# Visualizing oscillating NiO appear and disappear on the surface of Ni@Au catalyst driven by a hybrid water-hydrogen atmosphere

CLIMATE
Application Note

Xiaoben Zhang,[1] Fan Zhang,[1,2], Shaobo Han,[1] Dan Zhou,[2] Wei Liu[1]

## Experimental setup

| | |
|---|---|
| **TEM** | Thermo Fisher Themis ETEM @ 300 kV |
| **In situ system** | Climate G+, Vaporizer and Gas Analyzer |
| **Sample preparation** | Ultrasonication of NiAu bimetallic nanoparticle in ethanol for good dispersion |
| | Drop-casting the solvent on the bottom chip |
| **In situ parameters** | Temperature: 400 °C |
| | Gas: Various mixtures of $H_2O$, $H_2$ and He (carrier gas) |
| **Analysis techniques** | HRSTEM, mass spectrometry and calorimetry |
| This application note is the outcome of the collaboration between DICP[1](Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China) and DENSsolutions[2]. | |

**Keywords**
Dynamic Imaging, Reaction Oscillation, Water-Hydrogen Competition, MEMS Nano-Reactor.

**Field**
Heterogeneous Catalysis

**Goals**

- Realize the in situ observation of catalytic behavior under humid atmospheric conditions;
- Offer a solution to add water vapor to any gas mixture.

## Introduction

In situ and operando TEM have paved the way in studying materials' composition and structure down to atomic resolution in their working status.[1] Among catalyzed gas reactions, water can act as both a reactant and a product, like in water-gas shift reactions (WGS) and reversed WGS. Water's negative effects on metal corrosion and catalyst deactivation are also well-known and have been under study for decades. Insights into the role of water in catalytic reactions is important for unveiling reaction mechanisms, and thus critical for the optimization of the catalyst or for reaction recipes involving water.[2] Despite the importance, the study of water's influence on gas-solid reactions inside a TEM is limited. This is due to the lack of control over the flow rate and pressure of the water vapor, as well as the fear of contaminating the high-vacuum TEM columns.

The DENSsolutions Climate Vaporizer was specifically developed to tackle these challenges. As shown in Figure 1, the Vaporizer component is strategically positioned directly before the TEM holder, where the mixed gas pressure and flow rate controller are located. This design delivers benefits such as avoiding the contamination of the original dry gas supply, a fast and wide range of water partial pressure switch (0 to 100% relative humidity (RH)) and the independent control of gas parameters like pressure, flow rate, gas composition and the level of water vapor. In this work, the Vaporizer was used to study the reconstruction behavior of the NiAu bimetallic core-shell nanoparticles, a catalyst system highly selective to CO in $CO_2$ hydrogenation[3], under a hybrid atmosphere of water and hydrogen.

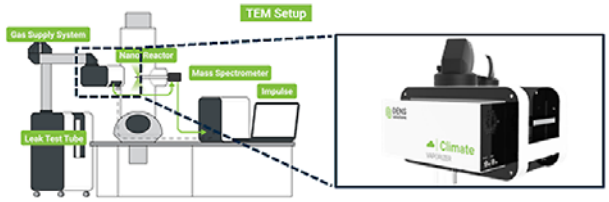


Figure 1. Schematic overview of the operando gas and heating TEM setup. The Vaporizer's location is marked in the dotted box and magnified on the right.

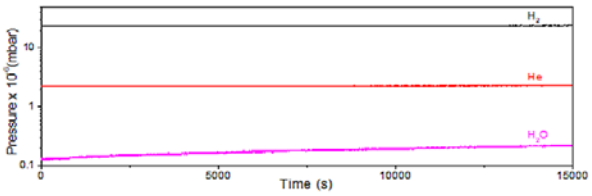


Figure 2. Mass spectra showing the partial pressure of $H_2$, He and $H_2O$ as the water pressure changes from 4.7 to 11.7 mbar (values measured with humidity sensor integrated in the Vaporizer)



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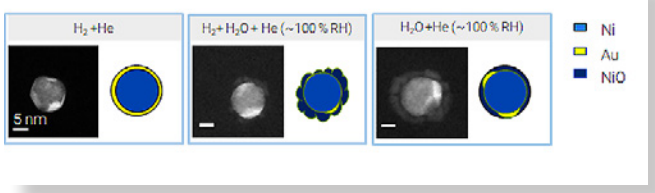



Figure 3. HAADF images and schematic views of the Ni@Au nanoparticles under different gas environments

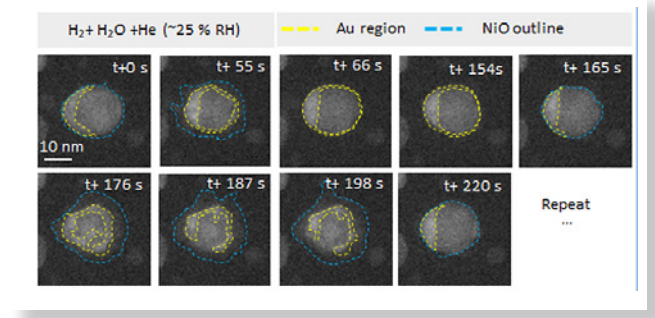



Figure 4 Reversible Ni-Au nanoparticle structure evolution under $H_2$ and lower water pressure (compared to Figure 3). The composition were concluded from HRTEM and EELS.

## Results

- Figure 2 shows the water and the carrier gas (mixture of $H_2$ and He) partial pressure measured from the Gas Analyzer (mass spectroscopy data with Y-axis shown in log scale) when changing water vapor pressure in the Vaporizer from 4.70 mbar to 11.74 mbar. As shown in Figure 1, the Vaporizer is located before the TEM holder, and the MS is located after. The increase of $H_2O$ in MS synchronized with Vaporizer measurements confirms the water partial pressure control inside the nano-reactor.

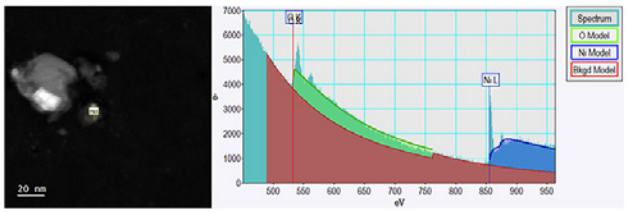
- Figure 3 shows three different architectures of a NiAu nanoparticle under three different gas conditions. In $H_2$ and He environment, a Ni core with ultra-thin Au shell architecture forms. Introducing 100% RH water vapor, i.e. $H_2$+$H_2O$+He, led to a loose NiO shell and Ni-Au side-by-side phase separation (different from core-shell phase separation). Under $H_2O$ and He environment (with about 100% RH), the loose NiO shell became compact and stable. These different observations can be attributed to only reduction, competition of reduction and oxidation, and only oxidation, respectively. Further data of high-resolution TEM images and EEL spectra are in the supplementary materials.

- Figure 4 shows the structure evolution of one NiAu nanoparticle under gas environment of $H_2$, He and 25% RH water vapor. The NiO outline is marked with a blue dashed line. Here t represents the starting time of the data presented. From t+0 s to t+55 s, the NiO shell grows as the oxidation process dominates. From t+55 s to t+66 s, the NiO shell disappears as an opposite reduction process occurs. Further data shows the reversibility of the oxidation and reduction processes.

## References

1. Huang, X. et al. Advanced Materials 2021, 33 (31), 2101772.
2 Saavedra, J. et al. Science 2014, 345 (6204), 1599.
3. Zhang, X. et al. Nature Catalysis 2020, 3 (4), 411-417.

## Supplementary materials




| Element | Shell | Signal(x10$^5$ e-) | Comp.(at.%) | Rel. |
|---|---|---|---|---|
| O | K | 5.55 ±0.015 | 48±3 | 0.93 |
| Ni | L | 4.29 ±0.008 | 52±3 | 1 |

Figure S1. EELS of the oxide shell. The quantified result in the table indicates the shell to be NiO.

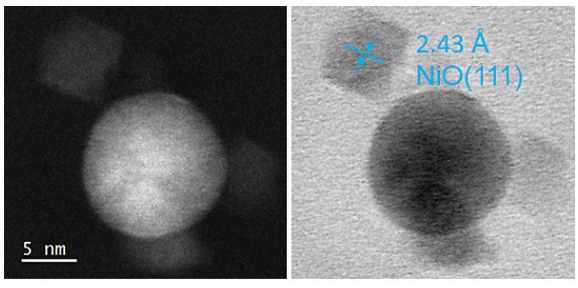



Figure S2. High-resolution STEM HAADF and BF images showing the outer shell to be NiO.



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