

Supplementary Information - Catalytic hot-spots in CO oxidation resolved by operando electron microscopy

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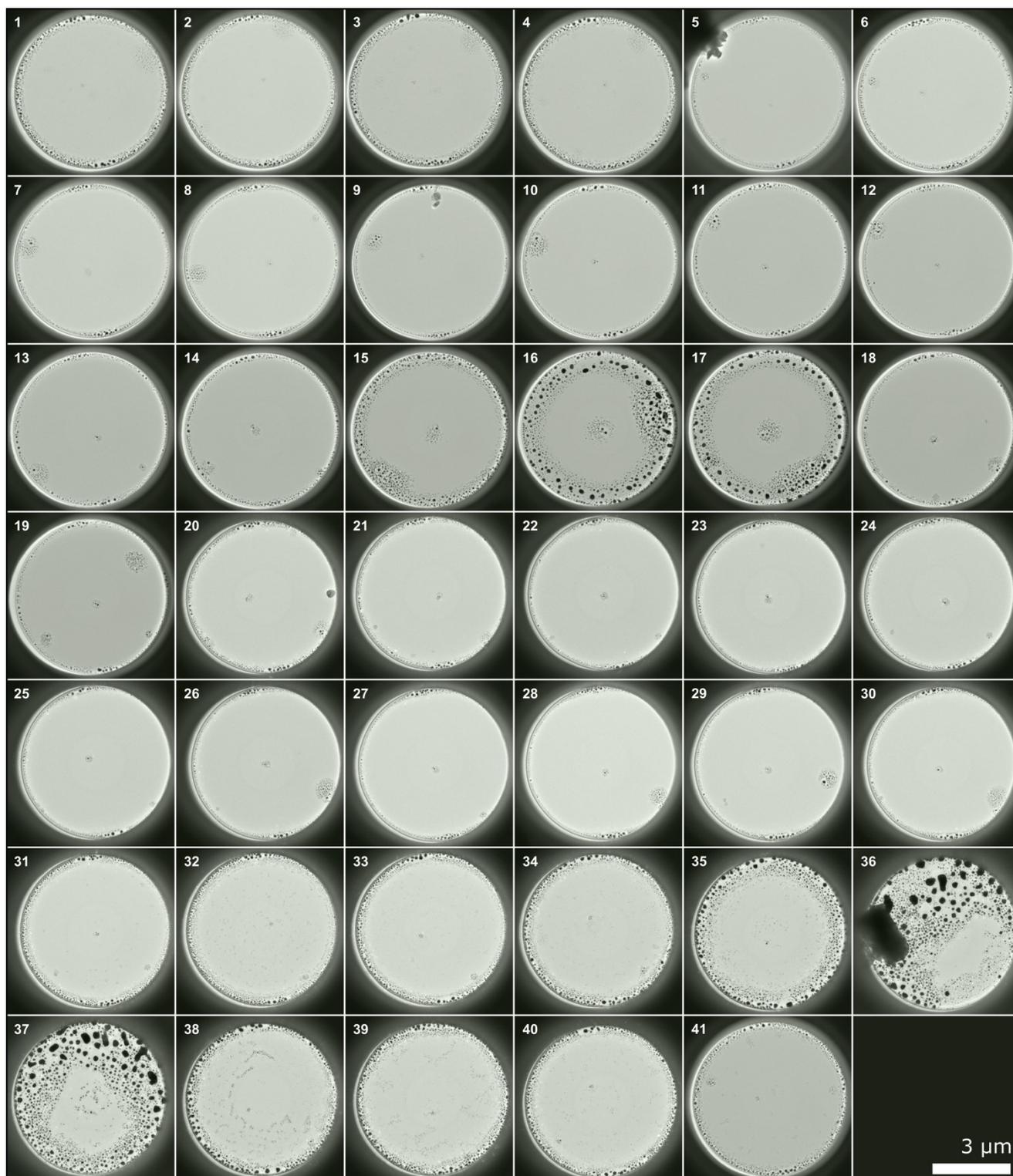


Figure S1. Overview of the Pt NPs coverage on the nanoreactor windows. The 41 electron transparent windows are displayed, illustrating the coverage of Pt NPs for each separate window. Each image measures $6.5 \mu\text{m} \times 6.5 \mu\text{m}$. During the heating-cooling cycles, transmission electron microscopy and spectroscopy data were obtained at window 33 (Fig. 2a), 13 (Fig. 2b), 36 (Fig. 2c) and 17 (Fig. 2d). Figure 4 reports electron microscopy observations from window 12, 13, 17, 33 and

36. For window 12, 17 and 36, the nanoreactor was heated up to 500 °C at 10 °C/s and subsequently cooled down to 100 °C at 10 °C/s. For window 13 and 33, the nanoreactor was heated up to 550 °C at 10 °C/s and cooled down immediately to 100 °C.

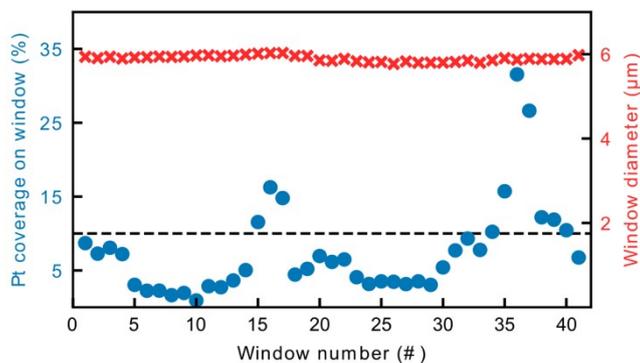


Figure S2. Estimation of the reactor coverage of Pt. The Pt coverage measured for all 41 electron transparent windows shown in Supplementary Fig. S1, as well as the measured window diameter. The dashed line illustrates the threshold of 10% used to define high and low loaded windows. The average coverage is 7.5 %, corresponding to a projected Pt area of 2.2 μm^2 per window.

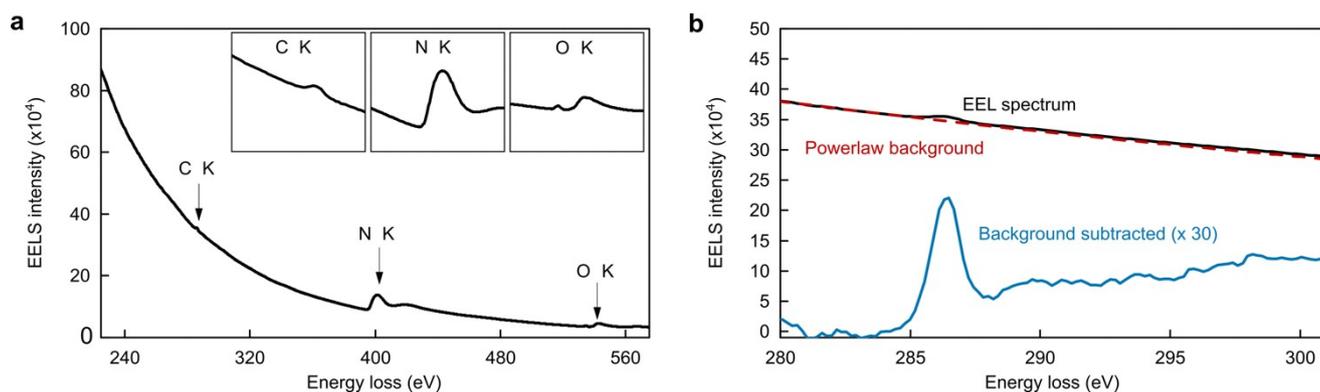


Figure S3. EEL spectrum. **a** EEL spectrum at the C K-ionization-edge of the nanoreactor showing the C K-edge (CO gas), N K-edge (SiN_x window material) and O K-edge (CO and O_2 gas, and SiO_2 on window surface). **b** Close-up of the C K-edge region showing the spectrum (black), fitted background (red) and background subtracted spectrum multiplied by 30 (blue). The spectrum was acquired with 1.0 bar of $\text{CO}:\text{Ar}:\text{O}_2 = 1:1:4$ entering the reaction zone and the temperature was 370°C .

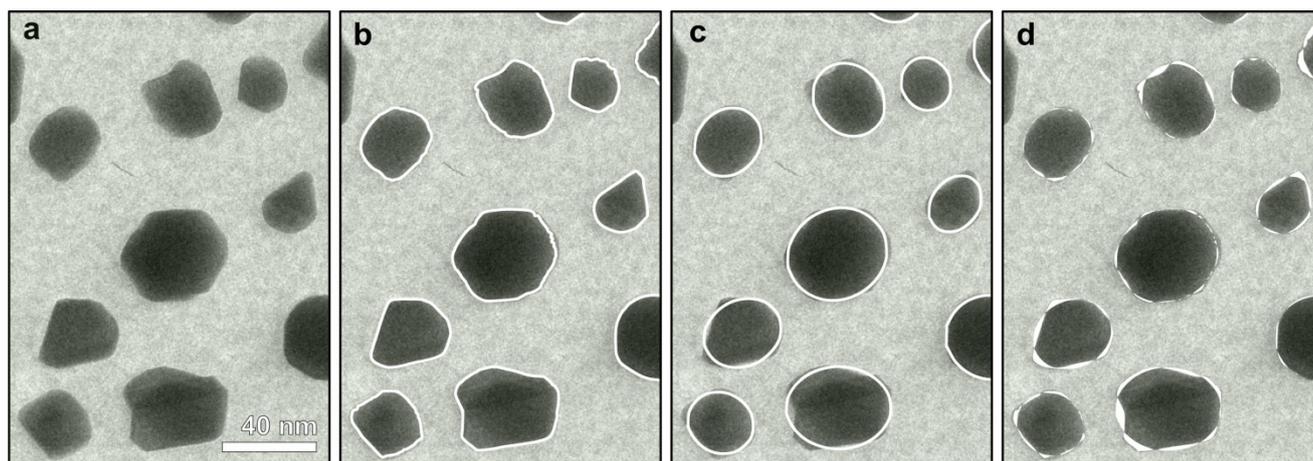


Figure S4. Determining the Pt nanoparticle shape factor. **a** A cutout of the ensemble of Pt nanoparticles recorded under the oxidation of CO at 380°C . **b** Nanoparticle outlines are shown in white, as determined by segmentation. **c** Depicts the outline of the best fit ellipse with the same area as the nanoparticle. **d** Illustrates the difference in projected area between the two outlines in **b** and **c**. This difference is a measure of the particle shape, i.e. round particles result in low shape factor and faceted particles result in a higher morphology factor.

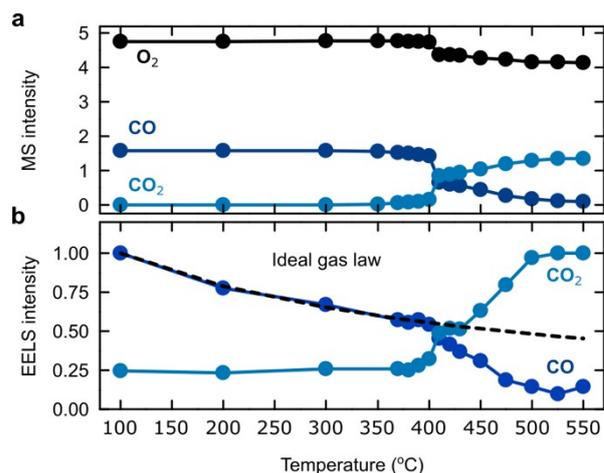


Figure S4. Global (MS) and local (EELS) measurements as a function of temperature for experiment shown in Fig. 1c. **a** MS intensity normalized to Ar signal. Onset of CO conversion at 350°C and light-off at 410°C. **b** EELS intensity as a function of temperature. Intensities normalized to 100°C (for CO, zero conversion) and 550°C (for CO₂, full conversion). The CO intensity follows the ideal gas law until 410°C where the signal drops below the extrapolated decay due to light-off of the CO oxidation reaction. The gas entering the reaction zone is 1.0 bar of CO:Ar:O₂ = 1:1:4.

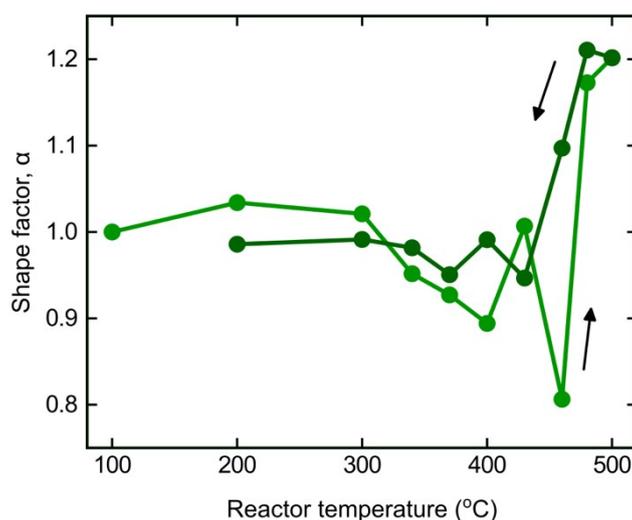


Figure S6. Shape factor as a function of temperature. Shape factor as a function of reactor temperature for a low-loaded region at the reactor outlet.