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Twinning-mediated anomalous alignment of rutile films revealed by synchrotron X-ray nanodiffraction

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Highlights
Nanotwinned TiO₂ film possesses stronger preferred orientation than its FTO substrate
State-of-the-art nanoscanned X-ray Laue diffraction is used to unveil the mechanism
Twinning-mediated heteroepitaxy mainly leads to the texture improvement
This work helps to stimulate the rational design and synthesis of nanotwin materials
Twinning-mediated anomalous alignment of rutile films revealed by synchrotron X-ray nanodiffraction

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SUMMARY
Nanotwin structures in materials engender fascinating exotic properties. However, twinning usually alter the crystal orientation, resulting in random orientation and limited performances. Here, we report a well-aligned rutile TiO2 nanotwin film with superior preferential orientation than its isostructural substrate. By means of the synchrotron X-ray Laue nanodiffraction technique, the crystal orientation, twin boundaries, and deviatoric stresses of the film were quantitatively imaged at unprecedented spatial resolution to unravel the underlying mechanism of this anomalous alignment. Massive {101}-type rutile nanotwins were observed, and a crystallographic relationship of the heteroepitaxy was proposed. The rapid twinning and twin-controlled heteroepitaxy are responsible for the texture improvement. This work would open up opportunities for rational design of better twin-based functional materials, and implies the powerful capabilities of X-ray nanodiffraction technique for multidisciplinary applications.

INTRODUCTION
Twinned crystals, especially the ordered and dense nanotwins, have attracted considerable interest due to their unique interface or defect structures, novel properties, and promising application prospects (Lu et al., 2009; Behrens et al., 2012; Nie et al., 2015; Zhu et al., 2018; Liu et al., 2018). Generally, a coherent twin boundary (TB) could be deemed as a stable two-dimensional (2D) high-pressure polymorph of the parent crystal due to its higher atomic density (e.g., rutile TiO2 {101} twin (Hwang et al., 2000)). Similar to high-angle grain boundaries (GBs), TBs can serve as barriers against dislocation motion, that is, the hardening effect (Lu et al., 2009; Zhang et al., 2004). The excess energy of coherent TBs is about one order of magnitude lower than that of the ordinary high-angle GBs, which together with the hardening effect make twinned materials possess higher hardness, higher stability, higher toughness, lower compressibility, and near zero thermal expansion (Tian et al., 2013; Huang et al., 2014; Lu et al., 2004, 2009; Zhu et al., 2018; Zhang et al., 2004). In addition, the electrical conductivity of coherent TBs is higher than that of high-angle GBs, and the enhanced ionic transportation along TBs was observed in compounds such as WO3 and SnO2 (Lu et al., 2004; Aird and Salje, 2000; Nie et al., 2015). Moreover, the (photo)catalytic activity of a (photo)catalyst can be enhanced by nanotwin domains via twin-induced active sites or homojunctions caused by staggered band alignment (Behrens et al., 2012; Liu et al., 2011; Huang et al., 2018; Lu et al., 2020a, 2020b).

As an important class of multifunctional materials, rutile TiO2 can be twinned on (101) and (301) planes (Hwang et al., 2000; Li et al., 1999; Lu et al., 2012a, 2020a; Jordan et al., 2018; Gao et al., 1992; Daneu et al., 2007, 2014). However, the synthetic TiO2 twins generally possess lower texture because twinning trends to alter the growth direction or crystal orientation, which is detrimental to practical applications and the discovery of novel properties, whereas the natural rutile twin minerals can directionally form on their substrates (Li et al., 1999; Lu et al., 2012a; Jordan et al., 2018; Gao et al., 1992; Daneu et al., 2007, 2014; Lee et al., 2006; Sosnowchik et al., 2010). Recently, we have successfully synthesized rutile TiO2 nanotwin films on fluorine-doped tin oxide (FTO) glass substrates with the rare b-axis preferred orientation (instead of the c-axis in common self-aligned rutile films) via a rapid nucleation/twinning strategy (Lu et al., 2020a). In this study, to uncover the underlying mechanism of the anomalous alignment, we applied the state-of-the-art scanning synchrotron X-ray Laue nanodiffraction technique (XND, see supplemental
RESULTS AND DISCUSSION

Characterization of [010]-oriented rutile twin films

Several methods can be adopted to determine the crystal orientation and grain boundaries in materials, including electron backscatter diffraction (EBSD), transmission electron microscopy (TEM), and electron tomography (Hsiao et al., 2012; Schwartz et al., 2009; Langille et al., 2012; Fultz and Howe, 2008; Midgley and Dunin-Borkowski, 2009). Although EBSD can image the orientation and twin boundaries of the crystals on the surface, the surface of the sample is required to be flat and the angular resolution is limited to 1–0.1° (Schwartz et al., 2009; Hsiao et al., 2012). TEM and electron tomography can characterize the crystal structure and twin boundaries or flat interfaces in an atomic resolution (Fultz and Howe, 2008; Midgley and Dunin-Borkowski, 2009; Langille et al., 2012), but the specimen preparation is complicated or the sample should be small/thin (generally, size/thickness <100 nm) due to the low penetration depth of electron beam. X-ray diffraction (XRD) in laboratory provides the ensemble-average crystal structure of multiple grains (size >1 μm). Alternatively, the high-brilliance X-ray nanobeam with strong penetration capacity enables the quantitative and nondestructive mapping of crystal orientation and buried grain boundaries of bulk/thick sample with larger strain and surface roughness by X-ray nanodiffraction (Chen et al., 2016), which makes it suitable for studying nanotwinned materials and in situ probing the processes of the growth and transformation of materials at extreme conditions, e.g., high/low temperature and high pressure/stress.

The TiO₂ films (Figure 1A) were synthesized on the FTO glass substrates by a rapid reaction method (see transparent methods) (Lu et al., 2020a). The XRD patterns (Figures 1B and S2) show that the TiO₂ film and
FTO substrate are of rutile structure and a preferred orientation of TiO\textsubscript{2} film along the [010] direction, with a degree about 16 times stronger than that of the isostructural substrate. The scanning electron microscopy (SEM) image (Figure 1C) shows the ship-like rutile TiO\textsubscript{2} crystals inverted on the substrate, with predominant exposed \{111\} and \{110\} facets (Lu et al., 2020a). Notably, there is a handful of crystals with reentrant shape, symbolizing twinned crystals. The high-resolution TEM image (Figure 1D) demonstrates that the sample possesses twin structure with a composition plane of (101). The thickness of the rutile twin film is about 2 μm (Figure S3).

Laue nanoimaging of crystal orientation and twin boundaries
The dedicated XND setup of Taiwan Photon Source (TPS, beamline 21A) (Figure S1) can achieve an angular resolution down to 0.01°, with a nanoscale spatial resolution (~80 nm in this work), and the deviatoric strain tensors resolution of 10\textsuperscript{-4} (Chung and Ice, 1999). Figure 2A shows the SEM image of the rutile twin film surrounding the XND-scanned region. A representative XND image (No. 14993) of the film was indexed as rutile phase (see Figure 2B). The (0, K, 0) spot of TiO\textsubscript{2} located near the center of the Laue image indicates that the a- or b-axis preferred orientation of the grain as inferred from the geometric relationship of the X-ray, sample, and detector (Figure S1). In the scanned region, there are 40,401 images recorded and auto-indexed. As shown in Figure 2C, the crystal orientation map (overlapped with grain boundaries) of the film along the normal direction (z axis, other directions can be find in Figures S4A and S4B) is predominantly

Figure 2. Nanoimaging of morphology, crystal orientation, and twin boundaries of rutile film
(A) SEM image of the TiO\textsubscript{2} film around the scanning region (~20 μm × 20 μm).
(B) Typical indexed XND image of the film (No. 14993).
(C) Crystal orientation map for TiO\textsubscript{2} grains along the normal direction of film (z axis) overlapped with grain boundaries (GBs). The white or transparent area represents the patterns failed to be indexed as rutile structure due to the complex or weak diffraction patterns from the joint area of grains.
(D) Spatial distribution of ordinary grain boundaries (OGBs, gray), (101) twin boundaries (red), and (301) twin boundaries (blue). Scale bar (bottom left) for Figures 2C and 2D: 2 μm. Sample coordinate system (bottom) for Figures 2C and 2D: O-XYZ.
occupied by green area with only little blue and red area, revealing that the TiO₂ film is preferentially oriented with the (100) or (010) crystal planes parallel to the glass substrate.

Previous studies showed that in the synthetic rutile phase TiO₂ powder or natural rutile minerals, the {101} and {301} twins are usually present together, with around six times many former than the latter (Li et al., 1999; Lu et al., 2012a; Jordan et al., 2018; Gao et al., 1992; Daneu et al., 2007, 2014). In our case, the possible twin boundaries were identified from the ordinary grain boundaries by checking the rotation angle of adjacent gains and the parallelity of their rotation axis (Li et al., 2015). As shown in Figure 2D, the red dots or lines signify that the grain boundaries fit well with the (101) twin boundaries, judging from the fact that the rotation angle of the adjacent grains along the [010] axis is 114.4° for the rutile {101}/[010] twin. The blue dots represent that the GBs match well with the {301} TBs (the mutual rotation angle of the rutile {301}/[010] twin is 54.7° (Lee et al., 1993)). Obviously, massive {101}-type rutile twins were detected, whereas only a few blue dots are observed in the map, which suggests the ratio and weight of the rutile {301} twins in the film are much lower than that reported elsewhere. We note that there are lots of nanotwins with thickness less than 80 nm in the film, which have been demonstrated by TEM observation (Lu et al., 2020a).

Taking the XND image of No. 1998 as an example, the image can be indexed as two sets of Laue diffraction spots of rutile TiO₂ and one set of Laue diffraction spots of F-doped SnO₂ (Figure S5 and Data S1). The orientation of both crystals plotted as pole figures shown in Figure 3A reveal that two [010] poles and two (101) poles overlap, respectively, i.e., (101) as composition planes and [010] as a twin axis. The misorientation between both twinned components is 65.8°/0.0025 1.0000 0.0005], agreeing well with the theoretical 65.57°/0 1 0). Moreover, the XND image of No. 14993 was indexed as one set of Laue diffraction spots of rutile TiO₂ and two sets of Laue diffraction spots of F-doped SnO₂ (Figures 2B and S6). The corresponding pole figures (Figure 3B) indicate that the preferential [010] orientation of F:SnO₂ substrate is weaker than that of TiO₂ overlayer, which is consistent with the XRD spectra, crystal orientation maps, and pole figures (Figures 1B, S4, and S7).

**Formation mechanism of well-aligned nanotwin film**

During the process of rapid hydrothermal synthesis of our samples, there are roughly three mechanisms at play: (1) nucleation of twins in reactive solution, (2) attachment of twinned crystals or nuclei to the substrate, and (3) selective growth controlled by twin anisotropy. In growth twin, twinning is usually related to the stress partially generated by the presence of defects and impurities or the accidental attachment of crystalline grains during the initial stages of crystal growth (Penn and Banfield, 1998, 1999; Lebensohn and
To reveal the mechanisms of twinning and attachment, crystallographic relationships and the stress distribution in the rutile nanotwin film were further analyzed. As shown in Figures 4A and S8, the uneven distribution of deviatoric stresses in rutile twin film suggests that the formation or attachment of twinned rutile crystals on the substrate is associated with the stress. In addition, twinned particles were discovered in the reaction solution, and their shape is related to that of twins grown on the substrate (Figure S9) (Lu et al., 2020a). During the dynamic dissolution of reaction precursor (TiN) at room temperature or rapidly elevated temperature, the generation of oxygen vacancies (Ti$^{3+}$, see the electron paramagnetic resonance data in our previous work (Lu et al., 2020a)) or N species would induce twin nuclei to reduce the system energy at the initial reaction stage. Then, the rutile twin seeds attach and continuously grow on the F:SnO$_2$ substrate. Hence, the F:SnO$_2$ substrate is not the prerequisite for twinning but profoundly impact the heteroepitaxial growth and the preferred orientation of the TiO$_2$ overlayer.

An atomic model of rutile {101} twin on SnO$_2$ was proposed, as shown in Figure 4C, based on the pole figures such as No. 1998, strain distributions, and previous studies (Lu et al., 2012b; Lee et al., 1993). Table 1 and Figure 4B show the lattice mismatch between rutile twin and substrate. It was found that the lattice mismatch between the isostuctural F:SnO$_2$ and one twin component (Grain A and twin boundary) is lower than 8%, which could facilitate its heteroepitaxy on F:SnO$_2$ grains and the formation of the other twin component (Grain B) with [010]-preferred orientation regardless of the large (tensile or compressive) stress in the Grain B region (Steidl et al., 2017). Similar effect can be obtained in the case of the rutile {301} twin formation (Figure S10). Rutile twin can be grown on some types of hexagonal substrates, such as sapphire (Al$_2$O$_3$) (Gao et al., 1992; Lee et al., 2006) and hematite (a-Fe$_2$O$_3$) (Rečnik et al., 2015) or formed from other hexagonal precursors, e.g., ilmenite (FeTiO$_3$) (Janssen et al., 2010; Stanković et al., 2015; Daneu et al., 2014). Interestingly, the (010)-oriented SnO$_2$ substrate possesses an approximatively hexagonal atomic arrangement, showing the importance of the lattice-matching attachment in the twinning and heteroepitaxial growth. The attachment of twinned rutile nanocrystals onto SnO$_2$ substrate may be controlled by some
mode of van der Waals-force-driven self-assembly processes, as described in references (Penn and B"{a}n-
field, 1998; Jordan et al., 2018). In this case, the orientation relationship between SnO$_2$ and TiO$_2$ is expected
to be imperfect, as shown by XND data (Figure S4).

In previous studies, the untwinned rutile TiO$_2$ films of nanorods or nanowires that were grown on FTO sub-
strates commonly possess the [001]-preferred orientation, although the preferential orientation of FTO
substrates is [010] direction (Lu et al., 2019; Liu and Aydil, 2009; Feng et al., 2008). The erected growth of
untwinned prismatic rutile on substrates could suppress the prostrate growth due to the fact that the fast-
est growth rate is along [001] direction, which can account for the self-aligned behavior of one-dimensional
rutile arrays on [010]-oriented substrates. From the view point of surface free energy, the tips of rutile nano-
rods or nanowires are commonly exposed with reactive high-energy facets ([111], [001], or [101]), which
favors the fastest growth along [001] direction and the formation of lateral low-energy [110] facets (Lu
et al., 2019, 2020a). However, in our case, after twinned TiO$_2$ is formed, the [001] direction ceases to be
the fastest growth direction. Instead, the twin plane becomes the fastest growth direction, pulling the
rest of rutile crystal along its way. This is supported by the fact that the ship-like rutile twins mainly are pre-
dominated with [111] facets (some capping species may be formed in the rapid reaction environments). In
effect, this type of geometric control actually governs crystal orientation in the TiO$_2$ film, whereas the sub-
strate only plays a minor role. Any crystals that have unfavorable orientations (with twin plane not vertical to
the substrate) will be blocked by surrounding seeds, and only those that have twin plane oriented vertically
to the substrate can grow freely. It is likely that they would grow in a similar manner on any substrate other
than FTO, as described for ZnO films by Podlogar et al. (Podlogar et al., 2012). Therefore, the discovered
texture improvement could be ascribed to the rapid formation of twinned seeds on the preferred orienta-
tion of FTO substrate in the special reaction environments.

CONCLUSIONS

In conclusion, the twin law and crystallographic texture in the anomalously aligned TiO$_2$ nanotwin film were
systematically analyzed by the synchrotron X-ray Laue nanodiffraction. The anomalous alignment was
mainly ascribed to the twin-mediated heteroepitaxy with low lattice mismatch. This study also presents
a state-of-the-art tool to investigate the twin structure, crystal orientation, and internal strain of functional
materials at sub-100 nm resolution and would stimulate the widespread application of X-ray Laue nanodif-
fraction in materials science, geoscience, solar cells, and electronic and optoelectronic devices. With the
rapid developments of X-ray focusing optics and advanced synchrotron light sources, we expect that
the X-ray Laue nanodiffraction system will further enable the quantitative 2D/3D imaging of materials at
several nanometers resolution.

Limitations of the study
It is not clear whether rutile {301} twins are present or not in the film. The orientation maps of FTO may be
distorted because the grain size is too small and the software (XMAS, 2018) cannot automatically remove
the indexed points from TiO$_2$ during the auto-indexing.

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Table 1. Lattice mismatch between the rutile TiO$_2$ (101) twin and F:SnO$_2$ substrate

|                      | Grain A region | Twin boundary | Grain B region |
|----------------------|----------------|---------------|----------------|
|                      | a (Å)          | c (Å)         | d (Å)          | h (Å)          | a or h (Å) | c or d (Å) |
| TiO$_2$              | 4.5940         | 2.9590        | 2.7322         | 4.9753         | 4.5940     | 2.9590     |
| F:SnO$_2$            | 4.7687         | 3.2036        | 2.8724         | 5.3644         | 5.3644     | 2.8724     |
| Mismatch             | 3.73%          | 7.94%         | 5.00%          | 7.53%          | 15.47%     | 2.97%      |
Data and code availability
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METHODS
All methods can be found in the accompanying transparent methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2021.102278.

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AUTHOR CONTRIBUTIONS
Conceptualization, Y.Lu and H.Y.; Methodology, Y.Lu, C.S.K., C.Y.C., Y.Li, and H.Y.; Investigation, C.Y.C., Y.Li, Y.Lu, and N.T.; Writing—Original Draft, Y.Lu; Writing—Review and Editing, Y.Lu, E.H., H.Y., and B.C.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental information

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Supplemental Information

Transparent Methods, Figures S1-S10, and Data S1

Transparent Methods

Synthesis

The well-aligned rutile TiO$_2$ twins were grown on fluorine-doped tin oxide (FTO) glass substrates by a rapid hydrothermal method (Lu et al., 2020). In a typical synthetic procedure, titanium nitride powder (40 mg, 99.5 wt%, size: 2-10 μm, aladdin), hydrochloric acid (26 mL, 5.0 M), and hydrogen peroxide (4 mL, 30 wt%) were placed in a Teflon-lined autoclave (100 mL in volume), in which two pieces of cleaned FTO conducting substrates were slantwise immersed with the conductive side facing down, then, heated quickly at 200 °C for 20 h in an electric oven (preheated to ~200 °C). After the hydrothermal procedure, the autoclave was took out and cooled naturally to room temperature. The obtained samples were washed with deionized water and dried in ambient environment.

Characterization

The crystal structure and preferential orientation of samples were investigated by the powder X-ray diffraction (XRD) on the X-ray diffractometer with Cu-Kα radiation (PANalytical X’ Pert Pro, $\lambda_{\text{K}\alpha_1} = 1.540598$ Å). The degree of the preferential orientation ($p$) of a film was estimated by the ratio ($R$) of peak intensity (e.g. $I_{020}$ / $I_{110}$) as compared with the ratio ($R^0$) of the reference powder without preferred orientation. That is, $p = R / R^0 = I_{020} / I_{110} / R^0$. We used JCPDS no. 96-900-4142 as the rutile reference ($R^0 = 0.071$), and JCPDS no. 01-077-0452 as the F:SnO$_2$ reference ($R^0 = 0.207$). The morphology and twin structure of samples were characterized by a field-emission scanning electron microscope (SEM, Hitachi SU8020) and a transmission electron microscope (TEM, FEI TECNAI G$^2$ S-TWIN). The cross-sectional TEM specimen (thinned TiO$_2$ ~ 80 nm) was prepared by a focused ion beam (FIB) and scanning electron microscope dual beam system (FEI Versa 3D).

X-ray Laue nanodiffraction experiments and data analysis

The synchrotron X-ray Laue nanodiffraction of film was conducted at the beamline BL21A of Taiwan Photon Source (TPS), where the FOrum x-Ray for Micro-Structure Analysis (FORMOSA) end-station provides an all-in-one solution including a large area hybrid pixel array detector (DECTRIS Pilatus3S 6M) on the top of the sample chamber and a built-in SEM (ORSAY PHYSICS) as an online real-time navigator (Chen et al., 2016). The TiO$_2$ film (on a holder) was mounted on an integrated hexapod scanner enabling the scanning measurements, and tilted 45° relative to the incident X-ray nanobeam. A series of scanning 2D polychromatic Laue diffraction patterns of sample were collected with an exposure time of 400 ms and the spatial resolution of ~80 nm at room temperature (Sample-CCD distance: 523.220 mm; Energy: 200-250 eV).
The crystal orientation and stress information were simultaneously determined from these patterns by the X-ray Microdiffraction Analysis Software (XMAS, Tamura, 2018) on personal computer and super-computer (Dell R220 computer clusters with 48 nodes, NSSRC). To map the crystal orientation, grain boundaries, and deviatoric stresses, the software automatically picked up the Laue pattern with the strongest intensity and indexed at least 6 reflections (or backscattering Laue points), i.e., only analyzed one TiO$_2$ grain per XND image. The twin law were determined by the self-developed software. The errors of both rotation angle and rotation axis of adjacent gains are less than 3° during the mapping of twin boundaries (Li et al., 2015). The used elastic stiffness tensor of rutile TiO$_2$ is

\[
M = \begin{bmatrix}
2.6700 & 1.6500 & 1.5200 & 0 & 0 & 0 \\
1.6500 & 2.6700 & 1.5200 & 0 & 0 & 0 \\
1.5200 & 1.5200 & 4.8300 & 0 & 0 & 0 \\
0 & 0 & 0 & 1.2200 & 0 & 0 \\
0 & 0 & 0 & 0 & 1.2200 & 0 \\
0 & 0 & 0 & 0 & 0 & 2.1200 \\
\end{bmatrix}
\]

(1)
Figure S1. Schematic layout of the scanning synchrotron X-ray Laue nanodiffraction with sub-100 nm spatial resolution, Related to Figures 2-4. The polychromatic X-rays spot was focused to tens of nanometer (inserted diagram) by focusing K-B mirror optics. The sample was fixed on a holder from which high–resolution diffraction patterns were collected by a PILATUS 6M detector.

Figure S2. Rietveld refinement of the experimental XRD data of the FTO conductive glass slice at ambient conditions, Related to Figure 1 and Table 1. The refinement was performed using the General Structure and Analysis System II (GSAS-II) (Toby and Von Dreele, 2013). The blue line denotes the difference between the experiment (grey X) and refinement (red).
Figure S3. SEM images of the FIB-prepared TEM specimen of the rutile TiO$_2$ twin film, Related to Figure 1.

Figure S4. Crystal orientation maps of TiO$_2$ and F:SnO$_2$ along different directions in the sample coordinate system, Related to Figures 2 and 3.  
(A-C) Crystal orientation maps of the TiO$_2$ nanotwin film.  
(D-F) Crystal orientation maps of the F:SnO$_2$ grains substrate. The black dots represent the patterns failed to be indexed as rutile structure.
Figure S5. XND image of No. 1998 indexed to tetragonal TiO$_2$ (A & B) and SnO$_2$ (C) structure ($a = 4.7687$ Å, $c = 3.2036$ Å), respectively, Related to Figure 3. Please find the indexed results in the Supplemental Data.
Figure S6. XND image of No. 14993 indexed to tetragonal TiO$_2$ (A) and SnO$_2$ (B & C) structure ($a = 4.7687$ Å, $c = 3.2036$ Å), respectively, Related to Figure 3.
Figure S7. Pole figures of TiO$_2$ for all indexed XND images, Related to Figure 3.

Figure S8. Spatial distribution of the normalized deviatoric stresses (overlapped with grain boundaries) in the rutile nanotwin film, Related to Figure 4.
Figure S9. SEM image (A) and shape model (B) of the precipitated twinned particles in the reaction solution, Related to Figure 1 and Table 1.

Figure S10. Scheme of the rutile TiO$_2$ $\{301\}$ twin on the SnO$_2$(010) viewed along the [010] direction, Related to Figure 2 and Table 1.
Data S1. Indexed reports of the XND image No. TiO\textsubscript{2}\_scan2\_0001998 (tif) from XMAS, Related to Figure 3.

1. Indexed results of TiO\textsubscript{2}\_A grain

| x(exp) | y(exp) | h   | k   | l   | Ener(keV) | 2theta(deg) |
|--------|--------|-----|-----|-----|-----------|-------------|
| 1106.695 | 1602.503 | 4   | 0   | 0   | 8.16582   | 82.75478    |
| 329.5151 | 2332.707 | 7   | 0   | -1  | 16.74797  | 70.58026    |
| 703.5555 | 501.1892 | 5   | 1   | 0   | 8.79855   | 102.8949    |
| 574.8782 | 216.6063 | 4   | 1   | 0   | 6.89485   | 107.5996    |
| 1982.293  | 1165.486 | 7   | 0   | 1   | 13.56202  | 91.02973    |
| 2369.085  | 1066.217 | 5   | 0   | 1   | 9.75535   | 92.80698    |
| 1973.84   | 100.3204 | 6   | 1   | 1   | 10.35671  | 109.7635    |
| 1986.335  | 1959.834 | 8   | -1  | 1   | 17.86347  | 76.66513    |
| 2261.803  | 2148.651 | 6   | -1  | 1   | 14.1077   | 73.80907    |
| 1313.163  | 2453.517 | 7   | -1  | 0   | 17.10203  | 67.82719    |
| 127.3696  | 1559.122 | 8   | 1   | -1  | 16.58127  | 83.85445    |
| 1715.04   | 469.8182 | 8   | 1   | 1   | 14.08803  | 103.7079    |
| 493.0877  | 2141.897 | 9   | 0   | -1  | 20.60028  | 73.49051    |
| 830.6199  | 813.3861 | 7   | 1   | 0   | 12.70187  | 97.39285    |
| 1777.531  | 1241.373 | 9   | 0   | 1   | 17.48984  | 89.60318    |
| 780.1652  | 684.0765 | 6   | 1   | 0   | 10.73812  | 99.70841    |
| 900.0615  | 990.7714 | 9   | 1   | 0   | 16.68744  | 94.15342    |
| 2166.246  | 525.0349 | 11  | 1   | 2   | 19.86192  | 102.4333    |
| 1575.416  | 690.8137 | 10  | 1   | 1   | 17.94053  | 99.79426    |
| 1636.77   | 593.6983 | 9   | 1   | 1   | 16.00582  | 101.5357    |
| 1821.293  | 311.0002 | 7   | 1   | 1   | 12.20069  | 106.3962    |
| 874.009   | 919.6783 | 8   | 1   | 0   | 14.70234  | 95.45995    |

dev1, dev2, pixdev= 0.0338600 0.0377700 0.0253900

matrix X Y Z -> h k l
0.02232 -0.02842 0.45798
0.17356 0.42498 0.01791
-0.27359 0.11088 0.02022

matrix h k l -> X Y Z
0.10577 0.82237 -3.12475
-0.13467 2.01436 1.26641
2.17001 0.08488 0.23089

Number of missing reflections: 35

Rfactor: 0.82745999
Rotangle(deg): 88.79728
Rodrigues vector: 0.16442 0.94101 0.21531 88.79728
Quaternion: 0.71449 0.11747 0.67234 0.15384
Euler angles: 79.66722 42.75689 82.67116
orsnr, orsirxy, orsirxz, orsiryz: 53.32627 67.78503 -51.50586 25.23834
Rotation matrix, unit cell to sample:
0.04859 0.37780 -0.92461
-0.06187 0.92507 0.37473
0.99690 0.03899 0.06832
Rotation matrix, sample to unit cell:
0.04859 -0.06187 0.99690
0.37780 0.92507 0.03899
-0.92461 0.37473 0.06832
Sum of integrated intensities: 8933603.00000
Average integrated intensity per peak: 446680.15625
scale: 0.00598000
depth: -0.175070
Unindexed reflections: 0
Xstage position: 43514.0
Ystage position: 11800.0
X map position: -22021
Y map position: 1
Izero: 10597.000
Channel A: 0.00000000
Channel B: 0.00000000
Channel C: 0.00000000
Channel D: 0.00000000
Channel E: 0.00000000
Exposure: 0.607000
Average intensity of the image: 92.838362
Average background of the image: 82.873988
## Indexed results of TiO$_2$ B grain

Number of grains found: 1
Grain no: 0  Grains list file index: 0
Number of indexed reflections: 27

| x(exp) | y(exp) | h  | k  | l  | Ener(keV) | 2theta(deg) |
|--------|--------|----|----|----|-----------|-------------|
| 1106.695 | 1602.503 | 0  | -4 | 0  | 8.16582   | 82.75478    |
| 2424.365 | 1929.563 | -1 | -3 | 0  | 6.8009    | 77.72577    |
| 284.0622 | 1732.038 | 2  | -10| 0  | 21.24706  | 80.73582    |
| 1909.466 | 1721.401 | -1 | -5 | 0  | 10.61332  | 80.82959    |
| 73.95251 | 1803.11  | 2  | -8 | 0  | 17.36535  | 79.703      |
| 2102.05  | 1787.395 | -1 | -4 | 0  | 8.67309   | 79.8079     |
| 1116.278 | 238.4037 | 0  | -7 | 1  | 11.97984  | 107.735     |
| 1973.84  | 100.3204 | -1 | -6 | 1  | 10.35671  | 109.7635    |
| 222.8259 | 58.89168 | 2  | -12| 2  | 20.74039  | 109.5519    |
| 1715.04  | 469.8182 | -1 | -8 | 1  | 14.08803  | 103.7079    |
| 494.1708 | 450.5739 | 1  | -8 | 1  | 14.10315  | 103.5517    |
| 522.5287 | 1669.975 | 1  | -7 | 0  | 14.5915   | 81.67837    |
| 1776.94  | 1685.652 | -1 | -6 | 0  | 12.58823  | 81.39429    |
| 1115.37  | 549.5213 | 0  | -9 | 1  | 15.8245   | 102.3036    |
| 1821.293 | 311.0002 | -1 | -7 | 1  | 12.20069  | 106.3962    |
| 389.9437 | 286.9494 | 2  | -14| 2  | 24.43778  | 106.1684    |
| 2000.909 | 1764.839 | -2 | -9 | 0  | 19.33087  | 80.1202     |
| 743.8867 | 237.2892 | 1  | -14| 2  | 24.05987  | 107.4615    |
| 695.955  | 1642.875 | 1  | -10| 0  | 20.65261  | 82.09056    |
| 654.776  | 1644.174 | 1  | -9 | 0  | 18.61041  | 82.08256    |
| 2158.033 | 714.6269 | -2 | -9 | 1  | 16.57559  | 99.12955    |
| 1577.617 | 692.2443 | -1 | -10| 1  | 17.944    | 99.76793    |
| 637.6443 | 679.6884 | 1  | -10| 1  | 17.95503  | 99.68447    |
| 383.8218 | 284.9153 | 1  | -7 | 1  | 12.21694  | 106.1928    |
| 1634.819 | 590.6048 | -1 | -9 | 1  | 15.99944  | 101.5917    |
| 406.287  | 942.7387 | 2  | -13| 1  | 24.2765  | 94.81672    |
| 680.4789 | 8.1313  | 1  | -12| 2  | 20.34551 | 111.1356    |

Dev1, dev2, pixdev = 0.0726400 0.0619900 0.0485500

Matrix X  Y  Z -> h  k  l

|   |   |   |
|---|---|---|
|   |   |   |

Matrix h  k  l -> X  Y  Z

|   |   |   |
|---|---|---|
|   |   |   |

Number of missing reflections: 72
Rfactor: 0.62246001  
Rotangle(deg): 86.42025  
Rodrigues vector: 0.93847 -0.00278 -0.04184 86.42094  
Quaternion: 0.72884 0.68400 -0.00203 -0.03049  
Euler angles: 86.31144 2.21962 -2.70861  
norsnr, orsirxy, orsirxz, orsiryz: 53.56714 2.39092 -0.67673 53.56610  
Rotation matrix, unit cell to sample:
0.99813 -0.04722 -0.03876  
0.04168 0.06243 0.99718  
-0.04467 -0.99693 0.06429  
Rotation matrix, sample to unit cell:
0.99813 0.04168 -0.04467  
-0.04722 0.06243 -0.99693  
-0.03876 0.99718 0.06429  
Sum of integrated intensities: 14591121.00000  
Average integrated intensity per peak: 583644.81250  
scale: 10.9890  
depth: -0.264670  
Unindexed reflections: 0  
Xstage position: 43514.0  
Ystage position: 11800.0  
X map position: -22021  
Y map position: 1  
Izero: 10597.000  
Channel A: 0.00000000  
Channel B: 0.00000000  
Channel C: 0.00000000  
Channel D: 0.00000000  
Channel E: 0.00000000  
Exposure: 0.607000  
Average intensity of the image: 92.838362  
Average background of the image: 82.873988
### 3. Indexed results of F:SnO$_2$ grain

The indexed reflections from TiO$_2$ were masked to reduce the interference.

| x(exp) | y(exp) | h   | k   | l   | Ener(keV) | 2theta(deg) |
|--------|--------|-----|-----|-----|-----------|-------------|
| 1575.453 | 1244.985 | -4  | 0   | 0   | 7.38595   | 89.50503    |
| 1968.467 | 2359.248 | -10 | -2  | 0   | 23.14313  | 69.89858    |
| 1034.028 | 235.7058  | -5  | 1   | 0   | 8.20737   | 107.7363    |
| 1208.45  | 523.1463  | -7  | 1   | 0   | 11.7619   | 102.8047    |
| 1868.458 | 2020.032  | -7  | -1  | 0   | 15.01524  | 75.49885    |
| 1298.06  | 682.6916  | -9  | 1   | 0   | 15.3738   | 99.94311    |
| 1184.172 | 1639.877  | -13 | 0   | 1   | 25.9119   | 82.06355    |
| 1138.206 | 403.6893  | -6  | 1   | 0   | 9.97449   | 104.8938    |
| 1911.1   | 2159.014  | -6  | -1  | 0   | 13.2699   | 73.15503    |
| 1283.73  | 2400.521  | -9  | -1  | 1   | 21.14641  | 68.68884    |
| 1645.708 | 140.9373  | -14 | 2   | -1  | 22.65584  | 109.3669    |
| 294.0976 | 495.5388  | -11 | 3   | 1   | 19.1628   | 102.5327    |
| 529.8547 | 583.9432  | -13 | 3   | 1   | 22.57164  | 101.2806    |

dev1, dev2, pixdev= 0.0818400 0.0648700 0.0430400

Matrix $X$ $Y$ $Z -> h$ $k$ $l$

| 0.03029 | 0.00120 | -0.47590 |
| 0.28079 | 0.38497 | 0.01884  |
| 0.25813 | -0.18906| 0.01595  |

Matrix $h$ $k$ $l -> X$ $Y$ $Z$

| 0.13320 | 1.23478  | 2.51518  |
| 0.00528 | 1.69292  | -1.84212 |
| -2.09279| 0.08286  | 0.15544  |

Number of missing reflections: 99

Rfactor: 0.69611001
Rotangle(deg): 92.27490
Rodrigues vector: 0.32784 -0.93915 0.30527 92.27490
Quaternion: 0.69293 -0.22717 -0.65076 0.21153
Euler angles: 85.17680 -38.86055 83.84298
orsnr, orsirxy, orsirxz, orsiryz: 53.28348 53.89382 46.65455 -88.82387

Rotation matrix, unit cell to sample:

| 0.06352 | 0.58882 | 0.80576 |
| 0.00252 | 0.80730 | -0.59014|
| -0.99798| 0.03951 | 0.04980 |
Rotation matrix, sample to unit cell:

\[
\begin{pmatrix}
0.06352 & 0.00252 & -0.99798 \\
0.58882 & 0.80730 & 0.03951 \\
0.80576 & -0.59014 & 0.04980
\end{pmatrix}
\]

Sum of integrated intensities: 200794.12500

Average integrated intensity per peak: 182540.82813

scale: -0.00419000

depth: -0.187010

Unindexed reflections: 0

X stage position: 43514.0

Y stage position: 11800.0

X map position: -22021

Y map position: 1

Izero: 10597.000

Channel A: 0.0000000

Channel B: 0.0000000

Channel C: 0.0000000

Channel D: 0.0000000

Channel E: 0.0000000

Exposure: 0.607000

Average intensity of the image: 92.838362

Average background of the image: 82.873988

Supplemental References

Chen, X., Dejoie, C., Jiang, T., Ku, C.-S., and Tamura, N. (2016). Quantitative microstructural imaging by scanning Laue x-ray micro- and nanodiffraction. *MRS Bull.* 41, 445-453.

Li, Y., Wan, L., and Chen, K. (2015). A look-up table based approach to characterize crystal twinning for synchrotron X-ray Laue microdiffraction scans. *J. Appl. Crystallogr.* 48, 747-757.

Lu, Y., Chiang, C.-Y., and Huang, E. (2020). Vertically nanotwinned TiO₂ photoanodes with enhanced charge transport for efficient solar water splitting. *Appl. Mater. Today* 20, 100707.

Toby, B. H., and Von Dreele, R. B. (2013). GSAS-II: the genesis of a modern open-source all purpose crystallography software package. *J. Appl. Crystallogr.* 46, 544-549.