In situ Imaging and Tracking of Reversible Metal-Support Interactions under CO_2 Hydrogenation over a $Cu@TiO_x$ Core@shell Catalyst

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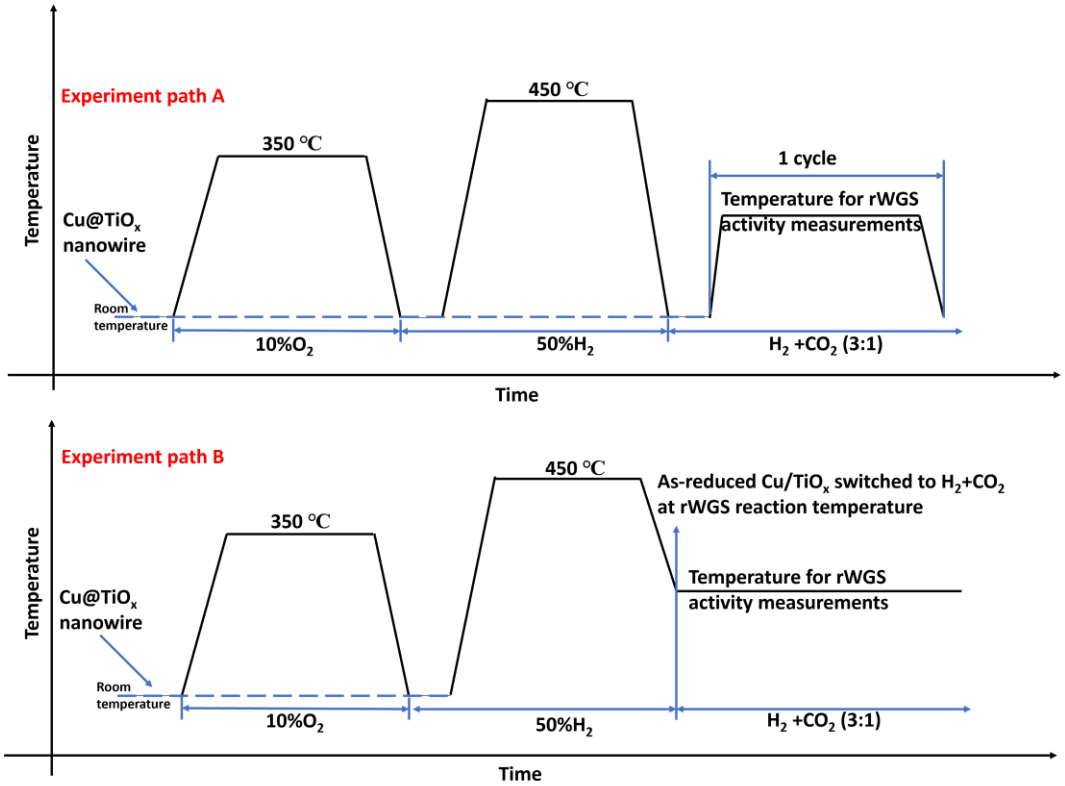
Methodology



Scheme 1. Paths A and B followed in our catalytic tests. The main difference is in the final set of experiments where the sample was cooled down to room temperature (path A) or directly to the reaction temperature tested (path B). Most of the activity measurements were done at 250 °C, with some at measurements at 350 °C.

Results

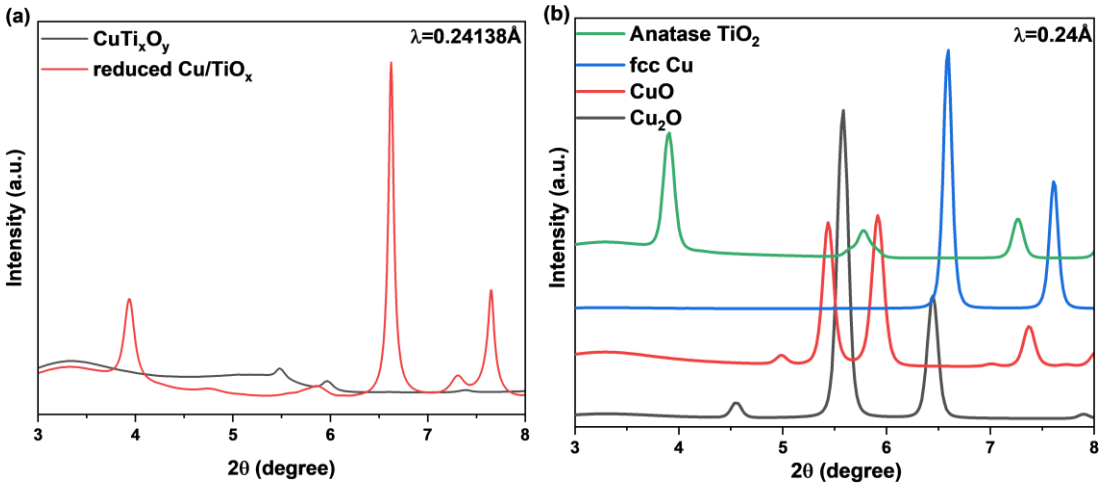


Figure S1. (a) XRD of a pristine $CuTi_xO_y$ solid solution, prepared by calcining the core@shell nanowires in 10%O_2/N_2 at 350 °C for 1 h along with the Cu/TiO_x sample prepared by reducing the $CuTi_xO_y$ in 50% H_2/N_2 at 450 °C for 1 h. (b) XRD diffraction patterns of several standards. In part (a), the reduced $CuTi_xO_y$ exhibits peaks for TiO_2(~ 3.9 and 7.4 degree) and Cu (~ 6.6 and 7.7 degree).

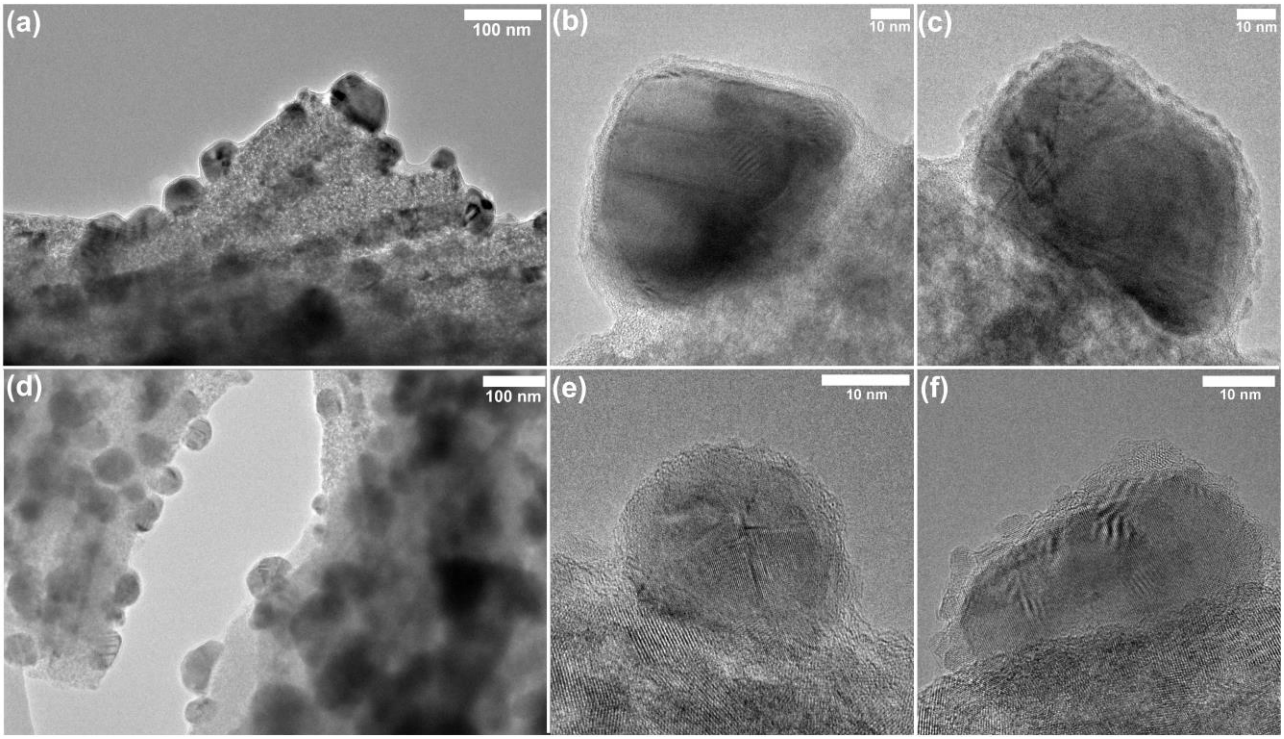


Figure S2. TEM images of two independent samples, (a-c) and (d-f), pre-reduced in a flow reactor (1 h in 50 v% H_2 at 450 °C). The bar in the top of the image denotes 100 nm (a and d) or 10 nm (b, c, e, and f).

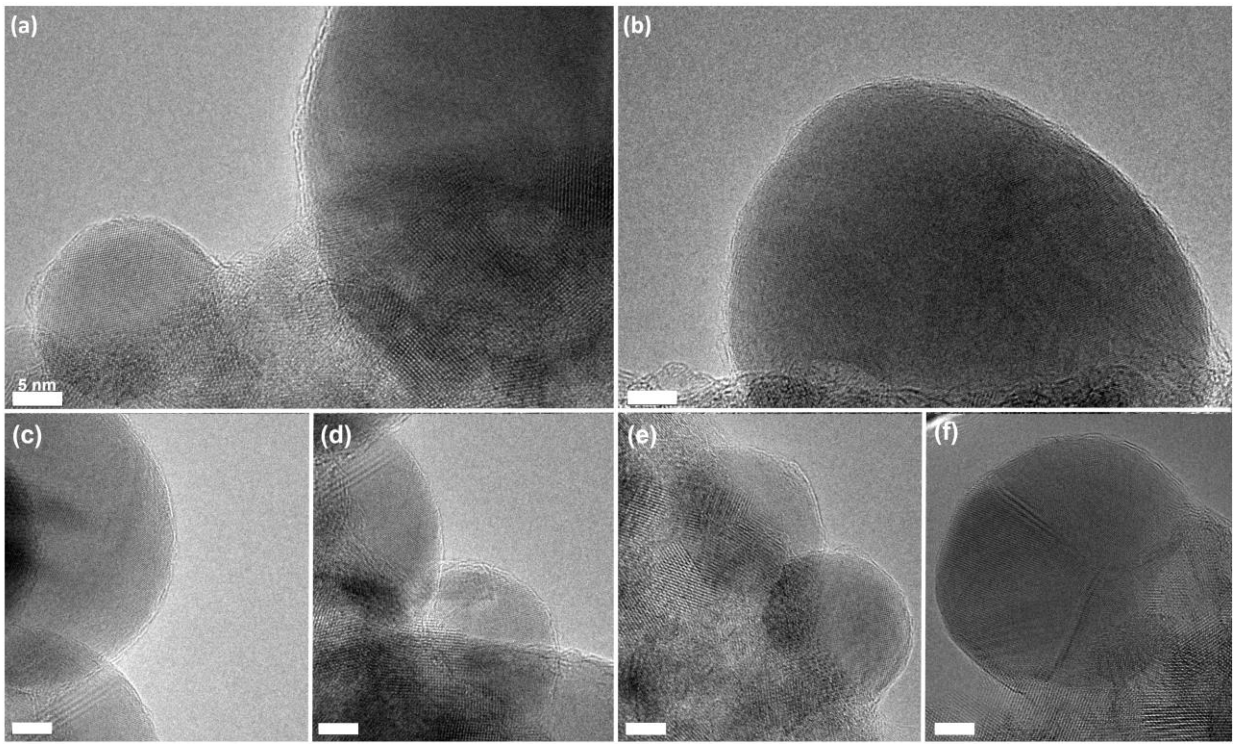


Figure S3. E-TEM images for a reduced Cu@TiO_2 catalyst. The sample was pre-reduced in a reactor (1 h in 50 v% H_2 at 450 °C) and then exposed to H_2 in the microscope (10 mTorr of H_2, at 450 ºC, for 30 min). The bar at the bottom of the images denotes 5 nm.

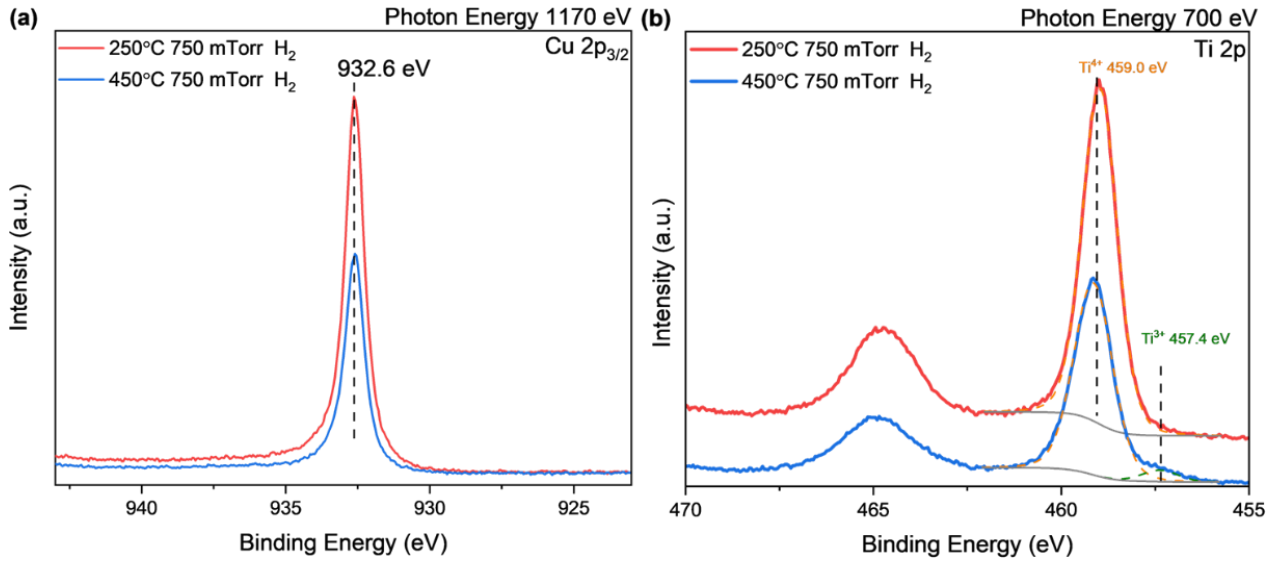


Figure S4. The synchrotron AP-XPS data collected on a pre-reduced Cu/TiO_x sample. The data were collected stepwise at 250 °C and 450 °C in 750 mTorr H_2. In green are shown the Ti^{3+} features.

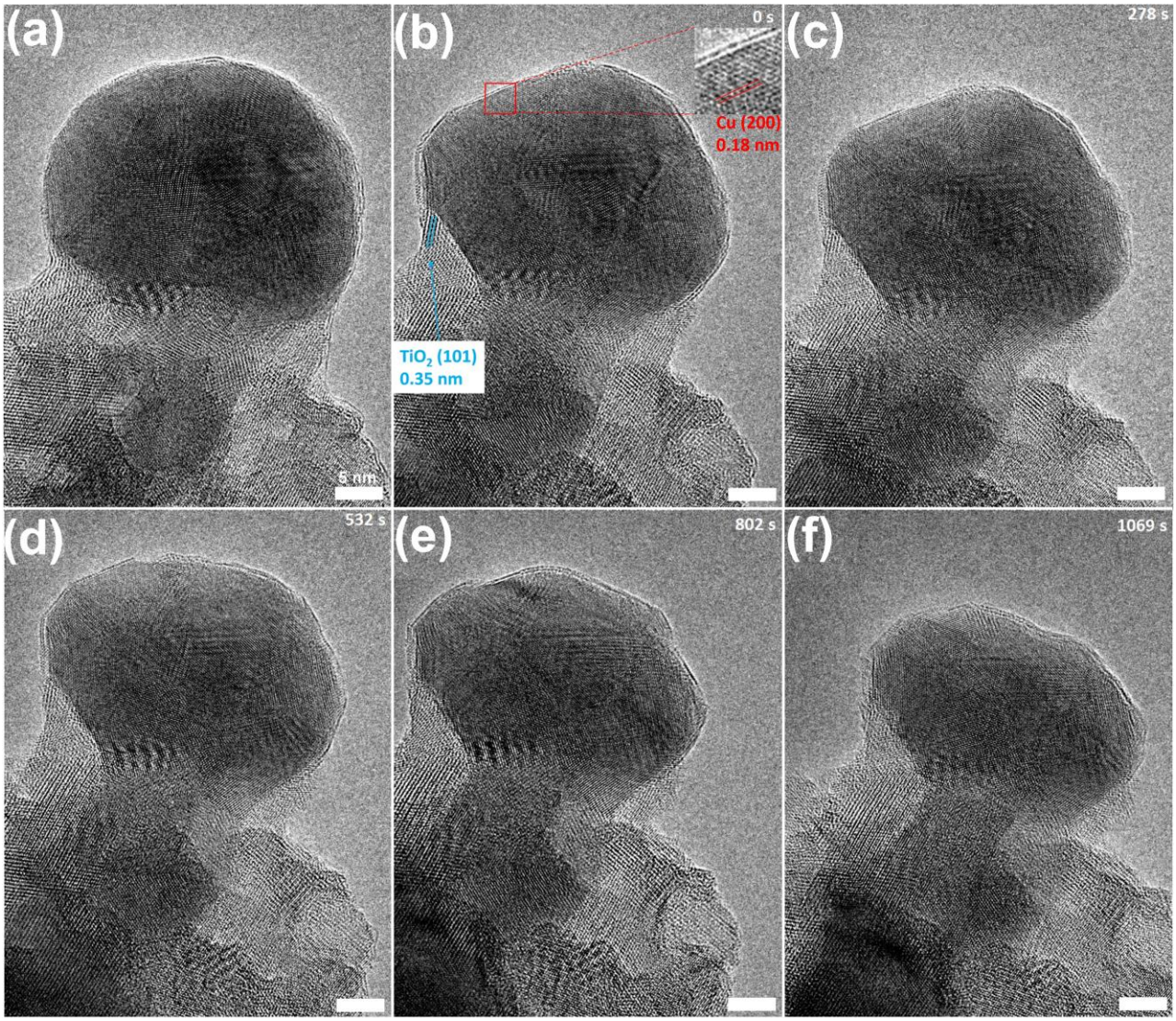


Figure S5. (a) A catalyst particle under 450 °C 10 mTorr of H_2**, (b)** after evacuating the H_2 gas and annealing the sample in 10^{-8} Torr vacuum at 450 °C for 1.5 hours without electron beam irradiation. **(b-f)** the structural evolution of a Cu@TiO_x particle under 450 °C 10 mTorr of H_2, "0 s" corresponds to the beginning of E-TEM study. In part (b) are shown areas with TiO_2(101) and Cu(200) orientations. The bar at the bottom of the images denotes 5 nm.

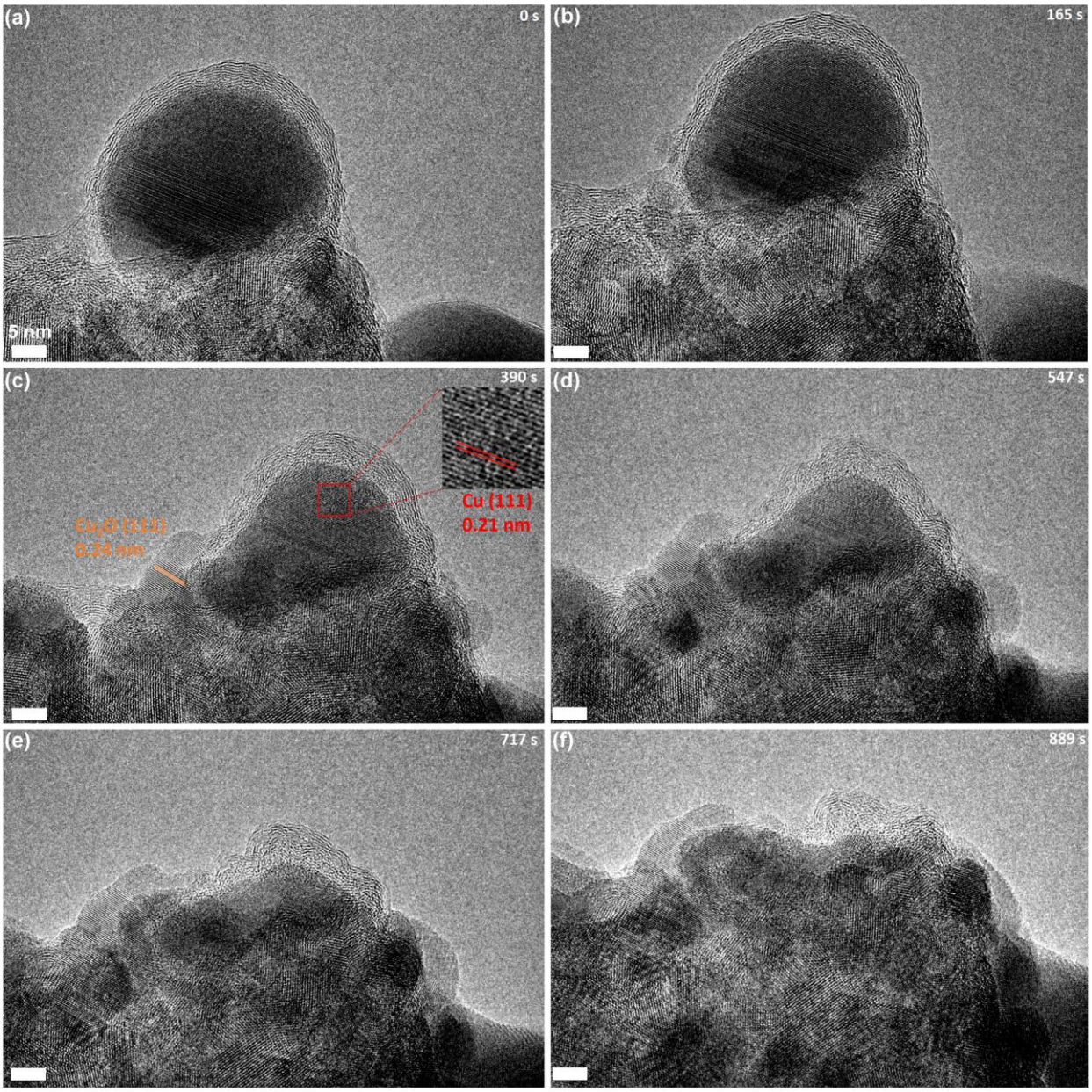


Figure S6. *In situ* oxidation of a pre-reduced Cu/TiO_x sample under 0.2 mTorr of O_2 at 350 °C. Before exposure to oxygen, the sample was pre-reduced at 450 ºC (see Figure S5). ¨0 s" corresponds to the beginning of E-TEM study. In part (c) are shown areas with Cu_2O[111] and Cu[111] orientations. The bar at the bottom of the images denotes 5 nm.

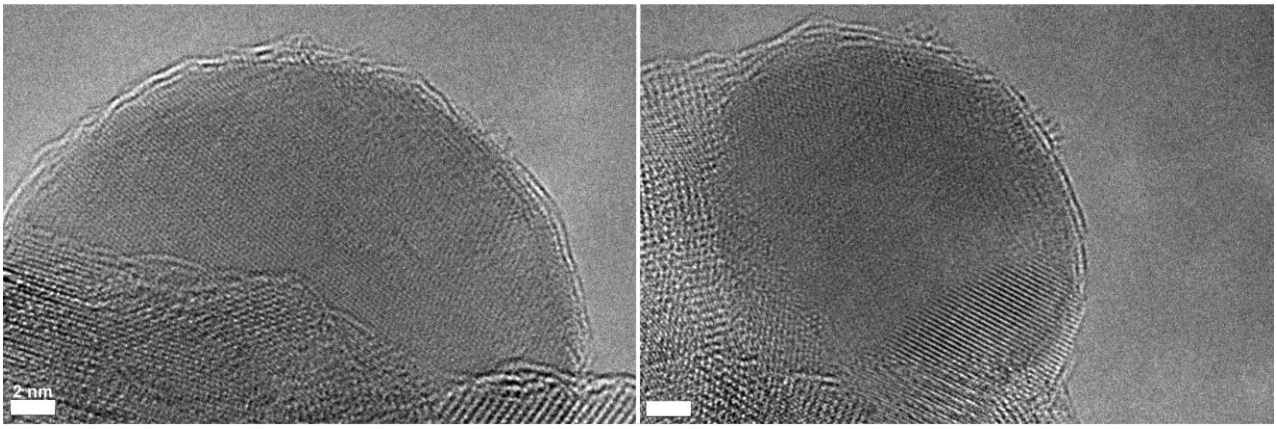


Figure S7. E-TEM images for a sample under 10 mTorr of H_2 at 450 °C. Initially the sample was exposed to 0.2 mTorr O_2 at 350 °C (see Figure S6). The bar at the bottom of the images denotes 2 nm.

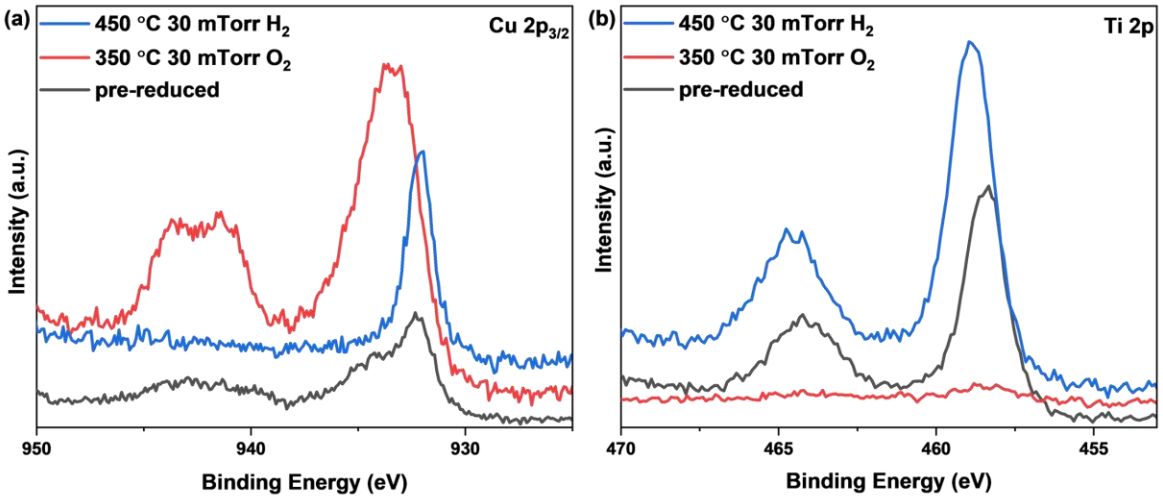


Figure S8. The AP-XPS results associated with the **(a)** Cu $2p_{3/2}$ and **(b)** Ti 2p peaks of the Cu/TiO_x sample with stepwise treatment in an 'pre-reduced' (black trace) condition, after a 350 °C / 30 mTorr O_2 treatment (red trace), and finally, after a 450 °C / 30 mTorr H_2 treatment (blue trace). The treatment with O_2 at 350 °C produces a massive formation of CuO that covers the titania component and decreases the Ti 2p signal. This effect is removed by final reduction on H_2 at 450 °C (blue trace).

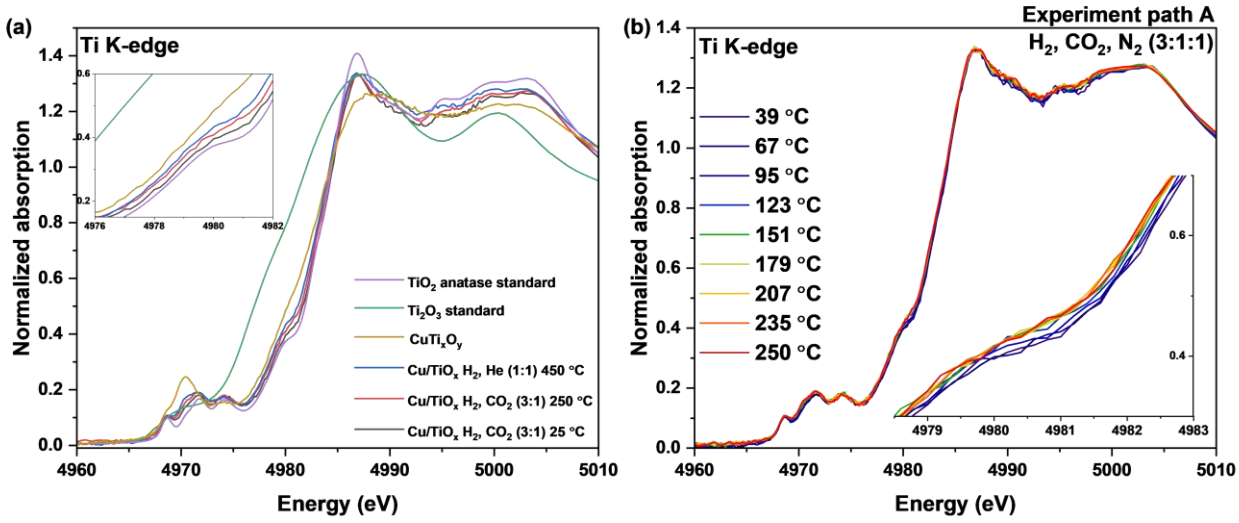


Figure S9. Ti K edge data collected during ramping from 25 °C to 250 °C with 7 °C /min ramping rate under 12 sccm H_2, 4 sccm CO_2, and 4 sccm He; The temperature shown is the average temperature obtained during the 3.7 min data collection. The *in situ* XANES experiments were carried out with a sample pre-reduced in H_2 at 450 ^oC.

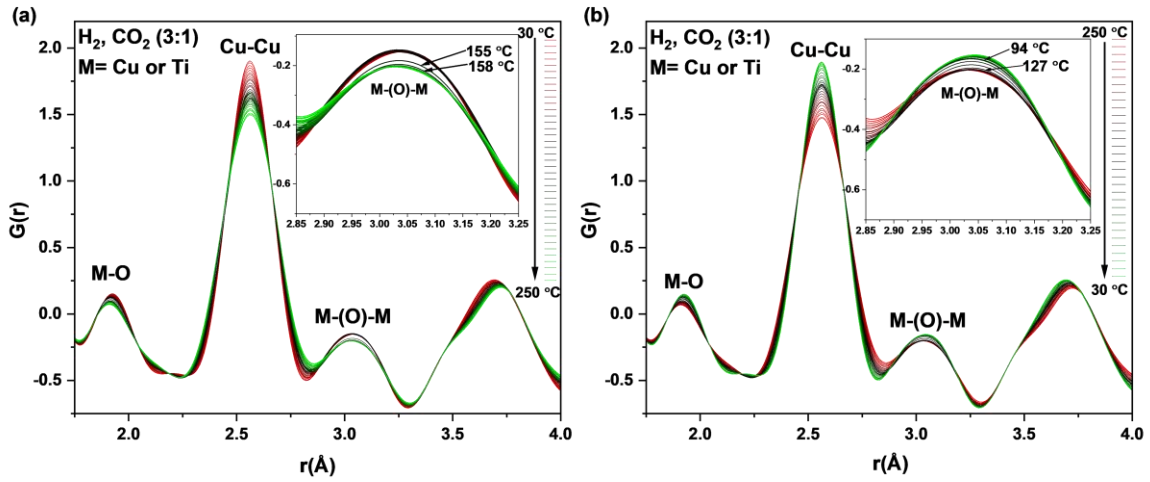


Figure S10. *In situ* PDF data collected **(a)** during ramping from 30 °C to 250 °C with 10 °C /min with a gas flow of 9 sccm H_2 and 3 sccm CO_2; **(b)** during the cooling from 250 to 30 °C 30 min. Data collection time for each spectrum was 0.5 min. The *in-situ* PDF experiments were carried out using a pre-reduced sample in H_2 at 450 ^oC.

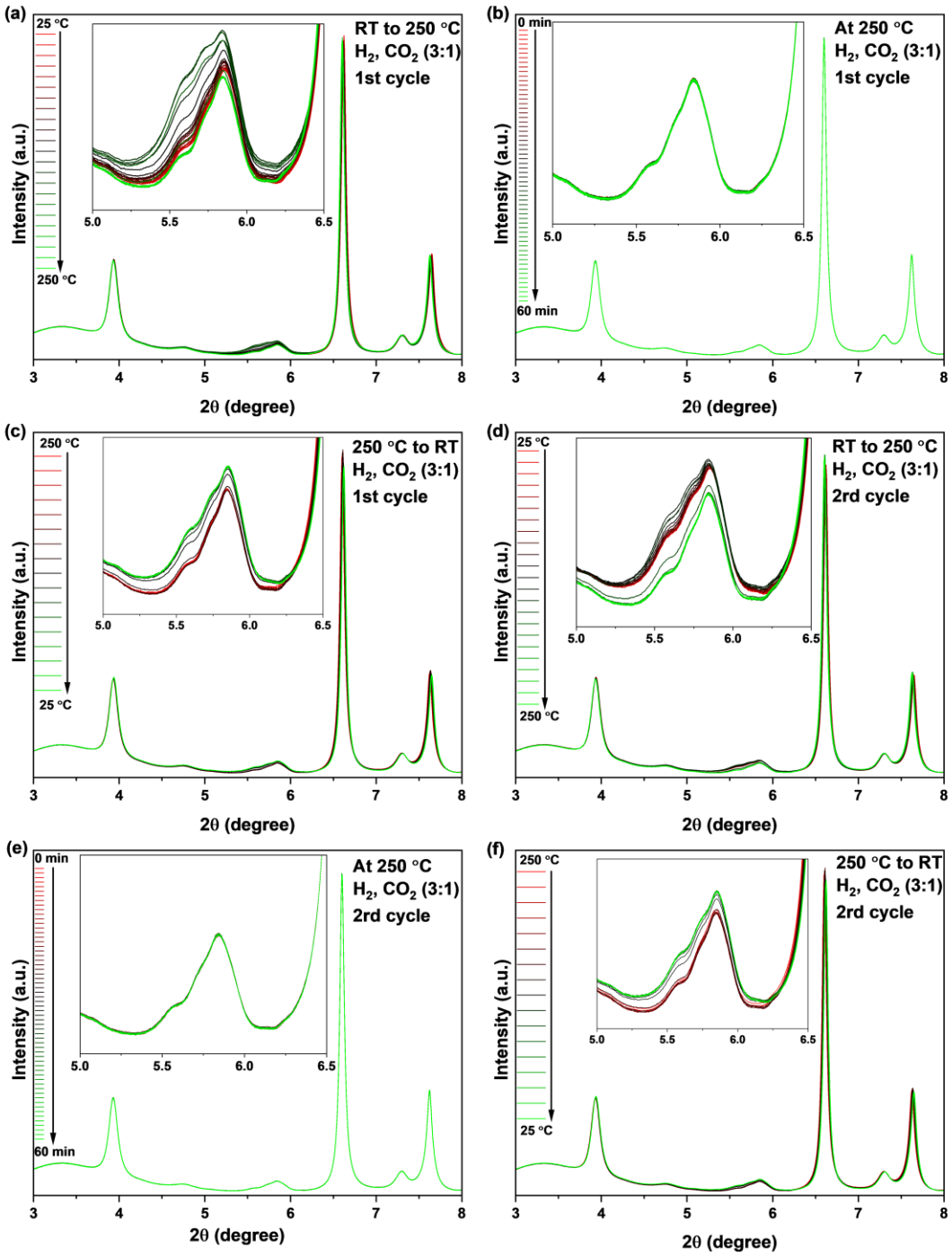


Figure S11. The *in-situ* XRD data were taken under a mixture of H_2:CO_2 (3:1) while heating from room temperature (RT) to 250 °C (**a** and **d**), holding at 250 °C (**b** and **e**), and while cooling from 250 to RT (**c** and **f)**. The *in-situ* XRD experiments were carried out using a pre-reduced sample in H_2 at 450 °C.

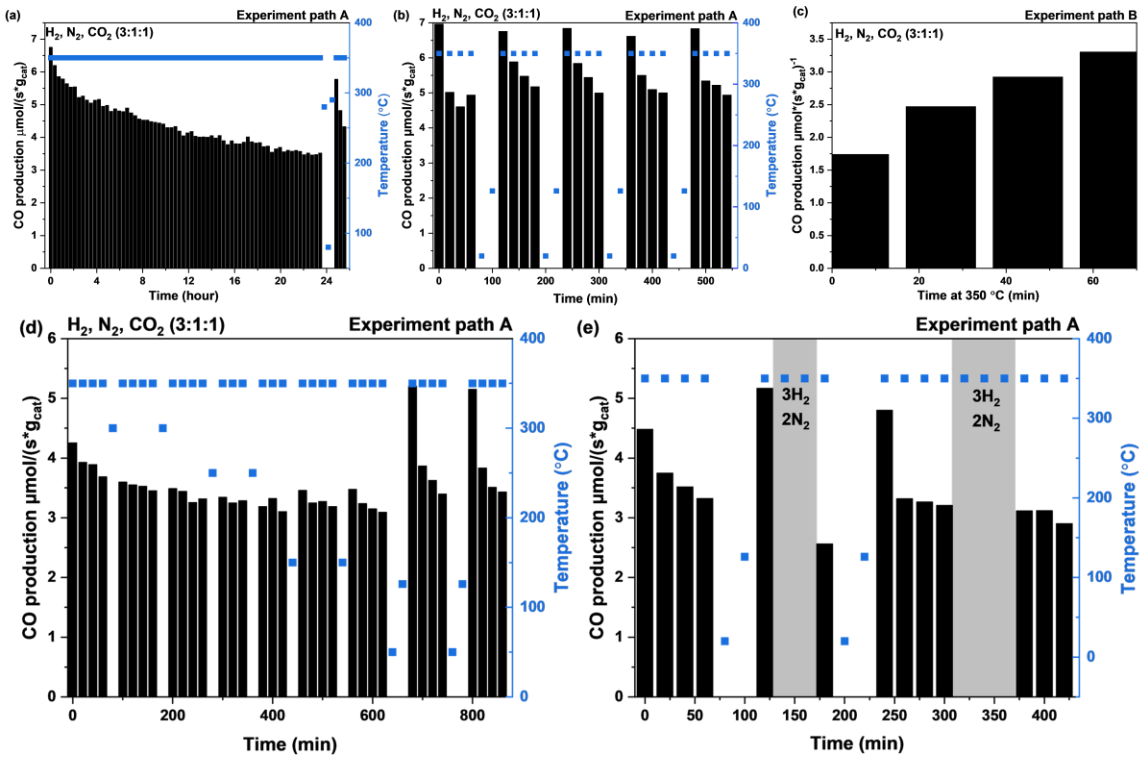


Figure S12. rWGS activity measurements at 350 °C using experimental paths A and B in **Scheme 1. (a)** The CO_2 hydrogenation activity was measured in a continuous experiment, which comprises three steps. In a v(H2): v(CO2): v(N2) = 3:1:1 mixture, a freshly reduced sample was switched to a reaction gas at room temperature, and then the temperature was raised to 350 °C. Subsequently, the sample was held at 350 °C for 24 h. Later, the temperature was cooled down to 30 °C and heated back to 350 °C. After that, the temperature was then held at 350 °C for another 1 h. **(b)** The CO_2 hydrogenation activity measured at 350 °C in a continuous experiment composed of 5 cycles. In each cycle, the temperature is raised from room temperature to 350 °C and then kept at 350 °C for 1 h prior to cooling down to room temperature in a reaction gas mixture composed of v(H2): v(CO2): v(N2)= 3:1:1. **(c)** The evolution of the CO_2 hydrogenation activity over time measured with experimental path B (**Scheme 1**). In a v(H2): v(CO2): v(N2) = 3: 1: 1 mixture with total flow rate of 10 sccm, an as-reduced sample was switched to reaction gas at 250 °C and held for 1 h. Then the temperature was raised to 350 °C, at which point the rWGS was measured as shown in the figure. **(d)** Measurement conditions are similar to **(b)** with the temperature cooling down from 350 °C to 300, 250, 150 and 50 °C. **(e)** Measurement conditions are similar to **(b)** with the flow switched from v(H2): v(CO2): v(N2)= 3:1:1 to v(H2): v(N2)= 3:2 at 350 °C and ultimately switched back.

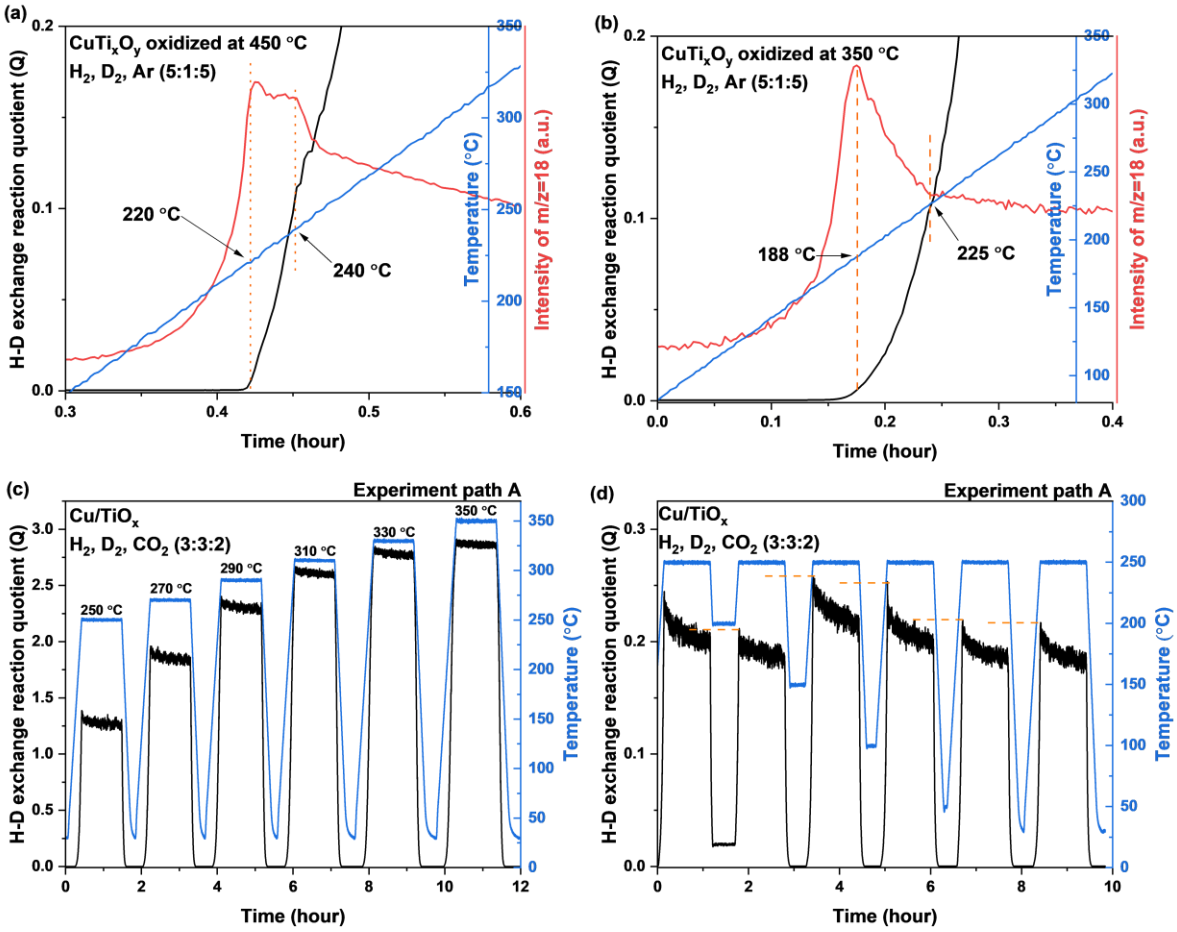


Figure S13 a-b temperature program reduction (TPR) profile of $CuTi_xO_y$ under H_2, D_2, Ar mixture (5:1:5). The $CuTi_xO_y$ was produced by reoxidation of a pre-activated Cu/TiO_x at (a) 450 °C (b) 350 °C. **(c)** H-D exchange quotient measured on Cu/TiO_x at (250, 270, 290, 310, 330, 350 °C) under CO_2 hydrogenation conditions (H_2, D_2, CO_2, Ar (1.5: 1.5: 1: 16)). The temperature was cooled down to 30 °C before catalytic measurements were conducted at different temperatures. **(d)** H-D exchange quotient measured on Cu/TiO_x at 250 °C) under CO_2 hydrogenation conditions (H_2, D_2, CO_2, Ar (1.5: 1.5: 1: 16)). Before the first measurement, the temperature was raised from 30 °C. Between two 1h measurements at 250 °C, the setpoints for cooling are different (stepwise cooled down to 200, 150, 100, 50, 30 °C).

References

1 Salvatore, K. L. *et al.* Optimized Microwave-Based Synthesis of Thermally Stable Inverse Catalytic Core–shell Motifs for CO_2 Hydrogenation. *ACS Applied Materials & Interfaces* **12**, 32591-32603, doi:10.1021/acsami.0c06430 (2020).

2 Rietveld, H. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography* **2**, 65-71, doi:doi:10.1107/S0021889869006558 (1969).

3 Toby, B. H. & Von Dreele, R. B. GSAS-II: the genesis of a modern open-source all purpose crystallography software package. *Journal of Applied Crystallography* **46**, 544-549, doi:doi:10.1107/S0021889813003531 (2013).

4 Nguyen, L. *et al.* Dual reactor for in situ/operando fluorescent mode XAS studies of sample containing low-concentration 3d or 5d metal elements. *Review of Scientific Instruments* **89**, 054103, doi:10.1063/1.5022738 (2018).

5 Ravel, B. & Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* **12**, 537-541, doi:doi:10.1107/S0909049505012719 (2005).

6 Jiang, N., Su, D. & Spence, J. C. H. Determination of Ti coordination from pre-edge peaks in Ti K-edge XANES. *Physical Review B* **76**, 214117, doi:10.1103/PhysRevB.76.214117 (2007).

7 Yamamoto, T. Assignment of pre-edge peaks in K-edge x-ray absorption spectra of 3d transition metal compounds: electric dipole or quadrupole? *X-Ray Spectrometry* **37**, 572-584, doi:https://doi.org/10.1002/xrs.1103 (2008).

8 Westre, T. E. *et al.* A Multiplet Analysis of Fe K-Edge 1s → 3d Pre-Edge Features of Iron Complexes. *Journal of the American Chemical Society* **119**, 6297-6314, doi:10.1021/ja964352a (1997).

9 Wu, Z. Y., Ouvrard, G., Gressier, P. & Natoli, C. R. Ti and O K edges for titanium oxides by multiple scattering calculations: Comparison to XAS and EELS spectra. *Physical Review B* **55**, 10382-10391, doi:10.1103/PhysRevB.55.10382 (1997).

10 Wu, Z. Y. *et al.* Structural determination of titanium-oxide nanoparticles by x-ray absorption spectroscopy. *Applied Physics Letters* **80**, 2973-2975, doi:10.1063/1.1470699 (2002).