

MEMS-based nanoreactor for in situ analysis of solid–gas interactions inside the transmission electron microscope

Hector Hugo Pérez Garza , Diederik Morsink, Jeff Xu, Mariya Sholkina, Yevheniy Pivak, Merijn Pen, Sander van Weperen, Qiang Xu

DENSSolutions B.V., Informaticalaan 12, Delft 2628 ZD, The Netherlands

✉ E-mail: hugo.perez@denssolutions.com

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A nanoreactor-based system for in situ analysis of solid–gas interactions inside the transmission electron microscope, referred to as the ‘climate system’, is introduced here. The latter uses an micro-electro mechanical systems (MEMS)-based device as a multi-functional sample carrier and micro-sized laboratory for simultaneous heating and gas experiments. To assemble the nanoreactor, two chips are sandwiched together to form a minimised chemical reaction chamber. The bottom chip contains a four-point-probe microheater, which controls and introduces the heating environment (up to 1300°C) around the sample. Similarly, it contains the spacers that define the height of the gas chamber. The top chip confines the gas in the microchamber while isolating it from the external environment. Both chips contain electron transparent windows that allow the electron beam to pass through for in situ imaging. The sample can be deposited or prepared directly on the windows, which are made of silicon nitride and can sustain pressures up to 1.5 bar and high temperatures while ensuring low background atomic resolution imaging.

1. Introduction: Green technology and sustainable energies are becoming part of everyday’s social and political discussion [1]. However, scientists are emphasising on three big problems on the top of the list: (i) energy [2], (ii) water and environment [3] and (iii) food shortage [3]. In on-going effort to solve these problems, research in different topics are taking place, but catalysis is emerging as the key most technology in the chemical industry, which can significantly reduce the environmental impact of chemical processes while maximising the energy required to carry them out [4]. Although many of the existing catalysts are considered to be very effective, the truth is that they are still far away from being perfect and there are still many needs and challenges that have to be addressed. As a result, understanding the solid–gas interactions is crucial for optimising a wide range of catalytic nanomaterials, which play an important role in the process of solving the previously mentioned problems [5]. In general, the performance and characteristics of these catalysts greatly depend on their atomic structure [6], while the latter is determined by the surrounding environment. Therefore, factors such as temperature, pressure and chemical composition of the interacting gases play a big role [7]. However, aiming at understanding these complex relations requires the appropriate tools to observe and characterise the dynamic events that occur as a function of different stimuli. A well-suited tool for observing the structure of materials with sub-atomic resolutions is the transmission electron microscopy (TEM). In conventional TEMs, the specimen of interest is usually transferred onto a copper (Cu) grid, which is then inserted with the help of a holder inside the TEM column. Nevertheless, these microscopes are limited to operate under a static environment (high-vacuum conditions of 10^{-7} mbar and room temperature). Similarly, the structural information can be only obtained at a fixed period of time. In the ideal scenario, the extreme resolutions offered by the TEM should be kept, while enabling sample environments that mimic the industrial conditions to which these materials are exposed. In other words, the capability to apply pressures equal or higher than atmospheric, temperatures up to 1000°C and using gases such as H₂, O₂ or different hydrocarbons. To achieve this, we replace the traditional Cu grids by an MEMS device acting as the new sample carrier. Such device, referred to as the nanoreactor,

consists of two chips that are sandwiched together to form a sealed gas microchamber (Fig. 1). The bottom chip contains a four-point-probe spiral-shaped microheater, which accurately controls the temperature to be delivered around the sample. Similarly, there is an inlet/outlet through which different gases can be flown. The gas is guided via a microduct that brings it toward the heated sample, which is located on an electron transparent window. Correspondingly, the top chip encloses the gas and isolates it from the external vacuum environment of the electron column of the TEM. The thickness of the gas layer is determined by the height of the microduct, which therefore acts also as a spacer. The developed ‘climate system’, compatible with JEOL and FEI microscopes, empowers the users to visualise solid–gas interactions in real-time, while mimicking the real-world and industrial conditions – gas pressure above 1 bar with thermal heating up to 1300°C.

2. Design of the nanoreactor: Different factors were considered for the design of the MEMS device: low-power consumption, negligible thermal drifts, thermal mass, temperature uniformity and thermal isolation from the surroundings. It consists of a double spiral-shaped microheater and was inspired by the work of Zandbergen [8], Creemer *et al.* [9] and Prasad *et al.* [10]. To assess the design, a thermal network model was done (Figs. 2a and b), which was later supported using electro-thermal finite element analysis (FEA) simulations using COMSOL Multiphysics. The microheater, made of molybdenum, is encapsulated with silicon nitride (Si₃N₄) to avoid interactions with the surrounding gas. Furthermore, it can withstand higher temperatures than platinum (Pt) without suffering morphological changes. Consequently, the heater can deliver temperatures up to 1300°C without the presence of a surrounding gas. The temperature is sensed by using a four-point-probe measurement of the resistance, which changes as a function of temperature. As confirmed by the FEA simulations, the chosen length/linewidth/thickness of the heater’s metal lines enable to reach $\sim 1300^\circ\text{C}$ with low powers of around ~ 10 mW (Fig. 2c). Similarly, these simulations allowed us to analyse the temperature homogeneity across the heater. This was crucial to define the optimum position of the electron transparent windows (represented by the white

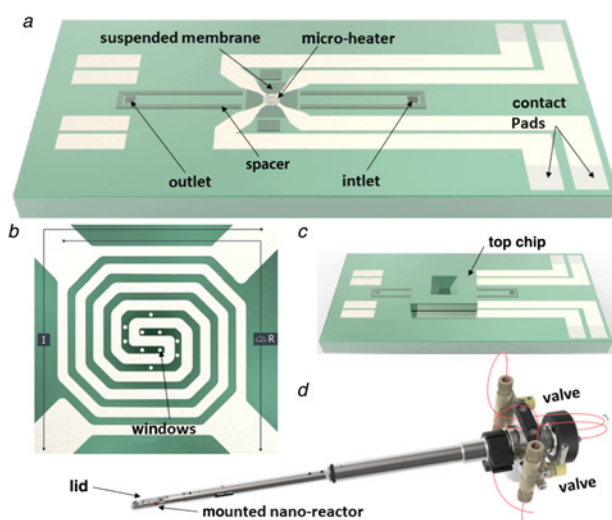


Fig. 1 Nanoreactor

- a* Architecture of the bottom chip including the microheater, contact pads, inlet/outlet and spacers
b Spiral-shaped microheater uses a four-point-probe technique to accurately determine the temperature
c Top chip encloses the gas and isolates it from the external vacuum environment
d When sealed and inserted in the functionalised holder, gas can be supplied in a continuous mode, as well as locking it with the valves in a static mode

circles). This ensures that all windows experience the same temperature at any moment, discarding confusions during the measurements that might arise from thermal gradients. Moreover, the Si substrate of the chip needs to remain at room temperature; otherwise, the heat losses of the microheater will result its thermal expansion. Such effect would lead to a significant drift of

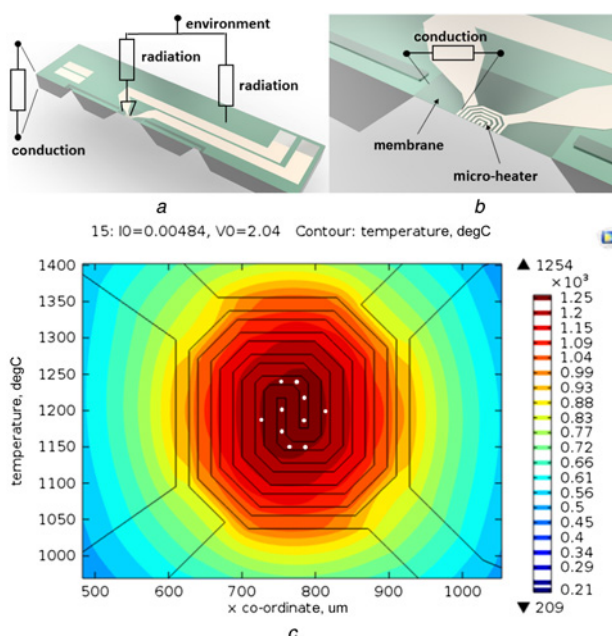


Fig. 2 Temperature distribution across the micro-heater

- a* A thermal network map was developed to understand the factors that would influence the temperature distribution, including the radiation from the MEMS into the environment
b Conduction between the different elements of the chip was also taken into account
c COMSOL simulations were used to define the position of the windows (white circles), to ensure that regardless of the selected temperature by the user, they will all be at the same temperature

the specimen, causing it to move out of the field of view of the microscope. Therefore, achieving high-resolution (HR) imaging for long times becomes impossible. To prevent this, the microheater is placed over a suspended Si_3N_4 membrane. The latter acts as a very efficient thermal insulator, preventing the conductive heat loss from reaching the Si frame of the device.

The window's design was also assessed with FEA simulations, to ensure electron transparency and the capability to withstand pressures above 1 bar. This resulted in circular shapes of $6\text{ }\mu\text{m}$ of diameter, with a thickness of 20 nm. Similarly, they were designed to be made of amorphous Si_3N_4 to prevent the superposition of periodic diffraction patterns. Once this was defined, FEA simulations were also used to determine the most favourable distance to have between neighbouring windows. To do this, stress distributions (mechanical and thermal) were taken into account.

When the nanoreactor is sealed, the microheater is switched on and the gas is introduced. The heat losses will differ from those of the microheaters operated in ambient air. The reason being is that the nanoreactor experiences the high-vacuum environment of the TEM column, but also convection by the gas that is introduced inside the chamber. The gas absorbs a certain power. Additionally, there is thermal conduction through the gas inside the chamber. Therefore, the top chip should also contain a suspended membrane whose dimensions are preferably as comparable with the bottom chip as possible, to thermally insulate its own frame. This would prevent the top Si from getting heated up, ensuring that a low-power consumption would still be required to do the gas-heating experiments. The top chip, similarly, must contain electron transparent windows which should be aligned to the bottom ones.

3. Development of the full 'climate system': To introduce the nanoreactor into the TEM, a holder is required. The latter allows the researcher to provide the different stimuli (heat and gas) to the sample inside the nanoreactor. The gas is introduced through the holder tip via tubing that connects the nanoreactor to a gas supply system. To change from a continuous flow mode to a static mode, the back of the holder contains manual valves that can lock a few microlitres of gas inside the microchamber. Additionally, the tip of the holder contains four electrical needles which create ohmic contact with the contact pads of the nanoreactor. Two needles act as the 'power' lines, supplying the current that warms up the microheater, while the other two needles act as the 'sensing' lines, necessary to read out the temperature supplied to the sample. There is a precision slot over which the bottom chip fits, having two o-rings that avoid any gas leakage around the inlet/outlet. Furthermore, an additional o-ring surrounds the top chip and seals completely the microchamber. The lid contains another small slot to fit the top chip, using a fourth o-ring that prevents leakage from the upper side of the chamber. Moreover, the holder has been developed to have a modular design. This means that all components can be detached from the holder (Fig. 3) including the inner tubing which can be

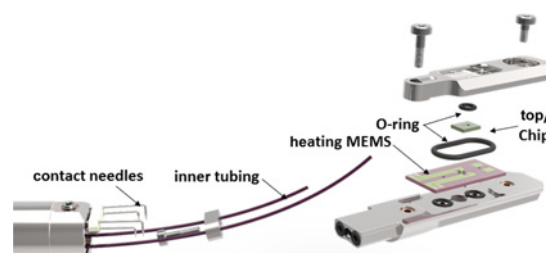


Fig. 3 Functionalised sample holder. To prevent cross-contamination between different experiments, the holder has a modular design which allows the user to detach, i.e. the tip and replace the inner tubing

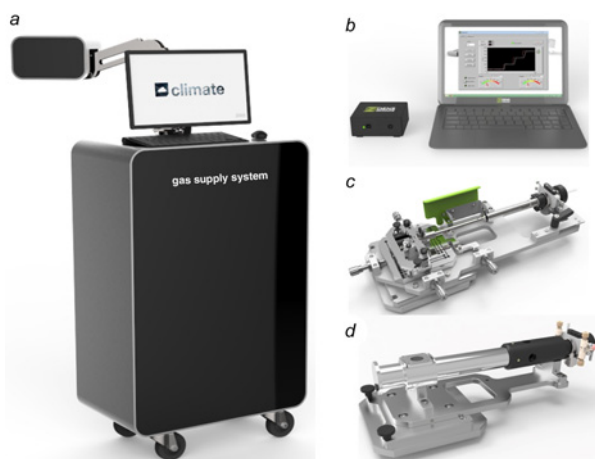


Fig. 4 Necessary tools for a total 'plug-and-play' Climate System

a Gas supply unit

b Temperature control software and heating control unit

c Alignment tool

d Leak-test tool

replaced by brand new tubing to prevent cross-contamination when necessary. This ensures easy cleaning of the system prior to new experiments.

Further improvements were required to create a complete 'plug-and-play' system. As shown in Fig. 4, additional tools were produced to enable full control on the experiments. To begin with, a gas supply system (Fig. 4a) was developed to enable on-site mixing. The cabinet contains three inlet lines with their own mass flow controllers to deliver the precise mixture of reactant gases. Similarly, the gas flow-rate and the gas pressure are defined digitally. Fast response during gas delivery is achieved via the expandable mechanical arm that shortens the distance from the gas cabinet to the holder. This is crucial when changing from one chemical environment to another one. The heating control box, as shown in Fig. 4b, supplies the power to the microheater and measures the real-time resistance changes, acting as temperature sensor. The software enables the user to set the temperature digitally and also allows to programme a temperature–time profile to enable an auto-heating experiment. Fig. 4c shows the tool used to align both top and bottom windows. Once the holder is inserted there, a set of micro-metre screws help to move the lid containing the top chip to the right location. Since this is done under an optical microscope, the user can easily visualise the position of the top windows with respect to the bottom smaller windows and correct for their positioning if necessary. Finally, Fig. 4d shows the leak-test tool used to confirm the absence of leakages in the nanoreactor. Such tool, connected to a turbo pump, corroborates the vacuum performance of the holder and gives the user the confidence that the membranes in the MEMS device are fully intact and that the gas is thus properly confined inside the reactor.

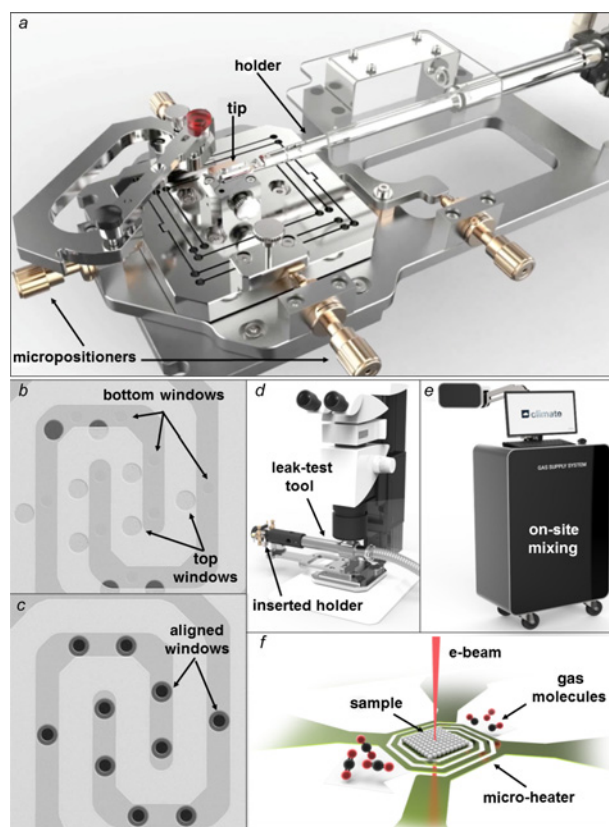


Fig. 5 Work flow

a After loading the sample on the bottom chip and closing the nanoreactor, the holder is introduced in the alignment tool

b Optical microscope allows the user to see the existing misalignment between top and bottom windows

c While the micropositioners allow to correct for that and ensure proper overlap

d Holder is then brought to the leak-test tool to ensure there is no leakage

e Gas supply system is used to set the gas pressure, composition and flow rates for the experiment

f Once inside the TEM, the user can visualise in situ the solid–gas interactions

4. Materials and methods: A series of different inspections using various techniques were done to inspect the geometry of the resulting nanoreactors. Scanning electron microscope (SEM) was used to inspect the linewidth of the heating lines, the lateral size of the suspended membrane and the inlet/outlet complex. The diameter and cleanness of the electron transparent windows were further inspected with atomic force microscopy (AFM) and (S)TEM to discard particle contamination which would have not been recognised with SEM due to small feature sizes. The spacer's height had also been inspected using white light interferometry. The thickness of the suspended membrane and the electron transparent windows were measured with ellipsometry and electron energy loss spectroscopy (EELS), respectively. The width/length of the chips were measured with micrometer to ensure that they were within the $\pm 20\ \mu\text{m}$ tolerance. This, due to the tight mechanical tolerances with which the slots in the tip and lid of the holder were made.

4.1. Heating performance: Temperature accuracy, lifetime and durability are important specifications of the microheater. Consequently, the bottom chip had to be calibrated in order to correlate the heater's resistance to the supplied temperature. The resistance was measured using the four-point-probe method. Since temperature measurements can differ, we used various methods including: (i) measuring the temperature of the heater with infrared (IR) pyrometer camera, (ii) measuring the temperature of the specimen (using Si powder) by Raman spectroscopy and (iii) measuring the chip temperature by heating up to a controlled temperature using a hot-plate with a Pt100 sensor. During the temperature calibration, we found that Raman spectroscopy gives the best local temperature information, although it is time consuming. The hot-plate with Pt100 is limited to a temperature range of 250–300°C. Therefore, for repetitive calibration the IR pyrometer camera was used, giving the most reproducible results in the temperature range 300–1300°C. However, the results obtained by IR pyrometer camera depend on the emissivity value of the heater. Therefore, the emissivity of our heater was found by cross-correlating the pyrometer temperature measurement with the Raman spectroscopy (Horiba Labram high resolution (HR) Raman spectroscope) measurements. The latter was also used to determine the temperature distribution over the spiral. The temperature of the Si powder sample was measured in the windows and between spiral lines. Nanoreactors are disposable (one per experiment). Therefore, they should perform according to specifications within a standard TEM session of 4 h. However, their lifetime testing was extended to 20–24 h.

4.2. Leak tightness: The bottom and top chips were tested for leak tightness. This was done using a Pfeiffer SmartTest HLT – IG 0100 BD. When the leak rate is $< 1 \times 10^{-9}$ mbar l/s, the chip is considered to be leak tight. As the chip is mounted, the leak-test machine was turned on to generate vacuum below the chip. Helium was then fed through the gas line located on the top cover. If the chip is leaking, the helium will pass through the membrane and can be detected by the helium detector in the leak-test machine.

4.3. Resolution and thermal drift: To explore the intrinsic thermal drift of the bottom chip, gold (Au) nanoparticles were deposited on the windows located across the microheater and brought up to 800°C. During this initial experiment, no gas was confined and two HRTEM images were taken from the same area at time 0 min and after 2 min. Both images were overlapped and analysed to measure the total shift given by the thermal drift.

4.4. Work flow: To carry the full experiment, a typical work flow was developed. This is shown in Fig. 5. It starts by loading the sample on the desired window and sealed with the top chip. The

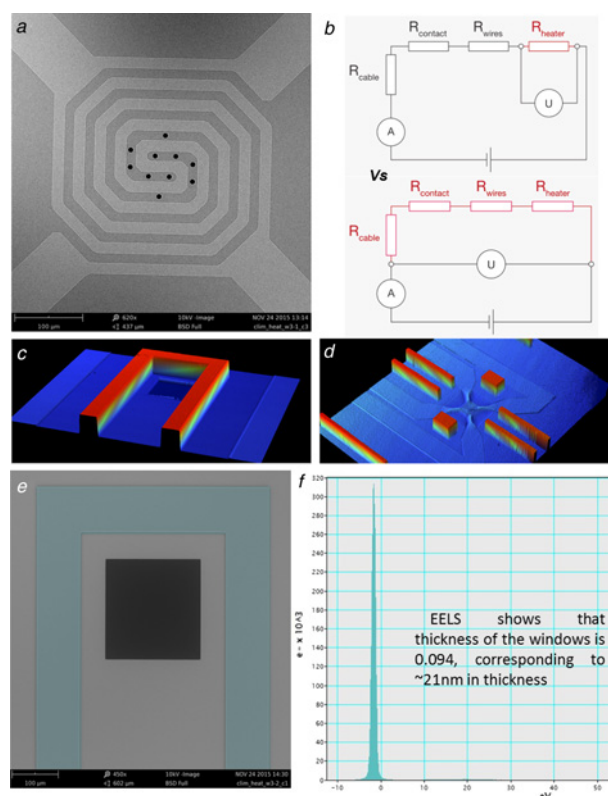


Fig. 6 Architecture of the device

a SEM inspection of the microheater, containing ten windows located in the region with same temperature homogeneity (as analysed from FEA simulations and Raman analysis). Note that the microheater has four contacts to perform 4-point-probe measurements
b Schematic of the representative circuit for the microheater (four contacts), compared with a 2-point-probe circuit
c, d White light interferometry images of the spacers around the inlet and the microheater
e Spacers (coloured in blue) surrounding the inlet/outlet define the gas duct and their thickness defines the height of the gas chamber
f EELS measurements showed a measured value of 0.094, corresponding to a window thickness of ~21 nm

latter is then inserted on the tip of the holder and brought to the alignment tool to ensure the top and bottom windows are well overlapped. This process is done under an optical microscope to corroborate the right positioning. Once aligned, gas can be supplied and the holder can be inserted in the high-vacuum leak-test tool to ensure the system is properly sealed and to verify the vacuum performance of the system. After introducing the holder into the TEM, the gas is brought inside the nanoreactor using the gas flow supply system. Reaction conditions such as gas pressure, flow rate, composition and temperature are then digitally set and controlled through the software user interface. Real-time dynamics of the gas–solid interaction can be observed within the nanoreactor's controlled reaction environment. Direct imaging of the reaction mechanisms at atomic level can be recorded.

4.5. Full experiment: in situ observation of $\text{CuO} + \text{H}_2$ reductive reaction: CuO particles were loaded on the desired window and sealed with the top chip. After inserting the holder into the TEM (FEI Titan), it was connected to the gas flow supply system to introduce pure N_2 , and then a mixture of $\text{H}_2 + 4\text{N}_2$. Reaction conditions such as flow-rate, pressure, composition and temperature were digitally set and controlled through the software user interface. Real-time dynamics of the gas–solid interaction within the nanoreactor's controlled reaction environment were

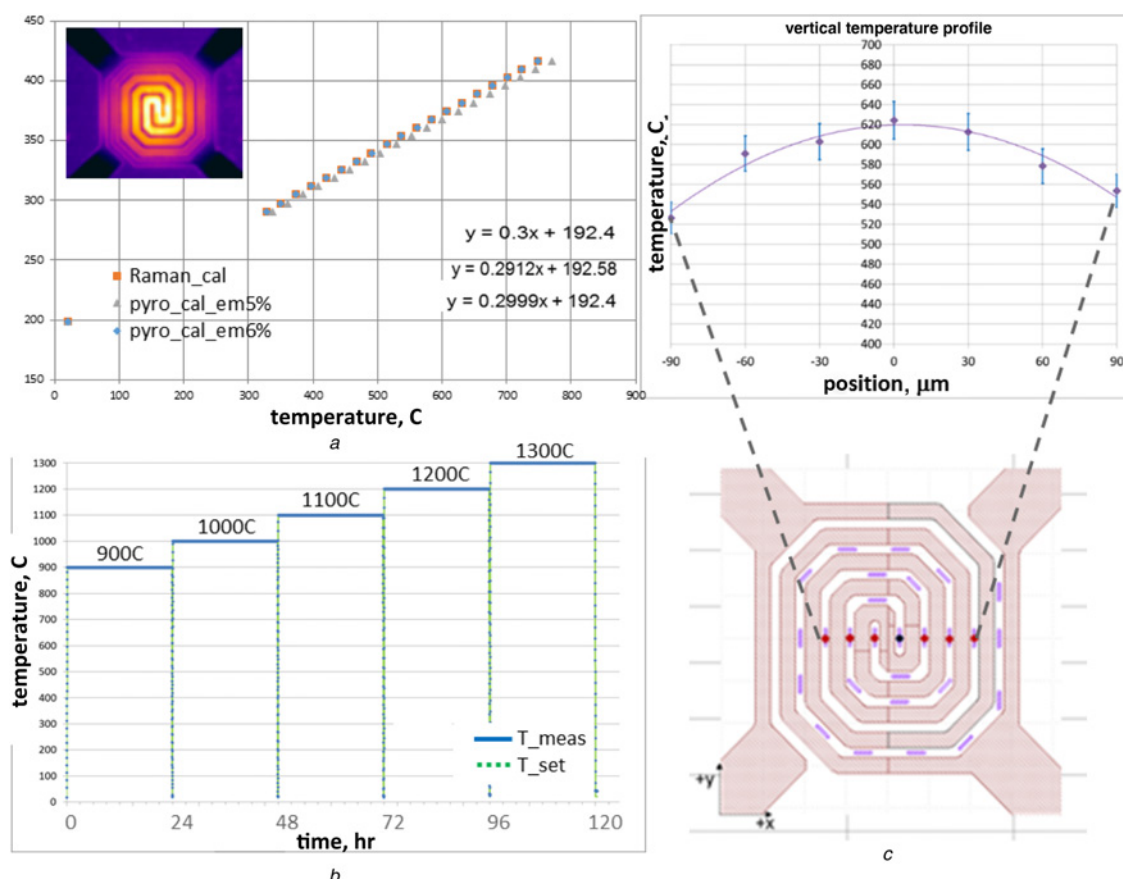


Fig. 7 Temperature calibration

a Raman and pyrometry calibration cross-correlation. The inset shows the IR image of the heating spiral taken with high end forward looking infrared imaging camera

b Measured and set temperature change during long exposure time

c Temperature variation in horizontal direction of the spiral. Error bars (3%) are also shown

observed and further monitored with diffraction and EELS. Direct imaging of the reaction mechanisms at atomic level was recorded. To explore thermal drift of the nanoreactor during the experiment, the reduced Cu particles were brought from room temperature to 650°C. A HR image was recorded at the beginning and end of the experiment, and then subtracted to measure the drift over time. For each of the images, the fast Fourier transforms of high resolution electron microscopy (HREM) were analysed to judge the resolution.

5. Results: The resulting chip (Fig. 6) had an encapsulated microheater covering an area of $-300 \times 300 \mu\text{m}$, located on top of a suspended Si_3N_4 membrane with a thickness of 400 nm and a

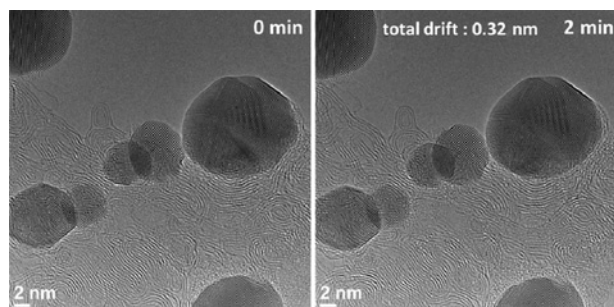


Fig. 8 Resolution and thermal drift. The total drift between (a) an image taken at the beginning of the experiment and (b) an image of the sample region of interest taken after 2 minutes is measured to be $<0.32 \text{ nm}$, giving an estimated drift rate 3 pm/s

lateral size of $800 \mu\text{m}$. The average resistance of the metallic heater was found to be 234Ω with a standard deviation of 5Ω .

When characterising its heating performance (Fig. 7), it was observed that from the temperature calibration using Raman and Pyrometry, the obtained 6% emissivity setting was in good agreement with the temperature data obtained from the Raman ($<0.5\%$). The temperature variation (maximum) was 6°C , meaning 1% at 600°C . Similarly, it was found that chips survived after 120 h of HT experiments in the range between 900 and 1300°C . The experiments showed that even at the highest temperatures the power generated never exceeded 20 mW.

5.1. Resolution and thermal drift: The test performed at 800°C using Au particles on the bottom chip alone showed negligible sample drift. Fig. 10 shows the HRTEM images taken from the same area at time 0 min (Fig. 8a) and after 2 min (Fig. 8b), the image shift is estimated to be $<0.32 \text{ nm}$. The apparent drift rate when no gas is confined is as low as 3 pm/s . Diffraction patterns showed resolutions better than $1 \text{ \AA}$.

5.2. Leak tightness: The pressure tests showed that bottom chips can withstand 1.5 bar for a maximum of 60 h without detecting any leak. Similarly, a top chip was able to withstand 3.2 bar of pressure for 20 h without any leak. Such chips were still leak tight after 6 weeks from the manufacturing date, helping to discard any aging effect.

5.3. Full experiment: in situ observation of CuO-H_2 reaction: The 'Climate System' empowered the precise control of the gas flow, gas mixture, pressure and temperature during the CuO-H_2

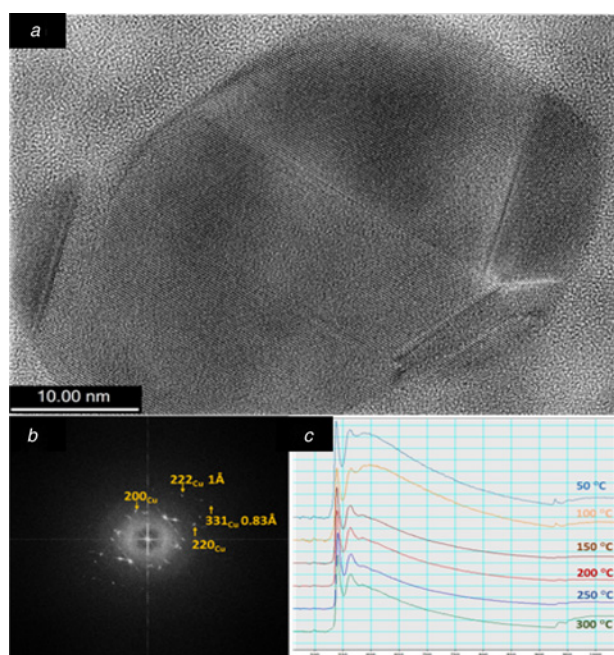


Fig. 9 *In situ* observation of CuO reduction
a HRTEM image of Cu taken at 300°C after reduced from CuO in 1 bar pressure of H₂ + 4N₂ with
b Resolution better than 1 Å. EELS measurements were taken from CuO in a reductive environment at various temperatures
c Showing the reduction of CuO to metallic Cu is accomplished around 250°C

reaction. In other words, the observation of real-time dynamics as the CuO particles reduced from 50 to 300°C and with 1 bar pressure of H₂ and N₂ mixture (Fig. 9a). Despite the 5 μm thickness (given by the spacers) of the mixed gas with 1 bar pressure, a resolution of 1 Å can be obtained (Fig. 9b) as confirmed by the diffractogram. Similarly, EELS confirmed the chemical valence state of the original CuO at room temperature is completely reduced to metallic Cu when the temperature is set above 250°C (Fig. 9c). Note that the outlet tubing is allowed to connect to a mass-spectrometer for end product analysis [11].

Drift rate tests performed during the CuO reduction experiment confirmed also a very low sample drift with metal-based MEMS heaters. On the basis of two HRTEM images taken from the same area at time 0 min (Fig. 10a) and after 1 min (Fig. 10b), the image shift is estimated to be <1.5 nm. The apparent drift rate is as low as 25 pm/s.

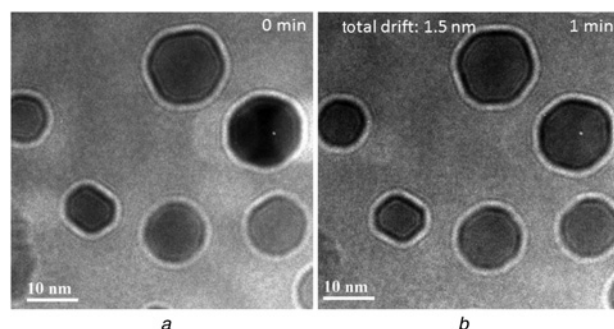


Fig. 10 *Thermal Drift.* The total drift between (a) an image taken at the beginning of the experiment and (b) an image of the same region of interest taken after 1 minute is measured to be <1.5 nm, giving an estimated drift rate of the nanoreactor of <25 pm/s

6. Discussion: The results obtained particularly during the heating experiments confirmed the advantage of using metallic heaters over, i.e. ceramics. Metals have much higher current densities and thus extremely fast linear responses. Such current densities, required to generate the Joule heating effects, are low enough to lead to appreciable electromigration, further helping to expand the lifetime of the heaters. Ceramics, on the other side, have a low response due to lower current densities and they are nonlinear. Moreover, despite the chemical inertness of ceramics, which can make them attractive, the Si₃N₄ encapsulation used here of our microheater ensures a non-conductive surface and it has been proven to prevent the surrounding gases from interacting with the metal. The appropriately chosen adhesion layers keep the metal in place and avoid delamination due to thermal stresses. Furthermore, there is a major advantage of having a four-point-probe configuration for our microheater. Two contact pads are used to supply the current and the other two to measure the changes in resistance. When the current flows through the system, the heater's resistance changes due to Joule heating effect, increasing the temperature. Using the electrical resistance of the metal as a temperature indicator offers considerable advantages as it can be used to operate independently from changes in external environments. A well proven linear dependence of the resistance versus temperature of the metal heaters over the whole temperature range facilitates temperature control and greatly improves time response. Additionally, the four-point-probe measurement is commonly accepted amongst the electrical engineers as the most accurate technique to locally measure a materials electrical resistance. This method discards the influence of the cable resistance, undefined contact resistance and lead wires resistance, by using separate pairs of current-carrying and voltage-sensing electrodes to make more accurate measurements than the simpler and more usual two-contact sensing. Sample stability at elevated temperature and during heating/quenching is the most important characteristic for microscopists. Therefore, the four-point-probe measurement in combination with our developed algorithm and the control unit results in a closed-loop feedback system that guarantees that despite potential thermal fluctuations inside the TEM column, the system will compensate for it to maintain the extreme temperature stability (Fig. 11). The presented device enables reduction of the drift rate to a minimum value.

Having a dual chip technology, as opposed to monolithic devices [12], empowers the user for direct and easy sample preparation and transferring, ensuring that the specimen will directly be on the field of view. This is a particular advantage for users wanting to work with focused ion beam (FIB) lamellas, as flowing them inside a monolithic device becomes nearly impossible. Similarly, the developed and suggested techniques to prepare and transfer the sample gives the user the full control on the amount of sample to be dispensed (i.e. by dispensing with the femtopipette [13]), or the capability to do the final thinning of the lamellas on-site, avoiding risks of losing or breaking the specimen. The modular design of the holder permits the user to avoid clogging and cross-

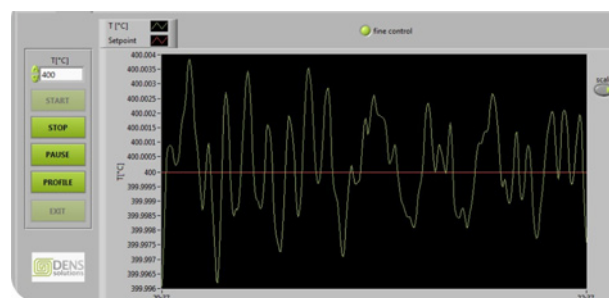


Fig. 11 *Temperature stability.* The closed-loop feedback system ensures that temperature will remain stable in the millikelvin regime

contamination that might arise from switching the type of gases between the different experiments. This is, therefore, one of the biggest value propositions that researchers can find on a holder of this nature. Finally, the 'Climate System' can act as the ideal platform not only to enable solid–gas interactions, but it could also be thought as a tool to allow liquid and heating experiments. Overall the nanoreactor acts as an 'all-in-one' nanolaboratory, as we can also record in situ EELS measurements (comparable with in situ xray photoelectron spectroscopy (XPS)) and in situ electron diffraction (comparable with in situ xray diffraction (XRD)), but giving the user the added value of doing it on a single nanoparticle level, increasing the accuracy of the measurement. In addition, it enables the user to cross-correlate calorimetry and mass-spectrometer data, which makes it more robust and accelerates the acceptance of the obtained results. Furthermore, there are on-going effort with Gatan to develop a fully integrated user interface that will ensure the correct correlation of the obtained data with the recorded images/movies. Such integration, which only works in combination with a Gatan camera/scanning system, will simplify the analysis of in situ experiments and help design a complete workflow together.

7 References

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