

Supporting Information Section

5 Rietveld Refinement Results for Anatase Nanoparticles

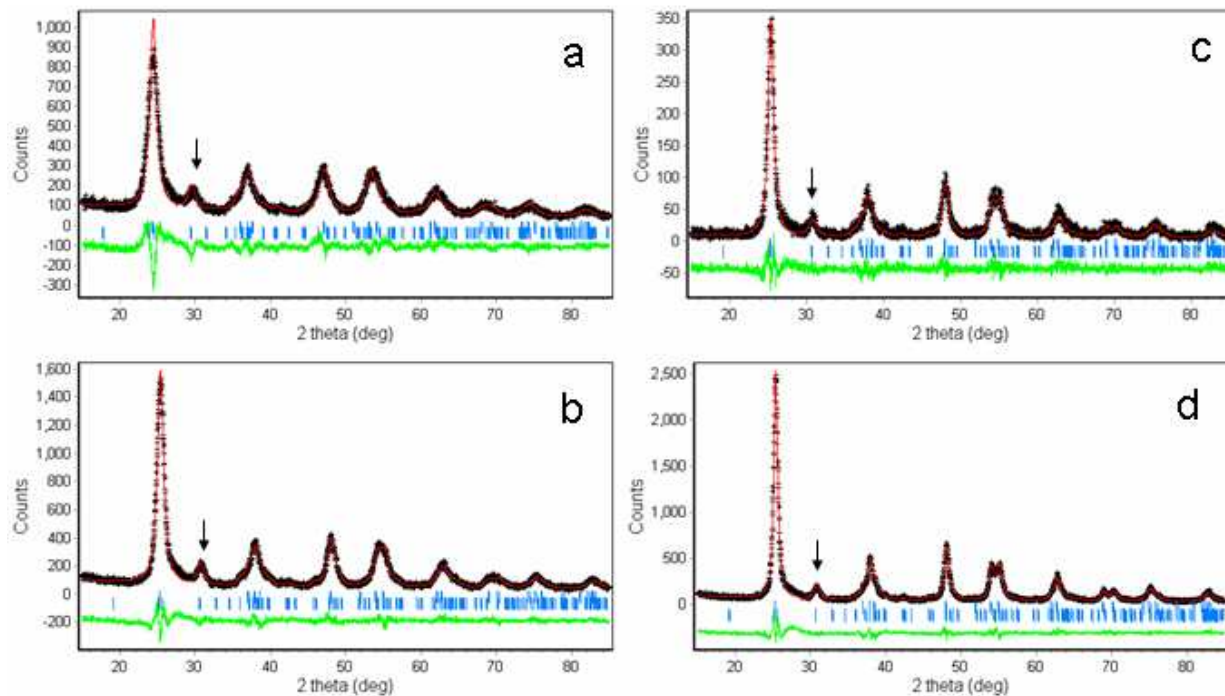


Figure A1. Rietveld refinements for a selection of hydrothermally ripened sol-gel anatase samples **(a)** 5 nm (AH4), **(b)** 7.6 nm (AH5), **(c)** 10.4 nm (AH6) and **(d)** 12.9 nm (AH7). The main reflection from a brookite impurity phase is indicated by the arrow at about 30 °2 θ .

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Comparison of particle diameter of AHx series of anatase samples compared with the particle diameters of the brookite impurity.

Sample	File	Temp. (°C)	<D> Anatase (nm)	<D> Brookite (nm)
AH4	VL111D	90	5.0	7.0
AH5	VL111A	155	7.6	3.21
AH6	VL111C	170	10.4	3.99
AH7	VL111B	200	12.9	5.78

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XRD of Rutile Nanoparticles of Increasing Dimension

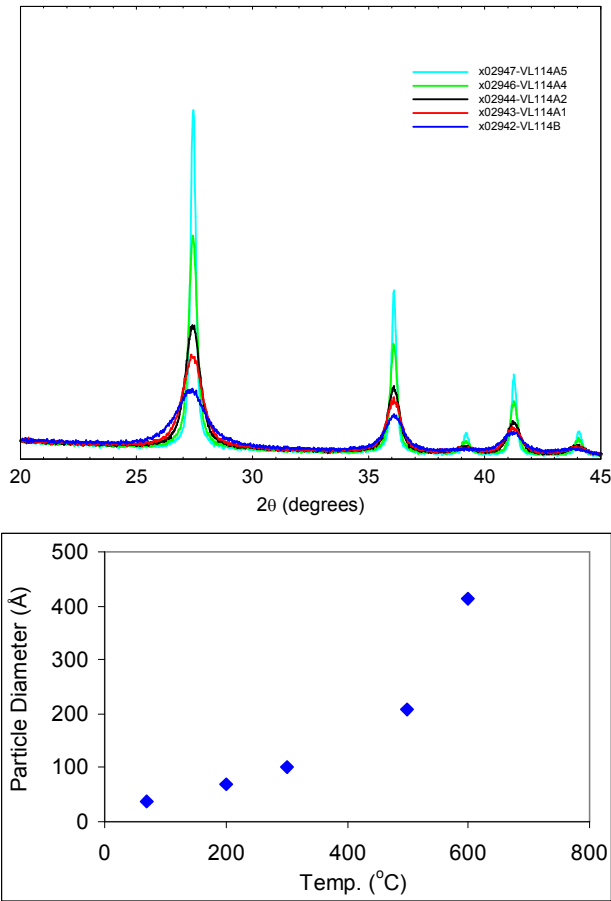


Figure A2. XRD powder patterns of rutile nanoparticles treated at various increasing temperatures.

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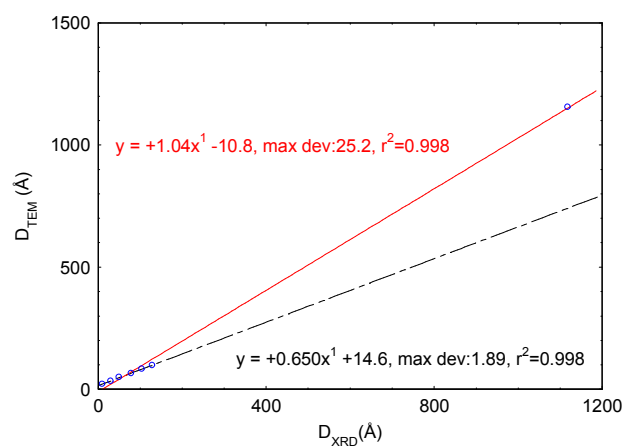
35 **Correlation for Particle Diameter Measurements from TEM and XRD**

Figure A3. Correlation between mean particle size determined by TEM and XRD for anatase particles of different sizes.

Raman Spectra of TiO₂ Polymorphs

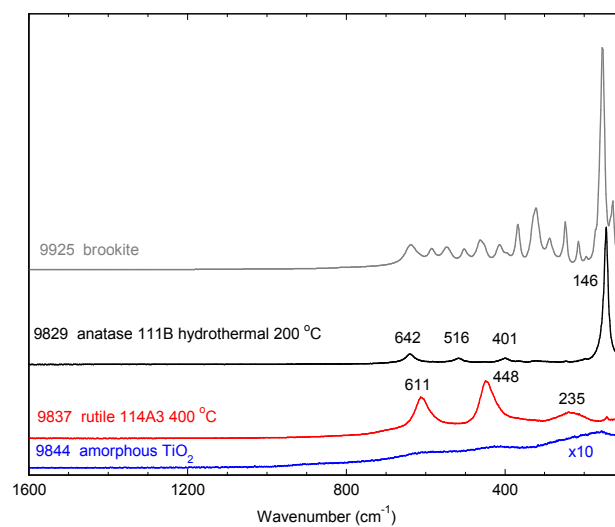
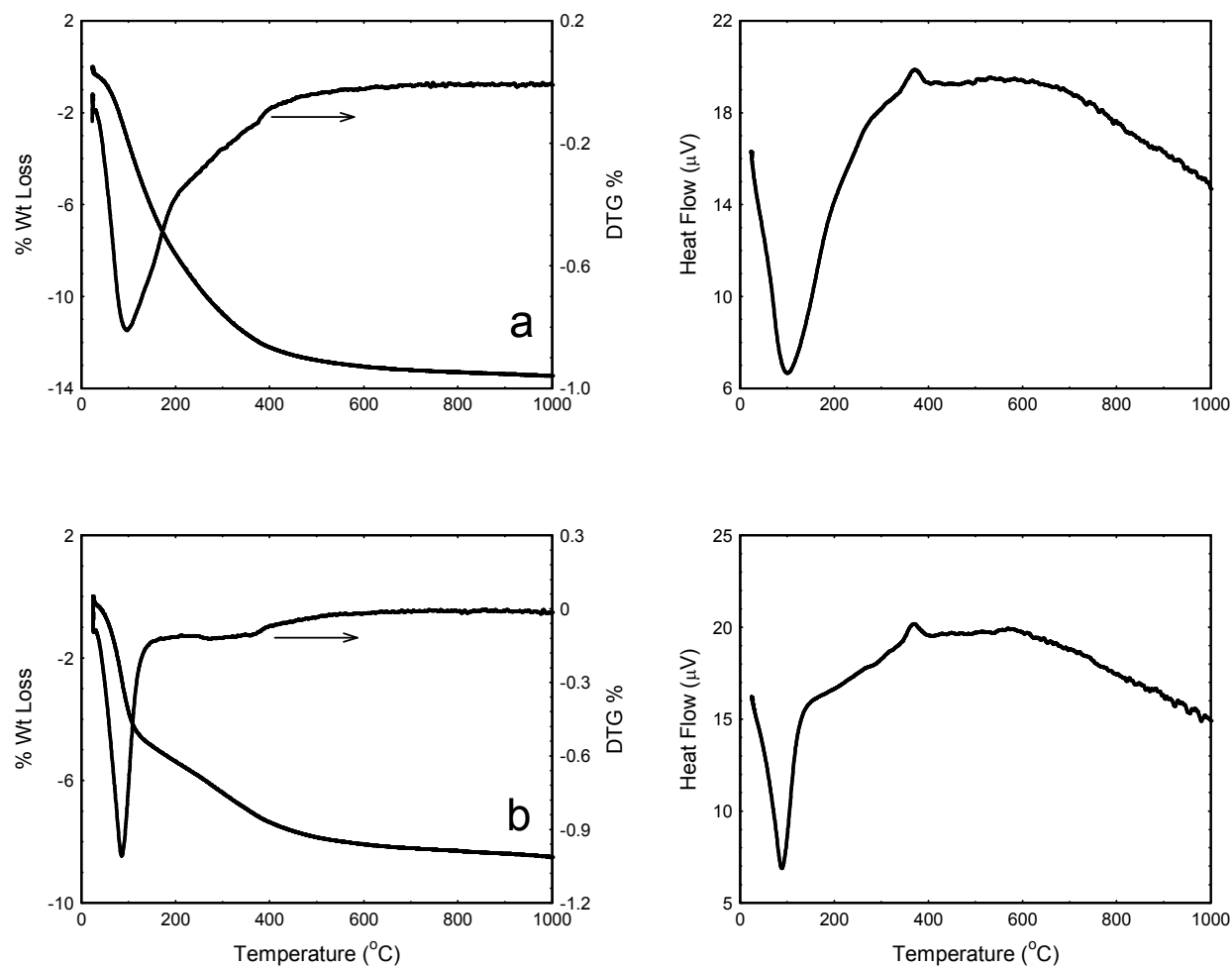


Figure A4. Raman spectra in the 1600 to 1500 cm⁻¹ range for a range of TiO₂ polymorphs.

TGA-DTA of Rutile Nanoparticles

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**Figure A5.** Thermal analysis data for nanocrystalline rutile samples **(a)** 3.6 nm, RC1 and **(b)** 6.9 nm, RC2.

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XANES preedge Fitting

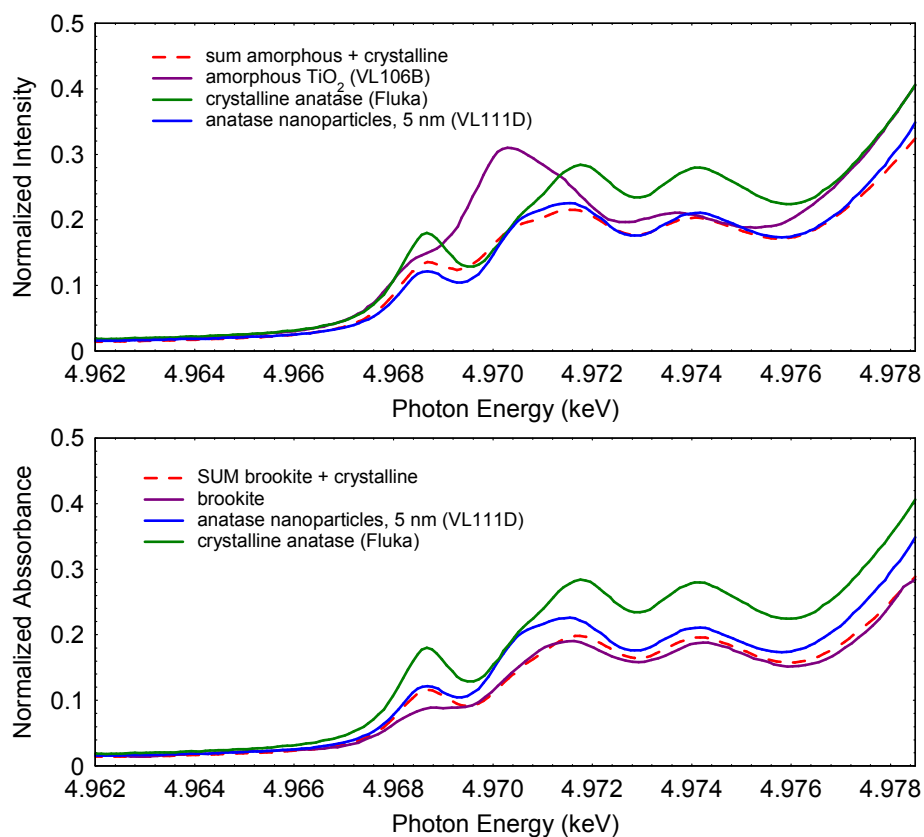


Figure A6. Attempted preedge XANES fits. Top is the attempted fit of the 5 nm anatase nanoparticles using a combination of amorphous TiO₂ and crystalline anatase and the bottom is a combination of brookite and crystalline anatase. Neither of the sum curves (---) represent good fits to the experimental data (blue).

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60 SAXS Measurements of Particle Diameters

Also used for particle size determination of these materials was small-angle X-ray scattering (SAXS) and once again good agreement was obtained through analysis of the Guinier region and the other methods. Example SAXS data for the 2 and 80 nm particles are shown in the figure below.

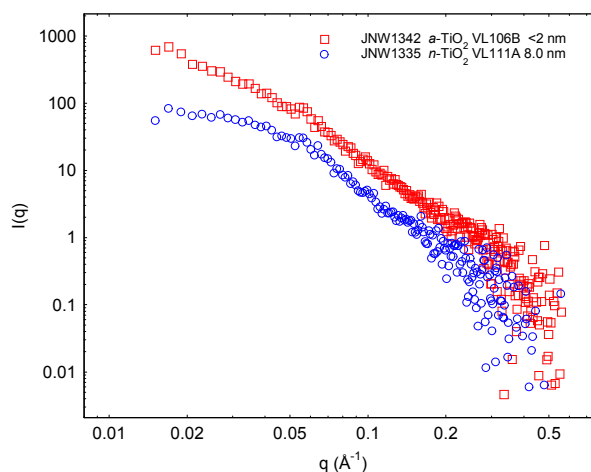


Figure A7. SAXS of (a) the as-prepared sol and (b) sol hydrothermally ripened a 155 °C.

SAXS-determined particle diameters in comparison with Scherrer values determined from XRD for AHx series of anatase samples are provided in the following table.

Sample	File	Temp. (°C)	<D> XRD (nm)	<D> SAXS (nm)
AH4	VL111D	90	5.0	
AH5	VL111A	155	7.6	8.2
AH6	VL111C	170	10.4	11.4
AH7	VL111B	200	12.9	14.1

Corroboration of Particle Dimension from N₂ Adsorption-Desorption Data

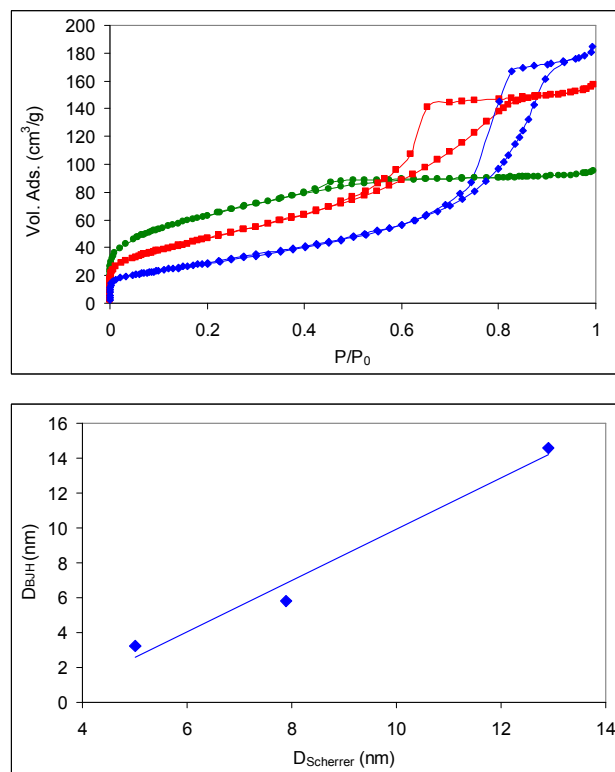


Figure A8. (a) Nitrogen adsorption-desorption isotherms for 5, 7.9 and 12.9 nm anatase nanoparticles produced by hydrothermal ripening method **(b)** correlation of particle diameter calculated from the XRD and the isotherms.