High-quality monolayer superconductor NbSe$_2$ grown by chemical vapour deposition

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The discovery of monolayer superconductors bears consequences for both fundamental physics and device applications. Currently, the growth of superconducting monolayers can only occur under ultrahigh vacuum and on specific lattice-matched or dangling bond-free substrates, to minimize environment- and substrate-induced disorders/defects. Such severe growth requirements limit the exploration of novel two-dimensional superconductivity and related nanodevices. Here we demonstrate the experimental realization of superconductivity in a chemical vapour deposition grown monolayer material—NbSe$_2$. Atomic-resolution scanning transmission electron microscope imaging reveals the atomic structure of the intrinsic point defects and grain boundaries in monolayer NbSe$_2$, and confirms the low defect concentration in our high-quality film, which is the key to two-dimensional superconductivity. By using monolayer chemical vapour deposited graphene as a protective capping layer, thickness-dependent superconducting properties are observed in as-grown NbSe$_2$ with a transition temperature increasing from 1.0 K in monolayer to 4.56 K in 10-layer.
Monolayer superconductors provide ideal models for investigating superconductivity in the two-dimensional (2D) limit, as well as superconductor-substrate interplay\(^1\)–\(^5\). Strong enhancement of the transition temperature \(T_c\) has been reported in the monolayer FeSe/SrTiO\(_3\) system\(^6,\,7\), which indicates that 2D ultra-thin films have the potential to be high-\(T_c\) superconductors. However, the superconductivity in most monolayers (Pb\(^8,\,9\), In\(^8,\,10\), FeSe\(^6\)) only survives on certain substrates, probably due to particular interface bonds\(^6,\,8\). Monolayer NbSe\(_2\), has recently been recognized as an intrinsic monolayer superconductor, due to the occurrence of superconductivity without the need of a special substrate\(^4\). NbSe\(_2\) crystallizes in the same layered hexagonal structure as \(2H\)-MoS\(_2\), where the niobium atoms sit at the center of trigonal selenium prisms. Compared with the bulk, 2D NbSe\(_2\) exhibits significantly different properties arising from reduced dimensionality, as exemplified by the observation of Ising superconductivity\(^1\), quantum metallic state\(^12\), and strong enhancement of charge density wave order\(^4\).

Defects in an ultrathin superconductor are known to be a critically detrimental factor to intrinsic 2D superconductivity\(^13,\,14\). Monolayer ambient-sensitive\(^15,\,16\) NbSe\(_2\) is predisposed to receive defects from the substrate and ambient environment. Therefore, the growth of superconducting NbSe\(_2\) monolayers is a great challenge. Though superconducting NbSe\(_2\) layers can be mechanically exfoliated from bulk NbSe\(_2\) crystals, it is not a scalable method. Also, the thickness and size of exfoliated NbSe\(_2\) flakes cannot be controlled. In the past few years, chemical vapour deposition (CVD) has been widely employed to synthesize ultrathin semiconducting transition metal dichalcogenides (TMDs) such as MoS\(_2\) and WSe\(_2\)\(^17\)–\(^24\). Recently, NbSe\(_2\) multilayers were prepared by selenizing pre-deposited Nb\(_2\)O\(_5\) films. However, none of the prepared NbSe\(_2\) was found to be superconducting\(^25,\,26\), probably due to the large concentration of defects created during growth. Currently,
superconducting NbSe$_2$ monolayers can only be grown by molecular beam epitaxial (MBE) under ultrahigh vacuum (UHV) and on a dangling bond-free graphene or h-BN substrate \cite{3, 27}, in order to minimize environment- and substrate-induced disorders/defects. However, MBE is expensive to perform because it requires a high-priced apparatus and a UHV environment. Furthermore, MBE growth of NbSe$_2$ is only available on specific graphene and h-BN substrates\cite{3, 27}, and the individual domain size is < 1 µm$^3$ \cite{27}. Therefore, it is desirable to develop a facile growth method to produce high-quality superconducting NbSe$_2$ layers.

In this work, we report the growth of the monolayer superconductor NbSe$_2$ at ambient pressure on a variety of substrates. Atomic-resolution annual dark-field scanning transmission electron microscope (ADF-STEM) imaging reveals the atomic structure of the intrinsic defects in the as-grown monolayer NbSe$_2$ crystal, such as point defects and grain boundaries, and confirms the low concentration of defects in both mono- and few-layer regions. Transport data indicate that even low concentration of defects exist in CVD-grown NbSe$_2$, they will not significantly affect the superconducting properties.

**Results**

**Growth of monolayer NbSe$_2$ crystals.** Atomically thin NbSe$_2$ crystals were grown on diverse substrates by ambient pressure CVD in a tube furnace (Supplementary Fig. 1). Partially oxidized niobium powder NbO$_x$ ($x \leq 2.5$) was chosen as the precursor (Supplementary Fig. 2). Briefly, the powder mixture of NbO$_x$ and NaCl was loaded in an alumina boat into the center of a fused quartz tube. Diverse substrates (SiO$_2$/Si, Si(100), quartz, etc.) were placed 1-3 mm above the powder mixture with the polished side faced down. Selenium powder was located at the entrance of the tube furnace, where the temperature was 300–340 °C during growth. Further details of the experiments are provided in the “Methods” section. Figure 1a shows the crystal structure of
monolayer NbSe₂ viewed from different angles. The as-deposited NbSe₂ crystals on SiO₂/Si are typically triangular or hexagonal in shape. Figure 1b shows the optical image of uniform hexagonal NbSe₂ crystals. A representative atomic force microscopy (AFM) measurement (inset of Fig. 1b) indicates the thickness of the NbSe₂ crystal is around 1.1 nm, which corresponds to a monolayer TMD.20, 28. As shown in Fig. 1c, the lateral domain size of monolayer CVD-grown NbSe₂ can reach 0.2 mm, which is ~10⁶ times as large as that of NbSe₂ prepared by MBE (<1 μm).3, 27. In addition to SiO₂/Si substrates, our CVD method can deposit NbSe₂ layers on arbitrary selenium-resistant crystalline and amorphous substrates, such as silicon (100), quartz, and CVD graphene (Supplementary Fig. 3). Different substrates may result in NbSe₂ flakes of varied morphologies (Supplementary Figs. 3 and 4), suggesting that the underlying substrate has an influence on the nucleation and growth of NbSe₂. Direct growth on diverse substrates makes it feasible to study the NbSe₂-substrate interaction and related properties.

The chemical states of the as-grown NbSe₂ samples were examined by X-ray photoemission spectroscopy (XPS) (Supplementary Fig. 5). Figure 1d is the Nb 3d core-level spectrum, and the two peaks at 203.4 and 206.1 eV can be assigned to Nb⁴⁺ 3d₅/₂ and Nb⁴⁺ 3d₇/₂ of NbSe₂. The absence of Nb⁵⁺ 3d₅/₂ and Nb³⁺ 3d₇/₂ peaks at higher binding energy (from 207.3 to 211.0 eV) indicates that the sample was not oxidized.30 The Se 3d core levels spectrum can be fitted with Se 3d₅/₂ (53.2 eV) and Se 3d₇/₂ (54.1 eV) peaks in agreement with the spectra of NbSe₂ (Fig. 1e).29, 30. Furthermore, the absence of Na 1s and Cl 2p peaks suggests that as-grown NbSe₂ was not contaminated by the NaCl precursor (Supplementary Fig. 6).

**Tuning the thickness of NbSe₂ layers.** In addition to producing monolayer NbSe₂, the proposed CVD method is also capable of acquiring NbSe₂ crystals with different thicknesses from 1.1 to 16 nm, which will be useful for investigating the thickness-dependent properties such as superconductivity, charge-density-wave order and their interplay in the 2D system. The NbSe₂ layer thickness was found to be sensitive to the heating temperature of selenium source (TSe). A portable thermocouple thermometer was used to measure the selenium temperature during sample growth. Figure 1f-h shows the thickness distribution statistics and representative morphologies (inset of Fig. 1f-h and Supplementary Fig. 7) of NbSe₂ crystals grown with TSe of (f) 300–340, (g) 360–420, and (h) 450–480 °C, respectively, while keeping all other growth parameters identical. Notably, the average thickness of obtained NbSe₂ increased with TSe. Monolayer NbSe₂ crystals were obtained only when selenium was heated to 300–340°C. In our experimental set-up, relatively higher TSe will induce a higher flow rate of the selenium vapour. Therefore, these results indicate that the thickness of NbSe₂ films highly relies on the flow rate of the selenium vapour. Supplementary Fig. 8 shows AFM images of NbSe₂ crystals with different thicknesses up to 16.2 nm. Raman spectra of the as-grown crystals show two characteristic peaks of NbSe₂ (Supplementary Fig. 9), including the in-plane E₂g mode at about 250 cm⁻¹ and the out-of-plane A₁g mode at about 225 cm⁻¹. The broad feature at about 180 cm⁻¹ is described as a soft mode because of its frequency behavior with temperature.4, 31. Thickness dependence of the Raman spectra of NbSe₂ is also shown in Supplementary Fig. 9. For monolayer NbSe₂, the Raman intensity of both A₁g and E₂g are very weak at room temperature. With the sample thickness increases, the intensity of A₁g and E₂g increase significantly.
exfoliated monolayer materials \(^3\), demonstrating the sufficiently low defect concentration in the film grown by our CVD method. The defect concentration is similar in multiple layers of NbSe\(_2\), as shown in Supplementary Fig. 10.

We further study the stacking sequence in the CVD-grown NbSe\(_2\) sample. Figure 2d shows two stacking orders that coexist in the bilayer region. While the lower bilayer is confirmed to be in 2\(H_a\) stacking, which is a stacking type commonly found in bulk NbSe\(_2\), where Nb atoms are aligned to each other between the layers (atomic model in the inset), the upper bilayer is revealed to be in 2\(H_c\) stacking, similar to the 2\(H_c\) stacking in MoS\(_2\). This is further evidenced by the equal intensity of each atomic column in the hexagonal rings, suggesting all the Nb atoms are aligned with the Se\(_2\) columns between the layers. Nevertheless, we found the dominating stacking in bilayers is the 2\(H_a\) stacking phase. This result implies that, though 2\(H_a\) stacking is rarely seen in bulk, it can still form in the CVD process presumably due to the weak van der Waal interlayer interaction, which can be overcome by the rapid nucleation process. EDX and EELS were used to identify the chemical constituents of the as-grown layers. Figure 2e shows the region that is used to perform the EDX and EELS experiment. Both EDX and EELS unambiguously show the as-grown NbSe\(_2\) film only contains Nb and Se without the presence of any other impurities (Fig. 2f, g). Similar defect and stacking structures are also observed in the NbSe\(_2\) layers that are directly grown on graphene substrate, as shown in Supplementary Fig. 11.

Due to the protection of the graphene sandwich structure, we were able to directly observe the grain boundary structure in the air-sensitive NbSe\(_2\) monolayer grown on SiO\(_2\)/Si by CVD method. Figure 3a displays a tilted grain boundary with a small misorientation angle (about 11\(^\circ\), determined by fast Fourier transform (FFT) in the inset). Interestingly, we found that two types of grain boundary structures coexist, as highlighted by different colored rectangles. The red region indicates the boundary that is atomically sharp, where two domains connects by distorted polygons to accommodate the strain due to the misorientation. The blue region represents another type of boundary, where the two domains overlap with each other, forming a vertically stacked structure. This is further evidenced by the selected FFT-filtered image shown in Fig. 3b, in which the two domains are separated according to the misorientation angles. Although both types of boundaries have been reported previously, it is commonly believed that only one of them can be formed depending on the dynamic energy between the growing frontiers of the misoriented domains during the growth process. The coexistence of both types in a single grain boundary structure suggests the formation energy between these two types of structures (atomically sharp and vertically stacked) is similar in NbSe\(_2\), where their co-growth can be induced by local fluctuation of the growing conditions. Figure 3c shows a similar tilted grain boundary without overlapping regions nearby. The ideal five-seven dislocation pairs are found periodically embedded along the grain boundary (highlighted by orange outline), which is similar to the case of other TMD materials \(^3, 36–38\) and consistent with the theoretical predictions \(^3\). In contrast, the polygons are found to be more distorted and did not have a periodic

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**Fig. 4 Superconductivity in monolayer NbSe\(_2\) devices.**

**a** Temperature dependence of the longitudinal resistance \(R_x\) for sample A—a monolayer NbSe\(_2\) device. **Upper left inset:** Optical image of a typical graphene protected monolayer NbSe\(_2\) device. Lower right inset:** Superconductivity in monolayer, 5-layer and 10-layer NbSe\(_2\) devices. **b** Superconductivity of sample A in different magnetic fields. **c** Temperature dependence of the upper critical field \(H_{c2}\). The solid line is the linear fit to \(H_{c2}\). **d** Voltage-current (\(V-I\)) characteristic at different temperatures on a logarithmic scale. The inset shows the temperature-dependent exponent deduced from the power-law behavior, \(V \propto I^n\). As indicated by the red dashed line, \(n\) approaches 3 at \(T = 0.8\) K.
distribution when the overlapping boundary is nearby, as shown in the red rectangular regions in Fig. 3a. This may be due to the alternation of the local strain profile in the atomically sharp grain boundary region induced by the overlapping area, which leads to the random formation of distorted polygons to release the inhomogeneous strain. These results reveal the local atomic structure of the grain boundaries, for the first time, in air-sensitive monolayer NbSe\(_2\) which is hard to observe due to its easy oxidation without any protection.

Transport properties of mono- and few-layer NbSe\(_2\). To further characterize the quality and dimensionality of as-grown NbSe\(_2\) crystals, a low-temperature transport experiment was carried out on Hall-bar devices. Because of its air sensitivity\(^{15}\), ultrathin NbSe\(_2\) was first covered with a continuous monolayer graphene film before device fabrication (see “Methods” section). Figure 4a shows the temperature \(T\) dependence of longitudinal resistance \(R_{xx}\) for sample A—a representative monolayer NbSe\(_2\) device (see Supplementary Note 1 and Supplementary Fig. 12 for more devices and data) at zero magnetic field. Consistent with previous studies\(^{3,11,12}\), the sample shows a metallic behavior (\(dR/dT > 0\)) at high temperatures. At \(T_{\text{onset}} = 1.5\) K, \(R_{xx}\) begins to decrease sharply and drops to zero at \(T_{\text{zero}} = 0.8\) K, indicating the occurrence of superconductivity. Additionally, we find the superconducting transition in our high-quality NbSe\(_2\) crystals can be tuned by changing the sample thickness. The lower right inset of Fig. 4a displays the normalized resistance \(R_{xx}/R_N\) as a function of temperature for NbSe\(_2\) with different thickness. It is evident that the superconducting transition critical temperature \(T_c\) (0.5\(R_N\)) can be tuned from 4.56 K for 10-layer, 4.2 K for 5-layer, to 1.0 K for monolayer. Due to its sensitivity to moisture and oxygen, even when protected by graphene, the superconductivity of NbSe\(_2\) sample degrades with increasing ambient exposure (Supplementary Fig. 13 and Supplementary Table 1), which is discussed in Supplementary Note 2.

To compare the quality of the monolayer NbSe\(_2\) prepared with different methods, the residual resistance ratio (defined as the ratio of the room temperature resistance \(R_{300\text{K}}\) to the normal-state resistance \(R_N\)) RRR, the superconducting transition onset temperature \(T_{\text{onset}}\), the critical temperature \(T_c\) (0.5\(R_N\)), the zero-resistance temperature \(T_{\text{zero}}\), and the inverse of the superconducting transition width \(1/\Delta T_c\) are summarized in Fig. 5. It is noted that our CVD-grown monolayer NbSe\(_2\) has a RRR = 2.0 very close to the reported value for MBE-grown NbSe\(_2\)\(^3\), but the CVD sample has a \(T_{\text{zero}}\) (0.8 K) almost two times as high as that of MBE NbSe\(_2\)\(^3\). Though a much higher zero-resistance temperature \(T_{\text{zero}} = 1.3\) K was reported in Se-capped MBE-grown monolayer NbSe\(_2\), however, the resistance did not really drop to zero\(^{40}\). Besides, the \(\Delta T_c\) in the CVD-grown sample is only 0.7 K, which is superior to all reported MBE NbSe\(_2\)\(^3,40\) and comparable to the best record in mechanically exfoliated samples\(^{15}\). The above data indicate that the CVD-grown NbSe\(_2\) samples are high quality.

Figure 4b shows the temperature and field dependence of \(R_{xx}\) for sample A (see Supplementary Note 1 for more devices and data) with the field perpendicular to the sample plane. Under a magnetic field, the critical temperature \(T_c\) is defined by where the resistance is 90% of the normal state value \(R_N\). With increasing the strength of magnetic field \(B\), \(T_c\) shifts to lower temperatures. Finally, the superconductivity is completely suppressed with a magnetic field of about 1.5 T at \(T = 0.3\) K. We summarize the \(H_{c2}-T_c\) phase diagram, where \(H_{c2}\) is the upper critical field, in Fig. 4c and find a linear relationship between \(H_{c2}\) and \(T_c\), which is a characteristics of 2D superconductors\(^{11-13}\) and can be explained by the standard linearized Ginzburg-Landau (GL) theory\(^{41}\),

\[
H_{c2}(T) = \frac{H_S}{2\xi_{GL}(0)} \left(1 - \frac{T}{T_{c}}\right) ,
\]

where \(\xi_{GL}(0)\) is the zero-temperature GL in-plane coherence length and \(\phi_0\) is the magnetic flux quantum. As shown in Fig. 4c, a linear fit between \(H_{c2}\) and \(T_c\) yields \(\xi_{GL}(0) = 18\) nm (see Supplementary Note 3 and Supplementary Fig. 14 for more transport data of NbSe\(_2\) grown on graphene substrate), which is about twice of the bulk value\(^{16}\). Based on the normal state resistance \(R_N\) and carrier density \(n_s\) as determined by Hall measurement (Supplementary Note 4 and Supplementary Fig. 15), the mean free path \(l_m = 1.3\) nm can be obtained, smaller than that in exfoliated sample\(^{12}\). On the other hand, the normal state sheet resistance \(R_S = 727\) \(\Omega\) (taken at \(T_{\text{onset}} = 1.5\) K) is much smaller than the quantum resistance \(R_S = \hbar/e^2 \approx 6.45\) K\(\Omega\), where \(\hbar\) is the electron charge and \(e\) is Planck’s constant, above which a disorder-induced superconductor-insulator transition emerges\(^{42}\). The above discussions indicate that our sample is in the low-disorder regime\(^{11,13,40}\).

For a 2D superconductor with the thickness \(d < \xi_{GL}(0)\), the superconducting phase transition is expected to be of the Berezinskii-Kosterlitz- Thouless (BKT) type\(^{13,44}\). Figure 4d shows voltage–current (\(V-I\)) behavior as a function of temperature on a
log-log scale. The $V-I$ relations change from a linear to a power-law dependence, $V \propto I^n$ at $T_c (0.5 R_S)$, which is consistent with expectations for a 2D superconductor based on the theoretical model of the BKT transition. In the inset of Fig. 4d, we plot the exponent $n$ vs. $T_c$, which is extracted from the slope of $V-I$ traces. The BKT transition temperature $T_{\text{BKT}}$ is estimated to be 0.8 K from where $n = 3$ interpolates. The above data confirm that monolayer NbSe$_2$ exhibits the characteristics of a true 2D superconductor.

**Discussion**

The developed CVD growth technology has enabled the realization of superconductivity in non-UHV grown monolayer materials. Our results also provide a comprehensive understanding of the defect structure, superconducting performance as well as the influence of ambient-induced defects on superconductivity of NbSe$_2$. It is evident that even though low concentrations of selenium vacancy-related defects remained in the CVD-grown NbSe$_2$, they will not significantly affect the superconducting properties. Our facile CVD technology not only provides an excellent platform for the investigation of many fascinating properties of NbSe$_2$, but also holds promise for large-scale synthesis of 2D superconducting NbSe$_2$ films for potential device applications. Future developments may also include investigation and understanding of NbSe$_2$-substrate interplay and related novel properties, inspired by the research on 2D high-$T_c$ Fe-chalcogenide superconductors, 6, 7, 45 (more discussion in Supplementary Note 5). More recently, monolayer NbSe$_2$ was suggested as a candidate for realizing topological superconducting phase and engineering Majorana fermions, 46, 47. Therefore, the present work offers possibilities for the study of topological physics.

More importantly, our work indicates that a UHV environment is not necessarily required for the growth of monolayer superconductors. In our salt-assisted CVD synthesis of NbSe$_2$, the role of salt is particularly important as no nucleation of NbSe$_2$ can be observed without salt. It is noted that all niobium oxides have melting points above 1510 °C, which make them difficult to vaporize and react with selenium in the CVD process. The products of reactions between molten salts and metal (Mo$^{4+}$, W$^{5+}$, and Nb$^{5+}$) oxides have been investigated in several works and found to be metal oxychlorides, which have much lower melting points compared with corresponding metal oxides. 48, 49, 50. Thus, it is suggested that in our CVD process, NaCl reacts with niobium oxides to give volatile niobium oxychloride, 48, thereby increasing the vapour pressure of precursor and facilitating the growth of NbSe$_2$. With the proposed salt-assisted CVD method, a number of other 2D and even monolayer superconductors (2H-TaS$_2$, 2H-TaSe$_2$, 1T-TiSe$_2$, and 1T-Cu$_2$TiSe$_2$, etc.) could be synthesized by substituting niobium oxides with corresponding metal oxides precursors. Considering that most of the mentioned monolayers have never been synthesized (even by MBE) and investigated, the new growth technology will enrich the research field of 2D TMDs superconductivity greatly.

**Methods**

**Atomically thin NbSe$_2$ crystals synthesis.** We used partially oxidized niobium powder NbO$_x$ ($x \leq 2.3$) as precursor for growing NbSe$_2$. In the first step, 5 g niobium powder (99.8%, 325 mesh, Alfa Aesar) was loaded into a both-ends-opened quartz tube equipped in a tube furnace. The niobium powder was ignited when furnace was heating to about 600 °C. After 1 min combustion, the niobium powder was rapid cooled to room temperature by moving it to cold zone. X-ray diffraction (XRD) analysis (Supplementary Fig. 3) indicated the obtained powder consisted mainly of Nb, Nb$_2$O$_3$, and NbO. Ambient pressure CVD growth of NbSe$_2$ was conducted in a 2-inch outer diameter fused quartz tube heated by a Lindberg/Blue M (HTF55322C) split-hinge furnace. Supplementary Fig. 1 shows the set-up of the CVD reaction chamber. The partially oxidized Nb powders NbO$_x$ (0.7 g) together with NaCl powders (0.1 g) were placed in an aluminia boat located in the center of the furnace. 285 nm SiO$_2$/Si or other substrates were placed 1-3 mm above the powder mixture with the polished side faced down. Selenium powder (2 g) (99.5%, Sigma-Aldrich) was placed at the upstream of the quartz tube, where the temperature ranges from 300 to 460 °C during the reaction. 120 sccm (cubic centimeters per minute) Ar and 24 sccm H$_2$ are used as carrier gases. The furnace is heated to 795 °C in 16 min and maintained at that temperature for 13 min to allow the synthesis of NbSe$_2$ layers.

The furnace was naturally cooled to 680 °C without changing the carrier gases. Then the top cover of the furnace was opened to allow fast cooling of the sample, with carrier gases switched to 250 sccm Ar and 4 sccm H$_2$.

**Device fabrication and transport measurements.** For fabricating ultrathin NbSe$_2$ devices, large-area monolayer CVD graphene was used to cover and protect the thin NbSe$_2$ deposited on SiO$_2$/Si. First, a rectangular frame consisted by adhesive tape was attached to the poly (methyl methacrylate) (PMMA)-coated graphene grown on Cu foil 28. Then PMMA/graphene was detached from the Cu substrate by a bubbling transfer method. The PMMA/graphene was rinsed in DI water for several times and then dried in air. Second, the PMMA/graphene film was directly attached to the NbSe$_2$ on SiO$_2$/Si substrate in an Ar-filled glove box, with the help of a drop of isopropanol added between. PMMA was then removed in acetone to form the graphene/NbSe$_2$ stacks. Finally, a thin film of PMMA was deposited on the prepared graphene/NbSe$_2$ layers, by spin-coating at 3 K rpm for 1 min. The PMMA film was cured at 140 °C for 6 min in an Ar glove box. Hall bar device was made by electron-beam lithography and the contact metal (5 nm Cz/50 nm Au) was fabricated by electron-beam deposition.

The transport experiment is carried out in a top-loading helium-3 cryostat in a superconducting magnet. An AC probe current $I_p$ = 10 nA at 30.9 Hz is applied from the source to the drain. Then a lock-in amplifier monitors the longitudinal $R_x$ through two additional electrical contacts.

**Fabrication of graphene/NbSe$_2$/graphene sandwich cell for STEM imaging.** First, mono- and few-layer NbSe$_2$ crystals were grown on 285 nm SiO$_2$/Si substrates. Second, with the same method described earlier in the device fabrication part, a continuous monolayer CVD graphene film was placed on top of the chip to form a graphene/NbSe$_2$-stacked heterostructure. Third, a thin PMMA film was spin-coated and cured on the chip, and then the PMMA/graphene/NbSe$_2$ film was detached from the SiO$_2$/Si substrate in HF. After rinsed in DI water, it was scooped up by a SiO$_2$/Si chip predeposited with monolayer graphene film to form a PMMA/graphene/NbSe$_2$/graphene structure on SiO$_2$/Si substrate. Fourth, the PMMA/graphene/NbSe$_2$/graphene film was detached from the substrate by etching SiO$_2$ layer in HF. After rinsed in DI water, it was scooped up by a TEM grid. Finally, the graphene/NbSe$_2$/graphene sandwich cell was created by removing PMMA in acetone.

**Sample characterizations.** XPS spectra were collected on a PHI Quantera II spectrometer using monochromatic Al-K$_\alpha$ ($h\nu = 1486.6$ eV) radiation, and the binding energies were calibrated with C 1s binding energy of 284.8 eV. AFM images were taken using the Asylum Research Cypher AFM in tapping mode. Raman spectra were recorded in vacuum by a Witec system with 530 objective lens and a 2400 lines per mm grating under 532 nm laser excitation. The laser power was fixed at 1 mW. STEM experiments were performed by a low acceleration voltage JEOL 2100F equipped with Delta correctors and GIF quantum spectrometer.

**Data availability.** The data that support the findings of this study are available from the corresponding author on reasonable request.

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Author contributions
Z.L., G.L. and E.H.T.T. directed the research; H.W. and Z.L. proposed and designed the experiments; H.W. performed the NbSe2 and NbS6/graphene heterostructure synthesis and did the SEM, AFM, and XPS measurements; X.H., J.C., and G.L. did the superconductivity measurements and data analysis; X.H., Z.C., Q.Z., and F.L. contributed to the device fabrication; J.L. did the STEM measurement and data analysis; Y.C. and H.W. did the Raman measurement; H.W. and J.Z. prepared the STEM sample. P.Y. and X.W. did the XRD measurement; H.H., S.H.T., W.G., K.S., F.M., C.Y., L.L., T.Y., and E.H.T.T. contributed to the results analysis and discussions. H.W., J.L., G.L. and Z.L. co-wrote the paper with input from all authors.

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