

General Framework Enabling Polarity-Tunable Time-Reversal Symmetric Superconducting Diode Effects in Gate-Defined Homojunctions

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Symmetry breaking underlies various nonreciprocal transport phenomena. A well-known example is the semiconductor p - n junction diode, a cornerstone of modern electronics. Its superconducting counterpart—the superconducting diode effect (SDE)—has recently attracted intense interest due to its potential in ultra-low-power superconducting circuits. While most SDEs reported so far involve either explicit or spontaneous breaking of time-reversal symmetry (TRS), a comprehensive theoretical framework remains elusive. Moreover, a general mechanism enabling TRS-preserving SDEs with minimal dependence on material or device architecture has yet to be established. Here, we report polarity-tunable SDEs without breaking TRS, realized in superconducting n - n , p - n , and p - p homojunctions defined via local protonic gates in multilayer NbSe₂. The local gates induce partial proton intercalation, generating a built-in proton concentration gradient across the transition zone between the gated and ungated regions—closely resembling the depletion layer in conventional semiconductor diodes. We find that the observed SDE arises from electric-field-driven variation of the proton concentration gradient in the transition region, which asymmetrically modulates the critical current: suppressing it in one direction and enhancing it in the other. This local-gate-driven, TRS-preserving mechanism offers a general and scalable strategy for realizing nonreciprocal superconducting transport. Our findings establish a material-agnostic platform for SDEs, broadly applicable across two-dimensional (2D) superconductors.

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I. INTRODUCTION

Nonreciprocal transport—the ability of a system to conduct current or other physical quantities differently, depending on direction—is a hallmark of symmetry breaking in condensed matter systems. It underpins a wide range of functional devices, from classical semiconductor

diodes to nonreciprocal magnetic and photonic responses in topological and correlated quantum materials [1–3]. In recent years, the pursuit of nondissipative, directionally selective transport has drawn increasing interest in the context of superconductors, where dissipationless current flow offers transformative potential for low-power electronics. Yet, achieving nonreciprocal superconducting transport poses fundamental challenges, as superconductivity inherently respects time-reversal and inversion symmetries. Overcoming these constraints has led to the discovery of the superconducting diode effect (SDE)—a phenomenon in which a supercurrent can flow preferentially in one direction while being suppressed or blocked in the opposite direction. Understanding and controlling this effect has become a central question in the design of next-generation superconducting quantum devices.

Recently, theoretical efforts have explored the SDE and other nonreciprocal superconducting transport phenomena

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in Josephson junctions and 2D superconductors [4–11], while experimental demonstrations have spanned a broad range of platforms, including noncentrosymmetric superconductors [12–15], Josephson junctions [16–26], superconductor/magnet heterostructures [27–29], twisted moiré systems [30–33], thin films [34,35], and patterned nanostructures or nanoflakes [36–41]. In most cases, the breaking of inversion symmetry alone is not sufficient to generate the SDE. Instead, breaking TRS is typically required, either explicitly—via applied magnetic fields or proximity to magnetic layers [12,17–21,23–29]—or implicitly, through trapped vortices [33,38,39], spontaneous or current-induced TRS breaking [22,30–32,40,41], or strain-induced electric polarization [15]. Despite this growing body of work, a unified theoretical framework for understanding SDEs remains incomplete, and the realization of TRS-preserving SDEs—-independent of magnetic fields or complex device architectures—remains a key challenge. A general and material-agnostic strategy for achieving non-reciprocal superconducting transport without breaking TRS would therefore be of broad significance.

In this study, we demonstrate a TRS-preserving SDE in multilayer NbSe₂, a conventional 2D superconductor, by creating superconducting *n-n*, *p-n*, and *p-p* homojunctions using localized protonic gates. SDEs are observed in all three homojunction types, with the *n-n* junction exhibiting diode polarity opposite to that of the *p-n* and *p-p* junctions. Crucially, the observed diode effect is accompanied by a symmetric magnetic-field dependence of the asymmetric critical current ΔI_c , indicating the absence of TRS breaking. We identify the underlying mechanism as an electric-field-driven variation of the proton concentration gradient across the transition zone between the gated and ungated regions, which modulates the local superconducting properties and directionally tunes the critical current. This local-gate-driven, TRS-preserving mechanism does not rely on exotic material properties or complex interface engineering, offering a broadly applicable platform for realizing non-reciprocal superconducting functionalities in a wide range of 2D systems.

II. RESULTS AND DISCUSSION

A. Carrier-dependent T_c in multilayer NbSe₂

Pristine NbSe₂ exhibits electron-doped superconductivity with an onset superconducting transition temperature of $T_c = 6.9$ K and a high electron carrier density [see Fig. S1(a) in Supplemental Material [42]]. Applying a protonic gate, however, we find T_c can be dramatically modulated. Figure 1(a) illustrates the gate-dependent superconducting transition temperature T_c in a typical NbSe₂ nanoflake (sample #1) with a thickness of 21 nm. Specifically, we find that a small gate voltage of $V_g = 2.6$ V can dramatically decrease the onset T_c to 6.56 K. Increasing the gate voltage from $V_g = 2.6$ V to 8.3 V, the onset T_c of sample #1 further decreases from 6.56 K to

5.85 K. Similar gate dependence of T_c is also observed in sample #2 [Fig. S1(b) in Supplemental Material [42]]. Besides the high tunability of T_c , both carrier density and carrier type can also be dramatically modulated by a protonic gate, as revealed by the gate-dependent Hall resistances in Fig. 1(b). The large modulation of both T_c and carrier density under a protonic gate allows for construction of a T_c -carrier density phase diagram of NbSe₂, as shown in Fig. 1(c). Upon applying a gate voltage, the electron carrier density n_e initially increases from $3.68 \times 10^{22} \text{ cm}^{-3}$ in pristine NbSe₂ to $10.1 \times 10^{22} \text{ cm}^{-3}$ accompanied by a suppression of T_c from 6.9 K to 6.38 K, resulting in $dn_e/dT_c < 0$ in sample #1. Interestingly, the carrier type switches from electrons to holes near a critical gate voltage V^* ($V^* = 5.5$ V in sample #1) with T_c at around 6.3 K, which is also in line with other gated samples [see Supplemental Material [42], Figs. S2(a) and S2(b)]. This behavior can be understood by the gating-induced Lifshitz transition (see Fig. S5 in Supplemental Material [42]). Subsequently, the hole carrier density n_h decreases as T_c decreases further, leading to $dn_h/dT_c > 0$, as can be seen in Fig. 1(c). Even more intriguingly, we find that the in-plane upper critical field $H_{\parallel c2}$ is significantly enhanced in proton-gated NbSe₂. According to the 2D Ginzburg-Landau theory, the temperature-dependent $H_{\parallel c2}(T)$ follows the relation $H_{\parallel c2}(T) = H_{\parallel c2}^*(1 - T/T_c)^{1+\chi}$. Figures 1(d) and 1(e) present the in-plane magnetoresistance of an ungated sample #5 and a gated sample #6 at various temperatures, respectively. Clearly, the upper critical magnetic field is substantially larger in the gated device compared to the ungated sample. Figure 1(f) shows the fitted temperature-dependent $H_{\parallel c2}^*$, which increases from 17 T in sample #5 to 24.2 T in sample #6 at $V_g = 6$ V. This finding is further confirmed in sample #7 (see Fig. S3 in Supplemental Material [42]), in which both in-plane ($H_{\parallel c2}$) and out-of-plane upper critical fields ($H_{\perp c2}$) have been enhanced by a protonic gate. Moreover, we also find that the anisotropy ratio of the upper critical field $H_{\parallel c2}/H_{\perp c2}$ increases from 5.67 at 0 V to 6.37 at 6.0 V in sample #7. Previous studies have shown that the intercalation of NbSe₂ bulk crystals with cations from ionic liquids can significantly expand the interlayer spacing, enhancing Ising superconductivity and resulting in a large $H_{\parallel c2}^*$ [43]. However, in proton-gated NbSe₂ multilayers, the interlayer spacing remains unchanged (see Fig. S4 in Supplemental Material [42]). First-principles calculations reveal that proton intercalation enhances the spin splitting at the K point, giving rise to large Ising-type SOC (see Fig. S5 in Supplemental Material [42]).

B. Superconducting *n-n* and *p-n* junctions

The high tunability of both carrier density (and type) and superconductivity enables the construction of superconducting homojunctions in multilayer NbSe₂ using local protonic gates. The gate-defined homojunction is composed of locally gated superconducting regions (*G*) and

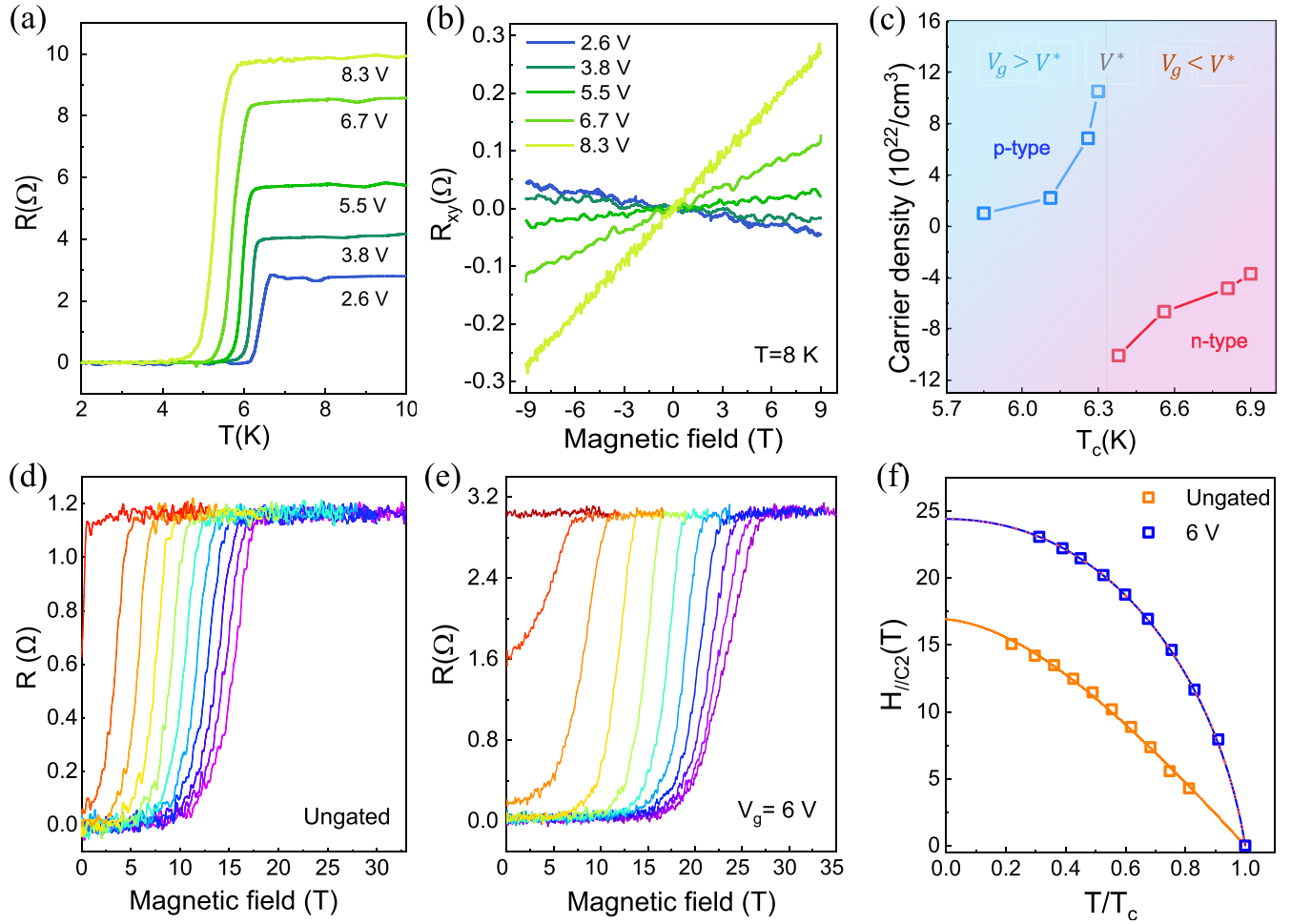


FIG. 1. (a) Gate-dependent R - T curves in a NbSe_2 multilayer (sample #1) with a thickness of 21 nm. The superconducting onset temperature T_c decreases from 6.9 K in pristine NbSe_2 to 5.85 K as the gate voltage is swept to 8.3 V. (b) Gate-dependent Hall resistance in sample #1 at 8 K. (c) T_c -carrier density phase diagram in gated NbSe_2 multilayers. Carrier type changes the sign at a critical voltage V^* with $T_c = 6.3$ K. (d) In-plane magnetic-field-dependent resistance under various temperatures in an ungated sample #5 (19 nm). The temperatures are 1.7 K, 2.2 K, 2.8 K, 3.3 K, 3.8 K, 4.3 K, 4.8 K, 5.3 K, 5.8 K, 6.3 K, and 6.8 K from the purple curves to the red curves. (e) In-plane magnetic-field-dependent resistance under various temperatures in a gated sample #6 (18 nm) at $V_g = 6$ V. The temperatures are 1.6 K, 2.5 K, 3 K, 3.5 K, 4 K, 4.5 K, 5 K, 5.5 K, 6 K, 6.5 K, and 7.5 K from the purple curves to the red curves. (f) Theoretical fitting of temperature-dependent upper critical field $H_{||c2}(T)$ via the 2D Ginzburg-Landau formula. Here, $H_{||c2}(T)$ is defined as the magnetic field at which the resistance drops to 50% of the normal-state resistance. The fitting yields an upper critical field $H_{||c2}^* = 24.2$ T in sample #6 at 6 V.

ungated superconducting regions (N), as illustrated in Fig. 2(a). Current is applied across the junction, and voltage is measured between the two sides of the junction, with a typical channel length of approximately $2\ \mu\text{m}$. Given the one-to-one correspondence among gate voltage V_g , carrier concentration $n_{e/h}$, and superconducting transition temperature T_c established above, we can now utilize T_c as a reliable parameter for identifying the types of superconducting homojunctions in the following discussion. When region “ G ” is tuned by a small local gate voltage such that its T_c lies between 6.3 K and 6.9 K, a superconducting n - n junction is formed, with electron Cooper pairs present on both sides. In this case, a small proton concentration

gradient is established in the junction region, as illustrated by the gray dashed line in Fig. 2(b). Figure 2(c) presents the temperature-resistance (R - T) curve of a superconducting homojunction (device J1) tuned by a local gate with $V_g = 3.2$ V. A single superconducting transition is observed with T_c at around 6.75 K, indicating the formation of a typical n - n junction. This single transition likely results from the short channel length and a relatively small proton concentration gradient across the junction. To examine the presence of nonreciprocal transport in the n - n junction, current is applied across the junction at 2 K under zero external magnetic fields with $I+$ ($I-$) defined as the current direction flowing from G (N) to N (G).

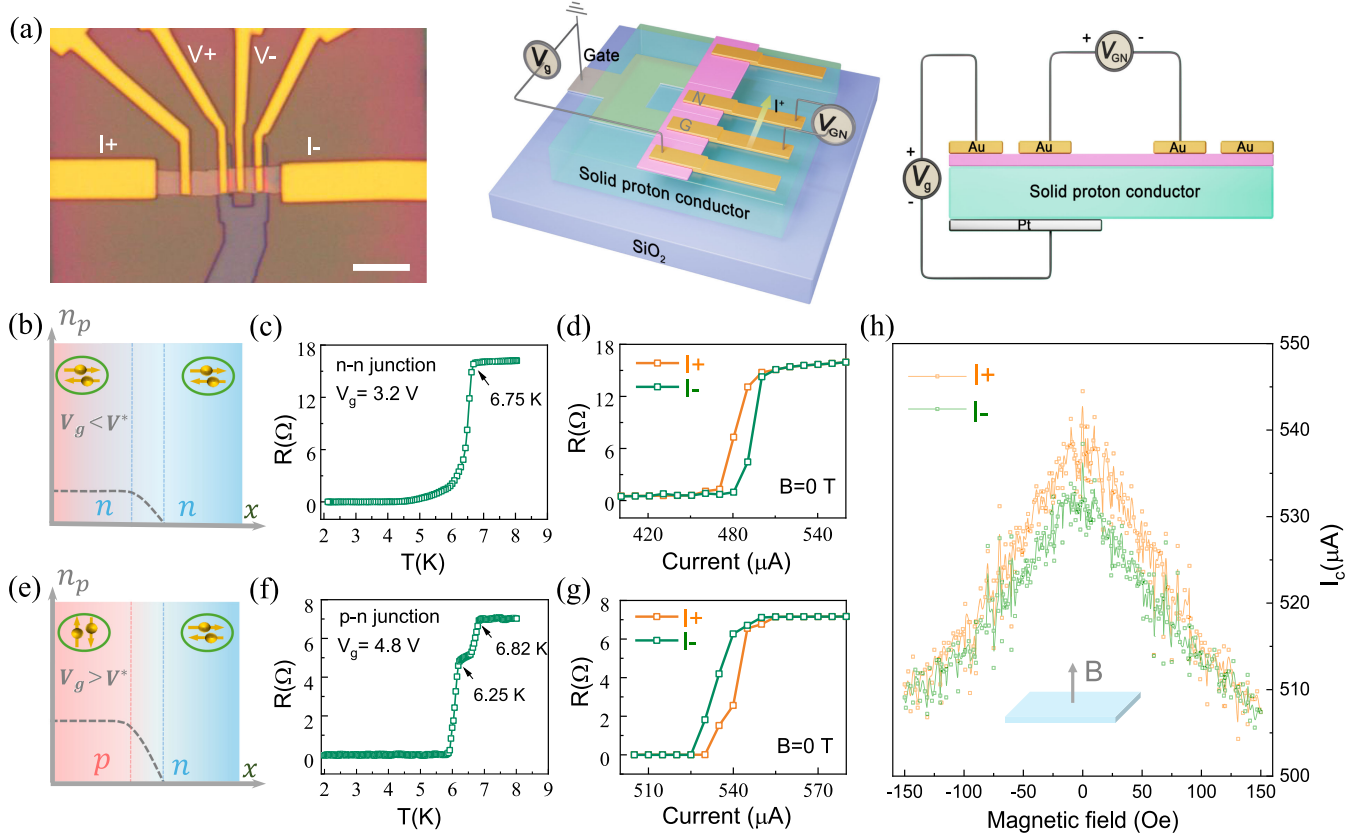


FIG. 2. (a) Optical image of a superconducting homojunction defined by a local protonic gate (left) and the schematic for device layout (middle and right). Scale bar: 10 μm . (b) Schematic for superconducting n - n defined by a local protonic gate. The area between two blue dashed lines denotes the junction region between two voltage probes. (c),(d) R - T curve and magnetic-field-free SDE in a superconducting n - n junction (device J1), correspondingly, with a local gate $V_g = 3.2$ V. (e) Schematic for superconducting p - n tuned by a local protonic gate. The area between the red and blue dashed lines denotes the junction region between two voltage probes. (f),(g) R - T curve and magnetic-field-free SDE in superconducting p - n junction (device J3), correspondingly, with a local gate $V_g = 4.8$ V. The diode polarity in the superconducting p - n junction is opposite to that in the n - n junction. (h) Out-of-plane magnetic-field dependence of asymmetric critical current ΔI_c in the superconducting p - n junction J3. SDE exhibits a symmetric dependence on out-of-plane magnetic fields.

The corresponding resistance of the homojunction is recorded. As shown in Fig. 2(d), the current-resistance (I - R) curves under opposite current directions reveal that the critical current in the forward direction, i.e., $I_c^+ < |I_c^-|$. Similarly, nonreciprocal behavior is also observed in another superconducting n - n junction (device J5), as shown in Figs. S6(a)–6(c) of the Supplemental Material [42]. These observations demonstrate a magnetic-field-free SDE in the superconducting n - n junction.

To further investigate the SDE in NbSe_2 homojunctions, we examine superconducting p - n junctions. To construct a superconducting p - n junction, the homojunction is tuned by a moderate gate voltage so that the gated superconducting region becomes hole doped ($T_c < 6.3$ K) while the ungated region remains electron doped (with $T_c > 6.3$ K), featuring hole Cooper pairs in region G and electron Cooper pairs in region N . In such a p - n junction, a larger

proton concentration gradient forms at the interface, as shown by the gray dashed line in Fig. 2(e). Such a p - n junction can be further proven by Hall measurements in different regions of the sample, as shown in Fig. S7 in the Supplemental Material [42], in which the gated region exhibits hole-type carriers while the ungated region has electron-type carriers. Figure 2(f) shows the typical R - T curve of such a p - n junction (device J3). In contrast to the n - n case, device J3, under a moderate gate voltage ($V_g = 4.8$ V), exhibits two distinct superconducting transition temperatures: with $T_c^1 = 6.82$ K and $T_c^2 = 6.25$ K corresponding to region N and region G . Interestingly, a magnetic-field-free SDE is also identified in this p - n junction at low temperatures but with reversed polarity compared to the n - n junction, i.e., $I_c^+ > |I_c^-|$, as illustrated in Fig. 2(g) as well as Fig. S8 in the Supplemental Material [42]. The gate-tuned transition from an n - n junction to a p - n junction with opposite diode polarity has also been

realized in device J5, as shown in Fig. S6 in the Supplemental Material [42].

To unveil the underlying mechanism of the SDE, we study the magnetic-field dependence of the asymmetric critical current $\Delta I_c = I_c^+ - |I_c^-|$. For simplicity, this analysis focuses on the p - n junction J3. As shown in Fig. 2(h), an out-of-plane magnetic field of approximately 80 Oe is sufficient to suppress the SDE. In contrast, the SDE remains robust under in-plane magnetic fields up to 3 T (see Fig. S9 in Supplemental Material [42]), likely due to the strong Ising-type spin-orbit coupling in proton-intercalated NbSe₂. More remarkably, the SDE exhibits a symmetric dependence on both out-of-plane and in-plane magnetic fields (see Figs. S10–S15 in Supplemental Material [42]), indicating TRS is not necessarily broken. This finding confirms the realization of a time-reversal symmetric SDE in both n - n and p - n superconducting homojunctions. Note that ΔI_c fluctuates with the applied magnetic field, as shown in Fig. 2(h) and Fig. S16 in the Supplemental Material [42], possibly due to the variation of proton displacement in each measurement caused by the applied magnetic field, current, or local proton dynamics.

C. Superconducting p - p junction

Because of their high mobility, protons can diffuse from region G to region N under a large local gate voltage. Consequently, the onset superconducting transition temperature T_c across the entire voltage channel can decrease to below 6.3 K, giving rise to a superconducting p - p junction with a significant proton concentration gradient at the junction interface, as illustrated by the gray dashed line in Fig. 3(a). To realize such a junction, a new homojunction device (J4) was fabricated and tuned by a large local gate voltage. Figure 3(b) [see also Fig. S17(a) in Supplemental Material [42]] shows the gate-dependent T_c of device J4. A single onset superconducting transition temperature in J4 is identified with $T_c = 6.22$ K at $V_g = 5.7$ V, indicating the formation of a superconducting p - p junction. As the gate voltage is increased from 5.7 V to 7.5 V, T_c decreases monotonically to 5.94 K, with each R-T curve displaying only one superconducting transition [see Fig. S17(a) in Supplemental Material [42]], probably due to the small variation of proton concentration between two voltage probes. Remarkably, large SDEs with asymmetric critical currents $I_c^+ > |I_c^-|$ are observed at zero magnetic field at 2 K with $V_g = 6.1$ V, 6.9 V, and 7.5 V, respectively, as shown in Figs. 3(c)–3(e). It is also evident that both ΔI_c and critical current I_c decrease as the gate voltage is swept to 7.5 V. Specifically, $\Delta I_c(I_c)$ decreases from 45 μ A (around 550 μ A) at $V_g = 6.1$ V to 24 μ A (around 230 μ A) at $V_g = 7.5$ V. The diode efficiency $\gamma = |\Delta I_c| / (I_c^+ + |I_c^-|)$ is found to be 4.2%, 5.7%, and 6.3%, at $V_g = 6.1$ V, 6.9 V, and 7.5 V, respectively. As previously discussed, the Ising-type SOC is enhanced as T_c decreases, resulting in a larger in-plane upper critical field. It can thus

be expected that the SDEs in the p - p homojunction with lower T_c will remain robust under high in-plane magnetic fields. This expectation is confirmed in Fig. 3(f) [see also Fig. S17(b) in Supplemental Material [42]], which shows that, while the critical current is significantly suppressed by an in-plane magnetic field of up to 9 T, the asymmetric critical current ΔI_c remains nearly unchanged. This robustness is consistent with strong Ising SOC induced by proton intercalation. The maximum diode efficiency was found to be 8.4% at $V_g = 6.1$ V with an in-plane magnetic field of 9 T.

The SDEs observed in NbSe₂ homojunctions occur in the absence of conventional TRS-breaking ingredients, such as external magnetic fields, ferromagnetic proximity effects, or intrinsic mechanisms causing spontaneous TRS breaking, which indicates the emergence of a new mechanism rooted in proton dynamics at the homojunction interface. Taking Fig. 3(c) as an example, regions I and III correspond to the fully superconducting and metallic states, respectively, and their I-R relationships are straightforward to understand. Therefore, we focus on understanding the I-R behavior in region II, which is key to uncovering the origin of the resistance difference ΔR . We note that the local critical current I_c depends on the local proton concentration, $I_c = I_c(n_p)$. Under an applied electric field, intercalated protons are displaced within a limited distance r_0 in the metal, described by

$$eE = D_0 \frac{d(\Delta n_p)}{dx} e^{l_0/r_0}, \quad (1)$$

where l_0 is the length of the metal region and Δn_p is the proton density variation. The exponential function is introduced to guarantee consistency for the full metal case. This picture can be specified further. Experimental data illustrate that $I_c(n_p)$ decreases monotonically with increasing proton intercalation, as can be seen in Figs. 3(c)–3(e), where I_c is reduced as the gate voltage is swept from 6.1 V to 7.5 V. An electric field (or a voltage drop) induces local displacement of protons intercalated between the layers, which is analogous to the gate-induced proton migration observed in 2D superconductors. Importantly, current-induced proton displacement can be ruled out, as no hysteresis is observed between the forward and reverse current sweeps, as shown by the SDEs in device J6 under various gate voltages (see Fig. S18 in Supplemental Material [42]). Note that the SDE polarity in device J6 exhibits a sign reversal in each measurement cycle which will be discussed later.

In a typical superconducting homojunction [Fig. 4(a)], a proton density gradient forms within the measurement region, directly breaking inversion symmetry—an essential prerequisite for the SDE. This region exhibits a series of superconductor-metal transitions at different proton concentrations, each characterized by distinct critical currents.

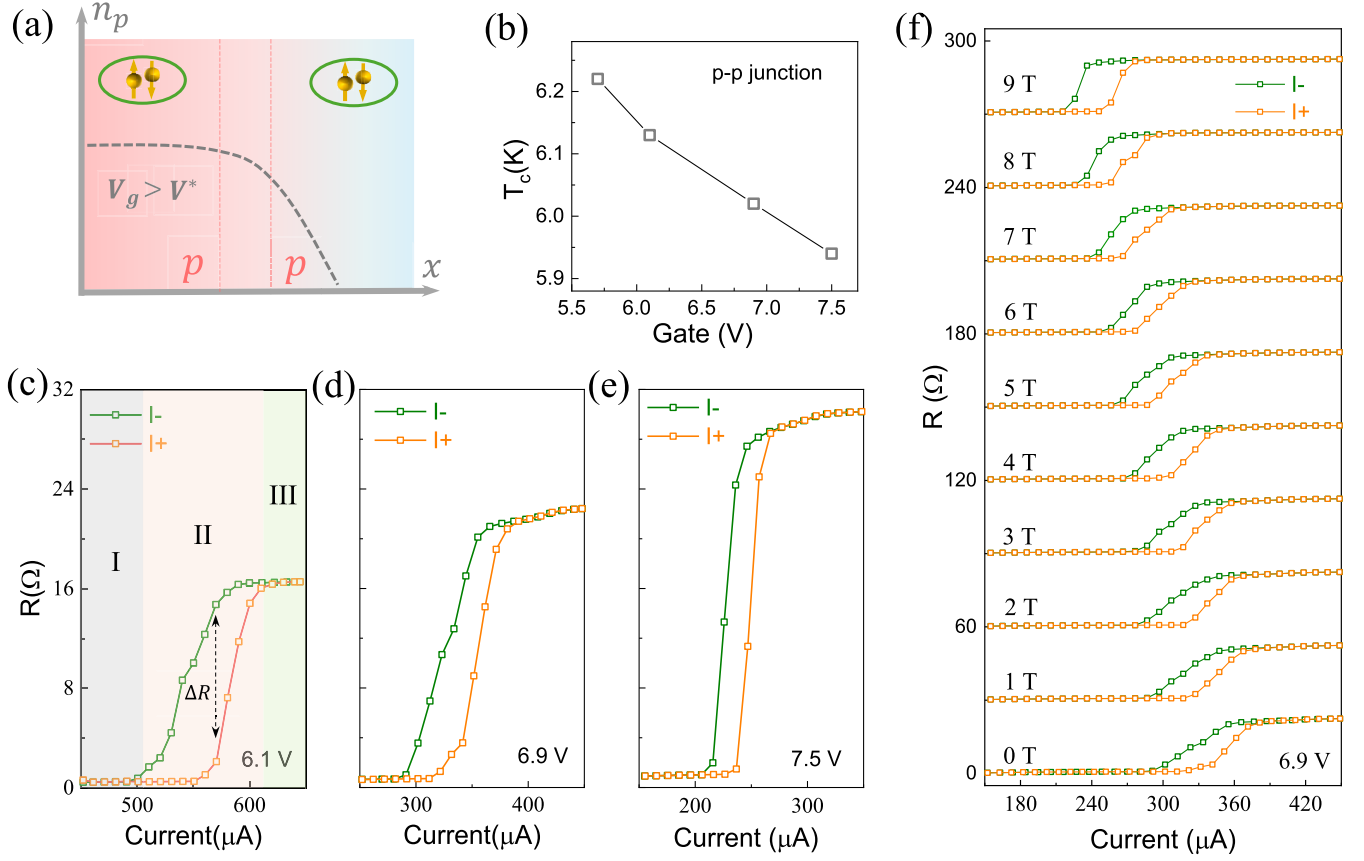


FIG. 3. (a) Schematic for a superconducting p - p junction. The area between two red dashed lines denotes the junction region between two voltage probes. (b) Gate-dependent T_c in device J4. Device J4 exhibits only one single onset temperature under each gate voltage (probably due to the small variation of proton concentration between two voltage probes) with $T_c < 6.3$ K, indicating the formation of a p - p junction. (c)–(e) Gate-dependent SDEs in device J4 at 2 K. Both amplitudes of ΔI_c and critical current are gradually suppressed as the gate voltage increases from 6.1 V to 7.5 V. (f) SDEs at 6.9 V in device J4 under various in-plane magnetic fields. SDEs still survive at a large in-plane magnetic field of 9 T, suggesting large Ising-type SOC. All curves are offset vertically for clarity.

For simplicity, we model the region as separated by a dynamic “transition wall,” between superconducting and metallic domains [Figs. 4(b) and 4(c)]. The observed SDE arises from electric-field-driven proton displacement, which induces two resistance differences, ΔR_1 and ΔR_2 .

- (1) Resistance asymmetry from transition-wall displacement (ΔR_1). When current flows forward from region G to region N [Fig. 4(b)], the local proton density near the transition wall increases due to electric-field-driven displacement, enlarging the metallic region. Upon current reversal, this region shrinks. The resulting resistance difference is

$$\Delta R_1 = 2\rho[n_{p0}(x_c)]\Delta x_c. \quad (2)$$

Here, $n_{p0}(x)$ is the initial proton density without current, x_c is the location of the transition wall, and $\pm\Delta x_c$ measures the enlarged or shrunken displacement of the transition wall.

- (2) Resistance asymmetry from nonlinear proton-modulated resistivity (ΔR_2). The local resistivity

$\rho(n_p)$ in the metallic region exhibits strong non-linearity mediated by proton concentration, which leads to an additional resistance asymmetry:

$$\Delta R_2 = 2 \int_{x_E}^{x_c} dx \left(\frac{\partial \rho}{\partial n_p} \right)_{n_p=n_{p0}(x)} \Delta n_p(x), \quad (3)$$

where $x_E = x_c - l_0$ is the coordinate of the metal region edge.

To analyze this result, we assume a linear proton distribution and a power-law resistivity model:

$$n_{p0}(x) = n_{pE} \left(1 - \frac{x - x_E}{L} \right), \quad \rho(n_p) = \rho_0 + \lambda \left(\frac{n_p}{\bar{n}_p} \right)^\nu, \quad (4)$$

with $\lambda, \nu > 0$ and a reference concentration $\bar{n}_p$. We always have $\Delta R_1 > 0$. However, $\Delta R_2 < 0$ when $0 < \nu < 1$, and $\Delta R_2 > 0$ once $\nu > 1$ (see Sec. IV). The total resistance asymmetry is

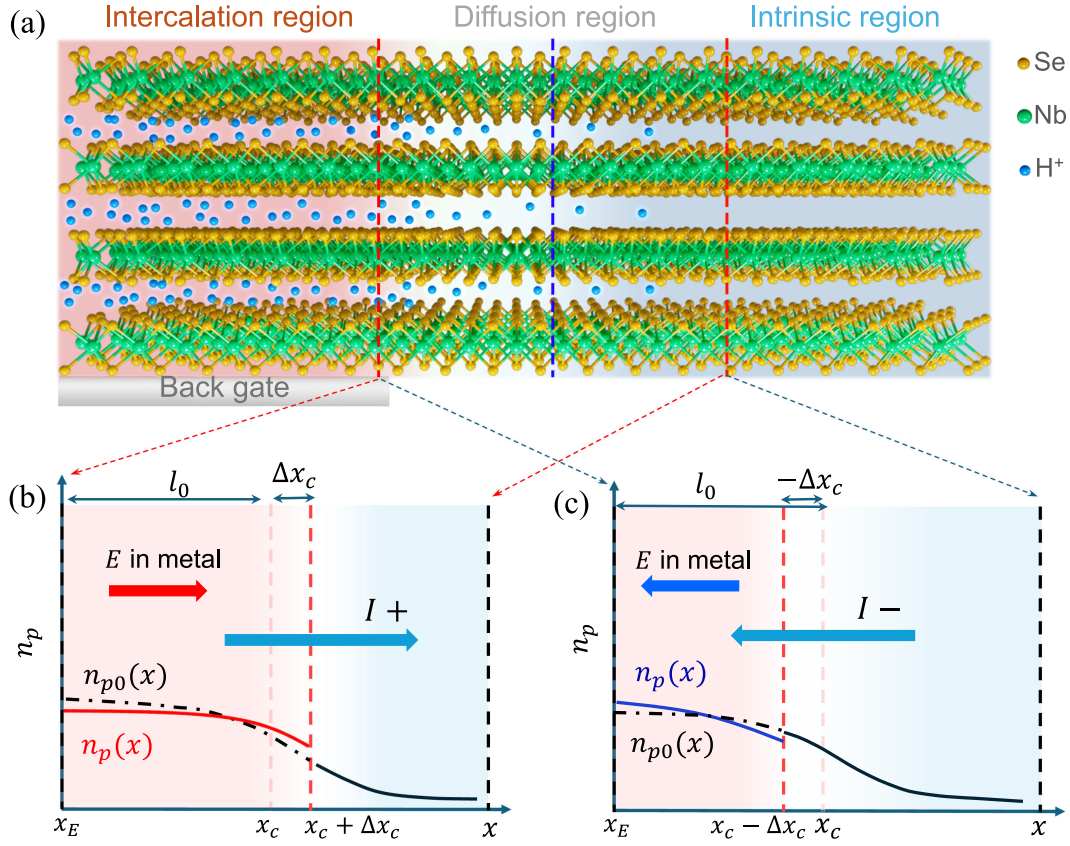


FIG. 4. (a) Schematic for the device. The red side is the gated region (G), and the blue side is the ungated region (N). The region between black dashed lines is where the experiment is implemented. The red dashed line indicates the transition wall between the metal and superconducting regions. The blue dots stand for protons. (b),(c) Displacement of transition wall under the proton dynamic. Here, x is the coordinate along the junction, and the y axis is for proton concentration. The metal and superconductor regions are highlighted by light red and blue, respectively. The light red dashed line labels the reference transition wall without applying current. The black dash-dotted line and the black solid line represent the proton density distribution in the metallic and superconducting regions, respectively, in the absence of applied current. When current is applied, the electric field E in metal aligns with the current. Accordingly, the dark red dashed lines denote the new balanced transition wall. The red and blue solid lines demonstrate the proton density redistribution in the metal region with forward and backward currents, respectively.

$$\Delta R = R^- - R^+ = \Delta R_2 - \Delta R_1. \quad (5)$$

Obviously, $R^- < R^+$ for a small ν , and $R^- > R^+$ for a larger ν , enabling a sign-tunable SDE.

Combining experimental observations and the above theoretical analysis, the mechanism behind the TRS SDE and polarity switch becomes clear. As illustrated in Fig. 1(b), the electron carrier concentration n_e increases as the proton concentration n_p increases, resulting in $dn_e/dn_p > 0$. Once $T_c < 6.38$ K, the carrier type changes from electron to hole, and n_h decreases as n_p increases further. Importantly, resistivity increases with proton concentration ($dp/dn_p > 0$) due to enhanced scattering [see Fig. 1(a)]. In n - n homojunctions (low n_p), although resistivity increases with the intercalation of protons ($dp/dn_p > 0$), the positive dn_e/dn_p indicates an increase of carrier density n_e , which may compensate for the

increase of resistivity, usually resulting in a relatively small ν . Hence, the SDE in an n - n junction is generally predominant by ΔR_1 , the total resistance difference $\Delta R = \Delta R_2 - \Delta R_1 < 0$, indicating $R^- < R^+$ (or $|I_c^-| > I_c^+$) on I-R curves near superconductor-to-metal transition, as shown in Fig. 2(c). In p - n or p - p homojunctions ($dn_h/dn_p < 0$), however, both increased n_p and decreased n_h cause a dramatic rise in resistivity, leading to a highly nonlinear dependence of $\rho(n_p)$ with large ν . The polarity of SDE in p - n or p - p junctions is mainly determined by the competition between ΔR_2 and ΔR_1 . For $\nu > 3$ (see Fig. S19 in Supplemental Material [42]), the total resistance difference in p - n or p - p junctions has $\Delta R = \Delta R_2 - \Delta R_1 > 0$ (or $|I_c^-| < I_c^+$), which explains the polarity-tunable diode effect observed experimentally. It is worth noting that gate-dependent resistivity is also influenced by intercalation sites and rates. Consequently, the value of ν in Eq. (4) fluctuates greatly in different devices and may even

have $\nu > 1$ in specialized n - n junctions. As a result, the competition between ΔR_2 and ΔR_1 may happen even in a superconducting n - n junction, leading to a polarity switch of SDE in a single measurement cycle. Such polarity switches of SDE can be seen in device J6 (Fig. S18 in Supplemental Material [42]). Half-wave rectifications were also obtained in device J6 in Fig. S20 of the Supplemental Material [42] to illustrate the high stability and practicality of the device. By employing the same method, we constructed superconducting homojunctions based on the 2D superconductor CsV_3Sb_5 and reproduced such SDEs as shown in Fig. S21 of the Supplemental Material [42], which illustrates the universality of this mechanism.

We note that the observed SDE is not a trivial consequence of the superposition of out-of-plane and in-plane electric fields but instead reflects a distinct mechanism for nonreciprocal superconducting transport. Unlike conventional SDEs, where no voltage is generated when the device exits the superconducting state, a finite voltage is always produced in the metal region of the NbSe_2 homojunctions due to the proton-concentration gradient induced by local protonic gating. This behavior is consistent with the flattened I-R characteristics observed in Fig. 3(c). More importantly, the essential origin of the SDE in NbSe_2 homojunctions lies in the electric-field-driven proton displacement in the metal region: The asymmetric proton distribution along the electric-field direction directly leads to $I_c^+ \neq |I_c^-|$, giving rise to nonreciprocal superconducting transport without breaking TRS. Furthermore, the polarity reversal of the SDE requires a nonlinear dependence of the resistivity on the proton-density gradient, which cannot be captured by a simple effective electric-field description but instead relies on the multiband electronic structure generically present near the Fermi energy in two-dimensional van der Waals superconductors. Based on these considerations, our work establishes a general route to realizing nonreciprocal superconducting transport while preserving TRS and provides concrete guidance for the choice of material platforms.

III. CONCLUSIONS

In summary, we have successfully engineered superconducting n - n , p - n , and p - p homojunctions in multilayer NbSe_2 tuned by local protonic gates. SDEs under TRS emerge in all three types of homojunctions induced by the electric-field-driven variation of the proton concentration gradient across the transition zone between the gated and ungated regions. Notably, we observe that the diode polarity in n - n homojunctions is reversed compared to that in p - n and p - p homojunctions. Remarkably, the large SDEs in superconducting p - p homojunctions are immune to high in-plane magnetic fields, a feature attributed to the strong Ising-type spin-orbit coupling induced by protonic gating in NbSe_2 multilayers. Our results offer a general framework for realizing nonreciprocal transport phenomena under TRS with minimal dependence on material or

device architecture, providing a versatile approach for engineering nonreciprocal superconducting transport in a wide range of materials.

IV. METHODS

A. Preparation of solid proton conductor

The solid protonic electrolyte was prepared by the sol-gel processes via mixing the tetraethyl orthosilicate (from Alfa Aesar), ethanol, deionized water, and phosphoric acid (as a proton source, from Alfa Aesar, 85% wt%). The mixed solution was stirred at room temperature for 2 h and annealed at 60 °C for another 2 h. Before the use of a solid protonic electrolyte, a local gate electrode (Pt) with a typical thickness of 10 nm was prepared on SiO_2 . To prepare a solid proton conductor, a PMMA window with a typical size of 80 $\mu\text{m} \times 80 \mu\text{m}$ on a Pt electrode was prepatterned by EBL followed by spin coating of a solid protonic electrolyte. Finally, the substrate was baked at 150 °C followed by a lift-off process.

B. Device fabrication and transport measurements

The 2H- NbSe_2 has a hexagonal lattice structure in the a - b plane and crystallizes along the c axis with space group $P6_3/mmc$ [44]. Multilayer NbSe_2 nanoflakes, typically 10–20 nm thick, were mechanically exfoliated from bulk crystals with an onset superconducting transition temperature of $T_c = 6.9$ K, close to that of the bulk. To investigate the effect of protonic gating, the NbSe_2 flakes were dry transferred onto solid proton conductors [45], followed by electron beam lithography (EBL) and deposition of Au/Ti electrodes via sputtering. Transport measurements were performed in a commercial Physical Property Measurement System (PPMS DynaCool) with a magnetic field up to 9 T. To decrease the leaking current during the gating, voltage was swept at 250 K. Once the resistance was changed, the sample was quickly cooled down to low temperatures for magnetotransport measurements.

C. Derivation of the resistance asymmetry

Combining Eq. (1), the conservation law of proton number, and Ohm's law, we find the variation for the proton concentration under a forward current density J is

$$\Delta n_p(x) = \frac{e|J|}{Dl_0} \int_{x_E}^{x_c} dx' \int_{x'}^x dx'' \rho(x''). \quad (6)$$

The displacement of the transition wall is determined by

$$\Delta x_c = - \left(\frac{\partial n_{p0}}{\partial x} \right)_{x=x_c}^{-1} \Delta n_p(x_c). \quad (7)$$

We deduce from Eq. (6) that $\Delta n_p(x_c)$ is always positive. Thus, Δx_c as well as ΔR_1 are always positive. Plugging in

Eqs. (2)–(4), (6) and (7), the analytical expressions for ΔR_1 and ΔR_2 become

$$\Delta R_1 = \frac{2e|J|\rho_0^2 L^2}{DX_0 n_{pE}} [1 + b_\nu(1 - X_0)^\nu] f(\nu, X_0), \quad (8)$$

$$\Delta R_2 = \frac{2e|J|\rho_0^2 L^2}{DX_0 n_{pE}} b_\nu r(\nu, X_0). \quad (9)$$

The dimensionless parameters are $X_0 = (l_0/L)$, $b_\nu = (\lambda/\rho_0)(n_{pE}/\bar{n}_p)^\nu$, and $D = D_0 e^{l_0/r_0}$. The dimensionless functions are

$$f(\nu, X_0) = \frac{1}{2} X_0^2 + \frac{b_\nu}{\nu + 1} \times \left\{ \frac{1}{\nu + 2} [1 - (1 - X_0)^{\nu+2}] - X_0(1 - X_0)^{\nu+1} \right\}, \quad (10)$$

$$r(\nu, X_0) = \frac{\nu X_0}{\nu + 1} [1 - (1 - X_0)^{\nu+1}] + \frac{\nu X_0 b_\nu}{(\nu + 1)(2\nu + 1)} \times [1 - (1 - X_0)^{2\nu+1}] - [1 - (1 - X_0)^\nu] \times \left\{ X_0 \left(1 - \frac{1}{2} X_0 \right) + \frac{b_\nu}{(\nu + 1)(\nu + 2)} \times [1 - (1 - X_0)^{\nu+2}] \right\}. \quad (11)$$

The sign of the function $r(\nu, X_0)$ is clear: $r(\nu, X_0) < 0$ when $0 < \nu < 1$, and $r(\nu, X_0) > 0$ when $\nu > 1$.

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G. Z. and M. T. conceived and supervised the project. H. Z. and C. W. fabricated the devices. H. Z., C. W., G. Z.,

S. P., J. C., H. W., C. X., and J. Z. performed the measurements. X. Z. grew the NbSe₂ crystals. R. W. and N. H. conducted the theoretical analysis. G. Z., R. W., and N. H. wrote the paper with the help from all authors.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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