Application Report XRD 31

D8 DISCOVER Plus

PDF Analysis on Titanium Dioxide Nanoparticles

The D8 DISCOVER Plus equipped with the ATLAS™ goniometer and the high-efficiency turbo X-ray source (TXS-HE) is a diffraction solution designed to meet current and future analytical needs in research and production. In this report, its capabilities for the analysis of the pair distribution function (PDF) are presented.

TiO_2 is a widely used metal oxide due to its low cost, low toxicity and chemical inertness. The properties of TiO_2 are highly dependent upon, among others, the crystal structure and the particle size, especially for very small sizes < 10 nm. The conventional particle size analysis using Rietveld structure analysis is limited to long range order, which obviously is not the case for nanoparticles.

The pair distribution function (PDF) describes the probability of finding two atoms separated by a distance *r*. The experimental PDF is determined directly from powder diffraction data making use of both Bragg and diffuse scattering intensities. The resulting reduced total scattering function *F(Q)* finally is Fourier transformed. PDF data is displayed in real space and, in contrast to Rietveld analysis, allows for comparative structural investigations at small and intermediate distance scales.

TiO_2 nanoparticles were prepared in a 1 mm glass capillary and measured on a D8 DISCOVER Plus with ATLAS goniometer, equipped with a TXS-HE (Mo anode), capillary stage, and a LYNXEYE XE-T detector. Data were collected from 2 - 147° 2θ using a variable counting time (VCT) strategy, with a total measurement time of 3.5 h. An empty glass capillary was also measured and data was used for background subtraction. The data collection strategy was planned using the WIZARD plugin of DIFFRAC.MEASUREMENT.

The calculation of the reduced total structure function, *F(Q)*, and its Fourier transform, the PDF *G(r)*, were done using PDFgetX3 [1]. Requirements on the data for PDF analysis include: 1) data measured over a wide Q-range, 2) good statistics especially at high-Q, and 3) low background scattering signal in order to see weak diffuse scattering signals. The D8 DISCOVER Plus perfectly meets these requirements: The TXS-HE with Mo anode allows data to be collected up to 17 $Å^{-1}$, while delivering a superior flux that gives good high-Q statistics even in a short measurement time (3.5 h). Figure 1 shows the raw data (top), and the resulting reduced structure function *F(Q)*, where high-Q diffraction features are clearly visible (bottom).

The experimental PDF was then fit against a model of TiO_2 with anatase structure over a range of 1.5 -50 Å using DIFFRAC.TOPAS V6 (Figure 2). Examining the fit, the anatase model agrees well with the experimental PDF above 8 Å, while the fit below 8 Å looks considerably worse. This would indicate that there is some disorder in the local structure of the nanoparticles. Table 1 shows the residuals to the fit using different fit ranges. The lowest R_{wp} (i.e. the best fit) comes when examining the non-local structure, while the highest Rwp is seen when looking at only the local structure.

Fit range (Å)	R_{wp} (%)
1.5 – 50	20.4
1.5 – 10	24.5
8 – 50	16.4

Table 1: Calculated residuals (R_{wp}) for fit ranges corresponding to full, local, and non-local structure.

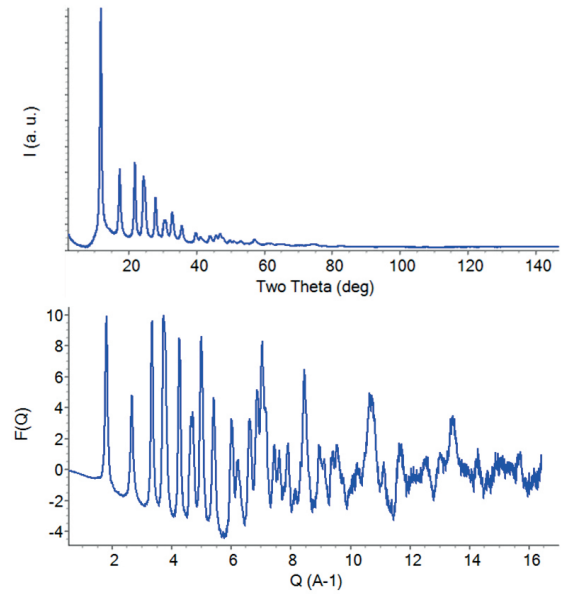

Figure 1: Raw diffraction data (top) and reduced structure function *F(Q)* (bottom).

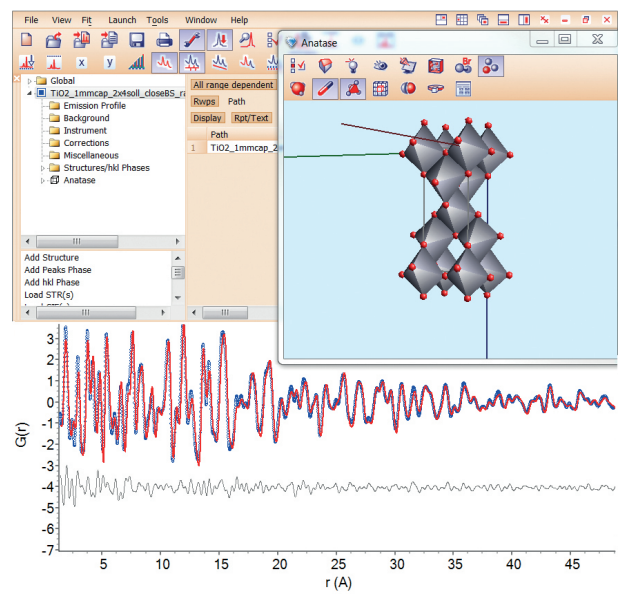

Figure 2: PDF refinement in DIFFRAC.TOPAS V6. There is good agreement between the anatase structural model and the experimental pattern above 8 Å, but a poorer fit in the short range structure region, implying structural defects.

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References

[1] P. Juhás and T. Davis, C. L. Farrow, S. J. L. Billinge, J. Appl. Cryst. 46, 560-566 (2013)

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