Supporting Information

Variable-Cell Double-Ended Surface Walking Method for Fast Transition State Location of Solid Phase Transition

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1. Performance of VC-DESW in different supercells

Table S1 The force/energy steps using VC-DESW with different supercells for TiO_2-B-to-anatase phase transition.

Size	a_{IS}/Å	b_{IS}/Å	c_{IS}/Å	a_{FS}/Å	b_{FS}/Å	c_{FS}/Å	Dist./ Å	N_{path}	N_{CBD}	N_{tot}
1×1×1	12.16	3.75	6.48	10.28	3.77	7.54	4.15	121	8	129
1×2×1	12.16	7.50	6.48	10.28	7.54	7.54	5.40	161	60	221
2×1×1	24.32	3.75	6.48	20.57	3.77	7.54	6.30	214	34	248
1×3×1	12.16	11.24	6.48	10.28	11.31	7.54	6.40	192	66	258
3×1×1	36.48	3.75	6.48	30.85	3.77	7.54	8.31	260	49	309

*The angles of lattice are α=γ=90º, β=75.8º for the IS and α=γ=90º, β=68.5º for the FS. The meaning of Dist, N_{path}, N_{CBD}, N_{tot} are as described in Table 1. Matsui-Akaogi empirical potential are utilized to describe the TiO_2 potential.

2. The Phonon spectrum of TiO_2-B-to-anatase

For solid phases, one needs to perform phonon calculations to confirm one and only one eigenvalue across the whole first Brillouin zone at the TS. We have demonstrated such phonon spectrum of ZrO_2 using VC-DESW in our recent published work in (Guan, S.-H.; Zhang, X.-J.; Liu, Z.-P., *J. Am. Chem. Soc.* **2015,** *137*, 8010-8013. [ref. 26]). In this work, we have confirmed the phase transition pathway of TiO_2-B-to-anatase using phonon calculations and the results are shown below in Figure S1. The interactions between the atoms during TS location and phonon calculation are described by Matsui-Akaogi potential (Matsui, M.; Akaogi, M., Mol. Simul. **1991**, *6*, 239-244).

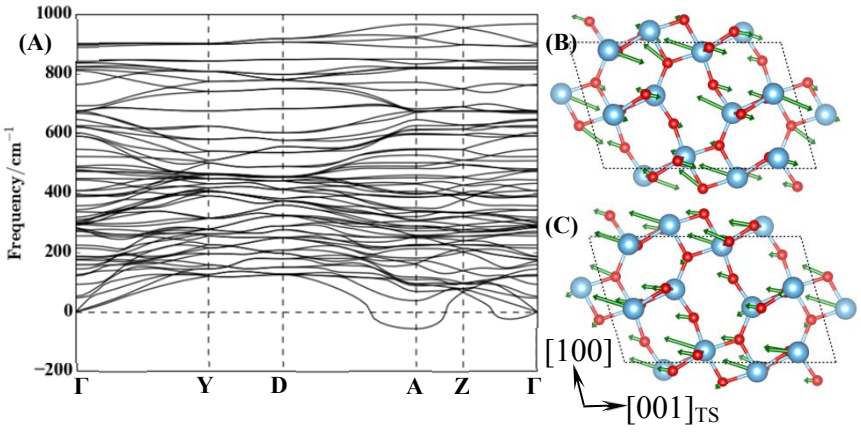

Figure S1 (Left) Calculated phonon spectrum for the TS of TiO_2-B-to-anatase phase transition. The high symmetry points of the Brillouin zone are denoted as Γ (0,0,0), Y (0,0.5,0), D(0,0.5,0.5), A(0.5,0,0.5), Z(0,0,0.5) (The maximum imaginary mode is located at A point). (B): The corresponding eigenvector associated with the maximum imaginary mode at A point. (C) The corresponding eigenvector associated with the

maximum imaginary mode point along Z to Γ.

3n+3 eigenvalues of the Hessian (24 atoms, in total 75 eigenvalues, unit eV/Å^2)

−0. 8720	0. 2744	0. 4394	0. 7269	0. 8466
1. 6662	1. 7677	1. 9414	1. 9951	2. 0598
2. 1715	2. 4486	2. 9039	3. 4464	3. 6706
4. 3107	4. 4345	4. 7462	4. 9895	5. 0616
5. 7418	5. 8122	5. 8281	6. 4548	6. 4975
7. 1935	8. 8482	9. 2049	9. 4061	10. 7611
11. 7292	12. 5461	12. 8895	13. 7827	14. 0591
14. 2321	14. 5745	14. 8048	14. 8481	18. 2570
18. 6766	19. 4872	19. 7891	20. 2012	20. 6614
22. 4766	22. 7884	24. 5265	24. 7677	28. 4700
32. 2654	33. 5906	36. 5748	37. 9587	37. 9824
38. 2607	38. 9207	39. 2786	41. 4728	42. 2522
44. 3438	46. 5870	46. 6186	46. 8535	46. 9204

Table S2 The eigenvector corresponding to the negative eigenvalue (-0.8720)

Atom	Label	x	y	Z
1	O	-0.179	0.000	-0.046
2	O	0.067	0.000	0.027
3	O	-0.179	0.000	-0.046
4	O	0.067	0.000	0.027
5	O	0.179	0.000	0.046
6	O	-0.067	0.000	-0.027
7	O	0.179	0.000	0.046
8	O	-0.067	0.000	-0.027
9	O	0.232	0.000	0.177
10	O	-0.053	0.000	0.022
11	O	0.232	0.000	0.177
12	O	-0.053	0.000	0.022
13	O	-0.232	0.000	-0.177
14	O	0.053	0.000	-0.022
15	O	-0.232	0.000	-0.177
16	O	0.053	0.000	-0.022
17	Ti	-0.210	0.000	-0.088
18	Ti	0.034	0.000	-0.058
19	Ti	-0.210	0.000	-0.088
20	Ti	0.034	0.000	-0.058
21	Ti	0.210	0.000	0.088
22	Ti	-0.034	0.000	0.058

23	Ti	0.210	0.000	0.088
24	Ti	-0.034	0.000	0.058
a	Lattice	-0.359	0.000	0.113
b	Lattice	0.000	0.015	0.000
c	Lattice	0.289	0.000	0.196

3. XYZ Coordinate of Structures

All the structures are displayed in VASP format (POSCAR file)

The structure of TiO_2-B, TS and anatase

TiO_2-B

1.00000

12.199800000	0.000000000	0.000000000
-0.000125532	3.785499998	0.000000000
1.654537004	0.000008687	6.404536388

O Ti

16 8

Direct

0.130037094	0.006137120	0.877458309
0.632865757	0.006153110	0.074678185
0.732168689	0.006113637	0.621287967
0.132858248	0.506186436	0.574681613
0.232169882	0.506192196	0.121311015
0.257724845	0.006210267	0.397495472
0.857031409	0.506112239	0.444083309
0.757729558	0.506150053	0.897482933
0.357037813	0.006201785	0.944080646
0.359891186	0.506213986	0.641256994
0.936495787	0.006147713	0.698455048
0.859890082	0.006094772	0.141262307
0.553407322	0.506106610	0.820274927
0.630015726	0.506088753	0.377517368
0.053396817	0.006107345	0.320292956
0.436486763	0.506225061	0.198458356
0.298869163	0.506231649	0.420189345
0.191033446	0.006198317	0.098566621
0.095694174	0.006198649	0.616430156
0.691024053	0.506119609	0.598559986
0.595690925	0.506187462	0.116440193
0.798864098	0.006159918	0.920188312
0.894210852	0.006126614	0.402330629
0.394207151	0.506225813	0.902312680

TS

1.00000

11.273100000 0.000000000 0.000000000

0.000154312 3.844099997 0.000000000

2.307985480 -0.000168368 6.852461272

O Ti

16 8

Direct

0.101069806 0.005664185 0.853428508

0.650332919 0.005208507 0.051658258

0.692736422 0.005243975 0.564070300

0.151045511 0.505807542 0.552237078

0.193114673 0.505798069 0.063839991

0.297453575 0.005342003 0.456801781

0.839157150 0.505691529 0.468696017

0.796997020 0.505675926 0.957238258

0.339804816 0.005300873 0.969387073

0.389935494 0.505506677 0.667622569

0.926387184 0.005436157 0.683909276

0.889219373 0.005446304 0.167482684

0.563854339 0.505479675 0.837206410

0.600096765 0.505422367 0.353475568

0.063779733 0.005555193 0.337183946

0.426298558 0.505564043 0.183742144

0.332647060 0.505619709 0.457268531

0.158187271 0.005513989 0.063935982

0.110319762 0.005532529 0.591134785

0.657530749 0.505549624 0.563692672

0.609932676 0.505524802 0.090767275

0.831961310 0.005367110 0.957108061

0.879881623 0.005402200 0.429852965

0.380193619 0.505601222 0.930250900

Anatase

1.00000

10.409000000 0.000000000 0.000000000

-0.000280160 3.821899990 0.000000000

2.793373199 0.000178080 7.116073653

O Ti

16 8

Direct

0.076827647 0.005777376 0.843585075

0.663109384 0.006370265 0.050734156

0.663110419 0.006371939 0.550734151

0.163108422	0.505899916	0.550633215
0.163109010	0.505904575	0.050632327
0.326786115	0.005943218	0.468118140
0.826786574	0.506427400	0.468014710
0.826785918	0.506425118	0.968017212
0.326786005	0.005947193	0.968118234
0.413075183	0.505903032	0.675186579
0.913076461	0.006530099	0.675097957
0.913078258	0.006533101	0.175101911
0.576827734	0.506405237	0.843668676
0.576828239	0.506402601	0.343670482
0.076826819	0.005778840	0.343582830
0.413074926	0.505901819	0.175185721
0.369982143	0.505948499	0.446553258
0.119912062	0.005878699	0.072219345
0.119912782	0.005872151	0.572219584
0.619913165	0.506403499	0.572320729
0.619914133	0.506400436	0.072321532
0.869983796	0.006478266	0.946447978
0.869984706	0.006481438	0.446449088
0.369984266	0.505954913	0.946550929

1. The structure of rutile, TS, MS and TiO_2-II

Rutile

1.00000

8.717100000	0.000000000	0.000000000
3.913571621	7.768836359	0.000000000
0.738743365	0.436968140	7.378144448

O Ti

32 16

Direct

0.376549538	0.252506718	0.125964878
0.851086507	0.226353551	0.412336195
0.457219018	0.289619622	0.743506189
0.957229867	0.789614902	0.743505936
0.497321671	0.830140465	0.662161397
0.560497092	0.436347471	0.993354936
0.916927608	0.293064347	0.044651886
0.060479719	0.936355162	0.993362843
0.810492073	0.686359896	0.493366011
0.351071377	0.726360391	0.412333039
0.273261071	0.105898207	0.875884213
0.126545477	0.002519424	0.625969694

0.563692318	0.896174493	0.294764083
0.747327801	0.080140309	0.162155079
0.773280675	0.605892770	0.875880569
0.247325819	0.580140470	0.162163566
0.523282706	0.355888559	0.375882895
0.313695861	0.646171322	0.794765650
0.997328328	0.330137619	0.662160698
0.207214290	0.039622639	0.243503018
0.601078328	0.976353848	0.912328023
0.666915746	0.043067239	0.544647334
0.416913563	0.793066192	0.044659979
0.063690349	0.396176328	0.294767931
0.166929231	0.543059356	0.544656359
0.626550194	0.502510569	0.625960122
0.707229777	0.539618545	0.243508706
0.813693704	0.146174555	0.794761702
0.023274825	0.855888035	0.375892866
0.101083968	0.476353102	0.912329370
0.876545891	0.752524900	0.125962311
0.310495814	0.186344543	0.493363257
0.955342709	0.560741539	0.681528416
0.294097811	0.397595798	0.356848385
0.330543662	0.435057093	0.932094142
0.794061450	0.897615659	0.356859930
0.455320328	0.060740402	0.681557106
0.544088992	0.647600077	0.856861835
0.919257962	0.522014810	0.107391838
0.419251729	0.021986910	0.107392538
0.580553089	0.685055020	0.432096285
0.705350897	0.310749521	0.181533766
0.080539655	0.185078744	0.432085093
0.169264700	0.771988341	0.607404476
0.669236304	0.272015206	0.607364942
0.830539087	0.935067633	0.932077295
0.205309877	0.810740170	0.181577662
0.044076132	0.147608347	0.856848504

TS

1.00000

7.767300000	0.000000000	0.000000000
1.825568558	7.549512690	0.000000000
0.097020982	0.081486472	8.353439187

O Ti

32 16
Direct
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0.486423176 0.277217032 0.742070487
0.986781667 0.776865803 0.741505986
0.440781967 0.802607997 0.594632405
0.546926839 0.468015977 0.991813761
0.886308944 0.306318165 0.045613307
0.048399581 0.967316392 0.991311813
0.796868147 0.716289564 0.491229063
0.326642866 0.666901838 0.341730282
0.294513994 0.168707260 0.946880430
0.187582494 0.026465192 0.696438758
0.576164921 0.867037170 0.295466909
0.689300625 0.055770573 0.092915346
0.794890032 0.668613928 0.946865499
0.188868601 0.555150548 0.094650076
0.548871148 0.414938710 0.446141251
0.325113385 0.617900260 0.798225385
0.940508164 0.303135640 0.593818236
0.238631009 0.026934379 0.240615281
0.571392885 0.922129574 0.847121527
0.638495583 0.055566325 0.547757500
0.387548752 0.805413060 0.046826588
0.076414693 0.365527670 0.295000982
0.138901461 0.555229764 0.546958765
0.688128444 0.525758984 0.697713821
0.738231192 0.526468981 0.241516588
0.825587927 0.117192549 0.797667918
0.051362430 0.913551098 0.444153704
0.072108525 0.421780263 0.846162054
0.935666314 0.778826852 0.194695219
0.297664397 0.215398852 0.490638228
0.931224114 0.564730705 0.680396852
0.289429749 0.423047903 0.353776958
0.335691829 0.410848994 0.933219614
0.788699614 0.923415140 0.355276240
0.431208536 0.065670685 0.680480740
0.538687759 0.675449986 0.855112590
0.944654136 0.518946046 0.102889962
0.445657423 0.018099839 0.101448519
0.584809291 0.659539117 0.429907780
0.681150598 0.315283891 0.181544102

0.086076056 0.158895639 0.429734258
0.195114006 0.768519427 0.607209980
0.695103556 0.269515434 0.606842197
0.836550828 0.910495892 0.933325729
0.180224643 0.816136844 0.183244883
0.039382440 0.174804433 0.854302839

MS
1.00000
8.013600000 0.000000000 0.000000000
2.039465718 7.750663832 0.000000000
0.257317802 0.197176573 7.672954906
O Ti
32 16
Direct
0.434187634 0.249572999 0.146567536
0.855247538 0.155208081 0.371957553
0.516038443 0.261975811 0.739934263
1.038409576 0.739504709 0.728485997
0.494505247 0.797160588 0.618912653
0.579512761 0.456467920 0.986913947
0.898998520 0.271740099 0.025554533
0.093138457 0.969496194 0.986884531
0.835775453 0.691796654 0.481528216
0.368873326 0.668236453 0.371928161
0.303525508 0.143200702 0.898938481
0.177922912 0.014245959 0.651953389
0.615264378 0.832469560 0.272483912
0.714773093 0.041930511 0.125004192
0.825896659 0.620729646 0.887490242
0.228398814 0.554958736 0.124974822
0.559787726 0.378530400 0.393552385
0.359001198 0.597141284 0.777869797
0.980879453 0.284132311 0.618941965
0.249930626 0.019775162 0.245996608
0.634982331 0.910435845 0.865865610
0.642734600 0.036412489 0.530940118
0.412624285 0.784768390 0.025525072
0.092893189 0.354940614 0.283932228
0.156360365 0.549440781 0.530910668
0.700294047 0.491774894 0.640505100
0.772301732 0.497304003 0.234548436
0.845375492 0.084113003 0.777899188
0.073413538 0.891558694 0.393522914

0.112611153 0.432906882 0.877313839
0.956558767 0.727101872 0.135119358
0.313404300 0.214267678 0.492976475
0.946672321 0.538206552 0.658434899
0.304067395 0.430250006 0.354017934
0.368343507 0.381172097 0.916837291
0.826438546 0.907778953 0.342569596
0.424301244 0.060677608 0.669883194
0.570175555 0.672450263 0.847955479
0.990749490 0.473040642 0.095615581
0.468378382 -0.004488166 0.107063759
0.624606211 0.616500916 0.411451053
0.680565074 0.296005685 0.164497401
0.102235096 0.138971920 0.422899321
0.248111357 0.750741233 0.600972408
0.734485582 0.237712947 0.601001796
0.890714692 0.858700992 0.905389079
0.194190881 0.809033939 0.164467960
0.047804359 0.194921348 0.859403677

TiO_2-II
1.00000
7.544200000 0.000000000 0.000000000
1.805320010 7.325216107 0.000000000
0.000227186 0.000311698 9.297699992
O Ti
32 16
Direct
0.464750849 0.263626896 0.242094132
0.839804761 0.138612112 0.296517759
0.464754204 0.263631256 0.742094396
0.964755452 0.763636072 0.742094468
0.409335942 0.819070746 0.546562369
0.534397720 0.444013363 0.992061107
0.909334191 0.319068376 0.046564911
0.034396294 0.944018360 0.992060420
0.784389561 0.694024184 0.492056584
0.339804539 0.638616725 0.296518973
0.284388825 0.194022655 0.992059428
0.214750506 0.013620113 0.742098321
0.589791564 0.888632687 0.296518149
0.659330633 0.069071146 0.046562751
0.784391421 0.694026529 0.992059285
0.159329169 0.569075215 0.046562297

0.534390096 0.444021714 0.492053496
0.339794652 0.638623376 0.796513570
0.909337074 0.319068095 0.546563569
0.214757234 0.013625922 0.242097341
0.589798015 0.888630898 0.796522260
0.659333380 0.069065018 0.546560496
0.409331554 0.819074094 0.046566553
0.089792272 0.388629047 0.296519963
0.159329203 0.569067489 0.546559640
0.714755582 0.513623806 0.742096250
0.714756950 0.513631432 0.242098531
0.839797837 0.138620339 0.796513348
0.034389073 0.944025926 0.492053871
0.089792578 0.388626749 0.796520510
0.964753169 0.763632676 0.242095388
0.284389683 0.194021948 0.492057930
0.937336539 0.541414338 0.644028261
0.312260642 0.416084697 0.393929724
0.312247337 0.416046477 0.893932899
0.812272626 0.916079789 0.393944096
0.437323243 0.041422150 0.644009706
0.562309734 0.666024316 0.893991384
0.937309119 0.541404138 0.144088731
0.437312601 0.041394932 0.144101535
0.562305641 0.666009729 0.393984808
0.687369113 0.291349483 0.143961423
0.062293826 0.166004607 0.393980759
0.187394284 0.791380400 0.644048483
0.687385159 0.291371428 0.644045169
0.812226989 0.916064665 0.893924601
0.187366951 0.791364352 0.143953839
0.062313219 0.166002161 0.893992677

The structure of α-quartz, TS and quartz-II

α-quartz

1.00000
9.500100000 0.000000000 0.000000000
4.731749786 8.203597999 0.000000000
-0.007095936 -0.000563240 5.399295308
O Si
24 12
Direct
0.054826086 0.150802007 0.227502726

0.349437086	0.946045153	0.106141968
0.205856450	0.847788514	0.436872922
0.445169866	0.706059345	0.771427276
0.650797458	0.795420943	0.894470779
0.793768856	0.553803723	0.563535205
0.554837819	0.650789803	0.227514661
0.293772838	0.553806193	0.563540967
0.150793774	0.795421148	0.894476252
0.945157217	0.706059537	0.771417249
0.349438875	0.446041121	0.106142202
0.205856911	0.347782370	0.436878782
0.445172259	0.206061083	0.771432808
0.650795403	0.295420926	0.894473502
0.793768388	0.053813649	0.563544372
0.554827726	0.150801178	0.227501574
0.705854141	0.847791351	0.436869721
0.849422034	0.946056842	0.106157336
0.849423739	0.446052828	0.106157589
0.705854565	0.347785194	0.436875501
0.945159258	0.206061238	0.771422450
0.150791733	0.295421089	0.894478869
0.293772339	0.053815764	0.563549803
0.054836166	0.650790714	0.227515799
0.220433515	0.499668048	0.333240290
0.500144242	0.780192167	0.999791333
0.500145522	0.280185661	0.999795317
0.720439444	0.499665512	0.333235528
0.779567568	0.720262499	0.666968851
0.279556467	0.220250696	0.666947176
0.720447088	0.999651880	0.333238784
0.000162501	0.280177195	0.999791623
0.779566495	0.220251700	0.666958395
0.220441150	0.999654717	0.333243664
0.279557932	0.720261110	0.666957617
0.000160932	0.780183713	0.999787518

TS

1.00000

8.236700000	0.000000000	0.000000000
4.121708774	8.703024697	0.000000000
0.002704494	0.361547052	5.444207459

O Si

24 12

Direct

0.043770772 0.145325032 0.215501832
0.358806141 0.942564448 0.103588308
0.190252599 0.852446229 0.442121114
0.469985153 0.714487977 0.738986762
0.685817556 0.783251184 0.917988443
0.802786614 0.555565959 0.553408715
0.543963450 0.645632528 0.215270431
0.302517709 0.555160378 0.553278257
0.186013101 0.783119091 0.918657465
0.970289820 0.714706982 0.738897561
0.358949586 0.442380636 0.103549184
0.190218895 0.352267202 0.442542527
0.469936405 0.214457574 0.739144025
0.685840801 0.283196889 0.918123744
0.802790534 0.055544269 0.553328085
0.544074209 0.145558180 0.215350068
0.690679263 0.852748238 0.442125008
0.858904857 0.942662984 0.103896900
0.858965587 0.442534130 0.103817096
0.690654866 0.352573275 0.442508066
0.970288586 0.214691385 0.739015543
0.185974049 0.283105783 0.918864633
0.302479937 0.055152322 0.553206160
0.043737279 0.645357052 0.215402247
0.219290293 0.498941673 0.328614925
0.494784309 0.781957330 0.999479808
0.494676750 0.282064688 0.999765141
0.719489617 0.499447417 0.328719709
0.778526832 0.715990057 0.657286164
0.277703689 0.215770313 0.657599332
0.719635501 0.999343444 0.328767591
-0.005031215 0.282078003 1.000698989
0.778484398 0.216033166 0.657204639
0.219373818 0.998890497 0.328650205
0.277814522 0.715722118 0.657595578
-0.004846132 0.781923997 1.000405678

Quartz-II

1.00000
6.814700000 0.000000000 0.000000000
3.397452666 8.682344323 0.000000000
-0.008099664 2.108352519 5.092398120
O Si
24 12

Direct

0.024733119	0.158335865	0.230107412
0.339373187	0.989920234	0.051036359
0.182351594	0.841769110	0.436532914
0.495539581	0.692232163	0.757576777
0.688186503	0.807753634	0.909035926
0.829792418	0.510060123	0.615717836
0.524734433	0.658334372	0.230101409
0.329771404	0.510038484	0.615711045
0.188176159	0.807746835	0.909030144
0.995536584	0.692229476	0.757581644
0.339361652	0.489905801	0.051029545
0.182348071	0.341761532	0.436533467
0.495532666	0.192227769	0.757581532
0.688178815	0.307745970	0.909033504
0.829774635	0.010035840	0.615712565
0.524732474	0.158331434	0.230104580
0.682359567	0.841771697	0.436533463
0.839362037	0.989905864	0.051031416
0.839377552	0.489919778	0.051036447
0.682348853	0.341764070	0.436533241
0.995542516	0.192232516	0.757576887
0.188182740	0.307751651	0.909038774
0.329792042	0.010059775	0.615720611
0.024728443	0.658329629	0.230098108
0.256884232	0.499915536	0.333356495
0.427820484	0.828127919	0.942537061
0.427842075	0.328147285	0.942539819
0.756870254	0.499895728	0.333349653
0.755336791	0.671915614	0.724103496
0.255336839	0.171921571	0.724108257
0.756877984	0.999906619	0.333350213
-0.072176929	0.328127604	0.942534433
0.755363052	0.171943204	0.724116778
0.256861984	0.999889505	0.333345175
0.255359847	0.671938964	0.724112018
-0.072153950	0.828149258	0.942543451