Supplementary Information for

Unifying the order and disorder dynamics in photoexcited VO$_2$

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Fig. S1. (A) The potential energy surface of the ground state VO$_2$ along with the distortion coordinate $\xi$ after correction. R phase corresponds to $\xi = 0$ Å and $M_1$ phase corresponds to $\xi = \pm 0.24$ Å. (B) Energies per VO$_2$ formula unit of the $M_1$ phase and R phase VO$_2$ obtained with our simulation and experiments (1, 2). All energies are given with respect to the R phase.
Fig. S2. Laser-induced excited electrons of VO$_2$. (A) The shape of the external electric field applied to VO$_2$ with laser strength $E_0 = 0$ to 0.5 Hartree/Bohr. The photon energy is 1.02 eV, corresponding to a 1.2 μm wavelength. The laser field value reaches the minimum strength at time $2t_0 = 35$ fs. (B) The number and percentage of excited electrons upon photoexcitation from the valence bands to conduction bands under different laser pulses.
Fig. S3. Photoinduced ultrafast phase transition in high electronic excitations. (A) Bond-length evolution under different laser pumping conditions. The blue and red dotted lines represent the bond lengths of each long and short bond, respectively. The blue and red solid lines represent the average bond length of long and short bonds. (B) Disorder degree evolution at different excitations before the phase transition time. (C) Phonon modes of V atoms during the phase transition, which are obtained from the normalized fast Fourier transform (FFT) of the average bond length of V-V bonds.
Fig. S4. Bond-length evolution under different laser pumping conditions on a longer timescale (~1000 fs). The blue and red dotted lines represent the bond lengths of each long and short bond, respectively. The blue and red solid lines represent the average bond length of long and short bonds.
Fig. S5. Photoinduced ultrafast phase transition in low electronic excitations. (A) Bond-length evolution under different laser pumping conditions. The blue and red dotted lines represent the bond lengths of each long and short bond, respectively. The blue and red solid lines represent the average bond length of long and short bonds. (B) Disorder degree evolution at different excitations.
Fig. S6. Time dependence of Bragg peaks for different photoexcitations. (A-D) Simulated Bragg peaks [(002)$_R$, (-1-13)$_M$] as a function of time at different excitations, which are obtained through the structure factors.
**Fig. S7.** Schematic of driving force caused by photoexcitation on vanadium atoms and oxygen atoms. The $F_P$ displays the driving force caused by photoexcitation, and the dotted arrows represent the components of $F_P$ along with the V-V bond and V-O bond directions, respectively.
Fig. S8. (A) In the rutile unit cell of VO$_2$, V atoms (imaginary orange atom) sites at the center of oxygen octahedrons, but in the monoclinic unit cell, V atoms (solid orange atom) derive from the orthorhombic center. There is a 90° rotation angle between the two adjacent oxygen octahedrons and a 45° rotation angle between the rutile crystallographic axes (solid arrows) and the geometric axes of the orbitals (dashed arrows). (B) Schematic diagram of $t_{2g}$ ($d_\parallel$ forming valence electronic states and $\pi^*$ forming conduction electronic states) orbitals along the geometric axes ($x$, $y$, $z$) of the orbitals.
Fig. S9. The bond-length evolution under the different laser pumping at the VO$_2$ system temperature ~ 1 K. The blue and red lines represent the evolution of V-V long and short bonds, respectively. The dotted and solid lines represent each pair and averaged V-V bond length.
**Fig. S10.** Real-space distributions of photoexcited holes and electrons on the (011) plane at the end of the laser pulses (~35 fs) for the case of photoexcited (A) 3.7%, (B) 5.1%, and (C) 6.3% valence electrons, respectively. As the number of photoexcited carriers increases, the holes near the O atoms increase significantly.
**Fig. S11.** Bond-length evolution at (A) 200 K and (B) 250 K. The blue and red dotted lines represent the bond lengths of each long and short bond, respectively. The blue and red solid lines represent the average bond length of long and short bonds.
Fig. S12. Photoinduced ultrafast phase transition under different electronic excitations at 200 K. (A) Bond-length evolution under different laser pumping conditions. The blue and red dotted lines represent the bond lengths of each long and short bond, respectively. The blue and red solid lines represent the average bond length of long and short bonds. (B) Disorder degree evolution at different excitations.
Fig. S13. Laser-induced excited electrons of VO$_2$. (A) The shape of the external electric field applied to VO$_2$ with laser strength $E_0 = 0$ to 0.14 Hartree/Bohr. The photon energy is 1.55 eV, corresponding to 800 nm wavelength. The laser field value reaches the minimum strength at time $2t_0 = 35$ fs. (B) The number and percentage of excited electrons upon photoexcitation from the valence bands to conduction bands under different laser pulses.
**Fig. S14.** Photoinduced ultrafast phase transition under different electronic excitations for the photon energy $\hbar\omega = 1.55$ eV. (A) Bond-length evolution under different laser pumping conditions. The blue and red dotted lines represent the bond lengths of each long and short bond, respectively. The blue and red solid lines represent the average bond length of long and short bonds. (B) Disorder degree evolution at different excitations.

**SI REFERENCES**

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