Supporting Information

Predicting New TiO_2 Phases with Low Band Gaps by a Multi-objective Global Optimization Approach

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Phonon calculations

The total energy of the new polymorphs discovered here is about 0.1 eV/atom higher than rutile. Therefore it's necessary to test the stability of PI and CI phases. We compute phonon dispersion by the finite difference method to test the dynamic stability. Figure S1 (a) and (b) show the computated results. As we can see in the graph, there is no imaginary phonon mode in the whole Brillouin zone.

Thermal stability

To check the thermal stability of these two new polymorphs, first-principles molecular dynamic (MD) simulations are adopted with a Nose-Hoover thermostat at 500 K. A $2 \times 5 \times 2$ supercell is used for the PI phase and a $4 \times 4 \times 2$ supercell is used for the CI phase. The time step of our simulations is 1.5 fs and total simulation time is 5~6 ps. Figure S2 (a) and (b) show the results of such MD simulations. Here we find no sign of structural destruction, and the curves of total potential energy soon become a quasi-SHO (simple harmonic oscillator). After 5.5 ps, we find no structure destruction to both the TiO_2 structure and could be returned to the original structure after relaxation at 0K. This indicates that the new polymorphs we discovered are thermal stable up to at least 500 K.

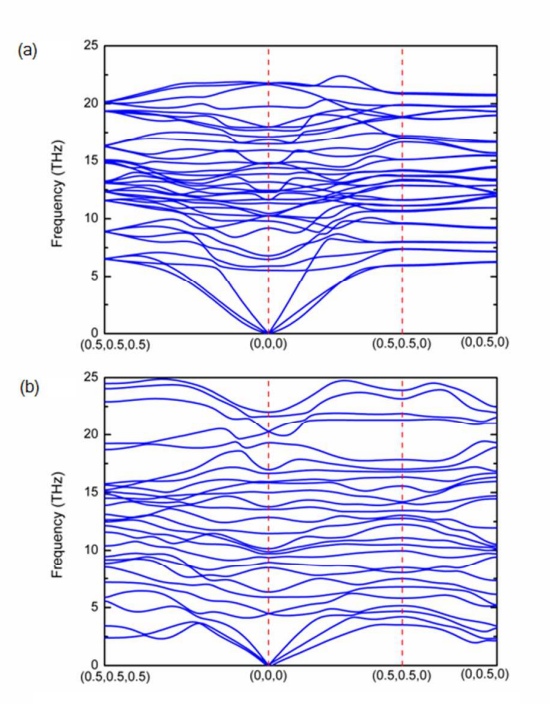

Figure S1. (a) and (b) The phonon dispersion of CI and PI from the local density approximation calculations. The absence of imaginary phonon modes indicates the dynamical stability of the new TiO_2 phases.

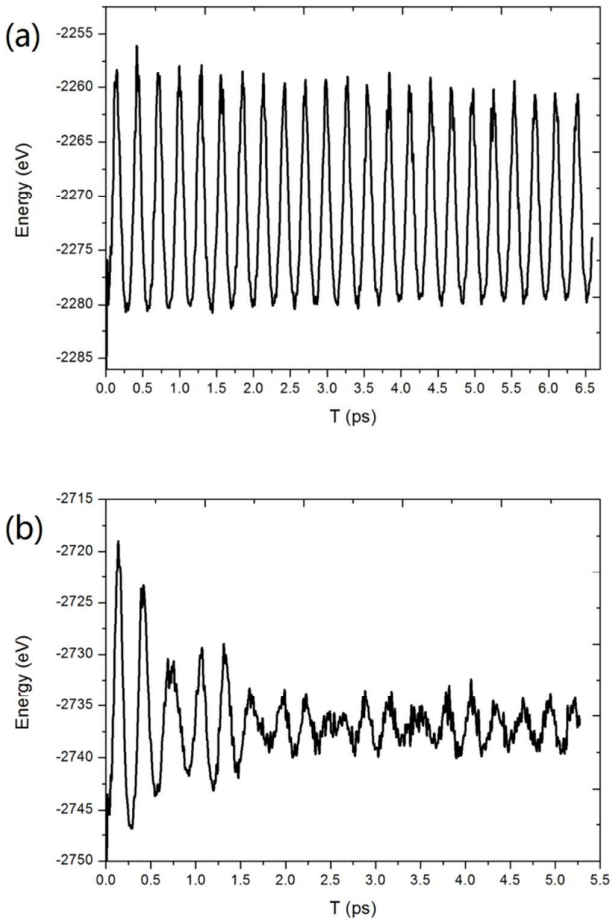

Figure S2. The the total potential energies of (a) CI and (b) PI supercell as a function of simulation time from first-principles canonical molecular dynamics simulations at 500 K.