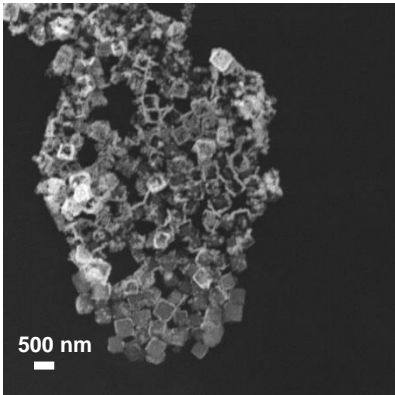
Ag@Cu₂O BF-STEM image



SEM image



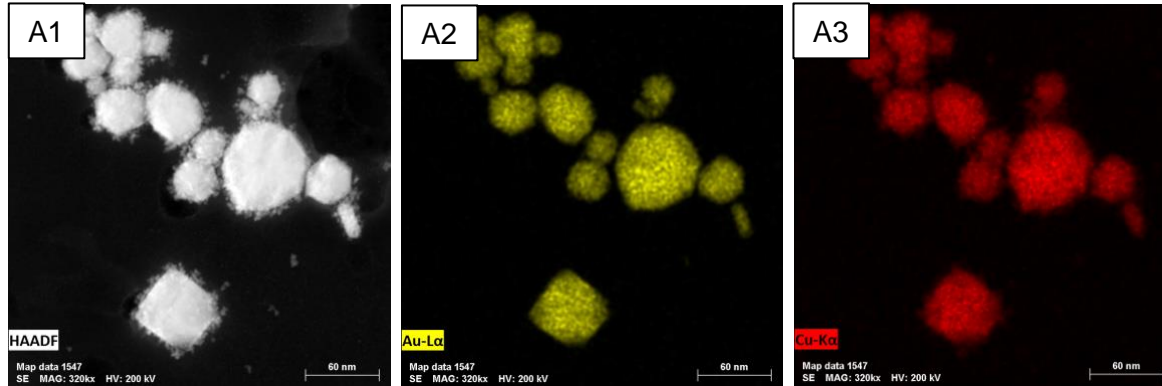
BF-STEM image, Au@Cu₂O COs



Au@Cu₂O NCs synthesis was performed also at Solaris, using *in situ* STXM. *Post mortem* analysis of the nanoparticles shows that the experiment was successful and nanocubes are hollow.

Cuboctahedrons were also used for the galvanic replacement reaction with Au, resulting in a hollow structure.

Cu₂O NCs synthesis *in situ*



A1) HAADF image of Au@Cu₂O NPs fabricated *in situ*; A2) EDS map of Au; A3) EDS map of Cu.

Cu₂O NPs synthesis was performed in LC TEM. However, the obtained nanoparticles were not cubic. The galvanic replacement reaction was also unsuccessful, the nanoparticles look rather like a core-shell or decorated. As we know, the pH is strongly modified in LC TEM, so we repeated the Cu₂O NPs *ex situ* synthesis in artificially decreased pH. The resulting nanoparticles morphology was indeed similar to the nanoparticles fabricated in LC TEM.¹⁸

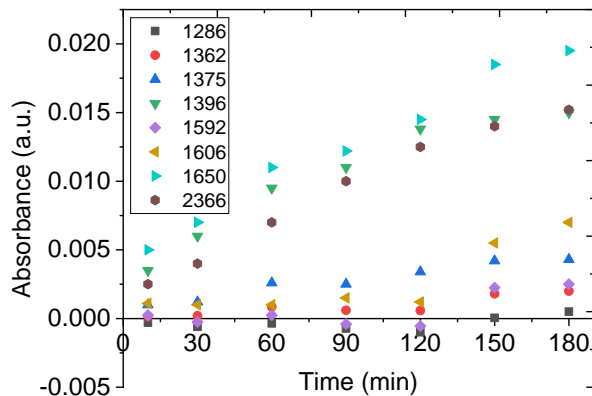
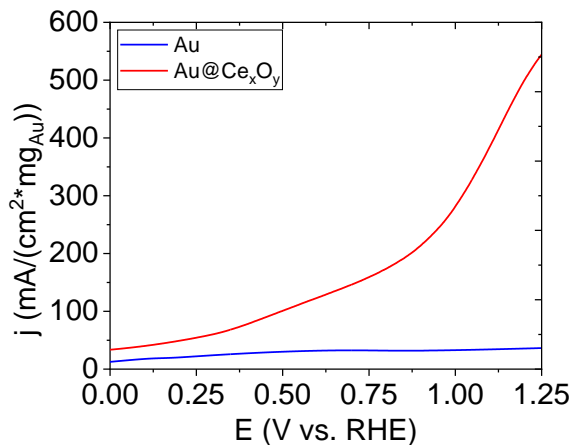
Chemical synthesis: CONCLUSIONS

- ✓ Parameters and reagents, which influence Cu_2O nanoparticles crystalization have been identified and examined.
- ✓ Cu_2O nanoparticles synthesis was performed inside LC-TEM, but the obtained structures were not cubes. Possible explanation would be the electron beam interaction with water and the resulting pH decrease. This hypothesis is supported by *ex situ* experiments in modified pH.
- ✓ During the galvanic replacement reaction inside the LC-TEM core-shell rather than hollow $\text{Au}@Cu_2\text{O}$ nanoparticles were obtained. Indeed, the electron beam creates reducing agents in the solution that stimulates metal crystalization.

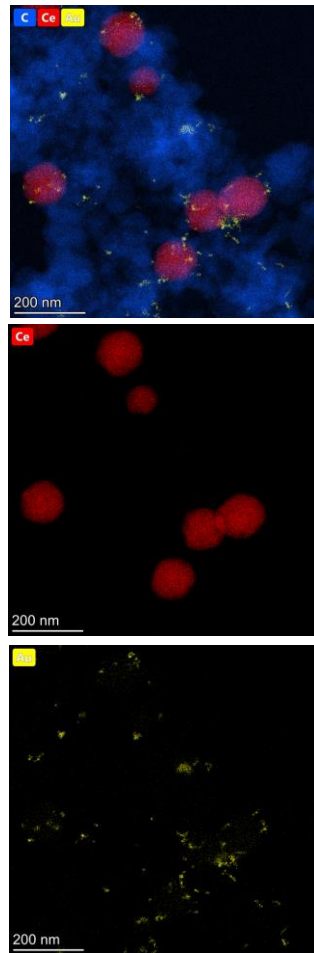
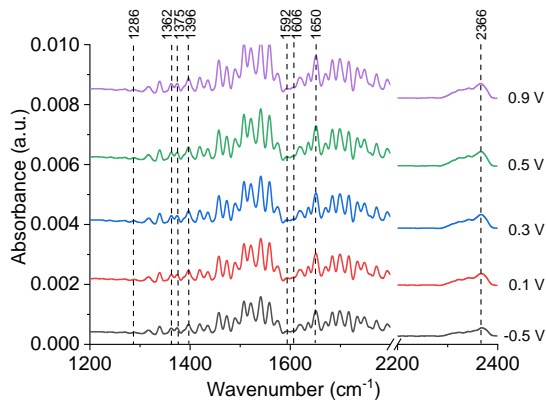
ELECTROCATALYSIS

The background of the slide is a dark, textured field of particles. It features a dense distribution of small, bright blue and yellow dots, interspersed with larger, more prominent clusters of red and orange particles. The overall effect is reminiscent of a microscopic view of a catalytic surface or a complex molecular structure.

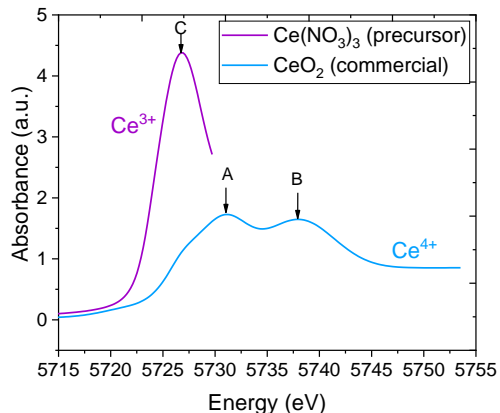
Ceria nanoparticles



Parameter	Au@Ce _x O _y	Au/C
ECSA (cm ² /mg _{Au})	24.74	51.53
onset potential (V)	0.03	0.30

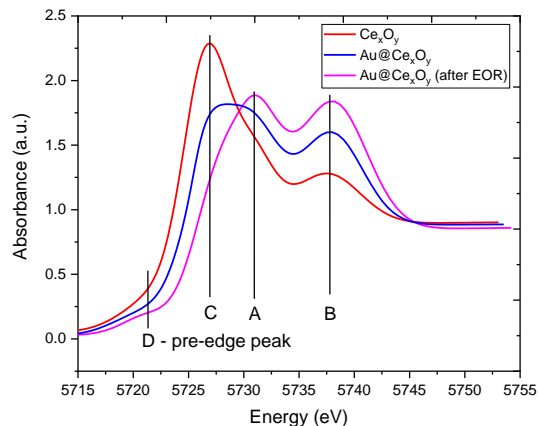


Ceria nanoparticles



XANES (X-ray Absorption Near Edge Structure) analysis performed in SOLARIS synchrotron centre for ceria, ceria with gold and the catalyst after ethanol oxidation reaction. Results show, that ceria was in fact composed of Ce(III) and Ce(IV) with ratio 58:42. However, the percentage of Ce(III) was different at every step of the experiment.

DFT calculations suggest, that Ce(III) is less stable than Ce(IV). Therefore, it spontaneously oxidizes into Ce(IV), using oxygen from environment.



Sample	Ce _x O _y	Au@Ce _x O _y	Au@Ce _x O _y after EOR
Percentage of Ce ³⁺ (%)	61	38	16

FUTURE PLANS

Performing electrocatalysis experiment
using LC TEM.

A microscopic image of plant cells, likely from a leaf, showing a network of green cell walls and large, dark, irregularly shaped chloroplasts. The cells are densely packed, and the green fluorescence highlights the cell walls and chloroplasts. Small, bright pink spots are scattered throughout the green tissue, possibly representing specific organelles or markers. The overall appearance is that of a highly organized, cellular structure.

Thank you for attention