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High-quality monolayer superconductor NbSe₂ 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—NbSe₂. Atomic-resolution scanning transmission electron microscope imaging reveals the atomic structure of the intrinsic point defects and grain boundaries in monolayer NbSe₂, 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 NbSe₂ with a transition temperature increasing from 1.0 K in monolayer to 4.56 K in 10-layer.

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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/SrTiO₃ 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}, FeSe⁶) only survives on certain substrates, probably due to particular interface bonds^{6, 8}. Monolayer NbSe₂ has recently been recognized as an intrinsic monolayer superconductor, due to the occurrence of superconductivity without the need of a special substrate⁴. NbSe₂ crystallizes in the same layered hexagonal structure as 2H-MoS₂, where the niobium atoms sit at the center of trigonal selenium prisms. Compared with the bulk, 2D NbSe₂ exhibits significantly different properties arising from reduced dimensionality, as exemplified by the observation of Ising superconductivity¹¹,

quantum metallic state¹², and strong enhancement of charge density wave order⁴.

Defects in an ultrathin superconductor are known to be a critically detrimental factor to intrinsic 2D superconductivity^{13, 14}. Monolayer ambient-sensitive^{15, 16} NbSe₂ is predisposed to receive defects from the substrate and ambient environment. Therefore, the growth of superconducting NbSe₂ monolayers is a great challenge. Though superconducting NbSe₂ layers can be mechanically exfoliated from bulk NbSe₂ crystals, it is not a scalable method. Also, the thickness and size of exfoliated NbSe₂ 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 MoS₂ and WSe₂^{17–24}. Recently, NbSe₂ multilayers were prepared by selenizing pre-deposited Nb₂O₅ films. However, none of the prepared NbSe₂ was found to be superconducting^{25, 26}, probably due to the large concentration of defects created during growth. Currently,

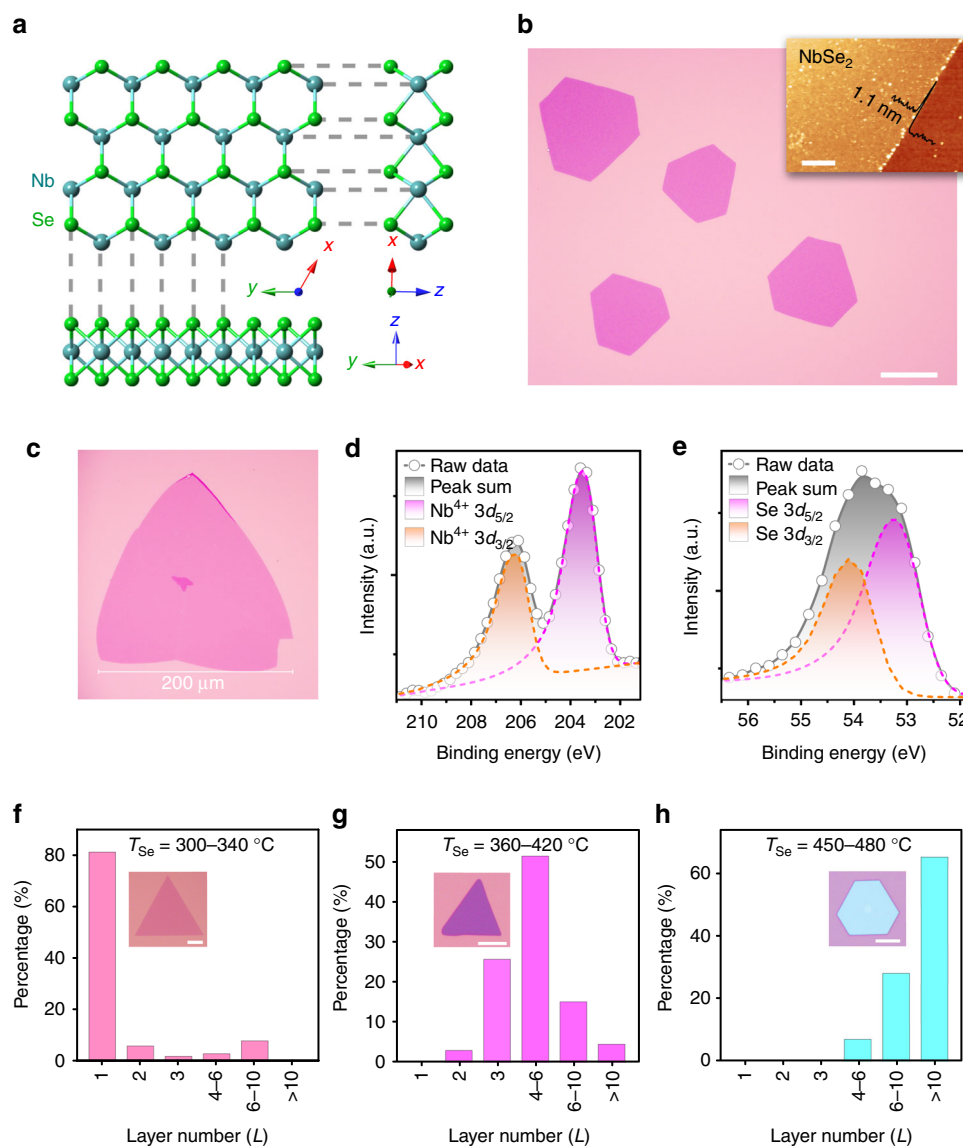


Fig. 1 Atomic structure, morphologies, and characterizations of NbSe₂ crystals. **a** Ball-and-stick model of monolayer 2H-NbSe₂ viewed from three different directions. **b** Optical image of uniform NbSe₂ crystals deposited on a SiO₂/Si substrate. Scale bar, 40 μm. A representative AFM image (inset; scale bar, 1 μm) shows the typical thickness is 1.1 nm. **c** A monolayer NbSe₂ crystal with edge length of 0.2 mm. **d**, **e** X-ray photoemission spectroscopy (XPS) spectra of the **d** Nb 3d and **e** Se 3d peaks from NbSe₂ crystals deposited on SiO₂/Si substrate. **f–h** Statistical thickness distributions and representative morphologies (inset) of NbSe₂ crystals synthesized with T_{Se} setting at **f** 300–340, **g** 360–420 and **h** 450–480 °C, respectively. Scale bars from inset of **f–h** are 20, 5 and 5 μm. Thickness of inset crystals of **f–h** are 1.1, 5.1 and 16.2 nm

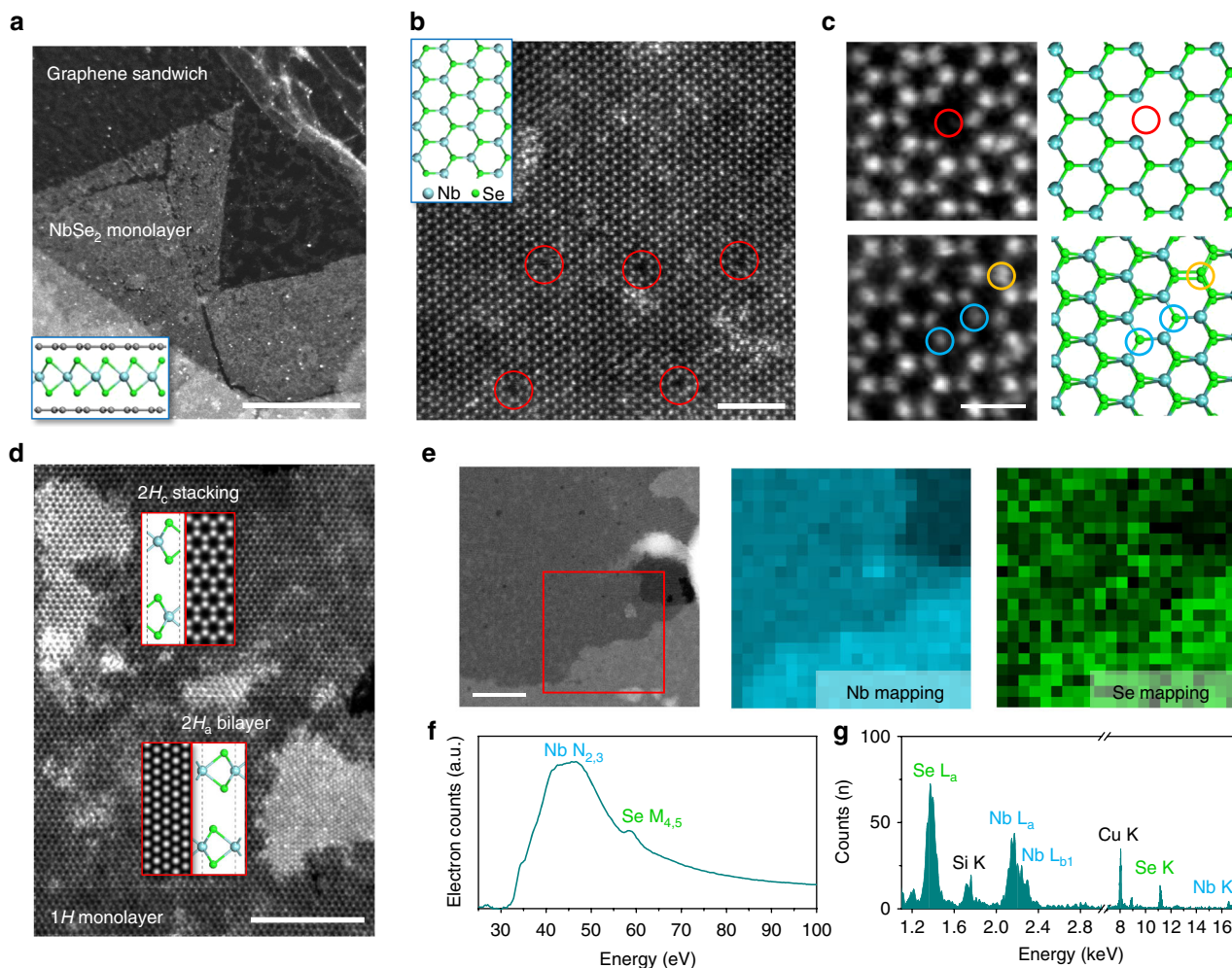


Fig. 2 ADF-STEM images, EELS, and EDX characterizations of the as-synthesized NbSe₂ atomic layers. **a** A low magnified annular dark-field scanning transmission electron microscope (ADF-STEM) image showing a large region of monolayer NbSe₂ encapsulated by the graphene sandwich. The schematic is shown in the inset. **b** Atomic resolution ADF-STEM image of the hexagonal NbSe₂ lattice. Diselenium vacancies are highlighted by red circles. The inset of panel **b** shows the structural model of 2H-NbSe₂, with cyan and green color indicating Nb and Se atoms, respectively. **c** Different point defects in monolayer NbSe₂ and their atomic models. Diselenium vacancy, monoselenium vacancy, and anti-site defect Se_{Nb} are highlighted by red, blue, and yellow circles, respectively. **d** Atomic resolution ADF-STEM image of two bilayer islands in NbSe₂, showing the coexistence of 2H_a and 2H_c stacking sequence. The insets are corresponding atomic models and simulated STEM images. **e** STEM image of a large region of NbSe₂ used for the collection of electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectrometry (EDX) spectra. The collected region is highlighted in red square. Nb and Se EELS mapping are provided next to it. **f** Typical EELS and **g** EDX spectra of the region shown in **e**. The Cu signal in the EDX spectra comes from the Cu grid. Scale bars, 500 nm (**a**), 2 nm (**b**), 0.5 nm (**c**), 5 nm (**d**), 50 nm (**e**)

superconducting NbSe₂ 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^{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 NbSe₂ is only available on specific graphene and *h*-BN substrates^{3, 27}, and the individual domain size is < 1 μm^{3, 27}. Therefore, it is desirable to develop a facile growth method to produce high-quality superconducting NbSe₂ layers.

In this work, we report the growth of the monolayer superconductor NbSe₂ at ambient pressure on a variety of substrates. Atomic-resolution annular dark-field scanning transmission electron microscope (ADF-STEM) imaging reveals the atomic structure of the intrinsic defects in the as-grown monolayer NbSe₂ 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 NbSe₂, they will not significantly affect the superconducting properties.

Results

Growth of monolayer NbSe₂ crystals. Atomically thin NbSe₂ 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 (SiO₂/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

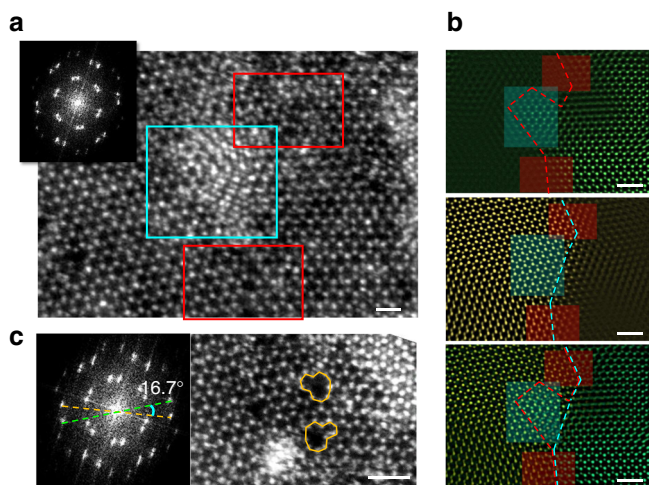


Fig. 3 ADF-STEM images of the grain boundary in monolayer NbSe₂. **a** A tilted grain boundary with misorientation angle of 11°. Both atomically sharp lateral interconnected (red rectangle) and vertically stacked (blue rectangle) boundary regions are found to coexist. The inset shows the fast Fourier transformation (FFT) of the image. The distorted polygons are also highlighted in the red rectangle. Scale bar, 0.5 nm. **b** Selected FFT-filtered image of the two domains and their overlap images. The overlapped image confirms the coexistence of the two types of grain boundaries. Scale bar, 1 nm. **c** Similar tilted grain boundary without an overlapping region nearby. The orange lines indicate the five-seven dislocation pairs, which is consistent with the theoretical predictions of the grain boundary structure. Scale bar, 1 nm

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 $\sim 10^2$ 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⁺ 3d_{5/2} and Nb⁴⁺ 3d_{3/2} of NbSe₂²⁹. The absence of Nb⁵⁺ 3d_{5/2} and Nb⁵⁺ 3d_{3/2} peaks at higher binding energy (from 207.3 to 211.0 eV) indicates that the sample was not oxidized³⁰. The Se 3d core levels spectrum can be fitted with Se 3d_{5/2} (53.2 eV) and Se 3d_{3/2} (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 (T_{Se}). 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 T_{Se} 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 T_{Se} . Monolayer NbSe₂ crystals were obtained only when selenium was heated to 300–340 °C. In our experimental set-up, relatively higher T_{Se} 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 E_{2g} mode at about 250 cm⁻¹ and the out-of-plane A_{1g} 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 A_{1g} and E_{2g} are very weak at room temperature. With the sample thickness increases, the intensity of A_{1g} and E_{2g} increase significantly.

Structural characterization. In order to examine the quality of the as-grown 2H-NbSe₂ atomic layers, the atomic structure and the chemical composition of the NbSe₂ layers were characterized by atomic resolution ADF-STEM imaging, electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectrometry (EDX). Since a bare NbSe₂ monolayer film is sensitive to the ambient environment, we transferred the NbSe₂ flakes grown on SiO₂ substrate with graphene encapsulation (see “Methods” section), constructing a graphene/NbSe₂/graphene sandwich structure for STEM imaging. Such structures have been demonstrated to be effective in protecting sensitive monolayer materials from being oxidized³². Figure 2a shows a low magnification ADF-STEM image of a large area of monolayer NbSe₂ sandwiched by graphene (schematic shown in the inset), where little oxidization is observed. Figure 2b shows a zoom-in image of the same area with atomic resolution, displaying the hexagonal atomic lattice of alternating bright and dark spots, which corresponds, respectively, to the Se₂ and Nb atomic columns as indicated in the atomic model, confirming its hexagonal phase. Diselenium vacancy can be directly visualized by their distinguishable contrast within the image, as highlighted by the red circles. Since the STEM image contrast is directly related to the atomic number and the number of atoms of the imaged species, more types of intrinsic point defects can be identified by carefully examining the image contrast of each atomic column. Figure 2c shows the atomic resolution image of three major types of point defects found in the monolayer NbSe₂ film, which are diselenium vacancy (V_{Se₂}, red), monoselenium vacancy (V_{Se}, blue), and anti-site defect where a Se₂ column replaces the Nb (yellow). These intrinsic point defects are similar to those found in MoS₂ and MoSe₂ with the same hexagonal phase^{33, 34} grown by CVD method. We can therefore calculate the defect concentration in certain area by counting the number of point defects. The defect concentration in Fig. 2b is estimated to be $\sim 0.18 \text{ nm}^{-2}$, which is similar to the case in mechanical

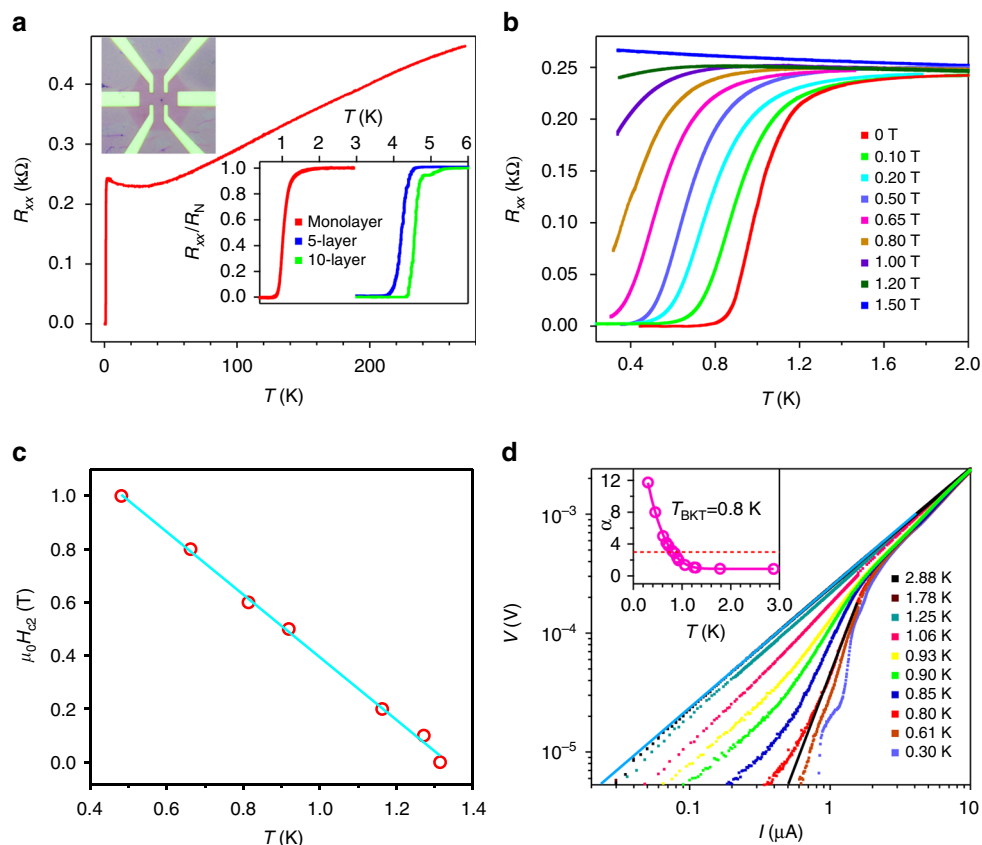


Fig. 4 Superconductivity in monolayer NbSe₂ devices. **a** Temperature dependence of the longitudinal resistance R_{xx} for sample A—a monolayer NbSe₂ device. *Upper left inset*: Optical image of a typical graphene protected monolayer NbSe₂ device. *Lower right inset*: Superconductivity in monolayer, 5-layer and 10-layer NbSe₂ 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 solid blue line indicates the Ohmic behavior at high temperature. The solid black line represents the expected $V \propto I^3$ behavior at the Berezinskii-Kosterlitz-Thouless (BKT) transition. The inset shows the temperature-dependent exponent deduced from the power-law behavior, $V \propto I^\alpha$. As indicated by the red dashed line, α approaches 3 at $T = 0.8$ K

exfoliated monolayer materials³⁵, demonstrating the sufficiently low defect concentration in the film grown by our CVD method. The defect concentration is similar in multiple layer of NbSe₂, as shown in Supplementary Fig. 10.

We further study the stacking sequence in the CVD-grown NbSe₂ sample. Figure 2d shows two stacking orders that coexist in the bilayer region. While the lower bilayer is confirmed to be in $2H_a$ stacking, which is a stacking type commonly found in bulk NbSe₂, where Nb atoms are aligned to each other between the layers (atomic model in the *inset*), the upper bilayer is revealed to be in $2H_c$ stacking, similar to the $2H$ stacking in MoS₂. 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 Se₂ columns between the layers. Nevertheless, we found the dominating stacking in bilayers is the $2H_a$ stacking phase. This result implies that, though $2H_c$ 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 NbSe₂ 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 NbSe₂ 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 NbSe₂ monolayer grown on SiO₂/Si by CVD method. Figure 3a displays a tilted grain boundary with a small misorientation angle (about 11°, 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^{36–38}, 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 NbSe₂, 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^{34,37} and consistent with the theoretical predictions³⁹. In contrast, the polygons are found to be more distorted and did not have a periodic

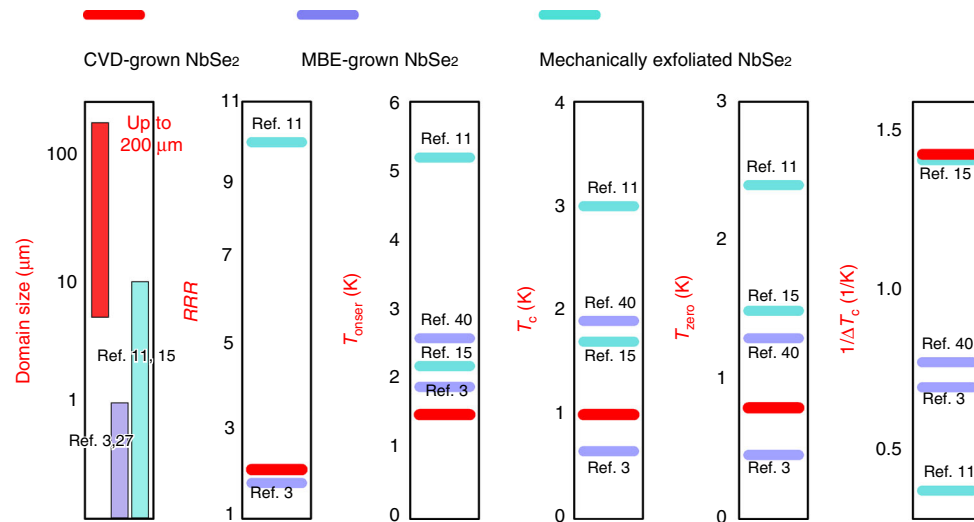


Fig. 5 Comparison of the superconducting performance of monolayer NbSe₂ prepared by CVD and other methods. From left to right: domain size, residual resistance ratio RRR, T_{onset} , T_c ($0.5 R_N$), T_{zero} , and $1/\Delta T_c$ for monolayer NbSe₂ samples prepared with different methods

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 NbSe₂ which is hard to observe due to its easy oxidation without any protection.

Transport properties of mono- and few-layer NbSe₂. To further characterize the quality and dimensionality of as-grown NbSe₂ crystals, a low-temperature transport experiment was carried out on Hall-bar devices. Because of its air sensitivity¹⁵, ultrathin NbSe₂ 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 NbSe₂ 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 NbSe₂ 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 NbSe₂ with different thickness. It is evident that the superconducting transition critical temperature T_c ($0.5R_N$) 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 NbSe₂ 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 NbSe₂ 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_{onset} , the critical temperature T_c ($0.5R_N$), the zero-resistance temperature T_{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 NbSe₂ has a RRR =

2.0 very close to the reported value for MBE-grown NbSe₂³, but the CVD sample has a T_{zero} (0.8 K) almost two times as high as that of MBE NbSe₂³. Though a much higher zero-resistance temperature $T_{\text{zero}} = 1.3$ K was reported in Se-capped MBE-grown monolayer NbSe₂, however, the resistance did not really drop to zero⁴⁰. Besides, the ΔT_c in the CVD-grown sample is only 0.7 K, which is superior to all reported MBE NbSe₂^{3, 40} and comparable to the best record in mechanically exfoliated samples¹⁵. The above data indicate that the CVD-grown NbSe₂ 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 characteristic of 2D superconductors^{11–13} and can be explained by the standard linearized Ginzburg-Landau (GL) theory⁴¹, $H_{c2}(T) = \frac{\phi_0}{2\pi\xi_{\text{GL}}(0)^2} \left(1 - \frac{T}{T_c}\right)$, where $\xi_{\text{GL}}(0)$ is the zero-temperature GL in-plane coherence length and ϕ_0 is the magnetic flux quantum. As shown in Fig. 4c, a linear fit between H_{c2} and T_c yields $\xi_{\text{GL}}(0) = 18$ nm (see Supplementary Note 3 and Supplementary Fig. 14 for more transport data of NbSe₂ grown on graphene substrate), which is about twice of the bulk value¹⁶. 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 sample¹². 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 $R_q = h/4e^2 \approx 6.45$ k Ω , where e is the electron charge and h is Planck’s constant, above which a disorder-induced superconductor-insulator transition emerges⁴². The above discussions indicate that our sample is in the low-disorder regime^{11, 13, 40}.

For a 2D superconductor with the thickness $d < \xi_{\text{GL}}(0)$, the superconducting phase transition is expected to be of the Berezinskii-Kosterlitz-Thouless (BKT) type^{43, 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, $V \propto I^\alpha$ at T_c ($0.5R_N$), 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 α vs. T , which is extracted from the slope of V - I traces. The BKT transition temperature T_{BKT} is estimated to be 0.8 K from where $\alpha = 3$ interpolates. The above data confirm that monolayer NbSe₂ 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 NbSe₂. It is evident that even though low concentrations of selenium vacancy-related defects remained in the CVD-grown NbSe₂, 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 NbSe₂, but also holds promise for large-scale synthesis of 2D superconducting NbSe₂ films for potential device applications. Future developments may also include investigation and understanding of NbSe₂-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 NbSe₂ 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 NbSe₂, the role of salt is particularly important as no nucleation of NbSe₂ 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 (Mo⁴⁸, W²⁸, and Nb⁴⁹) oxides have been investigated by several groups and found to be metal oxychlorides, which have much lower melting points compared with corresponding metal oxides^{28, 48, 49}. Thus, it is suggested that in our CVD process, NaCl reacts with niobium oxides to give volatile niobium oxychloride²⁸, therefore increasing the vapour pressure of precursor and facilitating the growth of NbSe₂. With the proposed salt-assisted CVD method, a number of other 2D and even monolayer superconductors (2H-TaS₂, 2H-TaSe₂, 1T-TiSe₂, and 1T-Cu_xTiSe₂, 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 NbSe₂ crystals synthesis. We used partially oxidized niobium powder NbO_x ($x \leq 2.5$) as precursor for growing NbSe₂. 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 680 °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. 2) indicated the obtained power consisted mainly of Nb, Nb₂O₅, and NbO.

Ambient pressure CVD growth of NbSe₂ 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 alumina boat located in the center of the furnace. 285 nm SiO₂/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 H₂ 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 NbSe₂ 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 H₂.

Device fabrication and transport measurements. For fabricating ultrathin NbSe₂ devices, large-area monolayer CVD graphene was used to cover and protect the thin NbSe₂ deposited on SiO₂/Si. First, a rectangular frame consisted by adhesive tape was attached to the poly (methyl methacrylate) (PMMA)-coated graphene grown on Cu foil⁵⁰. 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 NbSe₂ on SiO₂/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/NbSe₂ stacks. Finally, a fresh film of PMMA was deposited on the prepared graphene/NbSe₂ 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 Cr/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 $I_{\text{ac}} = 10$ nA at 30.9 Hz is applied from the source to the drain. Then a lock-in amplifier monitors the longitudinal R_{xx} through two additional electrical contacts.

Fabrication of graphene/NbSe₂/graphene sandwich cell for STEM imaging.

First, mono- and few-layer NbSe₂ crystals were grown on 285 nm SiO₂/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/NbSe₂-stacked heterostructure. Third, a thin PMMA film was spin-coated and cured on the chip, and then the PMMA/graphene/NbSe₂ film was detached from the SiO₂/Si substrate in HF. After rinsed in DI water, it was scooped up by a SiO₂/Si chip predeposited with monolayer graphene film to form a PMMA/graphene/NbSe₂/graphene structure on SiO₂/Si substrate. Fourth, the PMMA/graphene/NbSe₂/graphene film was detached from the substrate by etching SiO₂ layer in HF. After rinsed in DI water, it was scooped up by a TEM grid. Finally, the graphene/NbSe₂/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 α ($h\nu = 1486.6$ 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 $\times 50$ 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 NbSe₂/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., C.Z., 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.


Additional information

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