Supplementary Information

Design and Observation of Biphase TiO₂ Crystal with Perfect Junction

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1. Theoretical Methods

SSW and SSW-crystal method for PES exploration

The recently-developed SSW method¹⁻² and its extension for crystals to include the lattice degrees of freedom (SSW-crystal)³ is utilized to explore the PES of crystal and surfaces. The SSW algorithm features with an unbiased PES exploration ability using the second derivative information. The method is originated from the bias-potential driven constrained Broyden dimer (BP-CBD) method for transition state (TS) searching developed in the group ^{1, 4}, in which the barrier of reaction is surmounted by adding consecutively Gaussian bias potentials and the reaction coordinate (the direction where Gaussian is added) is refined continuously using the biased constrained Broyden dimer (biased-CBD) method. Different from the BP-CBD method, each SSW step (from one minimum to another) will choose a random direction and perturb structure along the direction that is always refined using the biased-CBD method. At the end of the SSW step, a structure selection module, e.g. in Metropolis Monte-Carlo scheme, is applied to accept/refuse the new minimum. The detail of the methodology can be found in the previous paper ^{1-2,3}. The SSW and SSW-crystal parameters utilized in this work is as those utilized previously^{1-2,3}, namely, the Gaussian width, $ds=0.6\ 0.6\ \text{\AA}$; the number of Gaussian, H=10; the lattice length in displacement, $\Delta L = 0.15 \times \sqrt{\sum l_{ij}^2}$, $l_{ij} \in L_0^n$ and the maximum CBD-cell cycle, $H_{Cell} = 5$.

Pathway sampling

For the pathway sampling between TiO₂ phases, first, we start from one single phase, the initial state (IS) phase (in this work it is TiO₂-B phase), and utilize the (SSW-crystal) method to explore all the likely phases nearby. The structure selection module is utilized to decide whether to accept/refuse once a new minimum is reached. If a new phase different from the IS phase is identified, we record/output the IS

structure and the final state (FS) phase (a new phase) of the current SSW step. Then, the program will return back to the IS by rejecting the new minimum to continue the phase exploration; On the other hand, if the new minimum identified is the same as the starting phase (e.g. the same symmetry but a permutation isomer with varied lattice), the program will accept the new isomeric structure and continue the structure exploration. Second, we repeat the whole procedure until a certain number of IS/FS pairs are collected, typical a few hundreds. The maximum number of the minima nearby visited is set as 5000 in this work. For TiO₂-B studied in this work, we collect 4500 IS/FS pairs in the database and 500 of them are found to lead to the anatase phase; Third, we utilize the variable-cell double-ended surface walking method (variable-cell DESW)⁵ to identify the TSs explicitly for all the IS/FS pairs ^{4, 6}, which is confirmed using numerical frequency analysis. The low energy pathways are thus determined according to the located TSs using the calculated barrier being the energy difference between the TS and the IS.

The pathway sampling for the surface phase transition is essentially the same as the above described for the pathway sampling of the bulk except that the lattice is always kept fixed for the surface phase transition. Because the pathway sampling is based on a state-to-state connection, we perform the pathway sampling for the surface phase transition step by step. First, we start from the perfect TiO₂-B(-201) surface and identify the lowest energy transition pathway, which is found to produce the one-layer anatase capped TiO₂-B i.e. 1-A/B, shown in Figure 5. Next, we start from the 1-A/B and identify the lowest energy transition pathway, which is found to produce the two-layer anatase capped TiO₂-B, i.e. 2-A/B in Figure 5. For the first layer transition, we collect 2241 pathway, 207 of them belonging to the lowest energy pathway; For the second layer transition, we collect 1444 pathways, 805 of them belonging to the lowest energy pathway.

Calculation details for TiO₂ system

Both the classical potential using Matsui-Akaogi (MA) interatomic potential ⁷ and density functional theory (DFT) calculations have been utilized for TiO₂ systems.

The classical potential calculations are mainly for sampling exhaustively the likely phase transition pathways and the latter are to refine and obtain the accurate energetics for the lowest energy pathways. The MA potential has been demonstrated to describe reasonably well the phase diagram of TiO₂ at different pressure conditions⁷⁻⁸. It should be mentioned that due to the huge amount of possible reaction pathways between different phases, the classical simulations are essential for the initial screening of the reaction pathways (up to 10⁴ pathways sampled for each phase) and provide a low energy database of the reaction coordinates (IS/FS pairs) for the phase transition, based on which the first principles calculations can then be performed to compare the energetics between different pathways.

The DFT calculations on the phase transition pathways are performed using SIESTA package ⁹ with optimized numerical double- ζ polarization basis set ¹⁰⁻¹¹ at the GGA-PBE exchange-correlation functional level. The energy cutoff for the real space grid used to represent the density was set as 250 Ry. An energy shift of 0.01 eV was used to determine the orbital-confining cutoff radii. For all the lattice studied, the **k**-point mesh utilized was Monkhorst-Pack set up to (4×4×4) for the bulk and (4×4×1) for the surfaces, which is verified to be enough to obtain good energetics.

2. TiO₂-B/anatase Phase junction model of literatures

There are two major models for the TiO₂-B/anatase phase junctions proposed by experiment in literatures. Yang et al. ¹² suggested $[010]_A//[010]_B + (001)_A//(100)_B$ orientation relation and Li et al. ¹³ suggested $[010]_A//[010]_B + [001]_A//[100]_B$. These two orientation relation are 17.3 degree difference from each other. We have constructed the interface model from both orientation relations but failed to yield the structurally matched interface. For example, in Figure S1 we show the interface model constructed by us using the Yang et al. model, where the too close contact between Ti ions or between O ions are present at the interface.

Comparing to our assignment, $(-201)_B//(103)_A + [010]_B//[010]_A$, it is obvious that all the three models acknowledge that $[010]_A$ and $[010]_B$ is a common axis; the other common axis is different. Our assignment is about 6.2 degree different from the Li et al. model, and 11.0 degree from the Yang et al. model.



Figure S1. The atomic model for the phase junction between TiO_2 -B and anatase phase formed according to the orientation relationship $(100)_B/(001)_A + [010)_B/[010]_A$ as suggested in literatures¹². (a): the top view of $(001)_A$ and $(100)_B$. (b-c) the structure of the phase junction from two different angles. The black dot line shows the interface between TiO_2 -B and anatase. (d): the enlarged view at the junction region (the circled area in (c)) shows the destroyed Ti octahedrons and too close contact between Ti ions

ref	Orientation	Synthesis	Characterization
	relations (OR)	method	Method
Materials Research	(-201) _B //(10-3) _A	Phase	Selected area
Bulletin, 1982, 17(3):		transition	electron diffraction
355-361.			(SAED)
J. Sol. State Chem. 2005,	No OR	Phase	no
178, 2179-2185	proposed	transition	
J. Phys. Chem. C. 2008,	[010] _A //[010] _B	Phase	HRTEM
112, 20539-20545	[001] _A //[100] _B	transition	
J. Mater. Chem. 2009, 19,	No OR	Phase	HRTEM
7055-7061	proposed	transition	
J. Am. Chem. Soc. 2009,	[010] _A //[010] _B	Phase	HRTEM
131, 17885-17893	(001) _A //(100) _B	transition	
Journal of Molecular	$(202)_{\rm B}//(202)_{\rm A}$	Phase	HRTEM
Catalysis A: Chemical,		transition	
2010, 316(1): 75-82.			
CrystEngComm. 2011, 13,	No OR	Phase	HRTEM
6643-6649	proposed	transition	
ACS Appl. Mater. Interf.	(001) _B //(100) _A	seeded-growth	HRTEM
2011, 3, 4444-4450			
J. Phys. Chem. Sol. 2012,	No OR	Phase	no
73, 757-761	proposed	transition	

Table S1 The orientation relation of TiO₂-B/anatase phases transition in literatures

3. Experimental Methods

Preparation of TiO₂-B/anatase bicrystalline material

The synthetic method of TiO₂-B in this work is as described previously¹⁴. In short, 6g TiO₂ anatase sample (synthesized in our own laboratory) was added to 15M 80 ml aqueous solution NaOH and stirred for 1 h. The white milk-like suspension was poured into a 100 ml Teflon-lined stainless steel autoclave and then placed in an oven

maintaining 180 °C for 72 h. The autoclave was then cooled to room temperature in air. The collected precipitates were filtered and repeatedly washed by distilled water for 3 times. The product (Na containing titanate) was washed by 0.1M HCl solution for 8 h under stirring, which leads to the ion-exchanged titanate. The white powder material was then filtered, washed with distilled water, and dried at 80 °C overnight, which finally produces H₂Ti₃O₇ nanofiber (XRD and SEM (Figure S2) were utilized to characterize the sample).

The TiO₂-B/anatase bicrystalline material was prepared by two methods. The first method is via wet chemical condition described as follows. The ion-exchanged titanate nanofiber was added into dilute 0.05 M HNO₃ acid solution¹⁵ and was maintained in hydrothermal condition 110°C for 20 h. The collected precipitates were filtered, wash, dried and finally heated to 400°C for 4 h in air, which produce the TiO₂-B/anatase bicrystalline material (as shown in Figure S3 and Figure S4). The second method is via the direct calcination of the pure TiO₂-B sample at 600°C for 4 h¹⁶ (as shown in Figure S3 and Figure S4). The pure TiO₂-B sample was obtained by heating the ion-exchange titanate nanofiber at 400°C for 4 h in air.

Preparation of anatase/rutile bicrystalline material

The synthetic method of bicrytalline rutile/anatase TiO₂ in this work is as described previously using a one-pot hydrothermal method ¹⁷. In short, 0.15 M TiCl₃ solution was prepared by dissolving 8.10 g TiCl₃ (20w%, in 3% HCl dilute aqueous; supplied by Alfa Aesar) in deionized water. Then, 0.50 g sodium dodecyl sulfate (SDS 99.9%; supplied by Alfa Aesar) was slowly added into the solution with strong stirring. The achieved violet microemulsion (70 mL) was poured into a Teflon-lined stainless steel autoclave (100 ml) and after stirring for 100 min it was placed in an oven maintaining 200°C for 3 h. The autoclave was then cooled to room temperature in air. The collected precipitates were centrifuged repeatedly and washed by deionized water for 3 times and by ethanol for 2 times to remove the surfactants organic reagents. Finally, the samples were dried at 80 °C overnight.

Characterization

The samples were characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer), Field Emission scanning electron microscopy (FESEM, FEI Nova NanoSEM450, USA, operated at 2-5kV), high resolution TEM (HRTEM, FEI Tecnai G2F20 S-Twin, USA, operated at 200kV). XRD measurements were conducted using Cu K α radiation at a scanning rate of 8°/ min in the range of 10-90°.

Photocatalytic activity measurements

The photocatalytic activity of TiO₂-B/anatase biphase material were tested by the photodegradation of methylene blue (MB) dyes. The aqueous solution of the MB dyes (0.01 g/L, ~2.7*10⁻⁵M, 100 mL) and the photocatalysts (50 mg) were placed in a 200 mL glass vessel (the cross sectional area is 50 cm2). Before irradiation, the suspensions were stirred in the dark for 4h to ensure the establishment of adsorption/desorption equilibrium. Under ambient conditions and stirring, the photoreaction vessel was exposed to the UV irradiation produced by a 50 W high pressure Hg lamp with the main wave crest at 365 nm, which was positioned 30 cm above from the vessel (intensity at wavelength of 365 nm at the catalyst mixture surface was 30μ W/cm2, estimated with a radiometer). The photocatalytic reaction was started by turning on the Hg lamp, and during the photocatalysis, all other lights were insulated. At given time intervals, a 5 mL sample solution was taken out and centrifuged to remove the catalyst completely. Then the solution was analyzed on a Varian UV-vis spectrophotometer by recording variations of the absorption band of MB. The conversion of MB was defined as the following (See Figure S12):

Conversion= $(C_0 - C)/C_0 \times 100\%$

where C_0 and C are the initial dye concentration and the dye concentration being analyzed at each time frame, respectively.

4. Supporting data from XRD, TEM and HRTEM



Figure S2. XRD and SEM images of H₂Ti₃O₇ nanofiber.



Figure S3. XRD of two different samples prepared under the wet and the dry conditions (see above for experimental procedure).



Figure S4 TEM images of two different samples prepared under the wet and the dry conditions (see above for experimental procedure).



Figure S5. HRTEM images of the junction of TiO₂-B/anatase prepared at the dry conditions.

The following data is for TiO₂-B/anatase phase junction



Figure S6. HRTEM images (Top) and the theoretical models (Bottom-Left: full atomic model; Bottom-right: only Ti ions are shown) for the junction of TiO₂-B/anatase prepared at the dry conditions, showing (011)_A, (100)_B and (110)_B.



Figure S7. HRTEM images (Top) and the theoretical models (Bottom-Left: full atomic model; Bottom-right: only Ti ions are shown) for the junction of TiO₂-B/anatase prepared at the dry conditions, showing $(001)_A$, $(020)_A$ and $(020)_B$.



Figure S8. HRTEM images (Top) and the theoretical models (Bottom-Left: full atomic model; Bottom-right: only Ti ions are shown) for the junction of TiO₂-B/anatase prepared at the dry conditions, showing (001)_B, (020)_B and (020)_A.



Figure S9. HRTEM images (Top) and the theoretical models (Bottom-Left: full atomic model; Bottom-right: only Ti ions are shown) for the junction of TiO₂-B/anatase prepared at the dry conditions, showing (011)_A, (1-12)_A, (103)_A, (-201)_B and (-110)_B facets.

The following data is for anatase/rutile phase junction



Figure S10. The SEM (a), TEM (b-c) images and XRD (d) pattern of the anatase/rutile biphase crystal samples.



Figure S11. The HRTEM patterns of the anatase/rutile phase junction of a anatase/rutile biphase crystal (shown in Figure S10-c) at two different zone axes. The theoretical atomic model for the anatase/rutile crystal containing phase junction are utilized to compare the dihedral angle of the planes. In (a), the experimental angle between $(-110)_R$ and $(004)_A$ is 47 degrees and the theoretical value is 43 degrees. In (b), the experimental angle between the $(200)_R$ and $(-101)_A$ is 80 degrees, and the theoretical value is 67 degrees. The deviation is as large as 13 degrees, indicating the structure of the junction is not perfect.

The atomistic model for the anatase/rutile crystal is constructed according to the orientation relation determined theoretically, i.e. $anatase(112)//TiO_2II(100)$, $anatase[-110]//TiO_2II[010]$ and $rutile(011)//TiO_2II(001)$, $rutile[100]//TiO_2II[100]$ (see our recent work in Ref³ and Figure **S13** below for the pathways and explanation). By comparing with the experiment, we found that the theoretical value for the dihedral angle is up to 13 degrees different from the experimental measured value (13 degrees are in fact quite large, if considering that different models on TiO₂-B/anatase phase

junction differs by at most 17 degrees, see section 2 above). The detailed characterization on the structure of the imperfect phase junction will be the focus of our ongoing work.



5. Photocatalytic activity test

Figure S12 Photocatalytic decomposition of MB with different TiO₂ photocatalysts under UV irradiation. TheTiO₂-B/anatase is obtained using ion-exchanged titanate nanofiber precursor at the hydrothermal 110°C for 20 h in dilute 0.05 M HNO₃ acid solution.

6. Supporting data from theory

Atomic Structures for the TiO₂-B/anatase phase junction



Figure S13. The theoretical atomic structure of the phase junction. The view angles are the same as those of the HRTEM images in Figure 4. (a): Figure 4c; (b): Figure 4d; (c): Figure 4e; (d): Figure 4f; (e): Figure 4g. The yellow dot lines indicate the interface between phases (above: anatase phase: below: TiO₂-B phase).



Figure S14. The DFT lowest energy connectivity map of the TiO_2 phases at zero pressure. The energy unit is eV per Ti_4O_8 cell. The energy of rutile is set to zero. *lepidocrocite typed layered structure (*Pmmn*, #59). The data is taken from our recent

work³.

According to the anatase to rutile lowest energy pathway (Ref. ³, also shown above in Figure S14), we have identified the orientation relation for the anatase to rutile phase transition, namely, anatase(112)//TiO₂II(100), anatase[-110]//TiO₂II[010] and rutile(011)//TiO₂II(001), rutile[100]//TiO₂II[100]. Based on these relations, we have constructed the theoretical atomic model for the anatase/rutile biphase crystal, as shown in Figure S12.

References

- (1) Shang, C.; Liu, Z. P. Stochastic Surface Walking Method for Structure Prediction and Pathway Searching. *J. Chem. Theory Comput.* **2013**, *9*, 1838-1845.
- (2) Zhang, X.-J.; Shang, C.; Liu, Z.-P. From Atoms to Fullerene: Stochastic Surface Walking Solution for Automated Structure Prediction of Complex Material. *J. Chem. Theory Comput.* **2013**, *9*, 3252-3260.
- (3) Shang, C.; Zhang, X.; Liu, Z. Stochastic Surface Walking Method for Crystal Structure and Phase Transition Pathway Prediction. *Phys. Chem. Chem. Phys.* **2014**,*16*, 17845--17856.
- (4) Shang, C.; Liu, Z. P. Constrained Broyden Dimer Method with Bias Potential for Exploring Potential Energy Surface of Multistep Reaction Process. J. Chem. Theory Comput. 2012, 8, 2215-2222.
- (5) Zhang, X.-J.; Shang, C.; Liu, Z.-P. Double-Ended Surface Walking Method for Pathway Building and Transition State Location of Complex Reactions. *J. Chem. Theory Comput.* **2013**, *9*, 5745-5753.
- (6) Shang, C.; Liu, Z.-P. Constrained Broyden Minimization Combined with the Dimer Method for Locating Transition State of Complex Reactions. *J. Chem. Theory Comput.* 2010, *6*, 1136-1144.
- (7) Matsui, M.; Akaogi, M. Molecular Dynamics Simulation of the Structural and Physical Properties of the Four Polymorphs of TiO2. *Molecular Simulation* **1991**, *6*, 239-244.
- (8) Dubrovinskaia, N. A.; Dubrovinsky, L. S.; Ahuja, R.; Prokopenko, V. B.; Dmitriev, V.; Weber, H. P.; Osorio-Guillen, J. M.; Johansson, B. Experimental and Theoretical Identification of a New High-Pressure TiO₂ Polymorph. *Phys. Rev. Lett.* **2001**, *87*, 275501.
- Soler, J. M.; Artacho, E.; Gale, J. D.; Garcia, A.; Junquera, J.; Ordejon, P.; Sanchez-Portal, D. The SIESTA method for ab initio order-N materials simulation *J. Phys: Condens. Mat.* 2002, *14*, 2745.
- (10) Junquera, J.; Paz, O.; Sanchez-Portal, D.; Artacho, E. Numerical atomic orbitals for linear-scaling calculations. *Phys. Rev. B* **2001**, *64*, 235111.
- (11) Anglada, E.; Soler, J. M.; Junquera, J.; Artacho, E. Systematic generation of finite-range

atomic basis sets for linear-scaling calculations. Phys. Rev. B 2002, 66, 205101.

- (12) Yang, D. J.; Liu, H. W.; Zheng, Z. F.; Yuan, Y.; Zhao, J. C.; Waclawik, E. R.; Ke, X. B.; Zhu, H. Y. An Efficient Photocatalyst Structure: TiO2(B) Nanofibers with a Shell of Anatase Nanocrystals. *J. Am. Chem. Soc.* 2009, *131*, 17885-17893.
- (13) Li, W.; Liu, C.; Zhou, Y.; Bai, Y.; Feng, X.; Yang, Z.; Lu, L.; Lu, X.; Chan, K.-Y. Enhanced Photocatalytic Activity in Anatase/TiO2 (B) Core– Shell Nanofiber. J. Phys. Chem. C 2008, 112, 20539-20545.
- (14) Armstrong, G.; Armstrong, A. R.; Bruce, P. G.; Reale, P.; Scrosati, B. TiO2 (B) Nanowires as an Improved Anode Material for Lithium Ion Batteries Containing LiFePO4 or LiNiO. 5Mn1. 5O4 Cathodes and a Polymer Electrolyte. *Adv. Mater.* 2006, *18*, 2597-2600.
- (15) Zhu, H.; Gao, X.; Lan, Y.; Song, D.; Xi, Y.; Zhao, J. Hydrogen Titanate Nanofibers Covered with Anatase Nanocrystals: a Delicate Structure Achieved by the Wet Chemistry Reaction of the Titanate Nanofibers. J. Am. Chem. Soc. 2004, 126, 8380-8381.
- (16) Kuo, H.-L.; Kuo, C.-Y.; Liu, C.-H.; Chao, J.-H.; Lin, C.-H. A Highly Active Bi-crystalline Photocatalyst Consisting of TiO2 (B) Nanotube and Anatase Particle for Producing H2 Gas from Neat Ethanol. *Catal. Lett.* **2007**, *113*, 7-12.
- (17) Hosono, E.; Fujihara, S.; Imai, H.; Honma, I.; Masaki, I.; Zhou, H. One-Step Synthesis of Nano–Micro Chestnut TiO₂ with Rutile Nanopins on the Microanatase Octahedron. ACS Nano 2007, 1, 273-278.