Superconductivity in a chiral nanotube

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Chirality of materials are known to affect optical, magnetic and electric properties, causing a variety of nontrivial phenomena such as circular dichroism for chiral molecules, magnetic Skyrmions in chiral magnets and nonreciprocal carrier transport in chiral conductors. On the other hand, effect of chirality on superconducting transport has not been known. Here we report the nonreciprocity of superconductivity—unambiguous evidence of superconductivity reflecting chiral structure in which the forward and backward supercurrent flows are not equivalent because of inversion symmetry breaking. Such superconductivity is realized via ionic gating in individual chiral nanotubes of tungsten disulfide. The nonreciprocal signal is significantly enhanced in the superconducting state, being associated with unprecedented quantum Little-Parks oscillations originating from the interference of supercurrent along the circumference of the nanotube. The present results indicate that the nonreciprocity is a viable approach toward the superconductors with chiral or noncentrosymmetric structures.
Chirality of crystal or magnetic structures in solids was recently recognized as a powerful source of unique optical and electronic properties and novel functionalities. For instance, it is well known that polarization of light or spin of electron are sensitive to the chirality of lattice or magnetic structure\(^1\) and electric transport reflecting the chiral structure are also reported\(^2\)\(^-\)\(^7\). Among them, effects of chiral structures on superconductivity have not been investigated so far because of the lack of suitable materials. One of the interesting superconducting materials with chirality is carbon nanotube (NT)\(^8\)\(^-\)\(^9\). Chiral structures and their relations to the electronic properties in carbon NTs have been well studied by Raman scattering\(^10\)\(^-\)\(^11\), scanning tunnel microscope\(^12\) and even magneto-chiral transport\(^6\). However, since superconductivity in carbon NTs\(^13\)\(^-\)\(^26\) has been investigated only in the assembled form of single, double or multi-walled NTs, relations between superconducting transport and the chirality in individual tubes have remained elusive.

Tungsten disulfide (WS\(_2\)) is a member of transition metal dichalcogenides (TMDs), which are now attracting significant attention as two dimensional (2D) materials beyond graphene with the potential application for electronics, photonics, spintronics, mechanics, as well as valleytronics\(^17\)\(^-\)\(^18\). Recent systematic studies clarified many TMDs including WS\(_2\), which are semiconductors without carrier doping, exhibit superconductivity under the ionic gating\(^19\)\(^-\)\(^20\). Importantly, TMD can form tubular structures with noncentrosymmetric chiral structures\(^21\)\(^-\)\(^26\). The semiconducting property of the WS\(_2\) NT was indeed demonstrated using the field effect transistor devices\(^24\). Superconductivity in such a noncentrosymmetric chiral cylinder, once it is realized, is a potential candidate for searching the exotic quantum phenomena and nontrivial Cooper pairing\(^27\)\(^-\)\(^28\). One of the manifestations of the chiral structure in the electronic transport is the unidirectional resistance. As shown in Fig. 1a,b, the two directions of current injection are not identical due to the chiral nature of the conducting substance when the magnetic field is applied parallel to the tube. Such nonreciprocity is highly anticipated to yield nontrivial quantum transport particularly in the superconducting states.

In this study, the transport properties of individual WS\(_2\) NT have been investigated by using the ionic liquid gating technique and resistance measurement on both first and second harmonic signals in alternative current (AC) mode. We have observed ambipolar transfer curve in electrostatic doping region and the emergence of superconductivity by electrochemical doping. The superconducting properties of individual WS\(_2\) NT have been further investigated, in which the observed anisotropy of the superconductivity and Little-Parks (LP) oscillation\(^29\) are consistent with tubular structure of WS\(_2\) NT. More importantly, we have experimentally discovered nonreciprocal superconducting transport via the second harmonic signal, being suggestive of chirality effect on superconductivity. Such nonreciprocal signal is largely enhanced in the superconducting state and affected by the magnetic flux quantum, showing periodic oscillations. The present study paves a route for studying the interplay between superconductivity and chirality or noncentrosymmetry.

**Results**

**Sample characterization.** WS\(_2\) NTs were synthesized following the literature\(^21\)\(^-\)\(^23\). Figure 1c shows a transmission electron microscope (TEM) image of a single WS\(_2\) NT (see Supplementary Fig. 1). The tube has a multi-walled structure, with the outer/inner diameters estimated as 132/107 nm, respectively, indicating that the layer number is \(\sim 20\). According to the literature\(^21\)\(^-\)\(^23\), the tube part has a 2H-polymorph-layered structure of WS\(_2\), where each tungsten atom is surrounded by six sulfur atoms in a trigonal biprism coordination (space group P\(_6\)3/mmc). The outer diameter distribution of tubes in the batch used for this measurement takes a broad maximum around 100 nm (See Supplementary Fig. 4). An electron diffraction pattern of a single WS\(_2\) NT is displayed in Fig. 1d. The red arrow and yellow hexagon represent the direction of tube axis and diffraction.
pattern from the zigzag type NT, respectively. The different walls of the tube can have different chirality. In addition to the contribution of the zigzag type NT, we can see the pair of tilted hexagonal pattern which confirms the co-existence of chiral structures in this NT. The TEM analysis indicates that the tubes used for the transport measurement are multi-walled WS$_2$ NTs with chirality, having the outer diameter of nearly 100 nm (See Supplementary Fig. 4).

**Ionic liquid gating on WS$_2$ NT and superconductivity.** We fabricated an individual tube device as shown in Fig. 1e,f, and measured gate responses of the transport characteristics. Based on our previous research on the systematic study of superconductivity in TMDs$^{19}$, we used KClO$_4$/polyethylene glycol electrolyte as the gate medium to facilitate electrochemical intercalation of potassium ions into the layered structure of WS$_2$.

Figure 2a displays the source-drain current ($I_{DS}$) of the individual WS$_2$ NT device against the gate voltage ($V_G$) between $-2$ and $3$ V. The device nicely operates in an ambipolar mode, in a similar manner to the 2D devices, showing marked contrast with the unipolar response of WS$_2$ NTs in the solid gated field effect transistor$^{24}$. This indicates the strong gate coupling of the presently used ionic medium. The transistor operation is most likely in the electrostatic mode in this regime, considering the ambipolar behaviour is reversible and repeatable. When $V_G$ was increased to $8$ V at a constant rate of $50$ mV s$^{-1}$, we found a saturation of $I_{DS}$ similarly to the case of 2D WS$_2$ (ref. 19). When $V_G$ was kept at $8$ V for a couple of minutes, we encountered another dramatic increase of $I_{DS}$ by more than two orders of magnitude as shown in Fig. 2b. This $I_{DS}$ increase is presumably attributed to intercalation of K$^+$ ions into WS$_2$ NTs.

When we cooled down the device to $2$ K keeping $V_G$ at $8$ V, superconductivity appeared at $T_c = 5.8$ K, defined as the temperature corresponding to the half of normal state resistance (Fig. 2c). In contrast to the K-intercalated 2D WS$_2$ multilayer with $T_c$ of $8.6$ K (ref. 19), the superconducting transition here is shifted to lower temperature and considerably broadened, potentially due to the reduced dimensions or lack of commensurability between the different walls.

![Figure 2](image-url)

**Figure 2 | Ionic gating effect on WS$_2$ NT and anisotropic superconducting behaviour.** (a) Ambipolar transfer curve ($I_{DS}$ versus $V_G$) measured from sample 1. (b) $I_{DS}$ as a function of $V_G$ and waiting time measured from sample 2. First and second increase of $I_{DS}$ observed at the electron-doped side can be attributed to the electrostatic and electrochemical doping, respectively$^{19}$. (c) Superconducting transition after ionic gating with $V_G = 8$ V. $T_c$ is $5.8$ K, defined as the temperature corresponding to the half of the normal state resistance. (d, e) Temperature dependence of the resistance under magnetic field $H$ parallel (d) and perpendicular (e) to the tube axis $z$ measured from sample 3. (f) Angle dependence of the critical magnetic field $H_{c2}$ measured at $3.5$ K. Circles and dashed line represent the critical magnetic field obtained from the experimental and theoretical fitting by the anisotropic Ginzburg–Landau model. We define $\theta = 0$ degree when the magnetic field is parallel to the tube axis. (g) Temperature dependence of the perpendicular and parallel critical magnetic field $H_{c2}$. Dashed line indicates the Pauli paramagnetic limit.
We then investigated the anisotropy of the observed superconductivity for sample 3 ($V_G = 6 \, \text{V}$). Figure 2d,e displays the temperature variation of the resistence under magnetic field $H$ for $H \parallel z$ and $H \perp z$, respectively. Here $z$ represents the tube axis direction. In the case of the $H \parallel z$, the superconductivity is robust against the magnetic field and remains undeformed even under $\mu_0 H = 9 \, \text{T}$ at $T = 2 \, \text{K}$, while the superconducting phase rapidly disappears for the $H \perp z$ configuration with increase of magnetic field. The anisotropic superconductivity was also confirmed by the angular dependence (Fig. 2f) and temperature dependence (Fig. 2g) of the upper critical field. In Fig. 2f, the estimated upper critical field at $T = 3.5 \, \text{K}$ are well fitted by the anisotropic Ginzburg–Landau model $\mu_0 H_{c2} = \frac{1}{\sqrt{(a \cos \theta)^2 + (b \sin \theta)^2}}$ with fitting parameters $a = 0.13 \, \text{T}^{-1}$ and $b = 0.75 \, \text{T}^{-1}$. The temperature dependence of the critical magnetic field (Fig. 2g) cannot be explained either by the simple 2D or 3D models, implying that the system is of intermediate dimension. Here we should note that the upper critical field at $T = 0 \, \text{K}$ for the $H \parallel z$ configuration seemingly exceeds the Pauli paramagnetic limit $\mu_0 H_{c2}^{PS} = \frac{\sqrt{\gamma}}{\pi \nu_0} \Delta \approx 1.84 \gamma r_c = 8.8 \, \text{T}$ ($\Delta$ is the superconducting gap at $T = 0 \, \text{K}$), being suggestive of a strong spin-orbit interaction and nontrivial Cooper pairing in the present system (See Supplementary Note 2).

**Little-Parks oscillations.** Figure 3a shows the AC magnetoresistance of sample 4 ($V_G = 12 \, \text{V}$) at various temperatures around $T_c$ in $H || z$ configuration. In addition to the robustness of the superconductivity discussed above, the magnetoresistance observed via the first harmonic signals in AC resistance ($R^0$) shows periodically oscillating behaviour in the low-magnetic field region. These oscillations during the superconducting transition known as LP effect originate from the interference of the superconducting current along the NT circumference and the resultant oscillations of $T_c$ (refs 29,30). During the application of a parallel magnetic field, the total flux piercing the NT should have a quantized value of $N \phi_0 = Nh/2e$ and induce the oscillation of the free energy, manifested by the resistance oscillation with the period of $\phi_0 = h/2e$ as observed in Fig. 3a ($h$ and $e$ represent the Planck constant and charge of the electron, respectively, while $N$ is an integer representing the number of flux quantum). Similar LP oscillations have been also observed in sample 3 (See Supplementary Fig. 11). We plotted the oscillating components at different temperatures in Fig. 3b after subtracting the polynomial background from Fig. 3a. The magnitude of the oscillating components reaches a maximum around $T_c$ (see also Fig. 4f). From the periods of LP oscillations $\Delta (\mu_0 H)$, we can estimate the effective diameter $d$ of the superconducting NT to be 100 and 80 nm for sample 3 and 4, respectively, according to the relation $\Delta (\mu_0 H) = \frac{\sqrt{\gamma}}{\pi \nu_0} \frac{h}{2e}$ (Fig. 3c). This is consistent with the diameter distribution histogram of the same batch shown in Supplementary Fig. 4. These results provide firm evidence that superconductivity occurs in the tubular region in the present WS$_2$ sample.

**Nonreciprocal superconducting transport in chiral WS$_2$ NT.** To clarify the characteristic properties due to the chiral structure, we have measured the second harmonic signals in the AC resistance ($R^{2h}$). In noncentrosymmetric systems, the cross term of magnetic field $H$ and electric current $I$ in the resistance is allowed on the basis of the symmetry argument, which indicates the difference between the forward and backward transports under magnetic field$^{5-7}$. This term generates the nonlinear voltage response, which can be measured as the second harmonic components in the AC resistance (See Supplementary Note 3).

Especially in chiral systems, this nonreciprocal electric transport called magneto-chiral anisotropy has been reported in several materials with different chiral degrees of freedom$^{5-7}$. Phenomenologically, magneto-chiral anisotropy can be expressed as

$$R^{2h} = \frac{1}{2} \gamma R_0 \mu_0 HI$$

where both the magnetic field $H$ and electric current $I$ are parallel to the chiral axis and $\gamma$ is the ratio of $R^{2h}$ to the normal resistance $R_0$. So far, there has been no report of such a phenomenon in
The observed second harmonic signals in AC resistance, together with LP oscillations in the first harmonic signals, are the direct manifestations of superconductivity in chiral NTs, however, the detailed mechanisms of the asymmetric electric transport and pairing symmetry (parity mixing) in the superconducting state needs to be further pursued. In light of this work, we expect various superconducting materials with broken inversion symmetry offer a similar transport, which provides a powerful
approach for probing the exotic superconducting state in a variety of noncentrosymmetric systems.

**Methods**

**Sample preparation.** The WS2 NTs were synthesized following the literature. The starting materials for the WS2 NT synthesis route were spherical tungsten oxide nanoparticles, which were sulfurized by solid-gas reaction with hydrogen and hydrogen sulfide at elevated temperatures (> 800°C). During this one-pot reaction, tungsten suboxide whiskers grow and are subsequently sulfurized into WS2 NTs of ~100 nm in diameter and up to 20 microns in length. These two main steps of the reaction—oxide whiskers growth and sulfurization—occur under the same H2/S2H6 gas flow regime and are not separated in space following each other in a self-controlled mechanism.

**Device fabrication.** WS2 NTs were dispersed in isopropyl alcohol solvent by ultrasonication for 20 min. A droplet of the suspension was spin-coated on a Si/SiO2(3,000 Å) substrate, and immediately covered by polymethyl methacrylate.

**Transport measurements.** All the transport properties have been measured in a Quantum Design Physical Property Measurement System with a horizontal rotator probe under He-purged and high-vacuum environments. High-vacuum mode was carried out TEM experiments, SEM measurement and characterization. F.Q., W.S. and M.Y. fabricated electric double-layer transistor devices and measured transport properties. T.K., D.I. and D.H. performed the growth and characterization of the WS2 nanotubes.

**Data availability.** All of the experimental data supporting this study are available from the corresponding author.

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**Author contributions**

F.Q., W.S. and T.I. conceived and designed the experiments. A.I. and D.H. performed the growth and characterization of the WS2 nanotubes. T.K., D.I. and D.H. measured transport properties. M.Y. fabricated electric double-layer transistor devices and measured transport properties. T.K., D.I. and D.H. measured transport properties. All authors commented on the manuscript.

**Additional information**

**Supplementary Information** accompanies this paper at http://www.nature.com/naturecommunications

**Competing financial interests:** The authors declare no competing financial interests.

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**How to cite this article:** Qin, F. et al. Superconductivity in a chiral nanotube. Nat. Commun. 8, 14465 doi: 10.1038/ncomms14465 (2017).

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