Signatures of excitonic insulating state in monolayer 1T-ZrTe₂

Yekai Song¹,²†, Chunjing Jia³,⁴†, Hongyu Xiong³,⁴,⁵, Binbin Wang⁶, Zhicheng Jiang¹, Kui Huang⁶, Jinwoong Hwang⁴,⁷,⁸, Zhuojun Li¹,², Choongyu Hwang⁸, Zhongkai Liu⁶, Dawei Shen¹, Jonathan A. Sobota³,⁴, Patrick Kirchmann³,⁴, Jiamin Xue⁶, Thomas P. Devereaux³,⁴, Sung-Kwan Mo⁷*, Zhi-Xun Shen³,⁴*, Shujie Tang¹,²*

¹State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China.

²2020 X-Lab, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China.

³Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA.

⁴Geballe Laboratory for Advanced Materials, Departments of Physics and Applied Physics, Stanford University, Stanford, California 94305, USA.

⁵Key Laboratory for Power Machinery and Engineering of MOE, School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China.

⁶School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China.

⁷Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.

⁸Department of Physics, Pusan National University, Busan 46241, Korea.

*Corresponding authors. Email: SKMo@lbl.gov, zxshen@stanford.edu, tangsj@mail.sim.ac.cn
The excitonic insulator (EI) is a Bose-Einstein condensate (BEC) of excitons bound by electron-hole interaction in solid, which could support high-temperature BEC transition$^{1-3}$. The material realization of EI has been elusive, which is further challenged by the difficulty of distinguishing it from a conventional charge density wave (CDW) state. Here we report an unexpected 2×2 CDW ground state emerging in epitaxially grown monolayer 1T-ZrTe$_2$ and its investigation by angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM). Our results show band- and energy-dependent folding behavior in a novel two-step CDW formation process, which signal preformed exciton and its condensation. The carrier dependent suppression of the CDW state is in good agreement with theoretical predictions for an EI. Our findings provide a versatile two-dimensional platform that allows tuning of the excitonic effect.

The macroscopic quantum phenomena such as superconductivity and BEC are crucial and attractive in basic research and potential technological applications. The EI was originally proposed as an analog of Bardeen-Cooper-Schrieffer (BCS) condensate in a weak-coupling limit$^{1-3}$. It may support novel transport properties$^{4,5}$ corresponding to the superfluidity in superconductors. With varying coupling strength, a wealth of exotic phenomena could stem from EIs$^{6,7}$, such as correlated Chern insulator and fractionalized Hall effect$^8$. However, the unequivocal experimental evidence for the realization of an EI state still lacks so far. Unlike singlet-paired superconductors, the singlet-paired electron-hole does not carry a net charge which provides no easy observable. Further complicating the issue, the EI state with finite-momentum exciton is characterized by a CDW state with periodic lattice distortion (PLD).

Hardly any difference is present in the ground state electronic structure due to the same symmetry-breaking behavior in the EI and a conventional CDW state from
electron-phonon coupling (EPC). The resulting states have similar band renormalization and a gap opening despite the different driving forces. Thus, experimental efforts to identify the excitonic effect are devoted to looking beyond the static electronic structure or constructing van der Waals heterostructures and separating electron and hole layers to avoid the fast recombination\textsuperscript{9,10}. For example, in the prototype CDW material 1T-TiSe\textsubscript{2}, the softening of the plasmon mode around critical temperature\textsuperscript{11} and ultra-fast melting of the CDW order upon laser pumping\textsuperscript{12} were taken as evidence of the existence of the excitonic effect. However, the excitonic effect is usually intertwined with other interactions in the candidate materials, such as EPC in the 1T-TiSe\textsubscript{2}, calling for a new material platform to enhance the contributions from the excitonic effect and to provide a route to distinguish it in a cleaner way.

2D materials, especially the monolayer transition metal dichalcogenides (TMDC), possess unprecedentedly strong excitonic effect\textsuperscript{13-16}. In addition, they also provide opportunities to control key physical parameters of the excitonic effect through strain, carrier doping, and varying dielectric environment. Thinning down EI candidates, such as 1T-TiSe\textsubscript{2}, to monolayer limit may be a viable route to enhance the excitonic effect by suppressing the screening from the adjacent layers. Although a moderate increase in CDW transition temperature has been observed\textsuperscript{17}, the EPC, an alternative driving force of the CDW in bulk 1T-TiSe\textsubscript{2}, also persists down to monolayer and makes it hard to distinguish from the enhanced excitonic instability.

The semi-metallic 1T-ZrTe\textsubscript{2}\textsuperscript{18-21}, a sister compound of 1T-TiSe\textsubscript{2}, largely resembles the electronic structure of 1T-TiSe\textsubscript{2}, except for the lack of CDW state in bulk. The absence of CDW in bulk indicates the suppressed influence of EPC and a potential advantage in investigating the excitonic instability stemming from the characteristic band structure\textsuperscript{2}. Using molecular beam epitaxy (MBE), we have successfully grown
high-quality monolayer 1T-ZrTe$_2$. In-situ ARPES and STM measurements reveal an emergence of a 2×2 CDW ground state in low temperature (LT), in a clear contrast to the bulk material, with strong spectral weight (SW) transfer and band folding. Using carrier doping to suppress the interaction, we found a hidden phase and confirmed the CDW formation to be a two-step process, indicating the existence of a strong fluctuation or preformed exciton gas. More importantly, the melting of the CDW in higher temperature reveal band- and energy-dependent relaxation of the band folding, exposing a temperature regime well above the CDW transition temperature ($T_c$) but with excition bands fully developed. Such observations prominently deviate from the conventional CDW systems, but naturally occur in the preformed exciton gas scenario$^{22}$, which is confirmed by the calculations and rooted in the fundamental aspect that the PLD is a secondary effect in the excitonic condensation.

Figure 1a represents the crystal structure of the monolayer 1T-ZrTe$_2$, where two Te layers sandwich a Zr layer with octahedral coordination. Sub-monolayer 1T-ZrTe$_2$ were grown on bilayer graphene (BLG) terminated SiC substrate, which is known to induce the least amount of interaction between the MBE grown film and substrate$^{15}$. Figs. 1b and c show the reflection high-energy electron diffraction (RHEED) and low energy electron diffraction (LEED) images of the film, respectively, showing the hexagonal symmetry of the 2D crystal with the in-plane orientation aligned with the BLG substrate. Using the lattice constant of BLG ($a = 2.46$ Å) as a reference, the lattice constant of the film is estimated to be $4.0 \pm 0.2$ Å, consistent with the value of bulk 1T-ZrTe$_2$. The large-scale STM image at room temperature in Fig. 1d shows the typical morphology of monolayer 1T-ZrTe$_2$ domains, with the typical lateral size of ~ 50 nm.

At $T = 4.5$ K, a 2×2 superlattice is observed by atomically resolved STM image (Fig. 1e) and its 2D Fast Fourier transform (FFT) image (the insert in Fig. 1e),
indicating the occurrence of CDW order at LT. ARPES spectra (Fig. 1f) taken from the monolayer 1T-ZrTe2 along Γ-M direction further confirm the existence of the CDW state. For the 2×2 CDW state, the first and second valence bands below Fermi energy (E_F) at the Γ point are folded into the M point. The SW transfer is distinctive in the system: the SW of the low energy valence band at the Γ point is nearly depleted around its maximum with most of the SW transferred to the folded band at the M point, while the SW of the conduction band at the M point is kept nearly intact close to E_F. Notably, such observations were also made in bulk 1T-TiSe2, and it is attributed to the formation of the EI23,24.

The temperature dependence of the CDW state evolution of monolayer 1T-ZrTe2 was studied using STM and ARPES. Fig. 2a shows the melting of the CDW order for selected temperatures from \( T = 4.5 \) K to \( T = 300 \) K. With increasing temperature, the superlattice contrast in the real space gets blurry (77 K) and then hardly visible (116 K). The 2×2 superlattice peaks in the FFT get weaker and diffused accordingly. Above some critical temperature, the superlattice peaks disappear, and only the Bragg peaks can be observed (a typical result at 300 K shown in Fig. 2a). The melting of the CDW order is also characterized in ARPES by the bandgap shrinking and the disappearance of the folded second valence bands at the M point (Figs. 2b & 2c). As temperature increases, the folded first valence band gradually shifts to lower binding energy and merges with the conduction band. The folded second valence peak also slightly moves towards E_F, and its SW (shaded area) in Fig. 2c gradually fades away up to \( T = 150 \) K. Note the presence of another feature from -0.2 eV to -0.8 eV that persists in all temperature. This is likely related to the existence of impurity phase or defect states25, which is not important to the current discussion.

The temperature evolution of bandgap size (defined by the energy difference
between the conduction and folded valence bands), the intensity of the folded second
valence band, and the intensity of normalized 2×2 superlattice peak are plotted in Fig. 2d. These three observables are indicators of the CDW order, showing the identical
temperature evolution. The T_c in the monolayer 1T-ZrTe_2 is thus determined to be about
130 ± 20 K. A detailed look into the valence band at 300 K (Fig. S3 in the
Supplementary Information) reveals that the valence band is well below E_F.
Surprisingly, a strong SW transfer of the first valence band, i.e., the depletion of SW at
the Γ point, persists well above T_c as in the 300 K data of Fig. 2b, which does not follow
the same trend with other three indicators. Such asynchronous behavior of the first
valence band implies the deviation from the conventional CDW picture.

To investigate the nature of the asynchronous band folding, we use carrier doping
to restore the screening in monolayer^{20} and therefore suppress the many-body
interaction^{13,15,26-28}. Upon surface K (potassium)-doping^{29}, the CDW order decreases
drastically and eventually dissolves completely (Fig. 3e). Compared to the CDW state,
a prominent valence band renormalization, from a flat band top to a nearly linear
dispersion, significantly shrinks the bandgap from ~ 70 meV to -100 meV, with a
concomitant recovery of SW at the Γ point. To rule out the potential band distortion that
K-doping may introduce^{30,31}, we also employed photo-excitation with laser pulses to
inject carrier into the system to mimic the process of screening building up. The band
dispersions before (t = -5 ps) and after (t = 100 fs) pumping at 12 K are plotted in Fig. 3g,
exhibiting a flattened valence band reshaped to a nearly linear dispersion upon
pumping at the Γ point, which is identical to the K-doped case. The direct comparison
of the valence band dispersions and their SW are plotted in Figs. 3i and 3j. It is striking
that the valence band dispersion at 300 K is very different from the well screened case,
but is essentially the same as the CDW state. This provides compelling evidence for the
exciton formation well above $T_c$.

The carrier-injection suppresses the many-body effect and leads to an interaction-suppressed state, which is corroborated by reproducing the main electronic features of the interaction-free state from DFT calculations (Fig. S4 in the Supplementary Information). It is feasible to summarize the experimentally observed states into a schematic band diagram (Fig. 4a), in which the formation of the CDW order is determined to be a two-step process. First, from the interactions-suppressed state to the intermediate state (normal state above the $T_c$), the first valence band renormalizes prominently, accompanied by a strong SW transfer, leading to an indirect bandgap opening. Next, the second valence band folded to the M point as the long-range CDW order sets in. In other words, the folding of the two different valence bands in the formation of the CDW state is asynchronous.

To understand such asynchronous behavior of band folding, we performed the model calculations based on the microscopic Hamiltonians obtained from first-principles calculations (see Methods), for the investigation of the electronic structures of monolayer 1T-ZrTe$_2$ lead by PLD and excitonic effect, respectively (Fig. 4b). In the case of PLD driven band folding, the SW of the two folded valence bands are comparable. In contrast, the excitonic interaction is much more energy-dependent, and the folded SW mostly concentrate on the energy bands near Fermi energy. The distinction reflects the fundamentally different roles that PLD and excitonic effect play in the formation of CDW state. In the case of PLD, the band folding is due to a superlattice potential, which acts on all the bands simultaneously. On the other hand, the excitons formed between conduction and valence bands with the binding energy overlapped near $E_F$ are more energetically favored, which makes the hybridization caused by the excitonic effect mainly concentrates on the top of the valence band and
the bottom of the conduction band (Fig. 4c).

Further, we discuss the reason for the two-step process of the CDW formation and the asynchronous behavior of band folding. Due to the lack of a clear nesting vector in the Fermi surface (FS) topology, the CDW state is less likely to be induced by the FS nesting. The EPC and excitonic effect are considered as the main candidate for many-body interaction. In the 2D CDW system, the fluctuations could be strong and lead to short-range CDW formation above $T_c$, corresponding to the intermediate state. However, fluctuation itself is incapable of containing the asynchronous band folding behavior. In the case of EPC-dominated CDW states in 2D materials, the folding behavior of different valence bands should always be consistent because of the same lattice distortion origin, which is contrary to the experimental observations. In the case of excitonic condensation, the fluctuation separates the phase diagram into exciton condensate (CDW state) and exciton gas state. Above the $T_c$, the excitonic effect hybridize and renormalize the valence and conduction band without EPC, and the preformed exciton is characterized by a folded valence band in photoemission process. Below the $T_c$, the exciton condensation drives a long-range CDW order formation, with PLD as secondary effect. On top of the purely electronically driven first valence folding, one expects a second valence band folding emerges upon the CDW formation, which is consistent with the experimental observations.

In addition, an identical two-step process with the asynchronous band folding are also found by changing the doping amount, as indicated in the plot of the SWs of the first valence band top at the $\Gamma$ point and the folded second valence band top at the M point as a function of carrier density amount in Fig. 4d. In which, the SW transfer of the second valence band, the indicator of the long-range CDW formation, is found to be very sensitive to the doping level. A critical doping amount of 2% electron per unit
cell could suppress the SW transfer, which is also consistent with the expectation of the excitonic instability induced CDW\textsuperscript{29}.

Our experiment establishes the monolayer 1T-ZrTe\textsubscript{2} as a promising EI candidate material with a highly tunable electronic structure. Moreover, its layered nature is advantageous in constructing van der Waals heterostructures, which is promising in exploiting excitonic physics, such as realizing spin supercurrent by embracing magnetism\textsuperscript{34}. Most importantly, we have found that the characteristic folding behavior induced by EI is fundamentally different from the one only with the EPC effect, which could be widely applicable to distinguish other EI candidates.
**Methods**

**Film growth and STM measurements.** The monolayer 1T-ZrTe$_2$ films were grown by MBE on bilayer graphene (BLG) epitaxially grown on 4H-SiC. The base pressure of the system was \( \sim 5 \times 10^{-10} \) mbar. Zr (99.95%) and Te (99.999%) were evaporated from an electron beam evaporator and thermal cracker cell, respectively. The substrate temperature was held at 330 °C during growth. The growth process was monitored by RHEED. After growth, the samples were transferred under vacuum to STM (VT, Omicron) chamber with a base pressure on \( \sim 3 \times 10^{-10} \) mbar for in situ characterization. Some samples were transferred through a vacuum suitcase to STM (LT, Omicron) for low temperature characterization. STM images were acquired at all temperatures using W-tips.

**ARPES measurements.** In-situ ARPES measurements were performed at Beamline 10.0.1, Advanced Light Source, Lawrence Berkeley National Laboratory. ARPES data were acquired by Scienta R4000 electron analyzer. The system energy resolution and the angular resolution were set to 12 meV and 0.2°. The potassium was evaporated from a SAES Getters alkali metal dispenser to surface dope the thin film samples at the temperature of 10 K. ARPES measurements were also performed at the 03U beamline of the Shanghai Synchrotron Radiation Facility (SSRF) equipped with Scienta-Omicron DA30 electron analyzer. The angular and the energy resolutions were set to 0.2° and 8 ~ 20 meV (dependent on the selected probing photon energy).

**trARPES measurements.** The grown films were transferred into the trARPES load-lock (pressure \( 1 \times 10^{-9} \) Torr) through a vacuum suitcase with a base pressure of \( 3 \times 10^{-10} \) Torr. The trARPES measurements were based on a Ti: Sapphire regenerative amplifier operating at a repetition rate of 300 kHz. We used 1.5 eV linearly polarized IR pulse to excite the sample and used 6.0 eV UV pulse to probe the transient populations of the
occupied and unoccupied band structure at a variable delay time. The overall time resolution of \(70 \pm 5\) fs was extracted from cross-correlations of pump and probe pulses, and \(t_0\) refers to both pulses overlapping in time. The beam profiles for IR and UV were \(69 \times 10^2 \, \mu m^2\) and \(23 \times 30 \, \mu m^2\), respectively. The photo-emitted electrons were collected by a Scienta R4000 analyzer in an ultrahigh vacuum with a base pressure less than \(7 \times 10^{-11}\) Torr. The energy resolution was 40 meV. During the measurement, the sample temperature was maintained at 12 K.

**Theoretical calculation.** The theoretical result as shown in the left panel of Fig. 4b was calculated using the following method: Firstly, the structural relaxation was performed for the \(2 \times 2\) supercell of the ZrTe\(_2\) structure using density functional theory calculation with generalized gradient approximation (GGA) functional implemented in quantum espresso\(^{35}\). The relaxed structure showed the CDW pattern. Secondly, the effective microscopic Hamiltonian for the CDW supercell, including the Zr 3\(d\) and Te 2\(p\) orbitals, was obtained using the Wannier downfolding, implemented in Wannier90\(^{36}\). An energy shift of 1 eV has been implemented on the on-site energies of the Zr 3\(d\) orbitals, in order to make the bandgap of the simulations consistent with the experiment. Thirdly, the bandstructure was calculated for the obtained tight-binding model Hamiltonian, with the wavefunctions projected on the primitive Brillouin zone associated with the original unit cell. Red and blue weights represent the orbital content for Zr and Te respectively.

The theoretical result as shown in the right panel of Fig. 4b was calculated using the following method: Firstly, the density functional theory calculation using quantum espresso\(^{35}\) and the Wannier downfolding for the Zr 3\(d\) and Te 2\(p\) orbitals using Wannier90\(^{36}\) were implemented for the unit cell of ZrTe\(_2\), obtaining the effective microscopic Hamiltonian. An energy shift of 1eV has been applied to the on-site energies of the Zr 3\(d\) orbitals to make consistent with the experimental bandstructure.
Secondly, the bandstructure for the primitive Brillouin zone was obtained using the tight-binding model Hamiltonian. Thirdly, the excitonic interactions were added between the top of the first (or second) valence band and the bottom of the first conduction band with momentum q difference. The Hamiltonian could be written as:

\[ H = H_{\text{tight-binding}} + \sum_{q=q_1,q_2,q_3} \sum_{k} \Delta_1 c_{k,v1}^+ c_{k-q,c1} + \Delta_2 c_{k,v2}^+ c_{k-q,c1} + h.c. \]

in which \( H_{\text{tight-binding}} \) is the tight-binding Hamiltonian obtained using Wannier90, \( q_1 = (0.0, -0.5), q_2 = (0.5, 0.0), q_3 = (-0.5, 0.5) \), \( v1 \) and \( v2 \) represent the first (top) and the second valence bands respectively, \( c1 \) represents the first conduction band, \( \Delta_1 = 0.07eV \) and \( \Delta_2 = 0.005eV \) in the calculation. The obtained bandstructure of this Hamiltonian was plotted on the right panel of Fig. 4B. Red and blue weights represent the orbital content for Zr and Te respectively.
Reference

1. Mott, N. F. The transition to the metallic state. *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics* **6**, 287-309 (1961).

2. Jérome, D., Rice, T. M. & Kohn, W. Excitonic Insulator. *Phys. Rev.* **158**, 462-475 (1967).

3. Kohn, W. Excitonic Phases. *Phys. Rev. Lett.* **19**, 439-442 (1967).

4. Lozovik, Y. E. & Yudson, V. Feasibility of superfluidity of paired spatially separated electrons and holes; a new superconductivity mechanism. *JETP Lett.(USSR)(Engl. Transl.);(United States)* **22**, 11 (1975).

5. Eisenstein, J. & MacDonald, A. H. Bose-Einstein condensation of excitons in bilayer electron systems. *Nature* **432**, 691-694 (2004).

6. Zenker, B., Ihle, D., Bronold, F. X. & Fehske, H. Slave-boson field fluctuation approach to the extended Falicov-Kimball model: Charge, orbital, and excitonic susceptibilities. *Phys. Rev. B* **83**, 235123 (2011).

7. Kunes, J. Excitonic condensation in systems of strongly correlated electrons. *J. Phys.: Condens. Matter* **27**, 333201 (2015).

8. Hu, Y., Venderbos, J. W. & Kane, C. Fractional excitonic insulator. *Phys. Rev. Lett.* **121**, 126601 (2018).

9. Wang, K. *et al.* Electrical control of charged carriers and excitons in atomically thin materials. *Nat. Nanotechnol.* **13**, 128-132 (2018).

10. Ma, L. *et al.* Strongly correlated excitonic insulator in atomic double layers. *Preprint at http://arXiv.org/cond-mat/arXiv:2104.05066* (2021).
11 Kogar, A. et al. Signatures of exciton condensation in a transition metal dichalcogenide. *Science* **358**, 1314-1317 (2017).

12 Rohwer, T. et al. Collapse of long-range charge order tracked by time-resolved photoemission at high momenta. *Nature* **471**, 490-493 (2011).

13 Ye, Z. et al. Probing excitonic dark states in single-layer tungsten disulphide. *Nature* **513**, 214-218 (2014).

14 Cheiwchanchamnangij, T. & Lambrecht, W. R. L. Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS$_2$. *Phys. Rev. B* **85**, 205302 (2012).

15 Ugeda, M. M. et al. Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor. *Nat. Mater.* **13**, 1091-1095 (2014).

16 Liu, G. B. et al. Electronic structures and theoretical modelling of two-dimensional group-VIB transition metal dichalcogenides. *Chem. Soc. Rev.* **44**, 2643-2663 (2015).

17 Chen, P. et al. Charge density wave transition in single-layer titanium diselenide. *Nat. Commun.* **6**, 8943 (2015).

18 Kar, I. et al. Metal-chalcogen bond-length induced electronic phase transition from semiconductor to topological semimetal in ZrX$_2$(X=Se and Te). *Phys. Rev. B* **101**, 165122 (2020).

19 Muhammad, Z. et al. Transition from Semimetal to Semiconductor in ZrTe$_2$ Induced by Se Substitution. *ACS nano* **14**, 835-841 (2019).

20 Tsipas, P. et al. Massless Dirac Fermions in ZrTe$_2$ Semimetal Grown on InAs(111)
by van der Waals Epitaxy. *Acs Nano* **12**, 1696-1703 (2018).

21 Villaos, R. A. B. *et al.* Evolution of the Electronic Properties of ZrX2(X = S, Se, or Te) Thin Films under Varying Thickness. *J. Phys. Chem. C* **125**, 1134-1142 (2021).

22 Rustagi, A. & Kemper, A. F. Photoemission signature of excitons. *Phys. Rev. B* **97**, 235310 (2018).

23 Cercellier, H. *et al.* Evidence for an excitonic insulator phase in 1T-TiSe2. *Phys. Rev. Lett.* **99**, 146403 (2007).

24 Monney, C. *et al.* Exciton Condensation Driving the Periodic Lattice Distortion of 1T-TiSe2. *Phys. Rev. Lett.* **106**, 106404 (2011).

25 Hoesch, M. *et al.* Disorder Quenching of the Charge Density Wave in ZrTe3. *Phys. Rev. Lett.* **122**, 017601 (2019).

26 Qiu, D. Y., da Jornada, F. H. & Louie, S. G. Optical Spectrum of MoS2: Many-Body Effects and Diversity of Exciton States. *Phys. Rev. Lett.* **111**, 216805 (2013).

27 Ramasubramaniam, A. Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides. *Phys. Rev. B* **86**, 115409 (2012).

28 Komsa, H. P. & Krasheninnikov, A. V. Effects of confinement and environment on the electronic structure and exciton binding energy of MoS2 from first principles. *Phys. Rev. B* **86**, 241201 (2012).

29 Chen, C., Singh, B., Lin, H. & Pereira, V. M. Reproduction of the Charge Density Wave Phase Diagram in 1T-TiSe2 Exposes its Excitonic Character. *Phys. Rev. Lett.* **121**, 226602 (2018).
30 Zheng, F. W. et al. Scaling law of the giant Stark effect in boron nitride nanoribbons and nanotubes. *Phys. Rev. B* **78**, 085423 (2008).

31 Zhang, K. N. N. et al. Widely tunable band gap in a multivalley semiconductor SnSe by potassium doping. *Phys. Rev. Mater.* **2**, 054603 (2018).

32 Rossnagel, K. On the origin of charge-density waves in select layered transition-metal dichalcogenides. *J. Phys.: Condens. Matter* **23**, 213001 (2011).

33 Fukutani, K. et al. Detecting photoelectrons from spontaneously formed excitons. *Nat. Phys.* **17**, 1024-1030 (2021).

34 Jiang, Z. Y. et al. Spin-Triplet Excitonic Insulator: The Case of Semihydrogenated Graphene. *Phys. Rev. Lett.* **124**, 166401 (2020).

35 Giannozzi, P. et al. Quantum ESPRESSO toward the exascale. *J. Chem. Phys.* **152**, 154105 (2020).

36 Mostofi, A. A. et al. An updated version of wannier90: A tool for obtaining maximally-localised Wannier functions. *Comput. Phys. Commun.* **185**, 2309-2310 (2014).
Acknowledgements

Research performed at ALS (thin film growth and ARPES) is supported by the Office of Basic Energy Sciences, US DOE under Contract No. DE-AC02-05CH11231. The work at Stanford University and SLAC National Accelerator Laboratory (thin film characterization, theory calculations) was supported by the Office of Basic Energy Sciences, US DOE under Contract No. DE-AC02-76SF00515. Part of this research used Beam line 03U of the Shanghai Synchrotron Radiation Facility, which is supported by ME2 project under Contract No. 11227902 from National Natural Science Foundation of China. A portion of the computational work was performed using the resources of the National Energy Research Scientific Computing Center (NERSC) supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-05CH11231. S. T. acknowledges the financial support from the National Natural Science Foundation of China (No. 11704395, No. 11974370), ‘Strategic Priority Research Program (B)’ of the Chinese Academy of Sciences (No. XDB04010600). D. S. acknowledges the support by National Natural Science Foundation of China (Grant No. U2032208). J. H. and C. H. acknowledge support from the NRF grant funded by the Korean government (MSIT) (No. 2020K1A3A7A09080369 and 2021R1A2C1004266).

Author contributions

S. T., S.-K. M. and Z.-X. S. proposed and designed the research. Y. S. and S. T. performed the MBE growth. Y. S. and S. T. carried out the ARPES measurements and analyzed the ARPES data with help from Z. J., D. S., K. H., J. H., S.-K. M., and Z. L. H. X., J. S. and P. K. carried out the trARPES measurements and analyzed the trARPES data. Y. S., B. W. and J. X. performed the STM measurements and analyzed STM data.
C. J. and T. P. D. carried out the density functional calculations and provided theoretical support. Y. S., S. T., S.-K. M. and Z.-X. S. wrote the manuscript with contributions and comments from all authors.

**Competing interests**

The authors declare no competing financial interests.
Figure 1. Structure and characterization of epitaxially grown monolayer 1T-ZrTe$_2$.

a. Schematic crystal structure of 1T-ZrTe$_2$. 1T-ZrTe$_2$ in the top (top panel) and side (bottom panel) views. b. RHEED patterns of graphene substrate (top panel) and sub-monolayer 1T-ZrTe$_2$ (bottom panel). c. LEED pattern after the film growing on the graphene. d. STM image of monolayer 1T-ZrTe$_2$ at 300 K [$V_{bias} = -2.8$ V, $I = 200$ pA, 200 nm $\times$ 200 nm]. Dark regions correspond to the BLG substrate, and the 1T-ZrTe$_2$ layer is orange, which is in the form of islands with straight boundaries, dressed with a small number of particles that might be amorphous Zr-Te compounds or tiny 1T-ZrTe$_2$ islands. Some 1T-ZrTe$_2$ islands with a corner angle of 120° are identified, implying a hexagonal symmetry of 1T-ZrTe$_2$ single crystal. e. Atomically resolved STM image of a CDW-related 2$\times$2 superstructure at 4.5 K [$V_{bias} = -50$ mV, $I = 200$ pA, 15 nm $\times$ 15nm]. The insert is the corresponding FFT. f. ARPES measured band structure along the $\Gamma$-M direction at $T = 15$ K.
Figure 2. Temperature dependence of CDW state in monolayer 1T-ZrTe₂.

Atomically resolved STM images of 10 nm × 10 nm and corresponding FFT images at 4.5 K [$V_{bias} = -50$ mV, $I = 200$ pA], 77 K [$V_{bias} = 50$ mV, $I = 250$ pA], 116 K [$V_{bias} = -150$ mV, $I = 280$ pA] and 300 K [$V_{bias} = -100$ mV, $I = 300$ pA].

b. The band structures measured along the experimental Γ-M direction at 14 K, 120 K, and 300 K.

c. EDCs measured exactly at M/Γ* (correspond to red dashed lines in Fig. 2b), as a function of temperature. Three peaks are clearly recognized in the spectra measured at $T = 50$ K, corresponding to one conduction band and two folded valence bands, respectively.

d. The evolutions of the size of the bandgap, the intensity of the folded second valence band, and 2×2 superlattice peaks in STM with temperature. At the high-temperature region, it is hard to tell whether the folded first valence band merges into the conduction band or disappears. Different fitting strategies (circles with different colors, see the Supplementary Information for more detail) are employed, and the results show an identical trend.
Figure 3. The two-step process of the CDW formation in monolayer 1T-ZrTe$_2$. a. and c. The band structures measured by ARPES along the Γ-M direction at 15 K (a) and 300 K (c) using 50.6 eV synchrotron radiation light. e. ARPES data along the Γ-M direction taken from surface K-doped sample. The corresponding EDCs are shown in b, d, and f, respectively. g. ARPES snapshots taken before optical pumping and at characteristic pump-probe delays at the Γ point. h. MDCs for the data shown in g. i. and j. Band position (bands are shifted by aligning the second valence band to 15K data for comparison) (i) and spectral weight (normalized by dividing by the maximum spectral weight) (j) of the first valence band at the Γ point along Γ-M direction. There is no apparent difference in the band dispersions and SW of the first valence band between the CDW (15 K) state and the normal state (300 K). In contrast, the interaction-suppressed state (photo-excited and K-doped) shows considerable band renormalization and SW recovery, respectively.
**Figure 4. The origin of CDW phase in monolayer 1T-ZrTe₂.** a. The schematic band diagram of the formation of the CDW state. b. The calculated band structure along the Γ-M direction for CDW driven by PLD and excitonic effect, respectively. c. The schematic diagram of PLD and excitonic effect, respectively. d. The evolution of electronic structure features of CDW state with doping amount.