Supporting Information: Quantitative Structural Characterization of Catalytically Active TiO_2 Nanoparticles

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Single phase refinements of TiO_2 supports

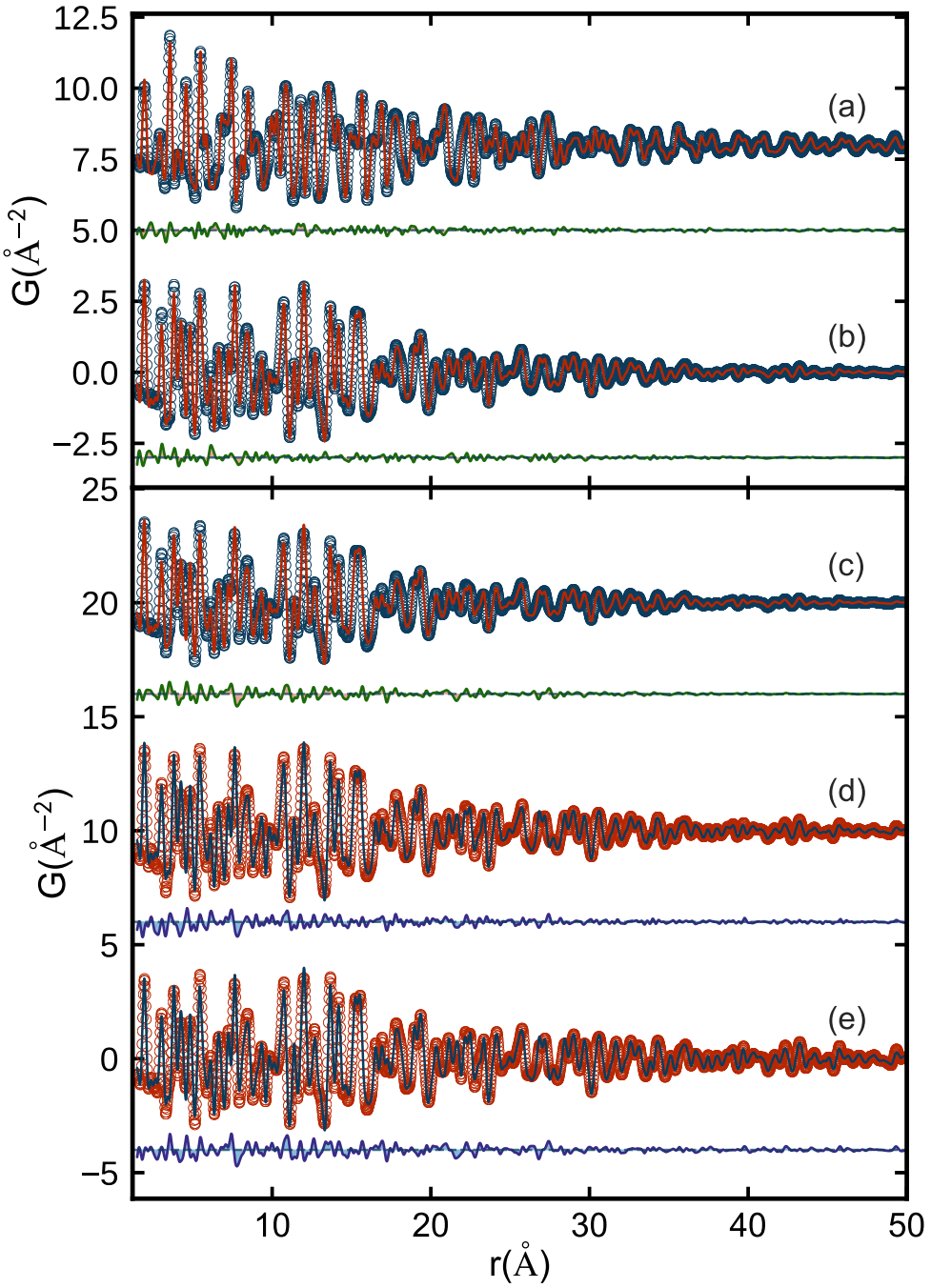

Fig. S1: Measured (open symbols) and calculated (solid lines) PDFs of pure rutile (a) pure anatase (b) a physical mixture of 90% anatase and 10% rutile (c) P90 (d) and P25 (e). The experimental PDF for rutile (a) is fit with a single phase rutile model while the phase pure and majority anatase PDFs (b-e) are fit with a single phase anatase model. Difference curves are offset below.

Table S1: Refined parameters from single phase refinements of pure (columns 1-2) and mixed (columns 3-5) TiO_2 samples using a single phase anatase model for the mixed nanomaterials, which are expected to contain a majority Anatase phase. See the main text for descriptions of the abbreviations below. Structure models were obtained from published crystal structures of bulk anatase and rutile.[1,2] For rutile (SG: $P4_2/mnm$), O is at the $2a$ $(0,0,0)$ site and Ti at $4f$ $(0.306, 0.306, 0)$. In anatase (SG: $I4_1/amd$), O is positioned at $4a$ $(0,0,0)$ and Ti at $8e$ $(0,0,0.208)$.

Sample	Anatase	Rutile	$Mix_{90:10}$	P90	P25
$a = b$ (Å)	3.785	4.592	3.783	3.785	3.785
c (Å)	9.504	2.958	9.498	9.487	9.492
Ti U_{iso} (Å^2)	0.006	0.006	0.007	0.005	0.005
O U_{iso} (Å^2)	0.016	0.016	0.017	0.015	0.014
SPD (Å)	69.78	152.4	68.66	93.27	161.06
R_w	0.104	0.109	0.155	0.163	0.181

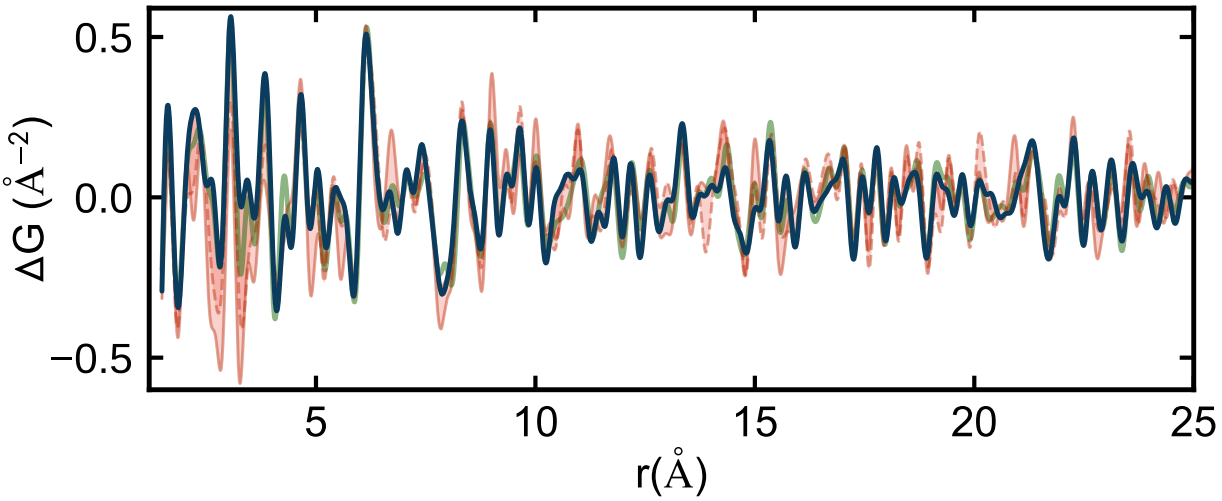

Fig. S2: Dark blue: unfit signal from a single phase refinement of pure anatase. Green: unfit signal from mixed phase refinement of the physical mixture. Red and dashed red: unfit signal from mixed phase refinement of P90 and P25, respectively. The pearson correlation coefficients between all mixed phase TiO_2 residuals and the pure anatase residual are > 0.75 for an r-range between $1.2 < r < 30$ Å.

Morphological tests with pure anatase nanoparticles

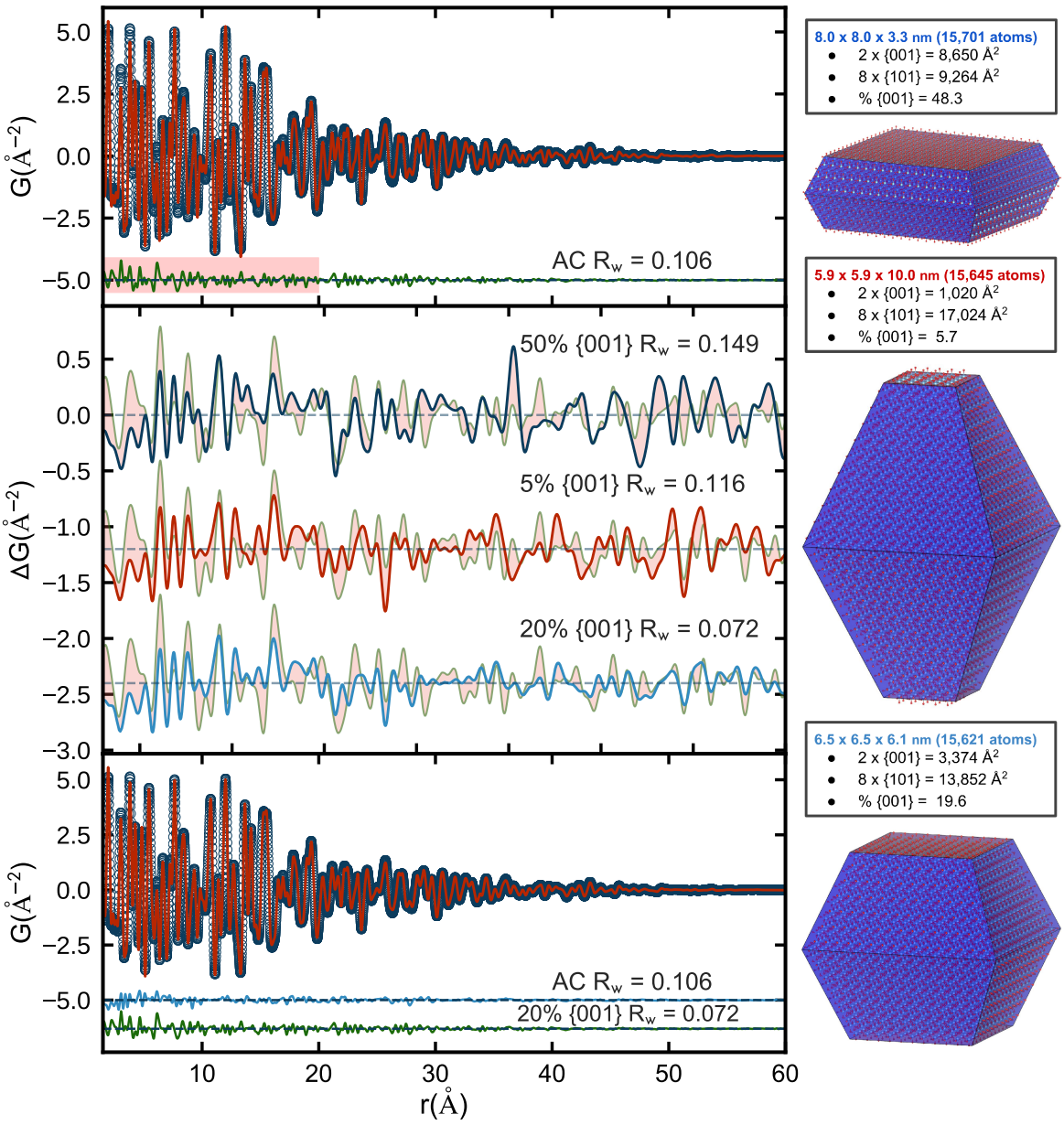

Fig. S3: Top panel: Measured (open circles) and calculated (solid lines) PDFs for pure anatase refined over the full-r range to the mixed phase AC model. Middle panel: difference curves, plotted over a truncated r-range (highlighted in the top panel) from discrete anatase models with different percentages of {001} surface facets (as labeled) fit to the pure anatase sample. The curves are overlaid with the mixed phase anatase residual in light green. R_w values are calculated over full-r. Right column: the particle morphologies used in the fits, with descriptions of the facet specific surface areas. {001} surfaces are shown in red and {101} surfaces in blue. Bottom panel: Measured (open circles) and calculated (solid lines) PDFs for pure anatase refined over the full-r range using the best candidate discrete structure (19.6% {001} faceting).

Supplementary TEM images

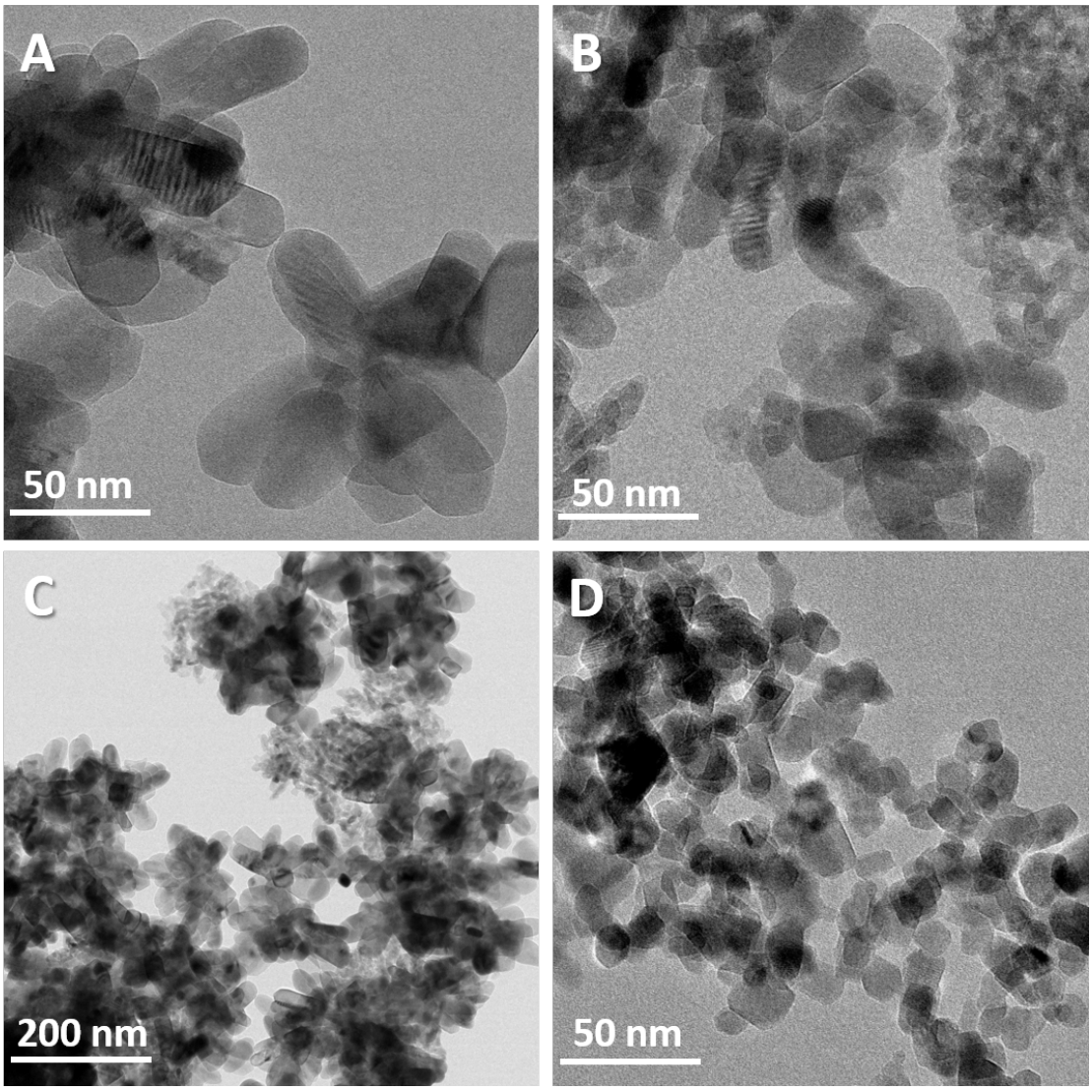

Fig. S4: TEM micrographs of TiO_2 nanoparticles (a) pure rutile (b) pure anatase (c) a physical mixture with 90% anatase and 10% rutile and (d) P90

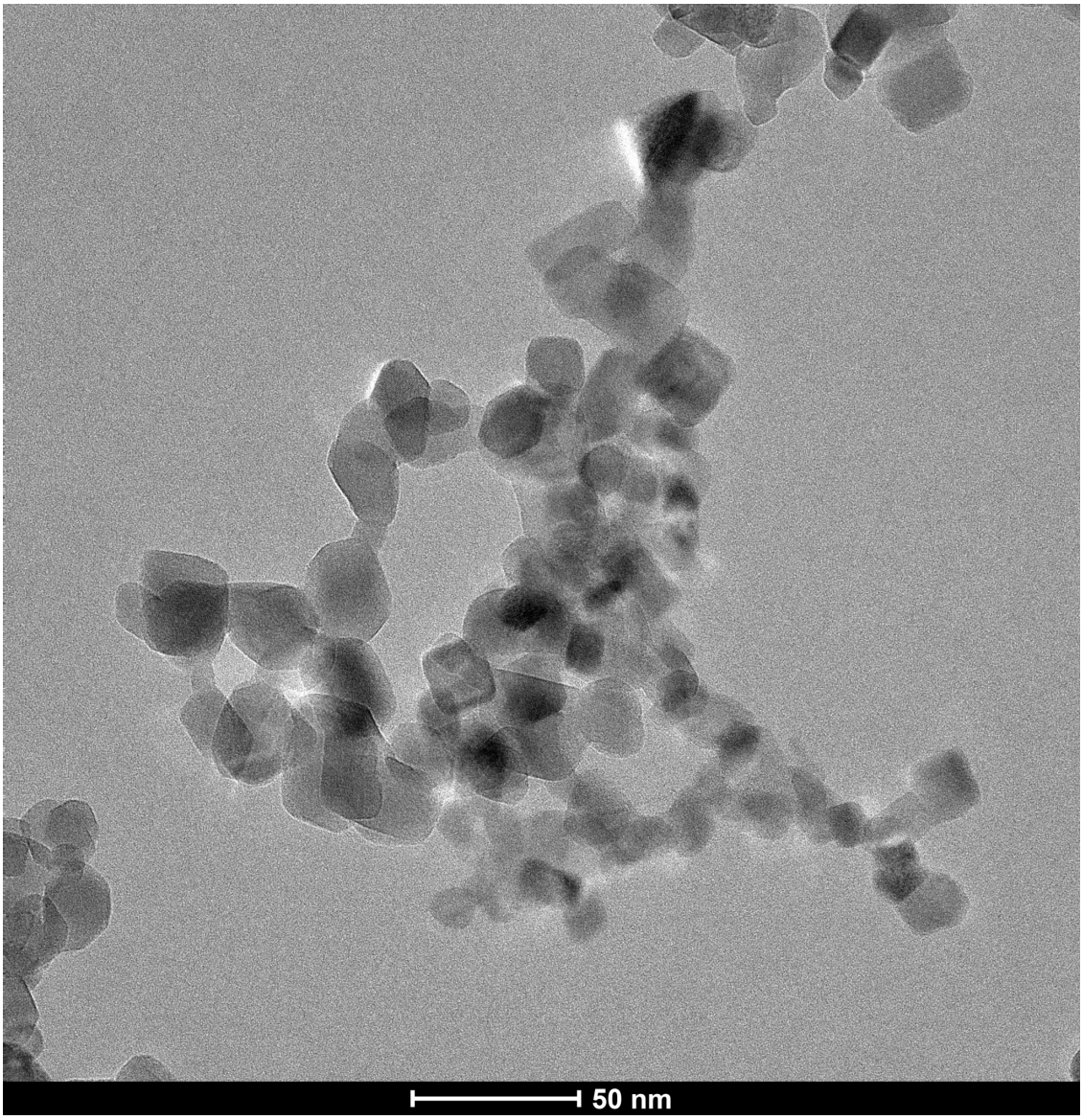

Fig. S5: TEM micrograph of P25

Reciprocal space data prior to PDF transformation

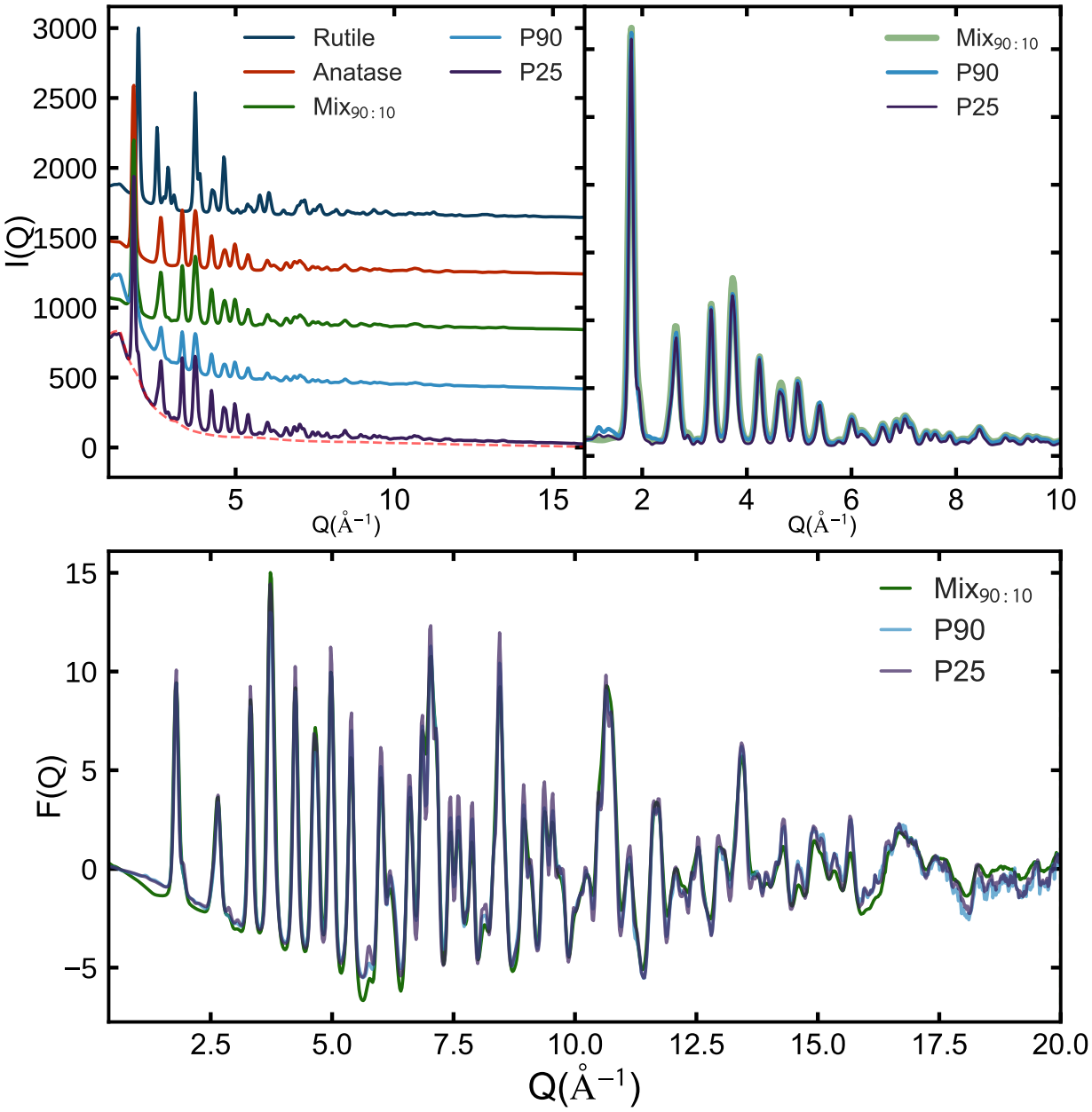

Fig. S6: Top left: Raw integrated diffraction patterns of samples used for PDF analysis, as labeled. Top right: a comparison of background subtracted and scale normalized $I(Q)$ for mixed TiO_2 samples. Bottom: an analogous comparison of the phase mixtures after transformation to $F(Q)$. See the PDF methods section for details.

References

1. Horn, M.; Schwerdtfeger, C. F. Refinement of the Structure of Anatase at Several Temperatures. *Z. Für Krist.* **1972**, 9.

2. Baur, W. H.; Khan, A. A. Rutile-Type Compounds. IV. SiO_2, GeO_2 and a Comparison with Other Rutile-Type Structures. *Acta Crystallogr. B* **1971**, *27*, 2133–2139.