Supporting Information

for

Pulsed supercritical water synthesis of anatase TiO$_2$ nanoparticles: Synthesis optimum revealed by *in situ* powder X-ray diffraction

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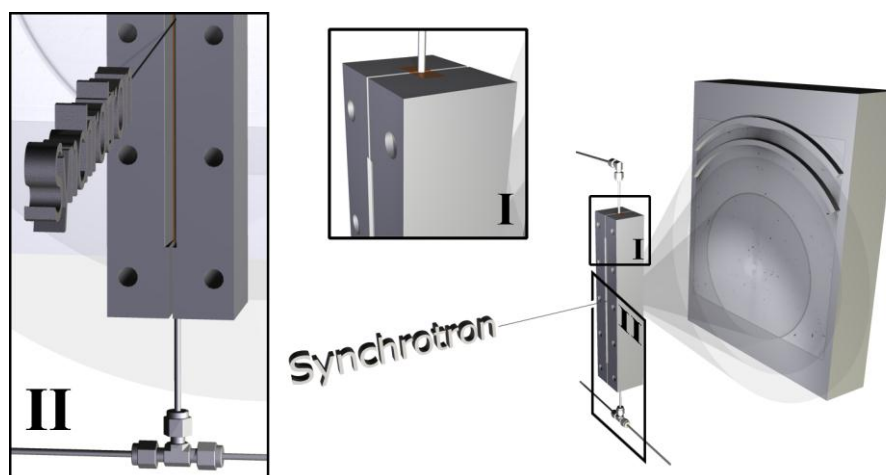**Detailed explanation of the in situ experiments**

Figure S1. Setup used for *in situ* diffraction experiments at ESRF. High-energy X-rays are directed at the reaction chamber and the resulting diffraction is recorded on the detector. Two steel rings are mounted directly on the detector to attenuate the diffraction from the steel reactor itself.

For the *in situ* experiments a heated steel reactor setup was used as depicted in Figure S1. Reactant and deionized water were pumped through the two bottom inlets, mixing in the T-piece before being injected into the heated reactor tube. Subsequently, nanoparticles formed in the reactor, while sequential X-ray scattering patterns were recorded with a time-resolution of 0.5 seconds, of which the exposure time was 0.4 s and readout was 0.1 s. As seen in the inset of Figure S1, the steel heat reservoirs are slotted to allow X-rays to penetrate the central reaction-chamber without being absorbed. The diffraction from the polycrystalline steel reactor saturates the detector and physical masking was therefore required. The (111) and (002) steel (austenite) Debye-Scherrer rings were attenuated by two semi-circular, 10 mm thick steel rings mounted on the detector (see Figure S1).
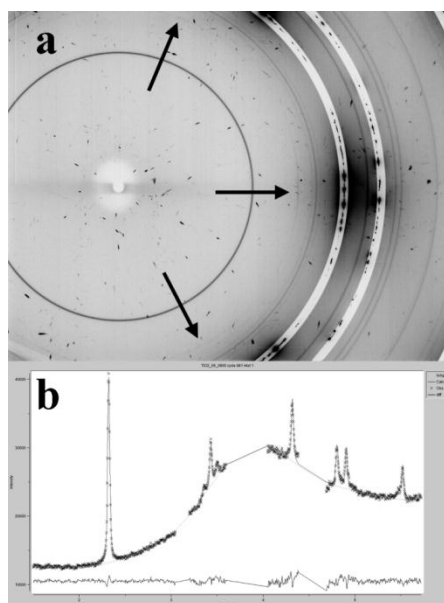

Figure S2. a) Summation of 431 frames from 400 s to 615 s in the 500°C series. The attenuation rings are apparent as light semi-circles. Air scattering from the diffracted beam from steel is clearly evident (dark areas around attenuation). Small spots are due to secondary scattering from steel. Arrows indicate a weak diffraction ring from an unknown substance, corresponding to the first excluded region in figure b (just above 3°). b) Fit of the frame at 400s from the 500°C series. Second and third excluded regions are due to steel attenuation, while the large background around 4° is due to air scattering from the steel-diffracted beams.

Figure S2a shows a sum of 431 detector frames, where the impact of steel diffraction is immediately clear. The steel diffraction penetrates the 10 mm thick attenuation rings as evident by the black spots inside the two light semi-circular bands on the right of the image. However, the attenuation is strong enough to avoid saturation of the detector. The air scattering caused by the diffracted steel beam is quite intense, producing the high background in Figure S2b. The tiny spots in Figure S2a are due to second order steel diffraction, where the scattered X-rays from steel are strong enough to scatter a second time with no "apparent" 2-theta dependence. The setup is controlled using an in-house programmed GUI, which offers direct monitoring of pressure, reactant consumption, temperature and more. Integration of the 2D data was performed using the program *Fit2D*.[1, 2] The sample to detector distance was initially calibrated using a standard (NIST LaB_6) placed inside the reaction chamber. The beam center on the 2D detector was found by fitting the strong (101)-peak of anatase, while all attenuation, air scattering and second order diffraction was masked to remove unwanted noise. All diffraction patterns were treated by sequential Rietveld refinement using the *GSAS* package.[3] The instrumental contribution to the peak broadening was corrected for by fixing GV, GW, LY and S/L to values found in a separate fit to the data measured on a NIST LaB_6 sample. Any additional peak broadening was ascribed to size-broadening using the Gaussian (GP) and Lorentzian (LX) broadening contributions for the syntheses at 450°C, 500°C and 550°C. For the syntheses at 300°C, 350°C and 400°C only the LX-parameter was used. When using both parameters a common FWHM (Full Width at Half Maximum) must be

calculated according to the formula: $\text{FWHM}_{\text{total}} = (\Gamma^5 + 2.69269 \cdot \Gamma^4 \cdot \gamma + 2.48243 \cdot \Gamma^3 \cdot \gamma^2 + 4.47163 \cdot \Gamma^2 \cdot \gamma^3 + 0.07842 \cdot \Gamma \cdot \gamma^4 + \gamma^5)^{1/5}$.[25] Here, Γ and γ are the Gaussian and Lorentzian FWHM's calculated from the refinement parameters. The volume weighted size of the coherently diffracting domains, here interpreted as crystallite size, is then calculated from the FWHM using the Scherrer formula. For all experiments scale factors, background and unit cell parameters were also refined. Atomic positions and atomic displacement factors were fixed for each temperature based on literature values.[4]

[1] A. P. Hammersley, *ESRF Internal Report* **1998**, *ESRF98HA01T*.

[2] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, D. Hausermann, *High Pressure Res* **1996**, *14*, 235-248.

[3] A. C. Larson, R. B. Von Dreele, *Los Alamos National Laboratory Report LAUR* **2004**, *86-748*.

[4] C. J. Howard, T. M. Sabine, F. Dickson, *Acta Crystallogr. Sect. B-Struct. Commun.* **1991**, *47*, 462-468.