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Observation of topological superconductivity in a stoichiometric transition metal dichalcogenide 2M-WS₂

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Topological superconductors (TSCs) are unconventional superconductors with bulk superconducting gap and in-gap Majorana states on the boundary that may be used as topological qubits for quantum computation. Despite their importance in both fundamental research and applications, natural TSCs are very rare. Here, combining state of the art synchrotron and laser-based angle-resolved photoemission spectroscopy, we investigated a stoichiometric transition metal dichalcogenide (TMD), 2M-WS₂ with a superconducting transition temperature of 8.8 K (the highest among all TMDs in the natural form up to date) and observed distinctive topological surface states (TSSs). Furthermore, in the superconducting state, we found that the TSSs acquired a nodeless superconducting gap with similar magnitude as that of the bulk states. These discoveries not only evidence 2M-WS₂ as an intrinsic TSC without the need of sensitive composition tuning or sophisticated heterostructures fabrication, but also provide an ideal platform for device applications thanks to its van der Waals layered structure.

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Superconductors and topological matter are two classes of quantum materials with fascinating physical properties^{1,2} and application potentials^{3,4}, and their combination may further give rise to a unique quantum phase, the topological superconductor (TSC). A TSC can host exotic emergent particles such as the Majorana fermion^{1,2}, a particle of its own anti-particle that can not only show remarkable phenomena such as thermal quantum Hall effect⁵, but also serve as a key ingredient for the realization of topological quantum computation—a promising approach to realize the fault-tolerant quantum computation^{1–4,6}.

However, TSCs are rare in nature. Up to date, intrinsic TSC candidates are only found in a few materials, which are either controversial (e.g., Sr_2RuO_4 ^{7,8}) or nonstoichiometric compounds (e.g., $\text{Cu}_x\text{Bi}_2\text{Se}_3$ ^{9,10}, $\text{FeTe}_x\text{Se}_{1-x}$ ^{11–13}, and $\text{Li}(\text{Fe},\text{Co})\text{As}$ ¹⁴) that require fine tuning in composition and inevitably consist of defects^{13,15} unfavorable for device applications. On the other hand, artificial structures combining conventional superconductors and nondegenerate spin states (e.g., topological insulators^{16–19}, quantum anomalous hall insulators²⁰, semiconductors with strong spin-orbit coupling^{21–23}, or ferromagnetic thin film and atomic chains^{24,25}) have been explored, but the need to construct sophisticated heterostructures and the requirement of long superconducting coherence length make this approach material selective.

Recently, a stoichiometric transition metal dichalcogenide (TMD), 2M- WS_2 was proposed as an intrinsic TSC with the highest intrinsic superconducting transition temperature ($T_C =$

8.8 K) among all TMDs in the natural form^{26,27}. The stoichiometry makes the synthesis of high-quality crystals possible, and the layered structure with van der Waals coupling makes it ideal for device fabrication for potential applications.

The superconductivity of 2M- WS_2 was recently confirmed by transport²⁶ and scanning tunneling microscopy/spectroscopy (STM/STS) measurements²⁷, and zero energy peaks in the STS spectra were observed in magnetic vortex cores²⁷, suggesting the possible existence of Majorana bound states (MBSs). However, compelling evidence for the topological electronic structure, including the direct observation of topological surface states (TSSs), the superconducting gap of the TSSs and its temperature evolution, are yet to be found.

In this work, combining the state of the art synchrotron- and laser-based angle-resolved photoemission spectroscopy (ARPES), we not only systematically investigated the band structure of 2M- WS_2 across the full three-dimensional Brillouin zone (BZ) thanks to the large photon energy range of the synchrotron light source, but also successfully observed the TSSs thanks to the high energy and momentum resolution made possible by the laser light source. Furthermore, by carrying out detailed temperature-dependent measurements, the superconducting gap from the TSSs (as well as the bulk states, BSs) was clearly observed below T_C , establishing the TSC nature of 2M- WS_2 .

The mechanism of the topological superconductivity in 2M- WS_2 can be briefly shown in Fig. 1a. Above the superconducting transition ($T > T_C$), 2M- WS_2 is a bulk topological semimetal

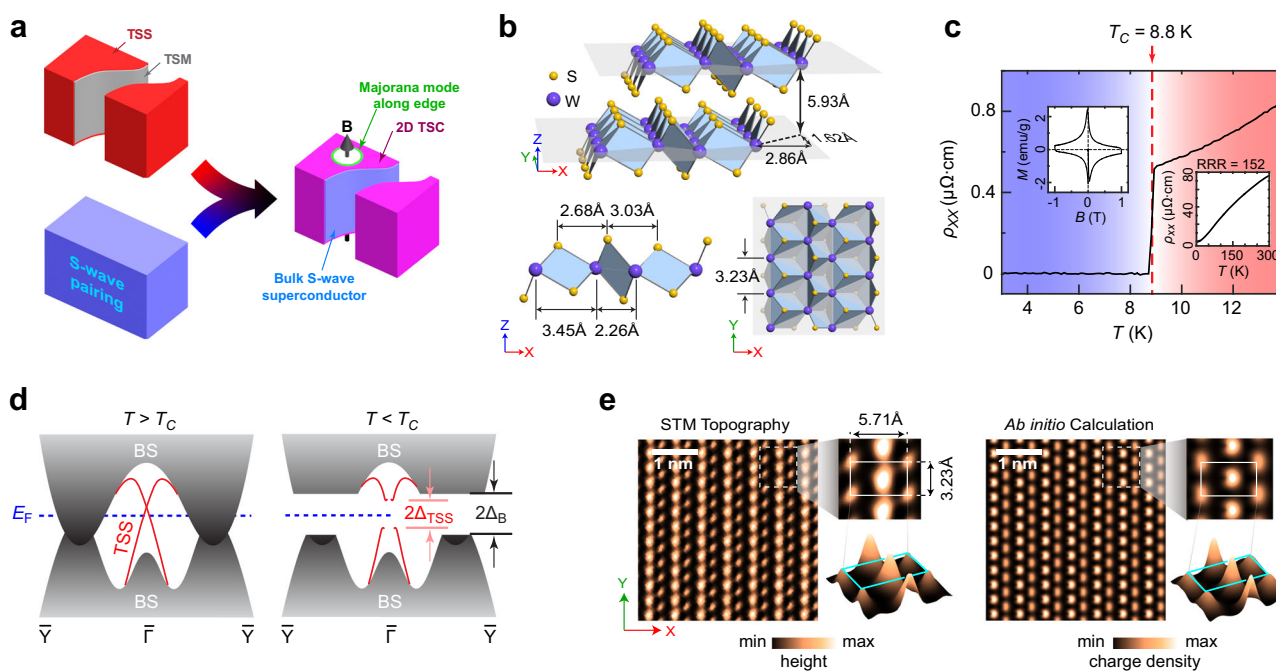


Fig. 1 Introduction to topological superconductivity and general characterizations of 2M- WS_2 . **a** Illustration on the formation of topological superconductivity in 2M- WS_2 (see text for details). Top panel: Topological surface state (TSS, red color) and the bulk topological semimetal (TSM, gray color) of 2M- WS_2 . Bottom left panel: Bulk s-wave superconductivity at $T < T_C$. Right panel: Surface (2D) topological superconductivity (TSC, magenta color) of TSS, induced by the internal proximity effect from the bulk s-wave superconductivity. Majorana state (green circle) can exist at the magnetic vortex core (illustrated by the black arrow and white color region). **b** Top panel: 3D view of the crystal structure, showing two adjacent WS_2 layers offset in the X- and Y-directions. Bottom left panel: Side view. Bottom right panel: Top view of a WS_2 layer. **c** Temperature dependence of resistance shows a sharp superconducting transition at $T_C = 8.8$ K. Left inset: Hysteresis loop of magnetization curve at 2 K showing the Meissner effect and the threshold field value. Right inset: Resistance curve at a large temperature range (3–300 K), showing a residual-resistivity ratio (RRR) of 152. **d** Illustration of the band structure of 2M- WS_2 in the normal (left) and superconducting states (right). The bulk states (BSs) are shown in solid gray color and the TSSs as solid red lines. In the superconducting states, the BSs and TSSs are both gapped (more details can be found in Fig. 4 below). E_F , Fermi energy. Δ_{TSS} and Δ_B , superconducting gap of the TSS and the BS, respectively. **e** Left panel: Surface topography of a cleaved sample from scanning tunneling microscopy (STM) measurement shows the perfect topmost S-atom layer without defects. Zoomed in plots with more information can be found in insets on the right. Right panel: Ab initio calculation of the charge density from the topmost S-atom layer shows excellent agreement with the STM measurement.

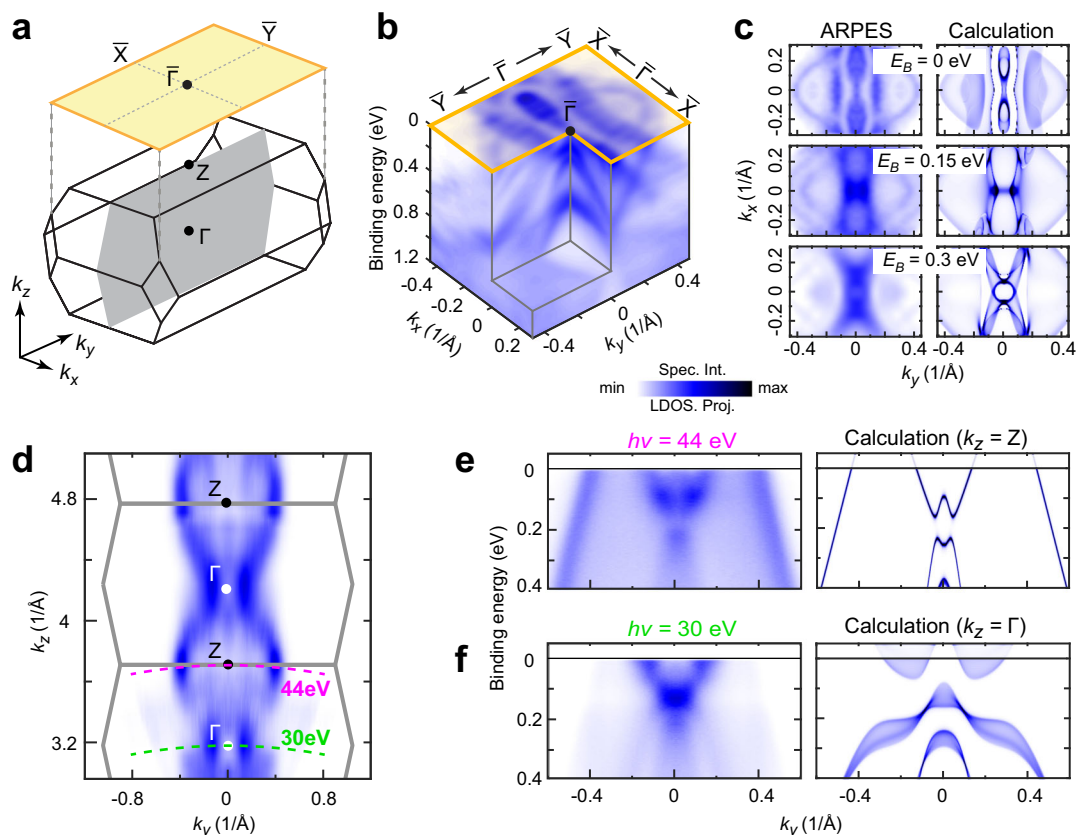


Fig. 2 Overall electronic structures across the 3D Brillouin zone. **a** Schematic of the bulk (bottom) and (100) surface (top) Brillouin zone (BZ) of 2M-WS₂ with high symmetry points labeled. The gray plane in the bulk BZ indicates the k_y - k_z measurement plane in **d**. **b** 3D intensity plot of photoemission spectra around the $\bar{\Gamma}$ point, showing the band dispersions and the resulting FSs. **c** Comparison showing nice agreement between experiments (left) and ab initio calculations (right) of three constant energy contours at different binding energies. For better comparison with calculations, the experimental plot has been symmetrized with respect to the $k_y = 0$ plane according to the crystal symmetry (same below). **d** Photoemission intensity plot of the k_y - k_z plane ($k_x = 0$, the gray plane in **a**), showing clear k_z dispersion (and thus the 3D nature) of 2M-WS₂. Green and magenta curves indicate the k_z momentum loci (probed by 30 eV and 44 eV photons, respectively) of the two band dispersions shown in **(e)** and **(f)**, respectively. **e, f** Comparisons between photoemission dispersions (left) and corresponding calculations (right) cutting across high symmetry k_z loci (around $\bar{\Gamma}$ and Z points, respectively, and k_z Integration window around $\bar{\Gamma}$ and Z points is $0.06 \pi/a$, where a is the out-of-plane lattice constant) in the bulk BZ as indicated in **d**.

(TSM) with nontrivial TSSs; while in the superconducting state ($T < T_C$), the bulk s-wave superconductivity can induce superconductivity to the TSSs by internal proximity effect, thus realizing a topologically nontrivial superconducting state of spin-helical electrons on the surface, as illustrated in Fig. 1a. In addition, if a magnetic domain is formed, the domain boundary (green line in the right panel of Fig. 1a) can host the MBS^{1,2,6}, which, if bound with a magnetic flux quantum, obey non-abelian statistics^{1,2} and can be used to form the quantum-bit for topological quantum computation^{1-4,6}. Similar self-proximity-induced TSC states have been proposed in iron-based superconductors¹¹⁻¹⁴ and PbTaSe₂²⁸.

Results

Sample characterization. Like many TMD compounds, 2M-WS₂ is a van der Waals layered crystal (space group $C_{2/m}$, No. 12). As shown in Fig. 1b, within each WS₂ layer, the distorted octahedral structure forms quasi-1D chains of W and S atoms along Y direction (see Fig. 1b); and the adjacent WS₂ layers are offset to each other along X- and Y-directions by $\Delta X = 2.86$ Å and $\Delta Y = 1.62$ Å, respectively (Fig. 1b, and more details on the crystal structure are shown in Supplementary Fig. 1). The high quality of the crystals used in this work was confirmed by X-ray diffraction (Supplementary Fig. 2), the large residual-resistivity ratio (RRR = 152, Fig. 1c, right inset), and the sharp superconducting transition

($\Delta T = 0.2$ K, Fig. 1c). In fact, the T_C (8.8 K) of 2M-WS₂ is the highest among all intrinsic TMD compounds under ambient conditions up to date²⁶.

The nontrivial topological electronic structure of 2M-WS₂ was theoretically proposed in a recent work^{26,29} and is confirmed by our ab initio calculations: 2M-WS₂ is a TSM in its normal state with the TSSs located at the center of the surface BZ (sketched in the left panel of Fig. 1d); in the superconducting state (right panel of Fig. 1d), both the BSs and TSSs are expected to be gapped (as observed in our measurements which will be discussed in details later).

Due to the weak van der Waals interaction between WS₂ layers, the cleaved surfaces for the ARPES study in this work are of high quality. As illustrated in Fig. 1e, a topography map from our STM measurement (left panel of Fig. 1e) reveals a defect-free region of the topmost S-atom layer with clear quasi-1D chains, in excellent agreement with the ab initio simulation (right panel of Fig. 1e and more details in Supplementary Fig. 3).

General electronic structure of 2M-WS₂. To investigate the overall electronic structure of 2M-WS₂, we first carried out synchrotron-based ARPES measurements, and Fig. 2b shows a typical set of experimental band structure, containing rich details that can be successfully reproduced by ab initio calculations (see Fig. 2c and Supplementary Fig. 4 for more details). Thanks to the

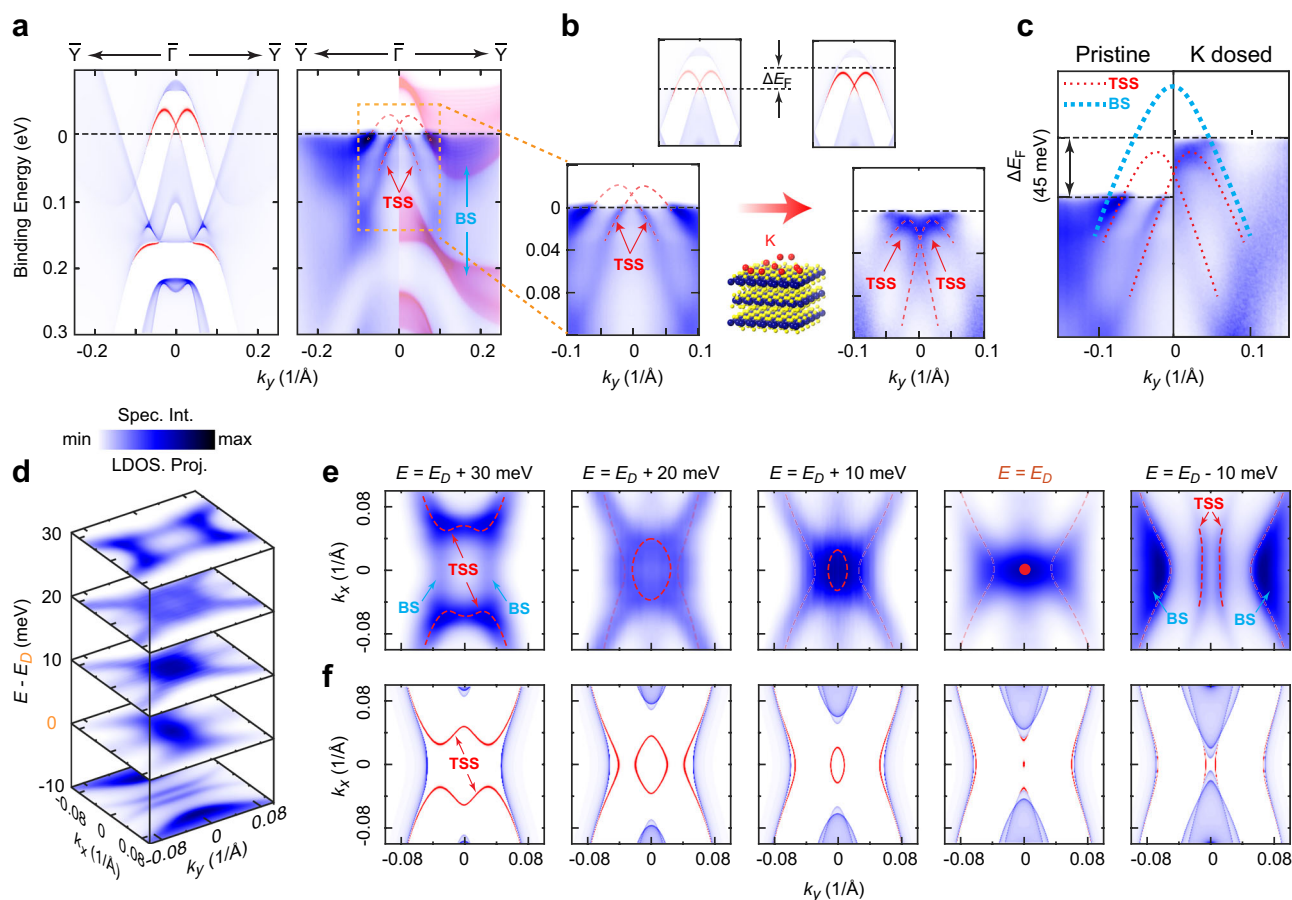


Fig. 3 Band structure of the topological surface states. **a** Comparison between slab calculation (left) and photoemission (right) band dispersions along $\bar{\Gamma} - \bar{\Gamma} - \bar{\Gamma}$ direction. The TSSs are highlighted by red color (left) and indicated by the red dashed lines (right). The bulk dispersions around Γ point (red shaded area, k_z integration window is $0.06 \pi/a$) are overlapped to better illustrate the TSSs (right). **b** Bottom left: Zoomed in dispersion of the TSS in the pristine sample covering the yellow box area in the right panel of **a**. The red dashed lines show the TSS dispersions. Top left: Schematic of the calculated dispersions for comparison and the E_F is marked as a black dashed line. Bottom right: Full dispersion of the TSS band observed after in situ potassium (K) doping (illustrated as the middle inset). Top right: Calculated dispersions with the new E_F position indicated after the K-dosing, showing a clear upshift ΔE_F . **c** Side-by-side comparison of TSS dispersions before (left panel) and after (right panel) K-doping, shows a ΔE_F of ~ 45 meV. **d** Stacking plots of the experimental constant energy contours (CECs) at different energy close to the Dirac point, showing rapid evolution. **e, f** Comparison between experimental (e) and ab initio calculated (f) CECs evolution near the Dirac point showing overall agreement. For clarity, the CECs of the TSSs are highlighted by red color. In **e**, the faded red dashed lines represent the less visible TSSs due to the hybridization to the bulk states.

wide photon energy range of the synchrotron light source, we were able to do detailed photon-energy-dependent measurements to examine the electronic structures across multiple 3D BZs along the k_z direction, as illustrated in Fig. 2d (see Supplementary Fig. 5). With the k_z electronic structures identified, we can study band dispersions at different k_z momenta using specific photon energies. As two examples, the dispersions cut across the bulk Γ ($k_z = 0$) and Z ($k_z = \pi/a$, where a is the out-of-plane lattice constant) points can be accessed by 30 and 44 eV photons, respectively (see Fig. 2d); and the comparison between experiments and ab initio calculations (Fig. 2e, f) shows nice overall consistency (see Supplementary Fig. 6).

Topological surface states of 2M-WS₂. According to our calculation and the previous theory work²⁶, the TSSs in 2M-WS₂ reside only in a close vicinity around the center ($\bar{\Gamma}$ point) of the surface BZ, thus very high energy and momentum resolution is needed to resolve the TSS band structures. Therefore, we adopted the laser-based ARPES ($h\nu = 6.994$ eV, $\Delta E = 0.9$ meV and $\Delta k = 0.003 \text{ \AA}^{-1}$) in the search for TSSs.

Indeed, as presented in Fig. 3a, the TSSs near the $\bar{\Gamma}$ in the calculation (left panel) were clearly seen in measurement (right panel). However, in the pristine sample, the upper part of the TSSs was above the Fermi-level (E_F) and could not be seen experimentally, and slight n-type doping was needed to lift the E_F to reveal the whole TSS dispersions. As expected, after in situ potassium doping, we successfully raised the E_F by ~ 45 meV and the whole TSS dispersions could be observed (Fig. 3b, c), in excellent agreement with the calculation. Besides the dispersions, the existence of the TSSs can also be seen in the constant energy contours of the band structures (Fig. 3d–f), again in good agreement with the calculations.

Superconducting gap of 2M-WS₂. Having identified the TSSs, we then investigate the superconducting state properties of the TSSs and BSs. The superconducting gaps of both the TSSs and BSs from a pristine sample are clearly seen in the left panel of Fig. 4a (spectra were symmetrized with respect to E_F to get rid of the Fermi-Dirac function cutoff), which disappear when $T > T_C$ (right panel of Fig. 4a). The evolution of the superconducting gap

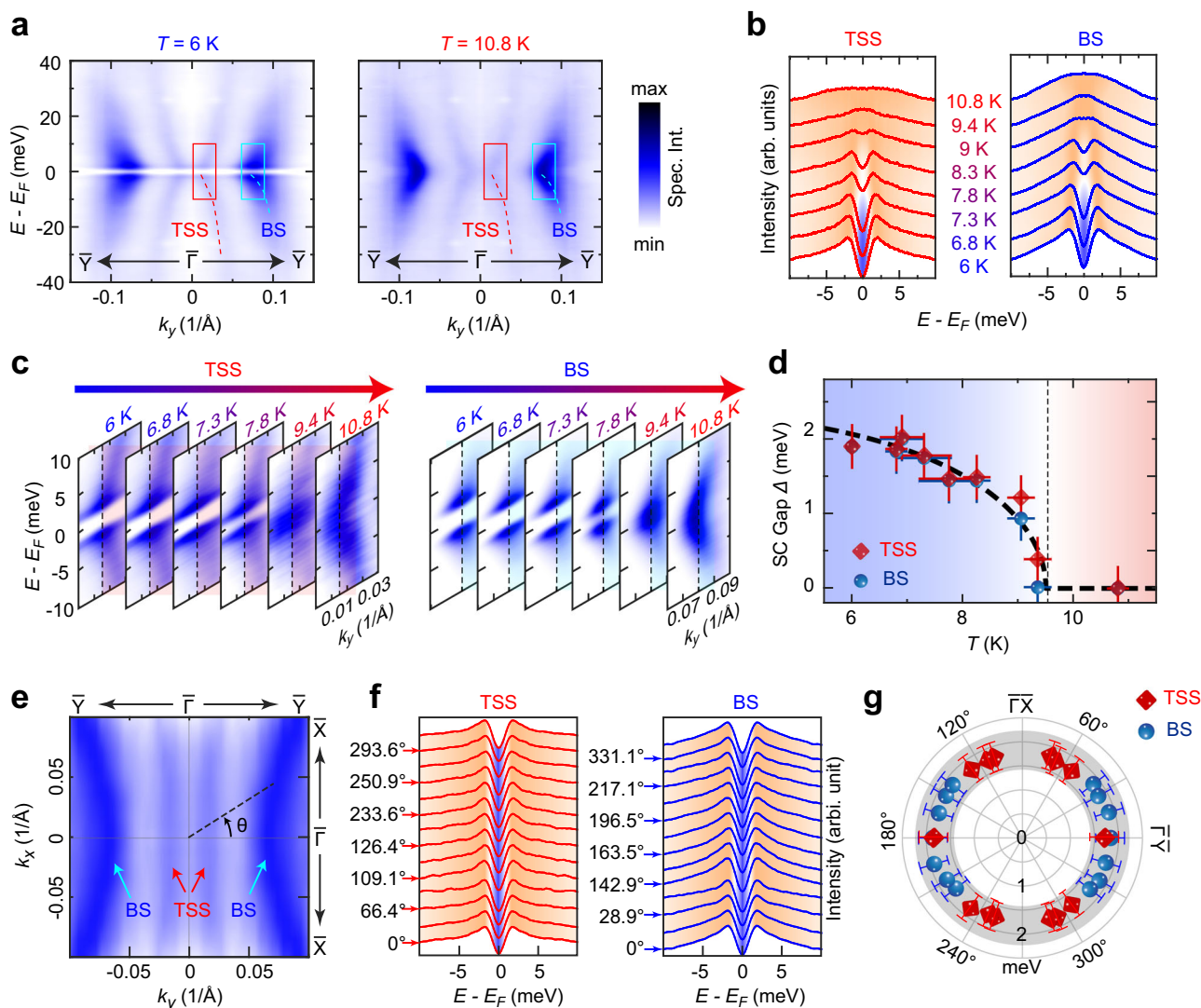


Fig. 4 Superconducting gap from the TSS and BS. **a** Photoemission spectra intensity plots of the band dispersions along $\bar{Y}-\bar{\Gamma}-\bar{Y}$ direction in the superconducting (left) and normal (right) states show clear superconducting gaps from both the TSS (red dashed lines) and BS (blue dashed lines, which show clear k_z broadening and form the bulk α pocket in Supplementary Fig. 5). Note that to better illustrate the gap, the spectra are symmetrized in energy direction with respect to E_F (same in plots **b**, **c**, **f** below). **b** Temperature dependence of the energy distribution curves (EDCs) at the Fermi momentum (k_F) of TSS (left) and BS (right) shows the opening of the superconducting gap below $T = 9$ K. **c** Temperature dependence of the band dispersions of the TSS (left) and BS (right) across k_F (the momentum and energy range plotted here corresponds to the red and cyan rectangle area marked in **a**, again shows the clear superconducting gap below T_C). **d** Temperature evolution of the superconducting gap from the TSS and BS (details on the gap extraction from the ARPES spectra function can be found in Supplementary Fig. 7) is consistent with a mean field temperature dependence, as indicated by the black dashed line. Horizontal error bars represent the temperature variance during the measurements. Vertical error bars represent the confidence intervals of the fitting under 95% confidence level. **e** Constant energy contour plot (intensity integrated between E_F to $E_F + 10$ meV) shows the k_F loci of the TSS and BS ($T = 6$ K). θ defined the angle used in **f**, **g**. **f** EDCs from the k_F loci of different θ angles at the superconducting state ($T = 6$ K) show that the superconducting gap magnitude of both TSS (left) and BS (right) are nearly isotropic. **g** Plot of the superconducting gap size as a function of θ angle for both TSS (red symbols) and BS (blue symbols), showing similar magnitude. Error bars represent the energy resolution determined by ARPES spectra on multi-crystalline gold.

with temperature can be seen in the energy distribution curves (EDCs, see Fig. 4b) or directly from the spectra plot (Fig. 4c). The superconducting gaps from both the TSSs and BSs are consistent with a mean field temperature dependence (Fig. 4d, more details about the gap extraction can be found in Supplementary Fig. 7).

Finally, benefited from the inherent momentum resolution of ARPES measurements, we were able to study the in-plane superconducting gap distribution (Fig. 4e–g), which shows a nodeless s-wave-like symmetry for both TSSs and BSs, making 2M-WS₂ an ideal system of 2D TSC on the surface¹⁶. In addition, the s-wave gap and the velocity anisotropy near the Dirac point of

TSSs revealed in our measurements (see Fig. 3e and Supplementary Fig. 8) suggest an anisotropy of the MBSS: the angular distribution of $\sim h v_F / \Delta$ (where h , v_F , and Δ are the Planck constant, Fermi-velocity, and the superconducting gap, respectively) from our experiment provides a direct momentum-resolved perspective that explains the recent STM report of such anisotropy²⁷.

Discussion

Our unambiguous observation of superconducting gap developed on the TSSs of 2M-WS₂ provide the key ingredient for TSC based

on the Fu-Kane proposal^{2,16}. The helical spin texture of the TSS is confirmed by previous first principle calculation²⁶ and should survive possible surface-bulk hybridization^{30,31} since it is well separated from the BS in both energy and momentum space. Moreover, spin polarization persists in the TSSs of n-doped topological insulators^{30,31}, topological metals³², and even the topological surface resonance states of Dirac semimetals³³, which exhibits robustness of spin texture in TSSs against surface-bulk hybridization. Therefore, the spin-momentum locked surface states could result in effective p-wave superconductivity in 2M-WS₂, namely a TSC state.

As shown in Fig. 3a–c, 2M-WS₂ hosts a Rashba-like TSS, which is a reminiscence of semiconductor–superconductor TSC scheme. As the upper and lower branches of the TSS must eventually merged in the spin unpolarized BSs, the E_F position is critical: (1) when only one pair of spin-polarized bands crosses E_F , 2M-WS₂ falls to the superconducting topological insulator scenario, as proposed in Cu_xBi₂Se₃^{9,10}, whereas (2) two pairs of spin-polarized bands cross E_F , 2M-WS₂ falls to the strong spin–orbit coupling semiconductor–superconductor scenario, as proposed in Al–InAs heterostructure²³. For the latter situation, the topology of the system can be tuned by the Zeeman coupling V_Z , which is due to the external magnetic field as shown in Fig. 1a, chemical potential μ , and the self-proximity-induced pairing gap Δ_0 ^{21,34}. The compatibility and versatility of the TSS configuration in 2M-WS₂ with the appearance of Majorana states require further investigation.

The formation of the TSC state in stoichiometric 2M-WS₂, together with its layered structure with van der Waals coupling, makes it ideal for device fabrication and thus a promising platform to explore the phenomena of MBSs and their application in topological quantum computation. Moreover, the discovery of the TSC state in 2M-WS₂ further enriches the interesting phenomena hosted by TMDs (e.g., gate and pressure-tunable superconductivity^{19,35–39}, charge density waves^{38–41}, Mott insulators^{38,39}, gyrotropic electronic orders⁴², moiré-trapped valley excitons⁴³, type-II Dirac and Weyl semimetals^{44–46}, etc.), thus enabling the study of these properties and their interplay, as well as the design of novel devices for new applications. We note that, after the acceptance of this manuscript, self-proximity induced TSC was also theoretically proposed in RRuB₂ (R=Y, Lu)⁴⁷.

Methods

Sample preparation. 2M-WS₂ single crystals were prepared by the deintercalation of interlayer potassium cations from K_{0.7}WS₂ crystals. For the synthesis of K_{0.7}WS₂, K₂S₂ (prepared via liquid ammonia), W (99.9%, Alfa Aesar) and S (99.9%, Alfa Aesar) were mixed by the stoichiometric ratios and ground in an argon-filled glovebox. The mixtures were pressed into a pellet and sealed in the evacuated quartz tube. The tube was heated at 850 °C for 2000 min and slowly cooled to 550 °C at a rate of 0.1 °C/min. The synthesized K_{0.7}WS₂ (0.1 g) was oxidized chemically by K₂Cr₂O₇ (0.01 mol/L) in aqueous H₂SO₄ (50 mL, 0.02 mol/L) at room temperature for 1 h. Finally, the 2M-WS₂ crystals were obtained after washing in distilled water for several times and drying in the vacuum oven at room temperature²⁶.

Angle-resolved photoemission spectroscopy. Synchrotron-based ARPES data were taken at Spectromicroscopy of Elettra Synchrotron, Italy (proposal no. 20190294), beamline I05 of Diamond Light Source (DLS), UK (proposal no. SI125135-1), and beamline BL5-2 of Stanford Synchrotron Radiation Laboratory (SSRL), Stanford Linear Accelerator Center (SLAC), USA (proposal no. 5069). The samples were cleaved in situ and aligned the $\bar{\Gamma} - \bar{Y}$ direction parallel to the analyzer slit. The measurements were under ultra-high vacuum below 5×10^{-11} Torr. Data were collected by an internal movable electron energy analyzer at Spectromicroscopy of Elettra Synchrotron, a Scienta R4000 analyzer at I05 beamline of DLS, UK, and a DA30L analyzer at beamline BL5-2 of SSRL, SLAC, USA. The total energy resolutions were 30 meV at Spectromicroscopy, and below 10 meV at beamline I05 of DLS and beamline BL5-2 of SSRL, respectively. The angle resolution was 0.2°.

High-resolution laser-based ARPES measurements were performed at home-built setups ($h\nu = 6.994$ eV) at ShanghaiTech University and Tsinghua University. The samples were cleaved in situ and aligned the $\bar{\Gamma} - \bar{Y}$ direction parallel to the

analyzer slit. The measurements were under ultra-high vacuum below 5×10^{-11} Torr. Data were collected by a DA30L analyzer. The total ultimate energy and angle resolutions were 0.9 meV and 0.2°, respectively.

Scanning tunneling microscopy/spectroscopy. In the STM experiment, cleaved single crystals were transferred to a cryogenic stage in the ultra-high vacuum ($< 2 \times 10^{-10}$ Torr) and kept at 80 K. Pt–Ir tips were used for imaging, which were all decorated and calibrated on the surface of silver islands grown on p-type Si (111) -7×7 .

Single-crystal X-ray diffraction. Single-crystal XRD was performed using Mo target by the Rigaku Oxford Diffraction at the Department of Physics, University of Oxford. The beam spot size is 10–200 μm in diameter. The data were collected and analyzed by the CrysAlisPro software.

Transport measurement. Transport measurements were taken in the Physical Properties Measurement System (PPMS) of Quantum design.

First principle calculations. The first principle calculations were carried out in the framework of the generalized gradient approximation (GGA) functional of the density functional theory through employing the Vienna ab initio simulation package (VASP) with the projector augmented wave pseudopotentials⁴⁸. The experimental lattice constants were taken, and inner positions were obtained through full relaxation with a total energy tolerance 10^{-5} eV. The SOC effect was self-consistently included. Modified Becke–Johnson (mBJ) functional was employed for the double check and the electronic structure and topological nature remains unchanged.

Data availability

The datasets that support the findings of this study are available from the corresponding author upon reasonable request. CCDC 1853656 contains the crystallographic data in the Supporting Information for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033.

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Author contributions

Y.L.C. conceived the experiments. Y.W.L. and H.J. Zheng carried out ARPES measurements with the assistance of Z.K.L., L.X.Y., Y.J.C., C.Chen, A.J.L., D.P., L.X.X., D.H.L., M.H., A.B., S.W.J., C.Cacho, and Y.H.; Y.W.L. and H.J. Zheng performed the data analysis on the ARPES results. Y.Q.F., J.P., and F.Q.H. synthesized and characterized the bulk single crystals. D.Q.Z., W.J.S., and H.J. Zhang performed ab initio calculations. H.J. Zheng, S.L., and M.X.W. carried out STM measurements. Y.W.L. wrote the first draft of the paper. Y.L.C., Z.K.L., L.X.Y., H.J. Zhang, Y.H., and L.F. contributed to the revision of the manuscript. All authors contributed to the scientific planning and discussions.

Competing interests

The authors declare no competing interests.

Additional information

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