Electronic Supplementary Information (ESI) for

In situ total X-ray scattering study of the formation mechanism and structural defects in anatase TiO_2 nanoparticles under hydrothermal conditions

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1. Time evolution of in situ PXRD

The in situ PXRD with the time resolution of 1 s is obtained from the total scattering experiment. The intensity of the amorphous peak at 2θ of 2.6° is constant before crystalline TiO_2 appears suggesting the amorphous precursor is not dissolved during the reaction. After the crystallization commences, the intensity of the anatase peaks rises while the intensity of the amorphous peak decreases suggesting a solid state transition mechanism.

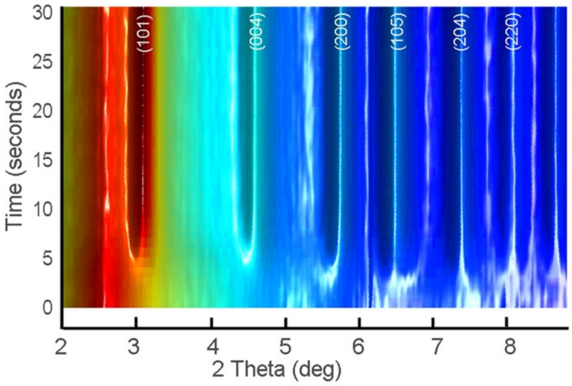

Fig. S1 Time evolution of the *in situ* PXRD patterns for the synthesis of TiO_2.

2. PDF refinements using ordered structure model and oxygen vacancy model

The refinement of the stoichiometric and ordered structure is based on crystallographic data of anatase TiO_2, and the oxygen vacancy model is implemented by refining the oxygen occupancy. Fig. S2 shows the comparison of PDF fits (1.5 Å $< r <$ 60 Å) at $t = 20$ min for (a) ordered structure model (R_w = 25.2%) and (b) oxygen vacancy model (R_w = 25.7%). The results show that the refinement for the oxygen vacancy model does not improve the quality of the fit compared with the ordered structure model in the full r range fits (1.5 Å $<$ $r <$ 60 Å).

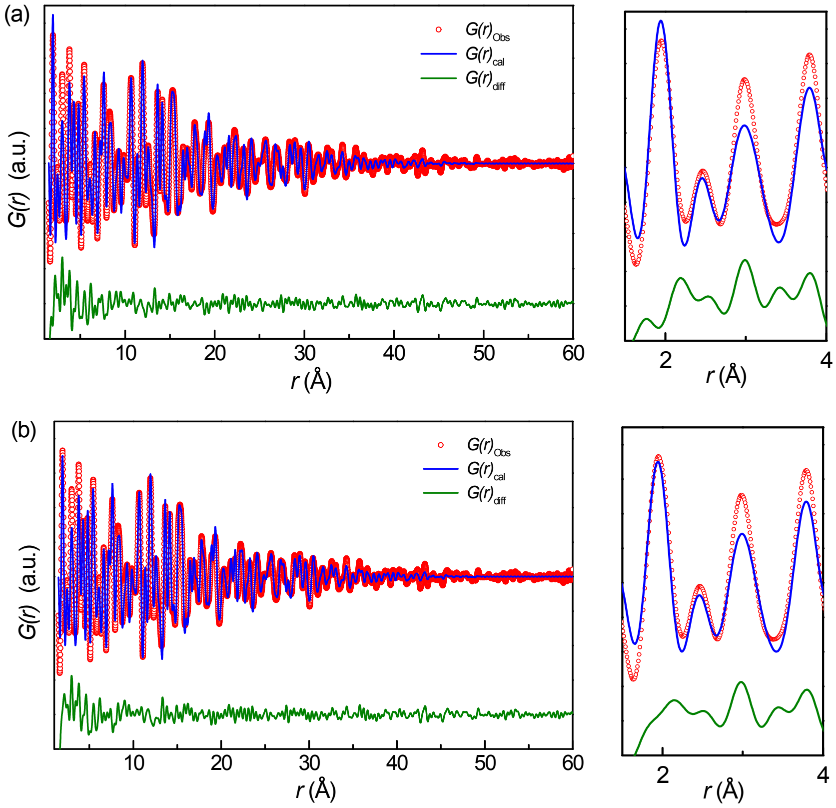

Fig. S2 Comparison of PDF fits (1.5 Å $< r <$ 60 Å) for (a) ordered structure model (R_w = 25.2%) and (b) oxygen vacancy model (R_w = 25.7%).

3. OH defect model

For the short *r* range (< 7 Å), the fits using the vacancy model or OH defects model should be similar because both models result in a lower coordination number of Ti atoms. An oxygen defect concentration of 72.7(6)% is obtained using the oxygen occupancy model. The OH defects were modeled by altering two oxygen atoms to hydroxyl (OH) groups in one anatase unit cell, which results in an OH defect concentration of 25%. As discussed in the manuscript, the model gives a reasonable fit of the PDF pattern in the local *r* range.

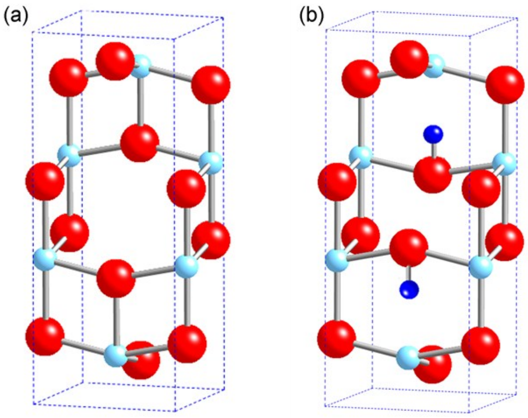

Fig. S3 The structures of (a) anatase and (b) the OH defect model

4. Rietveld refinement of the PXRD data

The PXRD data obtained from the in situ total scattering experiment ($\lambda = 0.18970$ Å) were refined using the anatase structure by the Rietveld method implemented in FullProf. A Thompson-Cox-Hastings pseudo-Voigt axial divergence asymmetry profile function was used. The background was modeled using linear interpolation with 30 points. Fig. S4 shows the observed, calculated and difference patterns of the PXRD data at the reaction time of 20 min. The data from 2.6 to 25° were included in the refinement. Sequential Rietveld refinements were carried out for the PXRD data at other reaction times. The occupancy (*Occ*) of Ti atoms was fixed to 1, while the occupancy of O atoms was refined for all the data. The thermal parameters (B_{iso}) of Ti and O atoms were refined for the data at the reaction time of 20 min, and they were then fixed with the obtained values of 20 min data for the refinements of the PXRD data at other reaction times. Table S1 gives a summary of the Rietveld refinement parameters and residuals for the data at the reaction time of 20 min. It can be seen that the occupancy at the O site is higher than the full occupancy. This can be explained by that the OH defects are averaged out for long range description and they are counted into the PXRD analysis, where the H atoms give rise to a higher occupancy at the oxygen sites. The particle size was calculated from the peak broadening. The instrumental broadening was small compared to the size broadening and was not corrected in the current refinement. It results in slightly smaller crystallite sizes of the nanoparticles than the values obtained from PDF calculation. Fig. S5 shows the refined oxygen coordinate z and the closest Ti-O distance (Ti-O bond) along c-axis as functions of reaction time. Though the unit cell parameter c decreases when the particle size decreases, it can be seen that the length of the Ti-O bond along c-axis increases with reduced particle size.

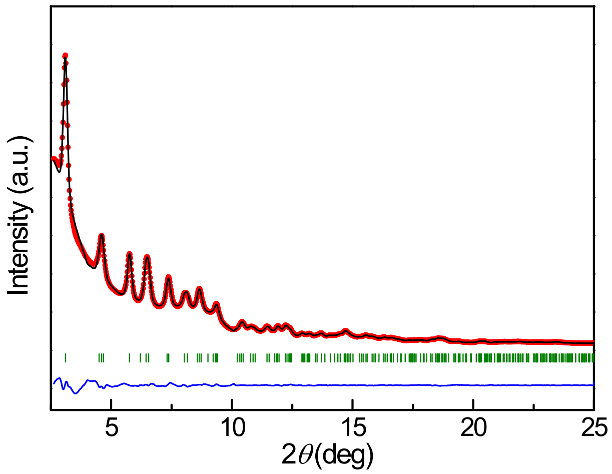

Fig. S4 Rietveld refinement of the PXRD data at the reaction time of 20 min.

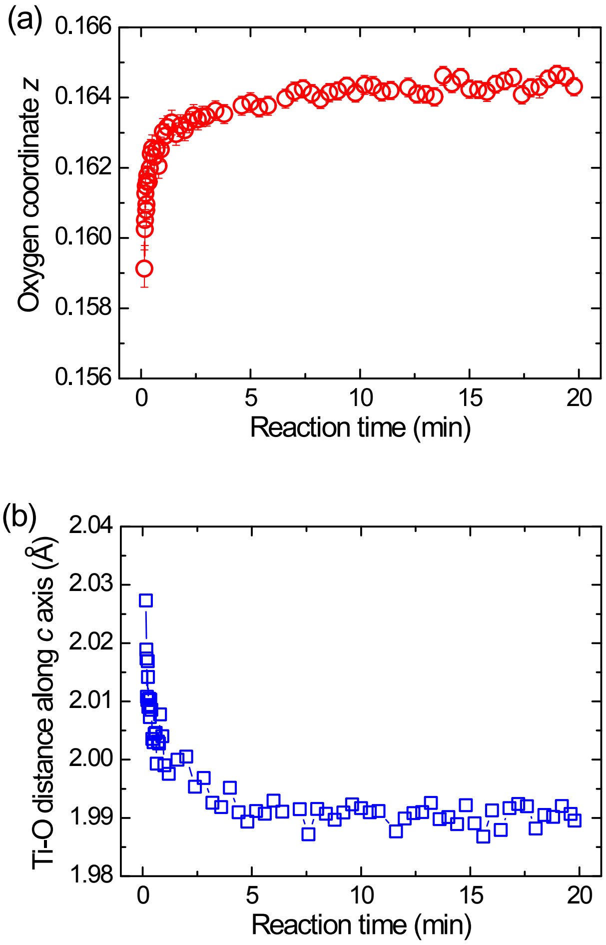

Fig. S5 Refined oxygen coordinate *z* (a) and the closest Ti-O distance along *c*-axis (b) as functions of reaction time.

Table S1 Reliability factors and refined parameters of the Rietveld analysis of the SR-PXRD data at the reaction time of 20 min.

Reaction time (min)	20
No. of data points	1091
No. of refined parameters	43
No. of reflections	326
R_P (%)	5.95
R_WP (%)	5.62
R_I (%)	1.34
R_F (%)	1.68
a (Å)	3.775(1)
c (Å)	9.443(1)
z (O)	0.164(1)
B_iso (Ti) (Å^2)	0.29(3)
B_iso (O) (Å^2)	0.47(7)
Occ (O)	1.05(5)
Particle size (nm)	3.45(5)

5. Calculation of crystallinity of TiO_2 nanoparticles

For determining the crystallinity, the TiO_2 product (0.06172 g) was mixed uniformly with an internal standard CaF_2 (0.07064 g) which is assumed to be 100% crystalline. Powder X-ray diffraction (PXRD) was then measured on a STOE powder diffractometer (STOE, Darmstadt, Germany) using Cu K_α radiation ($\lambda = 1.5406$ Å). The PXRD data were refined by the Rietveld method implemented in the FullProf program. A Pseudo-Voigt function was used to describe the profile. Fig. S6 shows the refinement of the PXRD pattern for the mixture of TiO_2 and CaF_2. The R_F factors are 2.62% and 2.97% for the TiO_2 and CaF_2 phases, respectively. Weight percentages of 40(1)% and 60(1)% are obtained for crystalline TiO_2 and CaF_2, respectively. Since CaF_2 is assumed to be 100% crystalline, there is 0.07064 g crystalline CaF_2 in the mixture. Crystalline TiO_2 is then calculated to be 0.04709 g. Thus, the crystallinity of TiO_2 product is 76.3%.

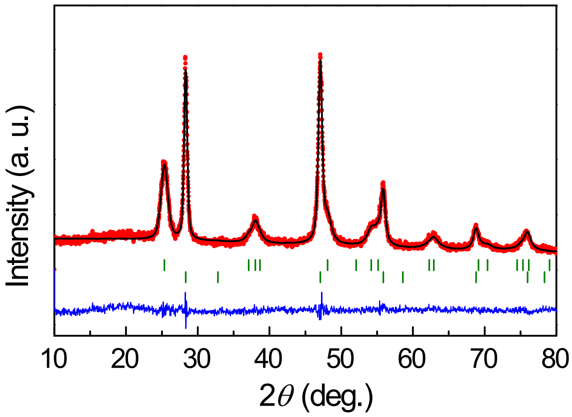

Fig. S6 Rietveld refinement of TiO_2 product and CaF_2 mixture.