

# In-situ STEM study on the morphological evolution of copper-based nanoparticles during high-temperature redox reactions

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## Electronic Supporting Information

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### 1. Nanoparticle synthesis

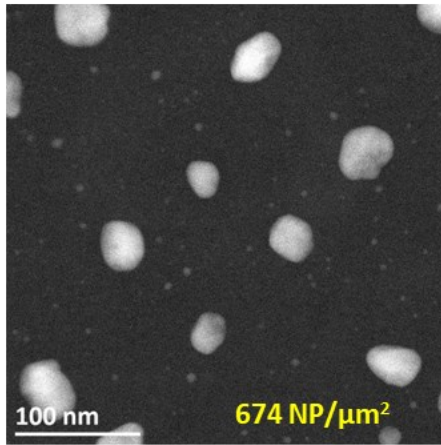
#### 1.1. Sputtered nanoparticles:

Three sputtering experiments were conducted varying the initial NP formation steps (presented in Table S1). The thickness of the film in the 1<sup>st</sup> experiment was 2 nm while in the 2<sup>nd</sup> and 3<sup>rd</sup> experiment 1 nm films were used. For all three experiments, the samples were heated from room temperature to 150 °C at 5 °C/min and kept for 2 hours. However, no particles were formed at this temperature, and the system had to be heated to 300 °C. For experiments 1 and 2, a slower heating rate of 5 °C/min was used in contrast to 5 °C/sec for the 3<sup>rd</sup> experiment.

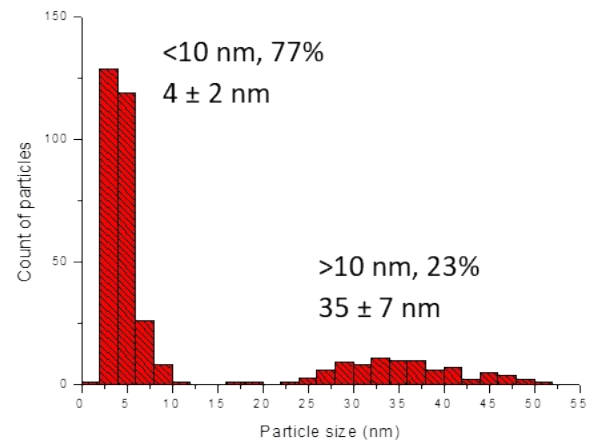
Table S1: Experimental parameters used for the formation of sputtered nanoparticles.

Samples	Film thickness	Gas atmosphere	Heating rate	Final Temperature	Duration	NP average size and density
Sputt-1	2 nm	0.5 bar H <sub>2</sub>	5 °C/min	300 °C	2 hours	4 ± 2 (<10 nm) 35 ± 7 (>10 nm) 675 NP/μm <sup>2</sup>
Sputt-2	1 nm	0.5 bar H <sub>2</sub>	5 °C/min	300 °C	2 hours	4 ± 1 (<10 nm) 21 ± 6 (>10 nm) 1015 NP/μm <sup>2</sup>
Sputt-3	1 nm	0.5 bar H <sub>2</sub>	5 °C/s	300 °C	2 hours	9 ± 4 nm 3730 NP/μm <sup>2</sup>

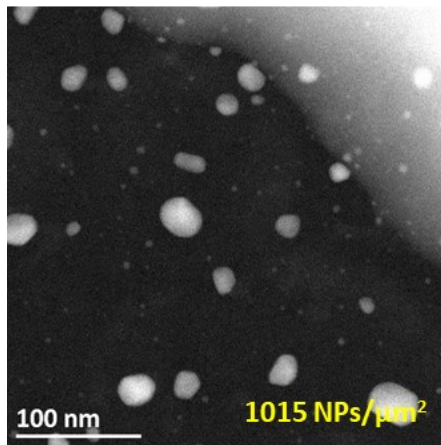
a) Sputt-1



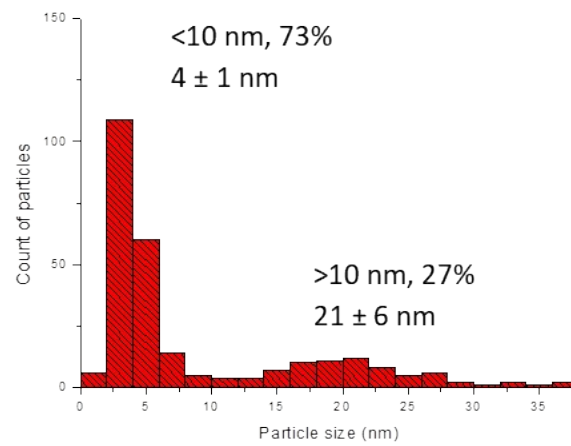
b) PSD, Sputt-1



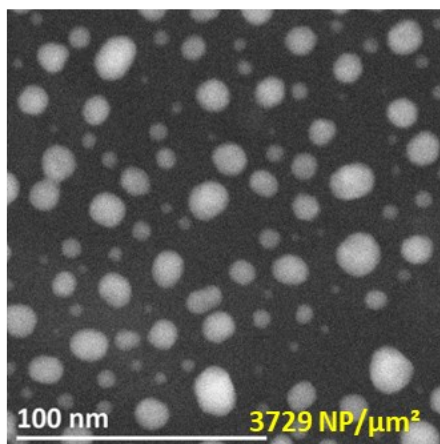
c) Sputt-2



d) PSD, Sputt-2



e) Sputt-3



f) PSD, Sputt-3

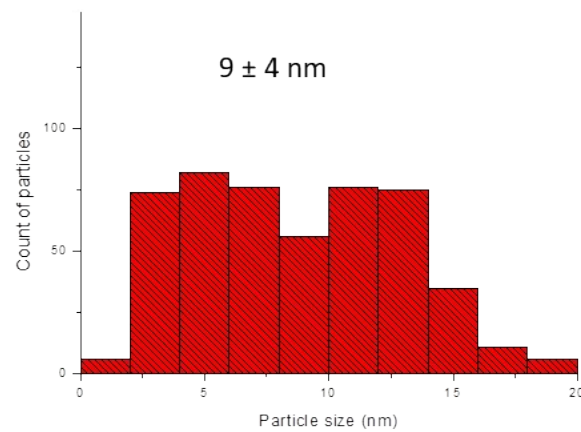


Figure S1: (a-c) Formation of Cu nanoparticles at different experimental conditions. (a) Sputt-1 (c) Sputt-2 (d) Sputt-3 and their corresponding particle size distribution in (d, e and f).

## 1.2. Chemically synthesized nanoparticles:

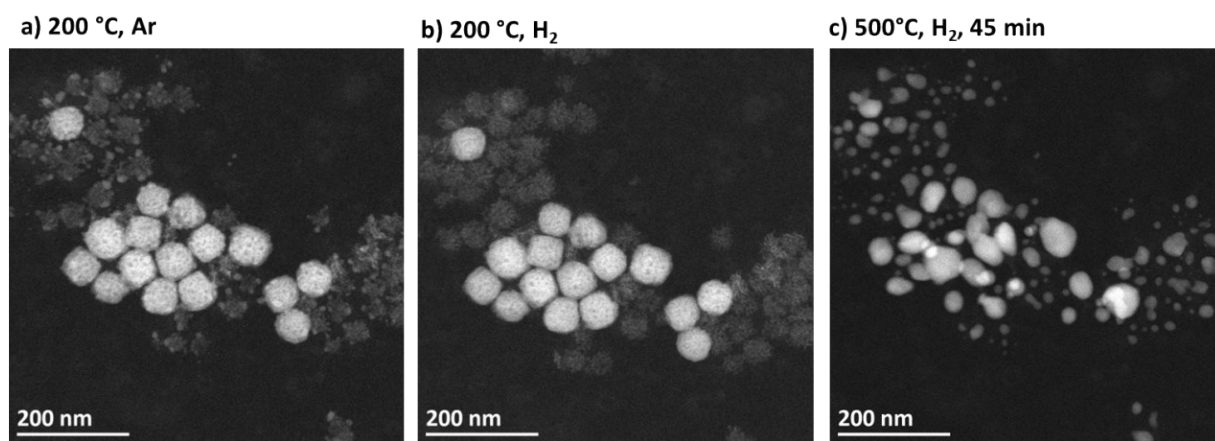


Figure S2: Heat treatment of sample: Syn-1: a) at 200 °C under Argon, b) at 200 °C under H<sub>2</sub> and c) at 500 °C after 42 min of gas flow.

Initially, the surface of the nanoparticles were passivated by organic ligands and large particles were rather composed of smaller nanoparticles, aggregated together. Upon heating at 500 °C, under H<sub>2</sub> for an hour the organic layer is removed and the initial porous structure is lost, forming compact nanoparticles of metallic copper.

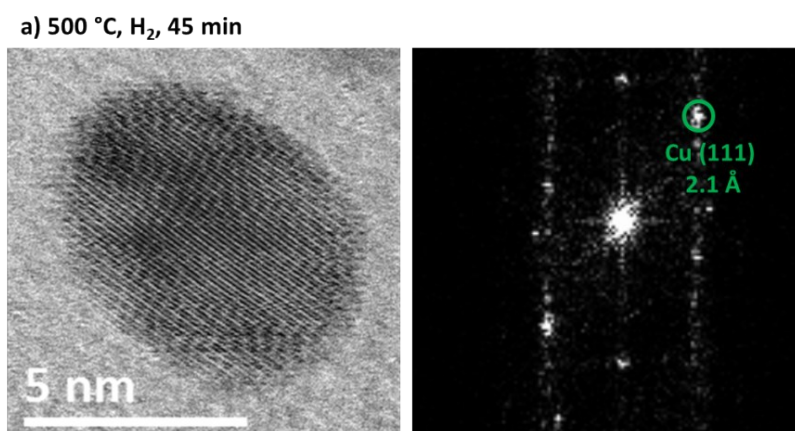


Figure S3: a) high resolution image (HR) of metallic copper after 45 min of heat treatment under H<sub>2</sub> at 500 °C and Fast Fourier Transform (FFT) of the HR image.

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## 2. In-situ STEM analysis

### 2.1. Oxidation of metallic Copper

#### 2.1.1. Phases present

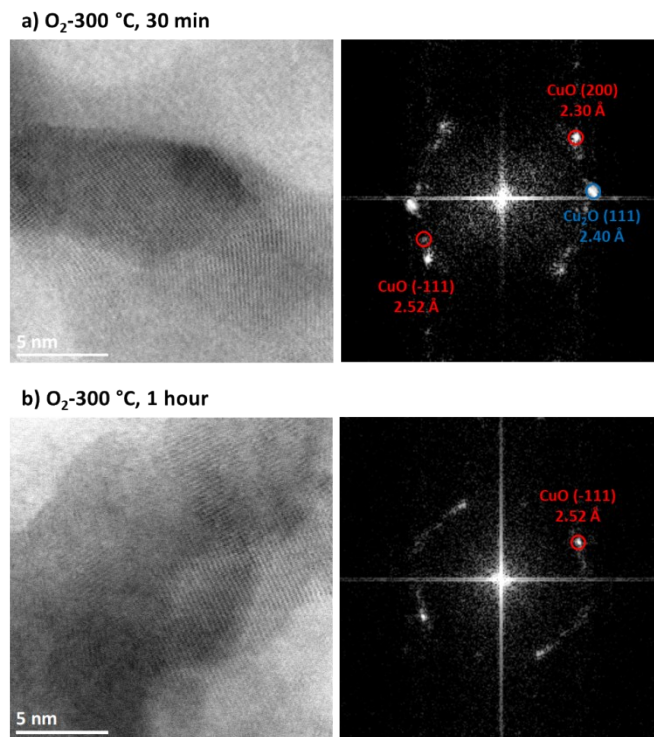
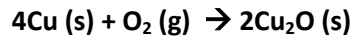


Figure S4: HR-STEM images of copper oxide during oxidation at 300 °C, a) after 30 min of oxygen flow and b) after 1 hour of gas flow (inset contains Fast Fourier Transformation (FFT) pattern of the HRSTEM image).

### 2.1.2. Kirkendall Void Formation



Calculations -  $\Delta g_{\text{Cu}_2\text{O}}$

$$\Delta g_{\text{Cu}_2\text{O}} = -339758 + 149.14T \quad ^1$$

#### Diffusion Coefficient (cm<sup>2</sup>/s):

Using the reaction-diffusion model developed by Svoboda et al. the self-diffusion coefficients of Cu in Cu<sub>2</sub>O is calculated to eventually determine the activation energy of diffusion and pre-exponential parameter to fit Arrhenius model for a temperature range of 323 – 773 K<sup>2</sup>.

$$t = \frac{ARTR_0^2}{D_{\text{Cu in Cu}_2\text{O}} |\Delta g_{\text{Cu}_2\text{O}}|}$$

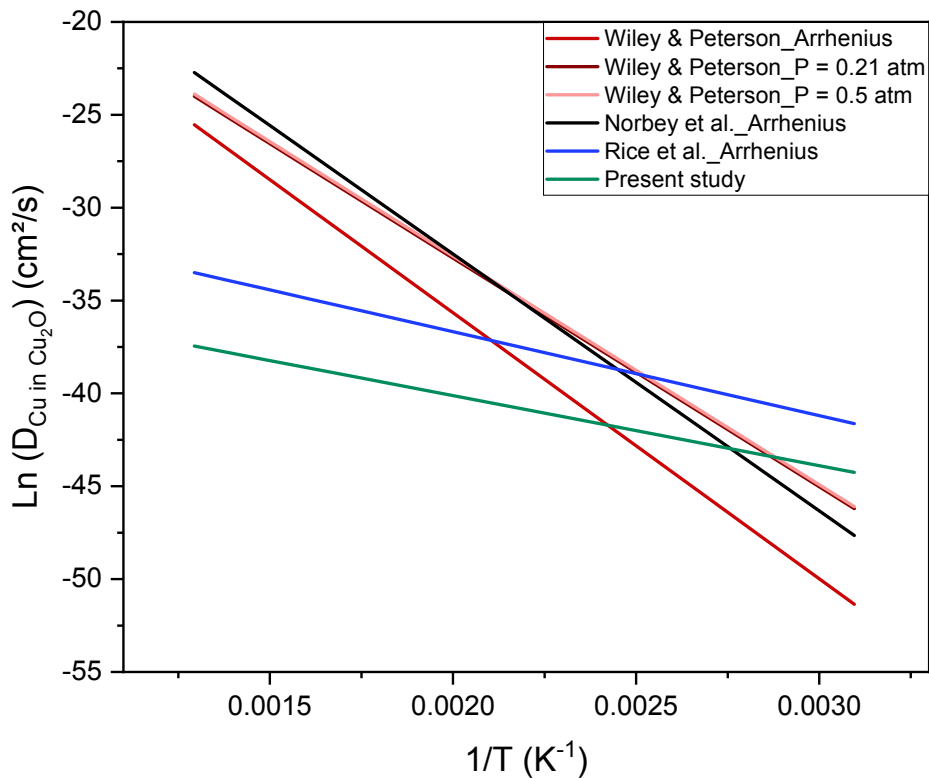


Figure S5: Comparison of self -diffusion coefficient of copper in Cu<sub>2</sub>O in bulk sample by Wiley and Peterson<sup>3</sup> and Norby et al.<sup>4</sup> and in nanoparticles by Rice et al.<sup>5</sup> and the current study.

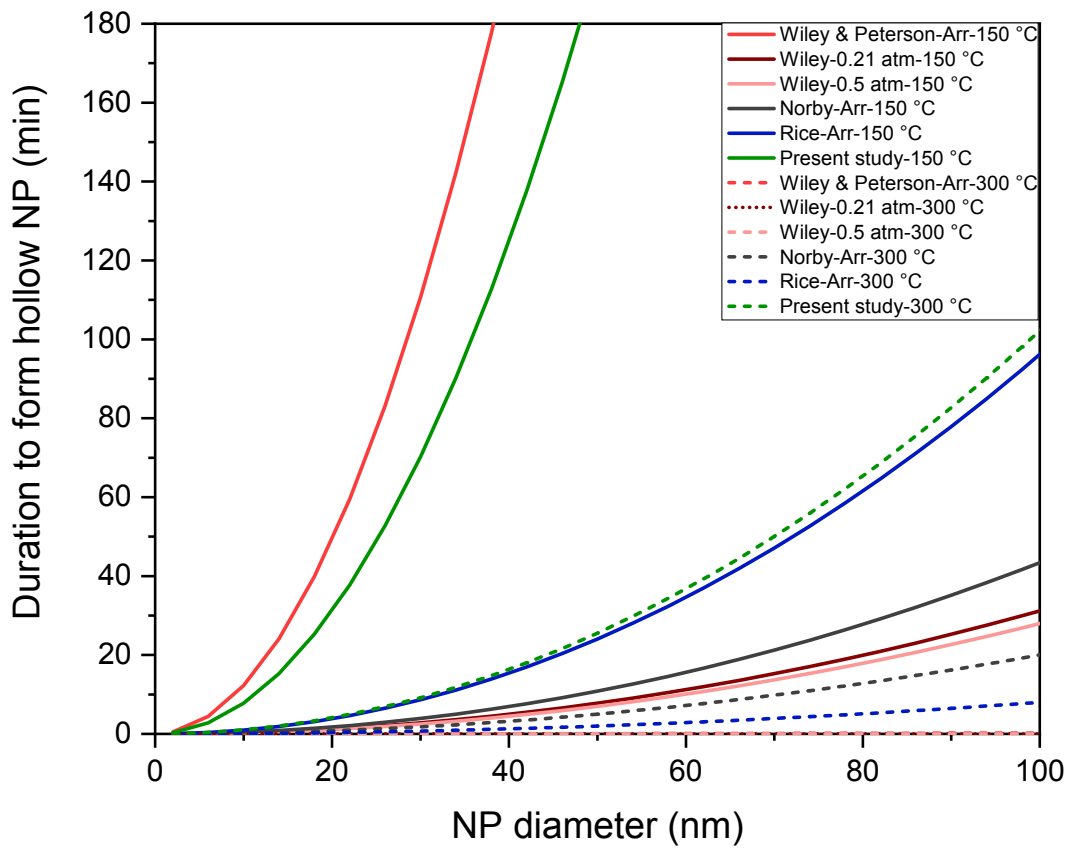


Figure S6: The duration of completion to form Kirkendall void as a function of nanoparticle diameter using the diffusion coefficients at a temperature of 150 °C and 300 °C.

## 2.2. Nanoparticle Size Distribution:

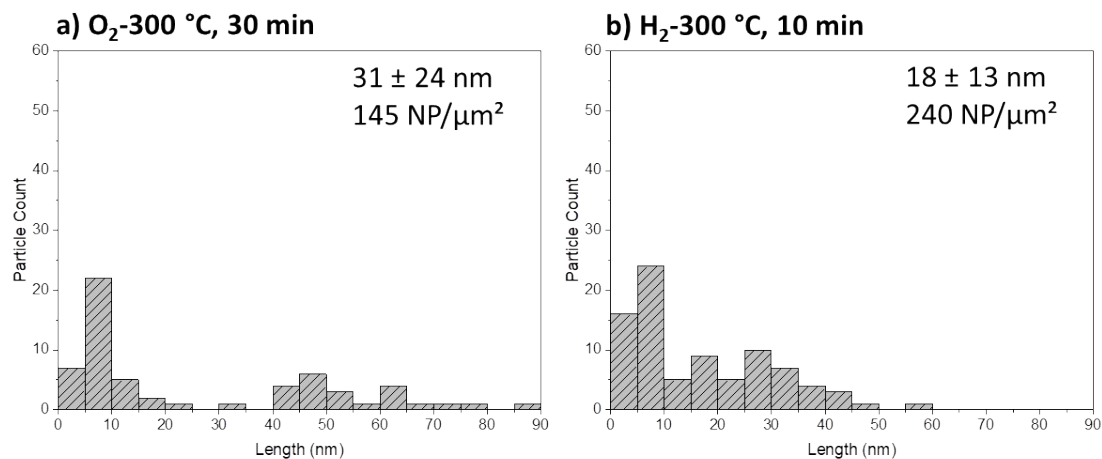


Figure S7: PSD for the NPs at 300 °C under a) O<sub>2</sub> after 30 min of oxidation and b) H<sub>2</sub> after 10 min . Sample: Sputt-1.

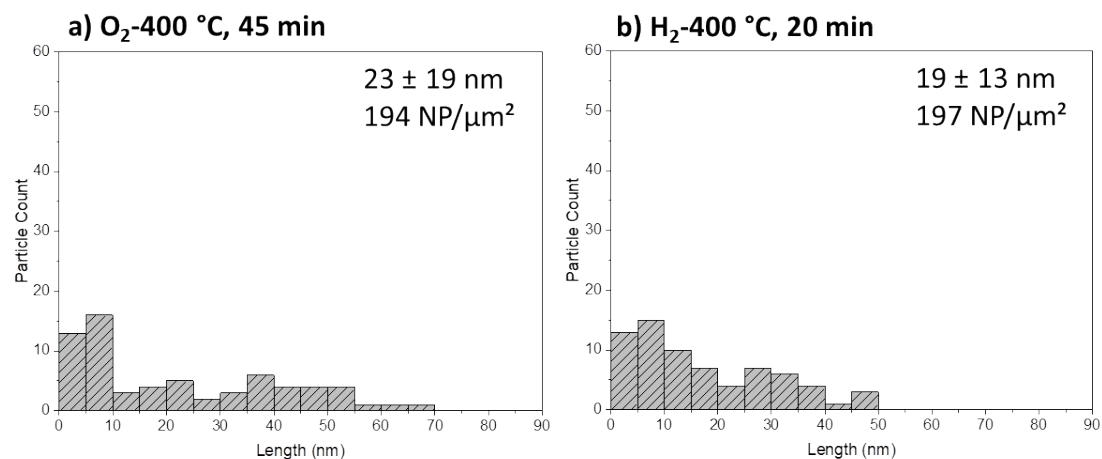


Figure S8: PSD of the nanoparticles at 400 °C, a) copper oxide NPs under oxygen after 45 min and b) under hydrogen after 20 min of gas flow. Sample: Sputt-1.

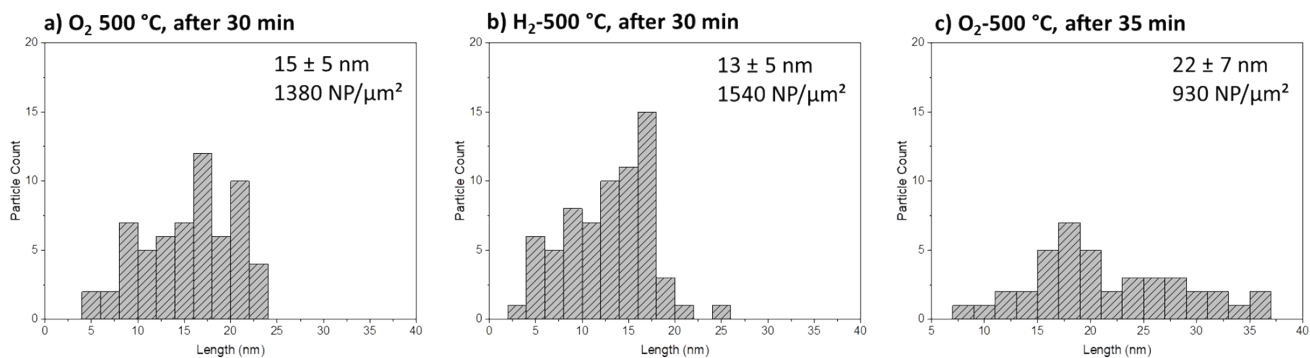


Figure S9: PSD of the NPs at 500 °C: a) under O<sub>2</sub> after 30 min of gas flow b) under H<sub>2</sub> after 30 min of gas flow and c) NPs after re-oxidation after 35 min of oxidation. The images are not from the same area of observation. Sample: Sputt-3.



## 2.3. Reduction of Copper Oxide Nanoparticles

### 2.3.1. Reduction of hollow NPs at 250 °C

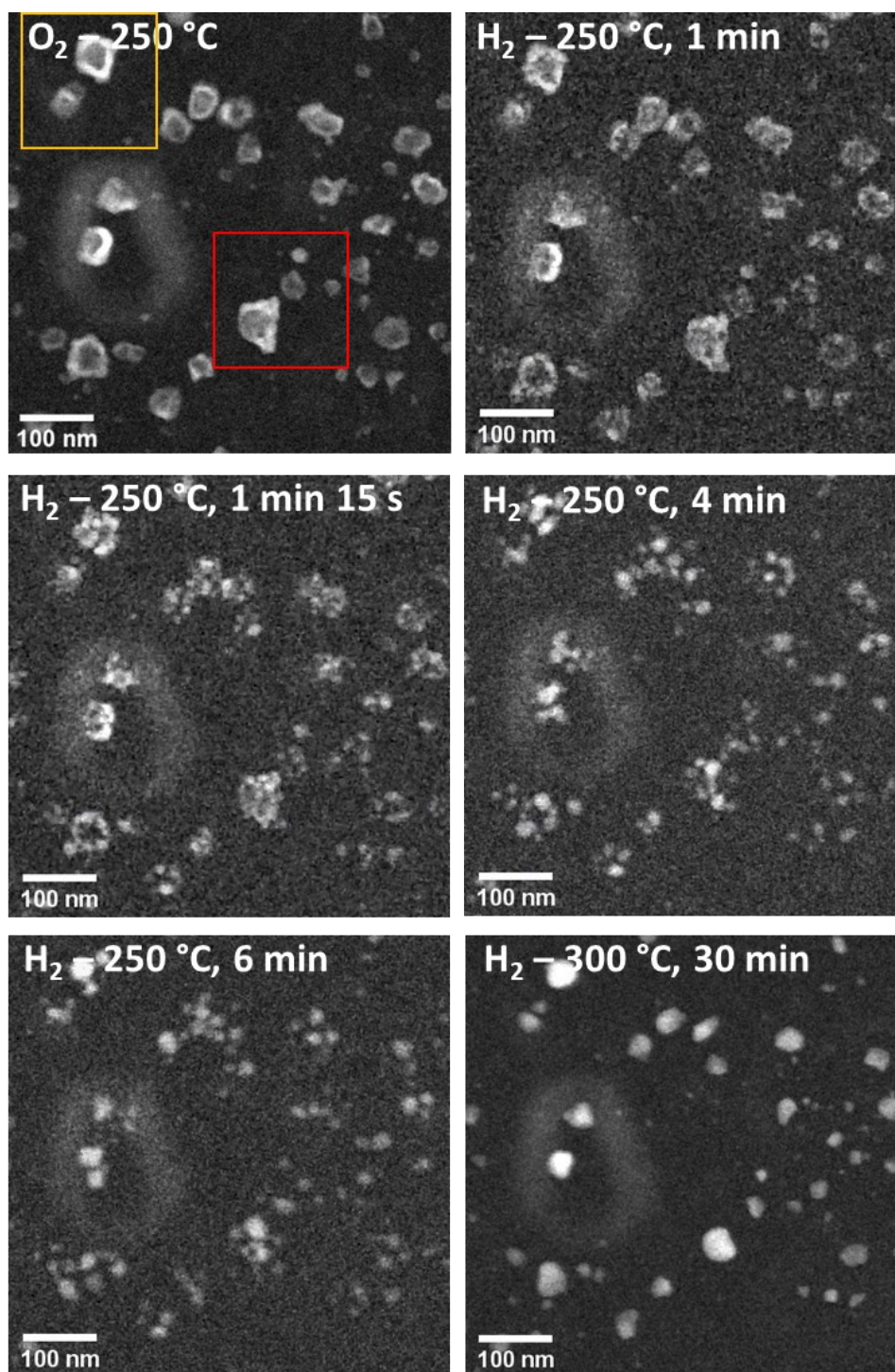


Figure S10: Reduction of hollow copper oxide nanoparticles under hydrogen at 250 °C up to 6 min and heated to 300 °C, after 30 min. Sample: Sputt-2.

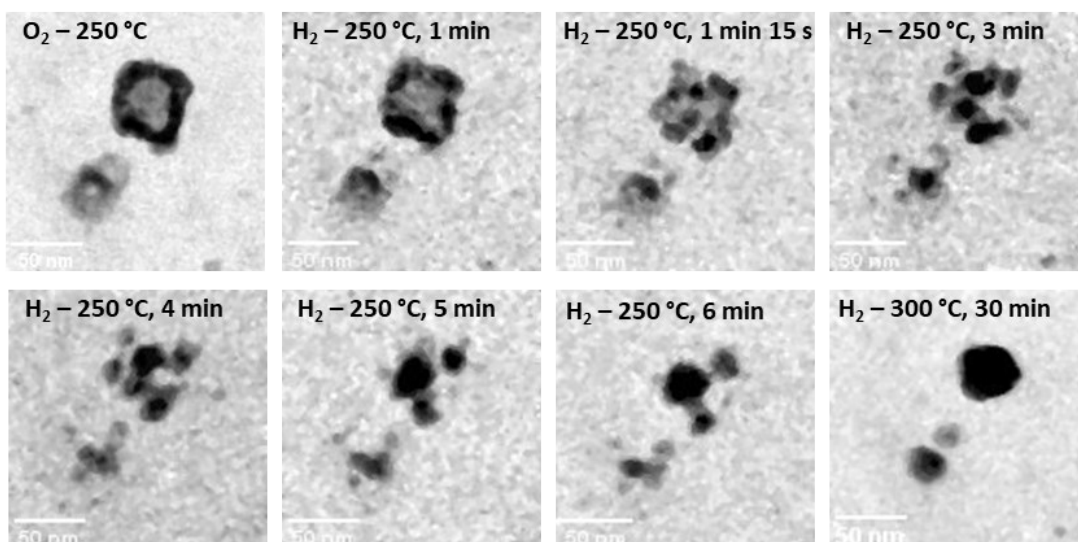


Figure S11: Reduction of hollow copper oxide nanoparticles under hydrogen at 250 °C up to 6 min and heated to 300 °C, after 30 min. Area marked by yellow square on Figure S9. Sample: Sputt-2.

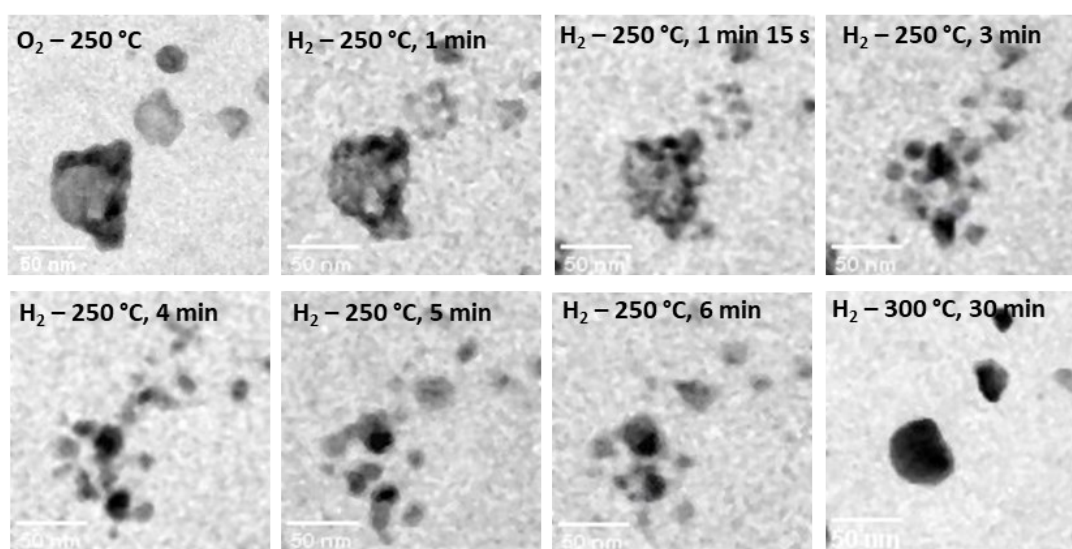


Figure S12: Reduction of hollow copper oxide nanoparticles under hydrogen at 250 °C up to 6 min and heated to 300 °C, after 30 min. Area marked by red square on Figure S9. Sample: Sputt-2.

### 2.3.2. Reduction of hollow and compact NPs at 400 °C

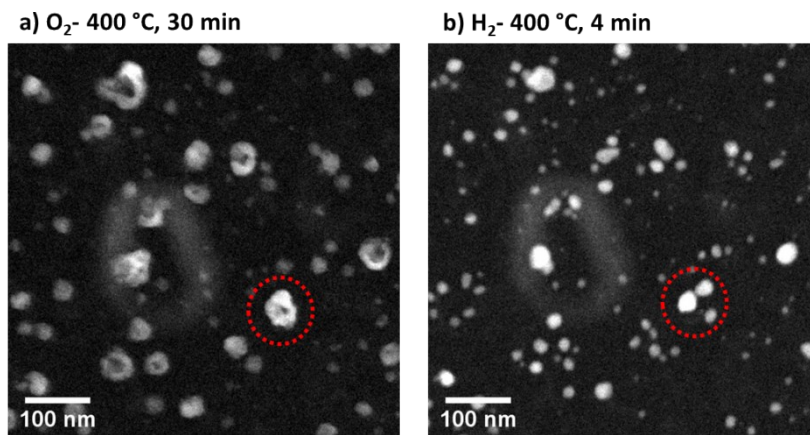


Figure S13: Reduction of Copper oxide nanoparticles at 400 °C, a) copper oxide NPs under oxygen after 30 min and b) under hydrogen after 4 min of gas flow. Sample: Sputt - 2

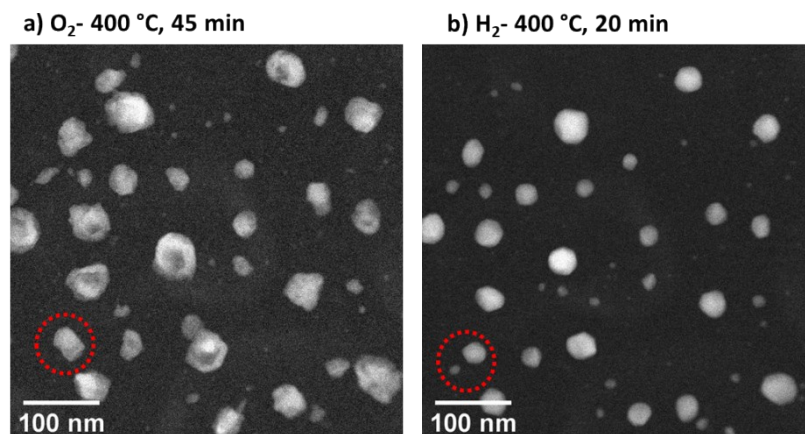


Figure S14: Reduction of Copper oxide nanoparticles at 400 °C, a) copper oxide NPs under oxygen after 45 min and b) under hydrogen after 20 min of gas flow. Sample: Sputt - 1

### 2.3.3. Reduction of compact NPs at 250 °C

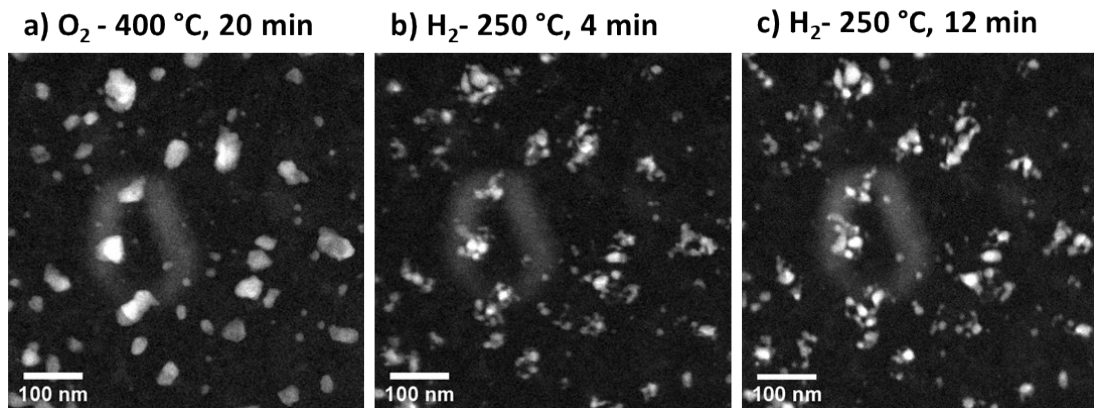


Figure S15: Reduction of Copper oxide nanoparticles at 250 °C, a) copper oxide NPs under oxygen after 20 min and under H<sub>2</sub> after 4 and 12 min of flow, respectively in b) and c). Sample: Sputt - 2

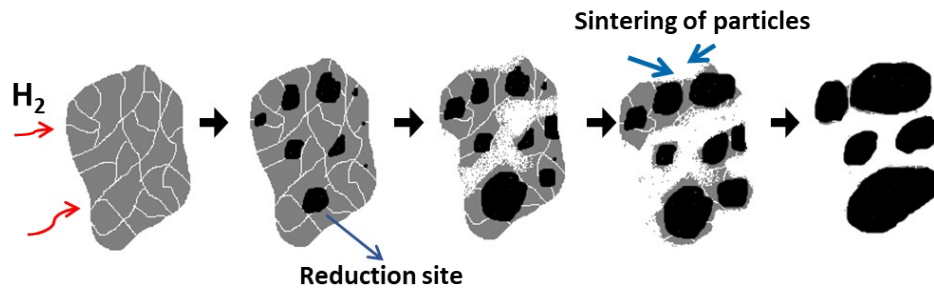


Figure S16: Schematic representation of Figure S15 illustrating the reduction of compact copper oxide nanoparticle which leads to the fragmentation into multiple nanoparticles of metallic copper.

## 2.4. Evaporation of the copper phase

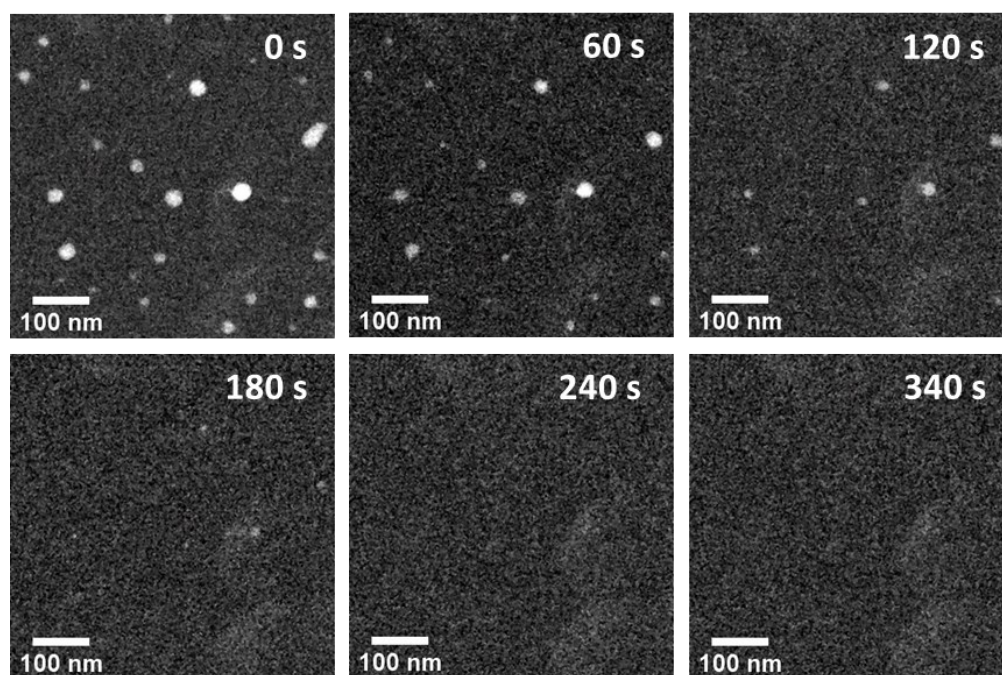


Figure S17: Evaporation of metallic copper NPs at 900 °C under H<sub>2</sub>

## References

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- 2 J. Svoboda, F.D. Fischer and D. Vollath, *Acta Materialia*, 2009, **57**, 1912–1919.
- 3 N. L. Peterson and C. L. Wiley, *Journal of Physical Chemistry Solids*, 1984, **45**, 281–294.
- 4 R. Haugsrudz and T. Norby, *Journal of Electrochemical Society*, 1999, **146**, 999–1004.
- 5 K. P. Rice, A. S. Paterson and M.P Stoykovich, *Particle & Particle Systems Characterization*, 2015, **32**, 373–380.