Atomic-Scale Investigation of New Phase Transformation Process in TiO_2 Nanofibers

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1. The characterization results

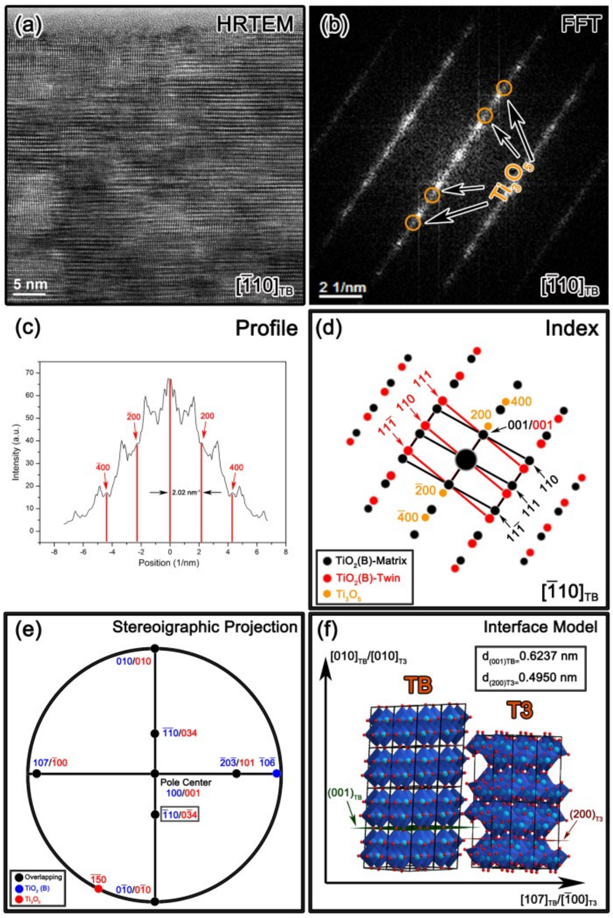

Fig. S1 The detailed TEM analysis on the mixed-phase $Ti_3O_5/TiO_2(B)$ nanofiber viewing along $[110]_{TB}$. (a) the HRTEM image; (b) the corresponding FFT image; (c) the intensity profile image; (d) the index of the two sets of diffraction patterns of Ti_3O_5 and $TiO_2(B)$; (e) the stereographic projection image to prove the COR of $[110]_{TB}//[034]_{T3}$; (f) the schematic interface between the two phases under this COR by using the Ti-O octahedron.

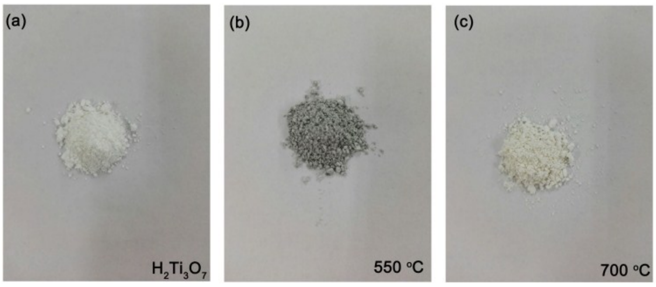

Fig. S2 The images of as-obtained $H_2Ti_3O_7$ (a), and the products calcinated at 550 ºC (b) and 700 ºC (c).

As it is known that the color Ti_3O_5 is black, the grey powder at 550 ºC indicates that the existing of Ti_3O_5 phase. When the temperature is up to 700 ºC, the color is back to the original white, proving that the anatase phase has been formed at this stage.

2. Invariant Line (IL) Model Explanation

In present study, the IL model was applied to study the phase transition from TiO_2 (B) to Ti_3O_5. According to the model, a habit plane must contain an edge dislocation with a Burgers vector *b* for diffusional phase transformation. The virtual unit vector $P_1 = b / |b|$ is invariant in both length and direction during deformation. The vector P_1 is equivalent to but not the same as the invariant line in real space. Q_1 is invariant normal perpendicular to the Burgers vector *b* (an edge dislocation in the habit plane). P_1 and Q_1 determine a one-step rotation matrix $R(u/\theta)$(R is the rotation matrix, u the unit rotation axis and θ the rotation angle). The rotation angle and the axis of a rotation matrix can be resolved by Euler's equation dealing with rigid-body rotation:

$$\frac{(P_2 - P_1)\times(Q_2 - Q_1)}{(P_2 + P_1)\cdot(Q_2 - Q_1)} = u\left(\tan\frac{\theta}{2}\right) \qquad (1)$$

Here, Q_2 is a deformation of vector Q_1 and B is the generalized Bain strain. The vectors P_2, Q_1 and Q_2 are given by

$$\begin{cases} P_2 = B\cdot b / \left|B\cdot b\right| \\ Q_1 = \left[hkl\right] \\ Q_2 = Q_1 \cdot B^{-1} \end{cases} \tag{2}$$

And
$$\begin{cases} P_1 \cdot Q_1 = 0 \\ \left|P_1\right| = \left|P_2\right| \\ \left|Q_1\right| = \left|Q_2\right| \end{cases} \tag{3}$$

A one-stop rotation operation $R(u/\theta)$ can be directly determined geometrically by using Euler's equation (1). Thus, having found the total strain A ($A = RB$), the eigenvalues, eigenvectors (including invariant line) and eigenplanes (including habit planes) can be found by linear algebra. The orientation relationship between the matrix and the new phase can be directly deduced by considering the rotation matrix $R(u/\theta)$ starting from the Bain strain lattice correspondence. Following this approach, it is very simple to define an OR.

2. The Detailed Calculation

The main strain matrix chosen in present calculation is:

$$B = \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix} = \begin{pmatrix} \frac{\left|[001]_{T3}\right|}{\left|[100]_{TB}\right|} & 0 & 0 \\ 0 & \frac{\left|[170]_{T3}\right|}{\left|[106]_{TB}\right|} & 0 \\ 0 & 0 & \frac{\left|[\bar{1}10]_{T3}\right|}{\left|[010]_{TB}\right|} \end{pmatrix} = \begin{pmatrix} 0.8108 & 0 & 0 \\ 0 & 0.7535 & 0 \\ 0 & 0 & 1.4042 \end{pmatrix}$$

Based on the observed TEM result, the first axis η_1 was chosen as $[001]_{T3}/[100]_{TB}$. Similarly, the $[\bar{1}10]_{T3}/[010]_{TB}$ was donated as the second axis η_2. The third axis η_3 was obtained through searching the vector which is perpendicular with η_1 and η_2 in the stereographic projection 2.0 software.[1] The obtained Bain strain lattice correspondence can be seen in Fig. S1.

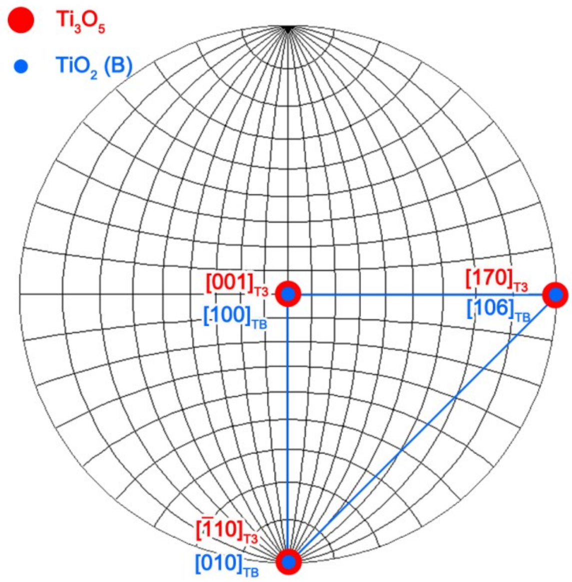

Fig. S3 The Bain strain lattice correspondence for the phase transition from TiO_2 (B) to Ti_3O_5.

As the $[100]_{TB}$ parallels to one of Bain strain lattice correspondence η_1, the IL model consequently was simplified to be two-dimensional case. Clearly, the rotation axis was $[100]_{TB}$.

As the total strain matrix for variant 1 can be written as:

$$\boldsymbol{A} = \boldsymbol{RB} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix} \tag{4}$$

We let (***A***-***I***)***X***=0, then we can obtain:

$$|\boldsymbol{A}-\boldsymbol{I}| = \left| \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix} - \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right| \tag{5}$$
$$= (\eta_1 - 1)[1 + \eta_2\eta_3 - (\eta_2 + \eta_3)\cos\theta] = 0$$

Therefore, the rotation angle θ can also be obtained as:

$$\cos\theta = \frac{1 + \eta_2\eta_3}{\eta_2 + \eta_3} \tag{6}$$

In order to calculate the eigenvalue λ_i of the lattice deformation matrix, we let |***A***-λ***I***|=0, then:

$$|\boldsymbol{A}-\lambda\boldsymbol{I}|=\left|\begin{pmatrix}1 & 0 & 0\\ 0 & \cos\theta & -\sin\theta\\ 0 & \sin\theta & \cos\theta\end{pmatrix}\begin{pmatrix}\eta_1 & 0 & 0\\ 0 & \eta_2 & 0\\ 0 & 0 & \eta_3\end{pmatrix}-\begin{pmatrix}\lambda & 0 & 0\\ 0 & \lambda & 0\\ 0 & 0 & \lambda\end{pmatrix}\right| \\ =(\lambda-1)(\lambda-\eta_2\eta_3)(\eta_1-\lambda)=0 \tag{7}$$

Therefore, the three eigenvalues are determined to be $\lambda_1=1$, $\lambda_2=\eta_2\eta_3$, $\lambda_3=\eta_1$. Obviously, one of the eigenvalues always equals to 1. Hence, eigenvectors V_i of the matrix A can be calculated by letting $\boldsymbol{AX}=\lambda\boldsymbol{X}$, then:

$$(\boldsymbol{A}-\lambda\boldsymbol{I})\boldsymbol{X}=\left(\begin{pmatrix}1 & 0 & 0\\ 0 & \cos\theta & -\sin\theta\\ 0 & \sin\theta & \cos\theta\end{pmatrix}\begin{pmatrix}\eta_1 & 0 & 0\\ 0 & \eta_2 & 0\\ 0 & 0 & \eta_3\end{pmatrix}-\begin{pmatrix}\lambda & 0 & 0\\ 0 & \lambda & 0\\ 0 & 0 & \lambda\end{pmatrix}\right)\begin{pmatrix}X\\ Y\\ Z\end{pmatrix} \\ =\begin{pmatrix}(\eta_1-\lambda)X\\ (\eta_2\cos\theta-\lambda)Y-(\eta_3\sin\theta)Z\\ (\eta_2\sin\theta)Y+(\eta_3\cos\theta-\lambda)Z\end{pmatrix}=0 \tag{8}$$

After putting the eigenvalues and rotation angles θ into Equation (8), we can obtain: when $\lambda_1=1$, the eigenvector can be obtained to $V=[0,3,2]$. This is the growth direction mentioned in paper. The eigenplane determined by the eigenvector can be calculated to be F= (100), and it is the habit plane in the phase transition.

Reference

1. Liu, H.; Liu, J. SP2: a computer program for plotting stereographic projection and exploring crystallographic orientation relationships. *Journal of Applied Crystallography* 2012, 45, 130-134.