Exotic phenomena can be achieved in quantum materials by confining electronic states into two dimensions. For example, relativistic fermions are realized in a single layer of carbon atoms, the quantized Hall effect can result from two-dimensional (2D) systems, and the superconducting transition temperature can be considerably increased in a one-atomic-layer material. Ordinarily, a 2D electronic system can be obtained by exfoliating the layered materials, growing monolayer materials on substrates, or establishing interfaces between different materials. Here we use femtosecond infrared laser pulses to invert the periodic lattice distortion sectionally in a three-dimensional (3D) charge density wave material (IT-TiSe$_2$), creating macroscopic domain walls of transient 2D ordered electronic states with unusual properties. The corresponding ultrafast electronic and lattice dynamics are captured by time-resolved and angle-resolved photoemission spectroscopy and ultrafast electron diffraction at energies of the order of megaelectronvolts. Moreover, in the photoinduced 2D domain wall near the surface we identify a phase with enhanced density of states and signatures of potential opening of an energy gap near the Fermi energy. Such optical modulation of atomic motion is an alternative path towards realizing 2D electronic states and will be a useful platform upon which novel phases in quantum materials may be discovered.

The control of macroscopic quantum phenomena is key to exploring quantum materials for applications. Ultrafast optical irradiation is an approach for manipulating quantum phases or even promoting the emergence of novel quantum phases, such as light-induced superconductivity, optical switching to hidden phases, coherent control of phases, ultrafast photon-induced metastable states, and light-modulated exotic phases. In particular, photons coherently coupled to the lattice vibrations or phase order parameter can largely drive the excitations far from equilibrium, which could be an effective method to realize novel phases in a material. However, the possibility of realizing novel phases by optically manipulating electronic dimensionality is still a largely open subject.

Ultrafast photon excitation in a charge density wave (CDW) material can induce a complete inversion of the phase order via an electron-phonon scattering process, and the symmetry of the inverted phase is equivalent to the original phase. Macroscopic domain walls, in which the electronic states are two dimensional (2D), possibly exist parallel to the surface at the interval between the inverted phase and the original phase. Photons-induced phase inversions were evident in SmTe$_3$, from an ultrafast X-ray diffraction experiment and in TbTe$_3$, from an ultrafast optical experiment and also expected in the quasi-one-dimensional CDW material K$_3$MoO$_6$ based on ultrafast X-ray diffraction data. However, such photon-induced 2D electronic states on the domain wall have never been identified in a material, and whether the states retain long-range order is still unclear experimentally.

Herein we report ultrafast photon-induced long-range 2D ordered electronic states at the surface in a 3D CDW material. We used infrared ultrashort laser pulses to pump the sample and monitored the electronic structure and lattice dynamics by high-resolution time- and angle-resolved photoemission spectroscopy (trARPES) and MeV ultrafast electron diffraction (UED), respectively (Fig. 1b, see Methods). With improved energy and pump fluence resolution, the trARPES experiments showed evidence of 2D electronic states on the surface owing to the ultrafast phase-inversion-induced macroscopic domain wall, which was confirmed by the temporal lattice distortion from high-resolution UED experiments and was consistent with the phenomenological theory based on a spatially and temporally dependent double-wall Ginzburg–Landau potential. Moreover, at the macroscopic domain wall we have identified a phase, to our knowledge previously unseen, with enhanced density of states and possible opening of an energy gap near the Fermi energy, $E_F$. 

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Ultrafast CDW evolution

The material we studied was 1T-TiSe₂ (the trigonal phase), for which the CDW transition at 202 K (T_c) is possibly a result of the cooperation of the excitonic interactions and the Jahn–Teller effect. Below T_c, the distortion of two adjacent Se–Ti–Se layers are anti-phase-locked, forming a commensurate 3D CDW with a 2 × 2 × 2 periodic lattice distortion (PLD). Our trARPES experiment at 4 K clearly showed a flattened sombrero-shaped dispersion in the Se 4px band, which is a signature of strong electron–hole interactions (Fig. 1c, left). Equilibrium PLD was evident from the diffraction patterns (Fig. 1b, left). Furthermore, we resolved the Se 4px bands folded from point A (A-4px) and the Ti3d₂₋₅ band folded from point L (L-3d₂₋₅) due to the PLD. At 0.5 ps after the photoexcitation with a pump fluence higher than the breaking threshold of the excitonic correlation and CDW order, the flattened Se 4px band could not be well defined near the band top (Fig. 1c, left), which was possibly due to the strong CDW fluctuations. The PLD superlattice peaks were almost indistinguishable (Fig. 1d, right) at the same delay time, indicating that both the electronic order and the PLD could be completely suppressed at such a high pump fluence. Both the L-3d₂₋₅ and the Se 4px band were restored at a delay time of 12 ps (Fig. 1c, right).

To track the ultrafast evolution of the CDW order, we will focus on the dynamics of the flattened Se 4px band at the Γ point. At an excitation fluence of 0.02 mJ cm⁻², the time-dependent photoemission spectrum and the PLD diffraction intensity clearly showed a band oscillation in both intensity and energy (Fig. 2a, c, d), which was a result of photon-induced coherent A₁g-CDW phonons. At the same high excitation fluence as that shown in Fig. 1c, the top of the 4px band was not resolvable until 1 ps after photon excitation, possibly owing to strong order fluctuations at high non-equilibrium electronic temperature (Fig. 2a). Two critical pump fluences with TR is identified (Extended Data Fig. 2). The white circle represents the 1.1 PLD peak. The intensity units of the colour scales for a and c are arbitrary, from low to high, as given in d.

In addition, intensity oscillations occur immediately after time zero at high pump fluence values, but detailed analysis showed that the oscillations were anharmonic, and the peak-to-peak distance was shorter than the period of the A₁g CDW phonon oscillations. Such an anharmonic oscillating state is a signature of a forced vibration, and the measured electronic states even temporarily enter inverted CDW at high pump fluence values, but detailed analysis showed that the oscillations were anharmonic, and the peak-to-peak distance was shorter than the period of the A₁g CDW phonon oscillations. Such an anharmonic oscillating state is a signature of a forced vibration, and the measured electronic states even temporarily enter inverted CDW.

| Fig. 1 | Time-resolved electronic structure and electron diffraction patterns in TiSe₂. a, Schematic of the CDW inversion in real space (side view). The position of the top surface was defined as z = 0. The normal state lattice was 1 × 1 × 1 with the order parameter Φ = 0. The CDW lattice was 2 × 2 × 2 with the order parameter Φ = 1. The inverted layers were anti-phase distorted with the order parameter Φ = −1. Upon photon excitation, phase inversion happens in the red dashed rectangle, and quasi-2D electronic states exist between the inverted and original CDW layers (red shaded area). b, Experimental geometry of time- and angle-resolved photoemission and ultrafast electron diffraction. Δt is the time delay between the infrared pump pulse and ultraviolet laser and 6.05-eV photon 126 fs. c, Typical UED patterns of TiSe₂ before and after photoexcitation with a pump fluence of 0.56 mJ cm⁻² at 90 K. The white circle represents the 1.1 PLD peak. The intensity units of the colour scales for a and c are arbitrary, from low to high, as given in d.
reappeared closer to time zero than the first oscillation peak at a low pump fluence, which was a result of pump-induced inhomogeneous PLD inversion in real space.

The above observations indicated the existence of photoinduced phase inversion in the TiSe_{2}, and were consistent with a simulation of the phase-inversion scenario based on the phenomenological theory of a spatially and temporally dependent double-wall Ginzburg–Landau potential (see Methods and Supplementary Information section I)\(^{23–35}\). The solved order parameter and PLD diffraction intensity from the phenomenological theory show behaviour similar to that of the anharmonic oscillations (Fig. 2g) and the reappearance of the PLD peak (Fig. 2h) at the highest pump fluence, consistent with the experimental results in Fig. 2c, d. From the phenomenological theory, the distribution of the domain wall perpendicular to the sample surface can be tuned by the excitation pulse energy (Fig. 2e, f). It can be expected that at certain pump fluences, transient macroscopic domain walls, which are possibly quasi-2D electronic systems, can be positioned near the sample surface (Fig. 3b, top) with a thickness of 2–3 unit cells (determined from Fig. 2f).

Optically induced 2D domain wall
TrARPES is an excellent tool for probing the transient electronic structure with surface sensitivity. Experimentally, by finely tuning the pump fluence, features of the domain wall should be also shown in the ARPES data. The detailed pump-fluence-dependent photoemission spectra at the Γ point at a delay time of 12 ps showed that the photoemission intensity just slightly increased until a large enhancement occurred above the excitation condensation critical pump fluence \( F_{c1} \) (Fig. 3a, b). Interestingly, the intensity shifted upward reaching a peak at the pump fluence of approximately 0.091 mJ cm\(^{-2} \) (I′), and then dropped to a minimum (dip) at approximately 0.116 mJ cm\(^{-2} \) (I) (Fig. 3b). Upon enhancing the pump fluence further, the intensity shifted to new maxima (at fluences of 0.156 (II′), 0.237 (III′), and 0.340 mJ cm\(^{-2} \) ) and then new minima (at fluences of 0.185 (II), 0.273 (III), and 0.371 mJ cm\(^{-2} \) ) alternately until reaching a point at which it monotonically increases at high pump fluences. The difference spectra in Fig. 3c clearly show reductions of the intensity near the Fermi energy at the Γ point between fluences I and I′ (Δ\( \Phi_1 \)) and between fluences II and II′ (Δ\( \Phi_2 = \Phi_3 \)). Further experimentation showed that the peak–dip feature lasted for longer than 30 ps (Extended Data Fig. 3d).

The above peak–dip features in the intensity are a result of changes in the band-folding from the A point, because the A–4\( \psi \)–3\( \psi \) band is slightly above the T–4\( \psi \)–3\( \psi \) band. Since the A–4\( \psi \)–3\( \psi \) band was much weaker in intensity and closer to the Fermi energy than the 4\( \psi \)–3\( \psi \) band, we attributed the left edge shift (green cut in the inset of Fig. 3d) as a result of the shift of the 4\( \psi \)–3\( \psi \) band, which monotonically
shifted upward with increasing pump fluence (Fig. 3d). Interestingly, the edge at the bottom right (red cut in the inset of Fig. 3d) of the $4p_{x,y}$-3$d_{x^2}$ band showed a similar peak–dip feature as in the intensity, and the edge at the upper right side (blue cut in the inset of Fig. 3d) of the $4p_{x,y}$-3$d_{x^2}$ band was similar to that at the bottom right but with a weaker peak–dip feature, which was also attributed to the folded A-$4p_{x,y}$ band. The observed dips described above were results of the lower folding intensity from the A-$4p_{x,y}$ band, indicating that the electronic states at the dips with fluences of I, II and III were possibly 2D. The reduced spectral linewidth at the fluences I and II (Fig. 3d) show further evidence for the 2D electronic states near the surface at those fluences, since—owing to the effect of momentum resolution perpendicular to the surface—photoemission spectral linewidth from 2D electronic states is narrower than that from 3D electronic states (energy distribution curves (EDCs) in Extended Data Fig. 4e). Consistent with the calculation based on a CDW-inversion-induced sharp domain wall (Extended Data Fig. 4a), the inset in Fig. 3d and the EDCs in Extended Data Fig. 4e show an increment of the binding energy of Se $4p_{x,y}$ band on the 2D domain wall (comparison between pump fluences I and I). From the solved order parameter (Fig. 2e), the 2D electronic structure was determined to be on the macroscopic domain wall where the Ginzburg–Landau potential $(V(\Phi))$ was a maximum (red curve in Fig. 3b).

It is interesting that the intensity of the L–3$d_{x^2}$ band showed a minimum (maximum) at the same fluences where the $4p_{x,y}$ band edge reached a maximum (minimum) (Fig. 3b, c) and lasted for 30 ps (Extended Data Fig. 3e, f), indicating that the density of states of the L–3$d_{x^2}$ band near the Fermi energy was enhanced in the photoinduced 2D electronic states (domain wall). The enhancement of the density of states of the L–3$d_{x^2}$ band cannot be a result of loss of excitonic order at higher pump fluence, since it was reduced with further enhanced pump fluence at II′ ($E_{2g}(II′) - E_{2g}(I)$) in Fig. 3c. Such photoinduced 2D electronic states, which result in the peak–dip features in the $\phi$-fluence-dependent intensity of the $4p_{x,y}$ band, could also be identified at equilibrium temperatures of 30 and 80 K but were absent at 295 K (Fig. 4a), which is above the CDW transition temperature.

A 2D electronic state with high DOS

Recently, superconductivity was discovered in pressurised, Cu-intercalated and electric-field-controlled 1T-TiSe$_2$ (refs. 36, 39). The existence of an incommensurate CDW phase with localized commensurate CDW domains separated by domain walls is common in superconducting 1T-TiSe$_2$, and the enhancement of the density of states at the domain wall is believed to be responsible for the superconductivity. The 2D domain wall reported herein also showed an enhancement of the density of states near the Fermi energy (the intensity of the L–3$d_{x^2}$ band at 0.116 mJ cm$^{-2}$ in Fig. 3b). Such an enhancement of the density of states might also result in superconductivity in 1T-TiSe$_2$. A close comparison of the EDCs for the pump fluences of 0.091 mJ cm$^{-2}$ (peak) and 0.116 mJ cm$^{-2}$ (dip) at 4 K showed the signature of leading-edge shift, indicating a possible energy gap of approximately 2 meV at the domain wall (Fig. 4c). A possible energy gap (approximately 1.5 meV) was also evident at the second domain wall on the surface as the pump fluence was increased further (in the EDCs measured at 0.156 mJ cm$^{-2}$ (peak) and 0.185 mJ cm$^{-2}$ (dip) in Fig. 4c), but no resolvable gap was
found away from the domain wall. Energy gaps were also identified at two other samples and were evidenced up to 30 ps only when the peak–dip features discussed in Fig. 3b were still resolvable (Extended Data Fig. 3c, f). We note that in the superconducting Cu-intercalated 1T-TiSe2, the estimated energy gap was about 0.5 meV (ref. 39), which was at the same scale as the domain-wall-induced energy gap. Interestingly, the electronic temperature estimated by fitting the Fermi edge to an energy-resolution-convolved Fermi–Dirac function was about 90 K, which is much higher than the equilibrium superconducting transition temperature in the pressurized, Cu-intercalated and electric-field-controlled samples.

The possible energy gap was still resolvable (approximately 1 meV) at 30 K, but absent at 80 K (Fig. 4c). A superconductor-like energy gap with a size comparable to the equilibrium superconducting gap was evident in K3C60 from the ultrafast optical spectra after pumping with an ultrashort far-infrared laser pulse at 100 K, which was much greater than its equilibrium superconducting transition temperature of 20 K (ref. 9). The possible energy gap observed in the phase-inversion-induced domain wall was similar to the observation for K3C60, in which the energy gap was comparable to the equilibrium superconducting gap in spite of its much higher electronic temperature. Such a pump-induced energy gap at a high electronic temperature may share the same non-equilibrium physics, although they may have different mechanisms of origin. The pioneering observations of light-induced coherent conductivity at high temperatures in cuprates in which the studied materials also possessed high-temperature CDW phases—also possibly originated from the pump-induced macroscopic domain walls. However, we note that the suggestive transient energy gap cannot be exclusive evidence of superconductivity and could also result from transient CDW, semiconducting and other novel phases that hold gapped electronic states. Further experimental and theoretical work is required to clarify this.

In summary, we detected photoinduced macroscopic CDW domain walls in 1T-TiSe2. The found domain walls existed parallel to the surface in the interval between the photo-inverted phase and the original phase and could be placed near the surface by finely tuning the excitation energy. This macroscopic domain wall exhibited the behaviour of a 2D electronic system, and thus it is a platform for realizing novel phases, for example, phases with superconductivity. Our work presents an approach for manipulating quantum materials using ultrafast laser pumping, and opens a window into ultrafast science with profound implications for next-generation devices with new functionalities. However, further studies are necessary to clarify the precise mechanism for producing such macroscopic domain walls, to determine if such methods are universal and applicable for other CDW materials or even other ordered solids, and—most notably—to identify if the observed energy gap was the result of photoinduced superconductivity.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41586-021-03643-8.
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**Methods**

**TrARPES**

In the trARPES measurements, infrared photon pulses with wavelength centred at 700 nm (1.77 eV) and pulse length of 30 fs were used to excite the sample, and the non-equilibrium states were probed by ultraviolet pulses at 205 nm (6.05 eV). Both of the pump and probe beams are s-polarized in our experimental geometry. The measurements were taken at \( k_z = 2 \) at the Fermi energy (\( E_F = 0 \)) by \( k_z = \frac{1}{2} [2m/((hv - W - |E_0|) \cos^2 \theta + V_0)] \) with photon energy \( hv = 6.05 \) eV, system work function \( W = 4.3 \) eV, nearly normal emission (\( \theta = 0 \)), and inner potential \( V_0 = 13.5 \) eV in our experiments. The excitation fluences of the pump beam can be precisely tuned by using a half wave plate and a polarizer, and the size of pump pulse is 8.5 times larger than the probe beam, ensuring a fluence resolution of 2.5% in the fluence-dependent measurements (Supplementary Information section II). Photoelectrons were collected by a Scienta DA30L-8000R analyser. The overall time resolution and energy resolution are 130 fs and 19 meV, respectively. The sample was cleaved at a pressure better than \( 3 \times 10^{-11} \) torr at 4 K. We note that for 605 eV photons, the top 4–5 layers of the unit cell can be probed. Limited by the photon energy, we cannot reach the Brillouin zone boundary on our trARPES system. With improved energy and momentum resolution for low-energy probe photons, the folded Ti3d\( z \) band can be clearly resolved near the Brillouin zone centre, making it possible to analyze the dynamics of the Ti3d\( z \) band indirectly.

**Determining the energy gap**

In Fig. 4c, we compare EDCs between the peak and dip to extract the energy gap, because at these two corresponding excitation fluences, the electronic temperature was comparable and the temperature effect on the EDC could be excluded. The energy gap here was obtained from the leading-edge shift between the EDCs at the two pump fluences, which is a common method for determining the energy gap with a non-apparent coherent peak and usually underestimates the energy gap. We note that a leading-edge shift did not appear in the inelastic-scattered electrons, which represented the Fermi–Dirac broadening at these pump fluences (Fig. 4b).

**MeV UED**

The structural dynamics was independently investigated by a MeV UED facility with a double bend achromat compressor. An 800 nm laser with about 30 fs pulse width was used to pump the sample and a 3 MeV electron beam was used to probe the dynamics. The electrons were produced in a photocathode radio-frequency gun and were further compressed to below 30 fs (FWHM) at the sample with the compressor. The size of pump pulse is 5 times larger than the electron beam, thus ensuring uniform excitation on the sample. An electron-multiplying CCD camera and a phosphor screen are used to measure the diffraction pattern. High-quality TiSe\(_2\) thin film with a thickness of 60 nm was prepared by exposing a bulk single crystal. The sample was tilted by several degrees to the normal incidence to avoid intensity cancellation in the PLD diffraction (Extended Data Fig. 1). During the experiment, the temperature of the sample was kept at ~90 K by liquid nitrogen.

**Domain-wall simulation**

The pump-induced macroscopic domain wall can be modelled by solving a motion equation based on a spatially and temporally dependent double-wall Ginzburg–Landau potential\(^{21,35}\). The potential \( V(\Phi, z) \), in which \( z \) is the depth away from the surface and \( \Phi \) is the order parameter, is

\[
V(\Phi, z) = \frac{1}{4} \eta \exp \left( -\frac{\tau}{\tau_p} \right) \exp \left( -\frac{z}{z_p} \right) - 1 \Phi^2 + \frac{1}{8} \Phi^4 + \frac{1}{2} \Phi^2 \left( \frac{\partial \Phi}{\partial z} \right)^2.
\]

Here \( \eta \exp \left( -\frac{\tau}{\tau_p} \right) \exp \left( -\frac{z}{z_p} \right) \) is the transient change on the potential energy after photoexcitation with the pump fluence coefficient \( \eta \), non-equilibrium quasiparticle recovery rate \( 1/\tau_p = 0.3 \) ps\(^{-1}\) determined by experiment, and pump penetration depth \( z_p = 17 \) nm (ref. \(^{21}\)), and the CDW coherence length at low temperature, \( \xi = 1.2 \) nm (ref. \(^{23}\)). The third term results from inhomogeneous order parameter\(^{41}\). The motion equation based on such a potential is

\[
\frac{1}{\omega_p^2} \frac{\partial^2 \Phi}{\partial t^2} + \frac{\gamma}{\omega_p} \frac{\partial \Phi}{\partial t} - \frac{1}{2} \left( 1 - \eta \exp \left( -\frac{\tau}{\tau_p} \right) \exp \left( -\frac{z}{z_p} \right) \right) \Phi + \frac{1}{2} \Phi^3 - \frac{\xi^2}{\tau_p^2} \frac{\partial^4 \Phi}{\partial z^4} = 0.
\]

The temporally and spatially dependent order parameter \( \Phi(z, t) \) can be numerically solved from the motion equation with the input of the above parameters in TiSe\(_2\) (Fig. 2f). The procedure to find the solution is introduced in Supplementary Information section I.

With the solved \( \Phi(z, t) \), the diffraction intensity of the PLD as a function of delay time (Fig. 2h) can be simulated by,

\[
I(t) = \int_{-\infty}^{\infty} \Phi(z, t) dz \int_{-\infty}^{\infty} \Phi(z, t) dz.
\]
order$^{13,12}$ and $F_{\text{c}}$ is the fluence that destroys the PLD$^{32}$. At fluence below $F_{\text{c}}$, photo carriers are mainly relaxed by $A_{\text{g}}$ phonons, and the recovery time may be mainly governed by the escape rate of the $A_{\text{g}}$ phonon, which is supposed to be a constant below $F_{\text{c}}$ from current data. Above $F_{\text{c}}$, hot carriers enhance Coulomb screening and destroy the excitonic interaction. The coupling between $A_{\text{g}}$ phonons and hot carriers is gradually weakened by enhancing the pump fluence, leading to an increase in the lifetime of populated hot carriers above $F_{\text{c}}$. Above $F_{\text{c}}$, the PLD and the associated CDW are completely destroyed, showing slower quasiparticle recovery rate owing to the temporally uncorrelated states.

The $k_z$ momentum resolution effect

In ARPES experiments, the final state is confined within the photoelectron escape depth $l$. From the Heisenberg uncertainty principle, such confinement results in intrinsic broadening of $k_z$, (momentum perpendicular to the sample surface) defined by $|\Delta k_z| = l$, and thus the measured spectrum is an average over the $\Delta k_z$ interval$^{44}$. For 3D electronic states, the photoemission spectra are usually broadened owing to the $k_z$ resolution, whereas in the 2D case, the photoemission spectra represent the intrinsic 2D electronic states since there is no dispersion along $k_z$. Owing to the $k_z$ resolution, it is usually possible to measure sharper ARPES spectra in 2D electronic states than in 3D electronic states. Taking Bi$_2$Se$_3$ for example, the photoemission spectra for the 2D surface states are much sharper than that of the bulk 3D states, for which the dispersion is not resolvable$^{48}$.

For higher pump fluence, the laser pulse usually pumps the electronic states to higher electronic temperature and the measured ARPES spectra should be broadened owing to enhanced scattering rate at higher electronic temperature. It is quite counterintuitive that with enhanced optical pump pulse energy the spectral linewidth from photoemission is narrower from the experiment. To our knowledge, it is only the dimension effect that can induce such a phenomenon experimentally. For the above reason, the measured bands getting sharper at higher pump fluence (I) than that at lower fluence (I') is striking evidence that the transient structure has 2D behaviour.

Additional measurements on two other samples

The peak–dip feature observed in Fig. 3 was quite reproducible, given that similar spectral intensities as a function of the pump fluence were taken in two other samples (Extended Data Fig. 3a, d), and was clearly evidenced in sample II until a delay time of 40 ps. Consistent with Fig. 3b, c, the difference of the photoemission spectra between fluence $I'$ and I clearly shows the enhancement of the density of states in the Ti3d$_{2z}$ band before 40 ps (Extended Data Fig. 3b, c).

The leading-edge shift between fluences $I'$ and I in Fig. 4c is robust and can be observed in other samples we measured at the same delay time (Extended Data Fig. 3c), and was seen between 9 and 30 ps in sample II (Extended Data Fig. 3f) and in sample IV, which is not shown here. It is clear that the possible energy gap is only shown when there is enhancement of the density of states. The absence of an energy gap at 3 and 6 ps is possibly due to the high transient electronic temperature close to time 0, and this is consistent with Fig. 4c, where the energy gap is not resolvable at 80 K, although there is still a clear peak–dip feature in the fluence-dependent measurement, indicating that the electronic temperature must be low enough to present the gapped states.

In addition, the leading-edge shift is a method to determine if there was gap opening and usually underestimates the size of the gap for a resolution larger than the gap size. For an example, the measured energy gap on the high-temperature superconductor Bi2212 (doped, $T_{c} = 78$ K) with an energy resolution of 30 meV from the leading-edge shift is 12 meV$^{10}$, which is about half that from high-resolution data from a similar sample$^{22}$. We note that for comparable spectral linewidth and electronic temperature, it cannot be concluded that there is no gap if there is no resolvable leading-edge shift, but on the other hand, if there is a resolvable leading-edge shift, there must be an energy gap, although it is hard to determine the exact value. Therefore, the real energy gap in the 2D electronic states on the domain wall should be larger than that obtained from the leading-edge shift.

The broadened spectra due to pump excitation and limited energy resolution makes it hard to determine the energy gap from the quasi-particle peak shift, but it is clear that the peak of the EDCs at the high pump fluence I shifts to higher binding energy at delay times 12, 15 and 18 ps, when the gap is mostly pronounced (Extended Data Fig. 3e).

First-principles density functional theory calculations

First-principles density functional theory (DFT)$^{14,49}$ calculations are performed using the VASP (Vienna Ab initio Simulation Package) code$^{50,51}$ with the projector augmented wave (PAW) method$^{52}$ and the PBE (Perdew–Burke–Ernzerhof) + $U$ approximation$^{53}$. A Hubbard interaction parameter $U = 3$ eV on the Ti 3d orbitals is used to obtain the electronic band structure. The lattice constants and displacements of the Ti and Se atoms in the CDW phase are adapted from experimental measurements$^{23}$.

To understand the electronic structure of the CDW domain wall, calculations are performed on $2 \times 2 \times 8$ periodic supercells of TiSe$_2$, in which the atomic displacements from the high-symmetry positions in one particular layer are scaled by a coefficient $c$. A single CDW phase without domain wall corresponds to $c = 1$, whereas $c = 0$ means that this one layer has no CDW distortion, and $c = -1$ means this one layer has a reversed CDW distortion, corresponding to a sharp CDW domain wall. Through band structure-unfolding analysis of the CDW phase, we have identified the $p_x$ and $p_y$ states that originated from the $\Gamma$ point of the high-symmetry phase. In the case of a sharp domain wall, the band structure is shown in Extended Data Fig. 4b, with the $p_x$ and $p_y$ domain-wall bands marked by red circles. The spatial distribution of the corresponding charge density is shown in Extended Data Fig. 4a, which exhibits a 2D electronic structure, being extended in the 2D layer while localized in the normal direction.

As the atomic displacements of the domain-wall layer are tuned continuously by the scaling coefficient from $c = 1$ to $c = -1$, we calculate the energy shifts of the $p_x$ and $p_y$ domain-wall bands relative to a reference energy. States localized at the domain wall are sensitively affected by the atomic displacements of the domain-wall layer, whereas delocalized states originating from band-folding in the layer-stacking direction are almost unaffected by the domain wall. Thus, these states are good references, and their average energy is used as a reference energy for calculating the shift of the domain-wall states. As the coefficient $c$ decreases from 1, a phase shift starts to form at the domain-wall layer and the energy gaps of the domain-wall states change, as shown in Extended Data Fig. 4c. In the initial stage, the energy of the domain-wall states remains almost unchanged. When $c = 0$, corresponding to a $\pi/2$ phase difference between adjacent layers, the energy shift is about $-0.3$ meV. When the distortion becomes larger at $c = -0.5$ and 1, the energy shifts become larger. In the case of sharp CDW domain wall ($c = -1$), the energy shift is about $-18$ meV.

Extended Data Fig. 4d clearly shows that the measured electronic structure (on the domain wall) at pump fluence I (dip position in Extended Data Fig. 4e, inset) is sharper than that at pump fluence I' (peak position in Extended Data Fig. 4e, inset). Since the electronic states near the $\Gamma$ point are complicated—in that they are the mixture of $\Gamma$-4$p_{x,y}$ and the $-3d_{2z}$ bands—the pump-induced photoemission linewidth and the energy of the 4$p_{x,y}$ band are analysed at the momentum $-0.13 \text{ Å}^{-1}$ away from the $\Gamma$ point. It is clear from Extended Data Fig. 4e that the photoemission spectral linewidth of the Se 4$p_{x,y}$ band is narrower for the pump fluence at I (dip) than that at I' (peak); the fluence dependence of the spectral linewidth as a function of pump fluence is shown in Fig. 3d.

It is qualitatively consistent with the DFT calculation that on the domain wall (fluence at I) the Se 4$p_{x,y}$ band moves to higher binding energy than the 3D states (fluence at I'). However, the calculation shows...
a downshift of the energy band of about 18 meV, whereas the experiment shows a downshift of about 3.5 meV as shown in Extended Data Fig. 4e. The discrepancy between the down-shifted energies from the calculation and experiment is possibly due to the following reasons: 1) a sharp domain wall with only one inverted layer is used in the calculation, whereas in the experiment the change from $\Phi = -1$ to $\Phi = 1$ is 2–3 unit cells; 2) the calculation was at zero temperature, whereas in the measurement the electronic temperature was about 90 K; 3) the down-shifted energy is estimated from the momentum away from the $\Gamma$ point, at which the energy shift is possibly larger; 4) the DFT calculation might overestimate the energy shift.

The agreement between the calculation and experiment about the energy shift of the band further suggests that the photoinduced electronic states on the domain wall are 2D.

**Data availability**

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request. Correspondence and requests for materials regarding trARPES experimental data and the simulation should be addressed to W.Z. and regarding UED experimental data should be addressed to D.X.

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**Author contributions**

W.Z. and D.X. proposed and designed the research. S.D., Y.Y., C.H., T.T. and W.Z. contributed to the development and maintenance of the trARPES system. S.D., Y.Y. and C.H. performed the DFT calculation. W.Z. wrote the paper with S.D., Y.C., W.L., D.Q., D.X. and W.Z. performed the phenomenological simulation. W.Z. and D.X. performed the trARPES experimental data and the simulation should be addressed to D.X.

**Competing interests**

The authors declare no competing interests.

**Additional information**

**Supplementary information**

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Extended Data Fig. 1 | Simulated and experimental electron diffraction patterns in TiSe₂. a, b, Simulated and experimental electron diffraction patterns based on the kinetical theory with the sample thickness of 60 nm. c, Experimental diffraction patterns at 12 ps with a tilted angle. Data were taken with the same pump fluence and equilibrium temperature as in Fig. 1d. The intensity units on the colour scale are arbitrary.
Extended Data Fig. 2 | Ultrafast electronic dynamics. a, Time-dependent photoemission spectroscopy intensity at different pump fluences. The intensity is the integration of non-equilibrium electrons between 0 and 0.03 eV above the Fermi energy. b, The decay rates of nonequilibrium electrons as a function of pump fluence. The three different regions separated by the two critical pump fluences are indicated by different colours in the background.
Extended Data Fig. 3 | Additional measurements on two other samples (samples II and III). a, Spectral intensity as a function of the pump fluence integrated from −0.1 eV (Se 4p, band top) to the Fermi level for samples II and III at a delay time of 12 ps. b, Photoemission spectra difference between fluences I' and I (I(I) − I(I′)) from 3 to 40 ps for sample II. The colour scale is in arbitrary units, and ‘−’ (green) indicates <0 and ‘+’ (red) indicates >0. c, EDCs at the momentum of the dashed line shown in the inset of Fig. 4b for pump fluences at I′ and I for samples II and III. EDCs are normalized to the same height. d, Spectral intensity as a function of the pump fluence integrated from −0.1 eV (Se 4p, band top) to the Fermi level for sample II. e, Original EDCs without normalization between 3 and 40 ps for sample II. f, Normalized EDCs from e.
**Extended Data Fig. 4** | **DFT calculations and experimental electronic structures of the bulk and 2D domain wall.**

**a**, Charge density isosurface plot of the domain-wall bands at the $\Gamma$ point. The Ti and Se atoms are shown in blue and green spheres, and the outer and inner surfaces of the density state isosurface on the domain wall are shown in purple and blue. **b**, Band structure of the periodic eight-layer supercell with domain wall. The $p_x$ and $p_y$ orbitals are projected to the three layers at the domain wall (shown in red circles); the symbol size denotes the relative weight of the orbitals. The reference bands are drawn in orange lines. **c**, Energy shifts of the domain-wall bands at different strengths of CDW displacements. The label ‘CDW’ means a single CDW phase, and ‘domain’ means the presence of sharp domain wall. **d**, Time-resolved photoemission spectra at 12 ps for pump fluences at $I'$ and $I$, as indicated in the inset to **e**. **e**, EDCs at the momentum of $-0.13 \text{ Å}^{-1}$ for pump fluence $I'$ and $I$, as indicated by the solid line cuts (the same colour as the corresponding EDC) in **d**. Inset shows the same spectra at 12 ps for sample II as that shown in Extended Data Fig. 3a. EDCs are normalized to the same height.