Tailoring Domain Morphology in Monolayer NbSe$_2$ and W$_x$Nb$_{1-x}$Se$_2$ Heterostructure

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ABSTRACT: Domain morphology plays a pivotal role not only for the synthesis of high-quality 2D transition metal dichalcogenides (TMDs) but also for the further unveiling of related physical and chemical properties, yet little has been divulged to date, especially for metallic TMDs. In addition, solid precursor as a transition metal source has been conventionally introduced for the synthesis of TMDs, which leads to an inhomogeneous distribution of local domains with the substrate position, making it difficult to obtain a reliable film. Here, we tailor the domain morphologies of metallic NbSe$_2$ and NbSe$_2$/WSe$_2$ heterostructures using liquid-precursor chemical vapor deposition (CVD). We find that triangular, hexagonal, tripod-like, and herringbone-like NbSe$_2$ flakes are constructed through control of growth temperature and promoter and precursor concentration. Liquid-precursor CVD ensures domain morphologies that are highly reproducible over repeated growth and uniform along the gas-flow direction. A domain coverage of ~80% is achieved at a high precursor concentration, starting with tripod-like NbSe$_2$ domain and evolving to the herringbone fractal. Furthermore, mixing liquid W and Nb precursors results in sea-urchin-like heterostructure domains with long-branch-shaped NbSe$_2$ at low temperature, whereas protruded hexagonal heterostructure domains grow at high temperature. Our liquid precursor approach provides a shortcut for tailoring the domain morphologies of metallic TMDs as well as metal/semiconductor heterostructures.

KEYWORDS: domain morphology, monolayer niobium diselenide, lateral NbSe$_2$−W$_x$Nb$_{1-x}$Se$_2$ heterostructure, liquid precursor, chemical vapor deposition

Two-dimensional (2D) van der Waals (vdW) layered transition metal dichalcogenides (TMDs) that possess various semiconductors and metals have attracted significant attention due to their intriguing physical and chemical properties. Semiconducting TMDs reveal a direct bandgap in the monolayer and a wide range of indirect bandgaps with the layer thicknesses, strong exciton binding energy, reduced charge screening, and strain-sensitive bandgap engineering. Meanwhile, metallic TMDs have been recently revisited because of their fascinating physical properties and promising applications such as Weyl semimetals, charge density waves, and superconductivity. Especially, homojunction vdW contacts without a transfer process between semiconducting and metallic TMDs (e.g., 2H-MoTe$_2$/1T’-MoTe$_2$ and WS$_2$/NbS$_2$) could significantly lower contact resistance, thus demonstrating excellent electrical performance compared with heterojunction TMD devices.

High-quality TMDs and their lateral heterostructures including metallic NbS$_2$/semiconducting WS$_2$ have been successfully synthesized on a large scale by chemical vapor deposition (CVD). There are three CVD approaches for growing TMDs, namely, (i) solid-metal-precursor, (ii) vapor-metal-precursor, and (iii) liquid-metal-precursor approaches. Solid-metal-precursor CVD provides high-quality TMDs with crystal domains of a few tens of μm in size, however, sample uniformity is often limited by the growth conditions. The vapor-metal-precursor approach, with metal–organic CVD as an example, provides a uniformly distributed sample on a 4 in. wafer, but the grown TMD suffers from low crystallinity (a few hundred nm domain) and low accessibility due to its toxicity. Meanwhile, the liquid-metal-precursor approach has several advantages. As the liquid precursors can simply be spin-coated onto a substrate, samples...
can be synthesized on the wafer scale in a highly uniform and reproducible manner. Moreover, a wide range of liquid-metal precursors are easily accessible through additional engineering of the precursor contents in combination with alkali promoters.

A variety of domain morphologies have been obtained through CVD growth, including heterogeneous defect domains in hexagonal WS$_2$, self-collimation in circular h-BN to form a single-crystalline film, and high hydrogen evolution reaction in dendritic MoS$_2$. Such diverse domain morphologies are certainly intriguing from a scientific point of view but are not controllable in terms of achieving uniformly distributed domains.

While control of the morphologies of semiconducting TMDs has been demonstrated that of metallic TMDs has rarely been reported. Furthermore, metallic TMDs are mostly grown by the solid-precursor CVD approach, which hinders the ability to precisely control domain morphology because of the low uniformity along the gas flow direction. To control the domain morphology of metallic TMDs precisely, it is essential to achieve high uniformity and reproducibility for CVD growth.

In this study, we develop a reliable growth platform for precisely tailoring the domain morphologies of NbSe$_2$ as well as NbSe$_2$/WSe$_2$ heterostructures through liquid-precursor CVD. Domain morphology and size are engineered by controlling growth temperature and the ratio of the Na-promoter concentration to the liquid-metal-precursor concentration, which results in a variety of morphologies, including triangles, hexagons, tripods, and herringbone-like dendritic fractals in the NbSe$_2$ monolayer and sea-urchin-like hexagonal forms in the NbSe$_2$/WSe$_2$ heterostructure.
RESULTS AND DISCUSSION

The liquid precursor for NbSe2 growth consists of aqueous ammonium niobite oxalate (ANO, the Nb precursor), NaOH (the Na promoter), and iodixanol. The ratio of the Nb precursor to the Na promoter is precisely adjusted with a micropipet. The mixed solution is uniformly spin-coated onto a 300 nm SiO2/Si substrate up to a 4 in. scale (Figure 1a and Figure S1). Note that the role of iodixanol is to improve the wettability and viscosity of the aqueous precursor so as to yield uniform spin-coating of the precursor on the SiO2/Si substrate. The precursor-coated substrate is then introduced to atmospheric-pressure CVD followed by annealing with a supply of Se vapor (see Methods). Various triangular NbSe2 flakes are well size-distributed to a maximum of ∼30 μm at a growth temperature of 800 °C, implying the emergence of a single crystal within the triangular flakes similar to a previous report (Figure 1b). The majority of monolayers in size are formed with small portions of bilayers and multilayers. The layer thickness is identified by an atomic force microscopy (AFM) height profile (Figure 1c).

The A1g mode near 225.7 cm⁻¹ and the E2g mode near 248.7 cm⁻¹ in the Raman spectra clearly identify the presence of NbSe2 (Figure 1d), in good agreement with previous reports. The frequency difference between the A1g and E2g peaks is an indicator of thickness, which was found to be 23 cm⁻¹ for the monolayer, 19.5 cm⁻¹ for the bilayer, and 17.9 cm⁻¹ for the multilayer. The broad feature at ∼180 cm⁻¹ corresponds to the soft vibrational mode associated with two-phonon scattering. The chemical composition of the CVD-grown NbSe2 is determined by X-ray photoelectron spectroscopy (XPS), with core level Nb 3d and Se 3d spectra shown in Figure 1e. All peaks are deconvoluted and dominant peaks (blue lines) are well-matched with those reported for NbSe2 (Nb4+ 3d5/2 = 203.4 eV, Nb4+ 3d3/2 = 206.1 eV, Se2− 3d5/2 = 53.3 eV, and Se2− 3d3/2 = 54.0 eV). The Se/Nb ratio is determined to be 2.03 (Figure S2). The additional side peaks in Nb (green and purple lines) and Se (green lines) that correspond to niobium oxide (NbO: 203.9 and 206.6 eV, Nb2O5: 207.5 and 210.3 eV) and selenium oxide (SeO2: 54.6 and 55.3 eV) are attributed to the air-sensitive nature of the metallic NbSe2 sample (Figure S3).

To tailor the domain morphology of NbSe2, we conduct a series of experiments depending on the growth temperature (750, 800, and 850 °C) and Na-promoter/Nb-precursor ratio in the liquid precursor (NaOH/ANO = 2, 2.5, and 3) (Figure 2a). Other CVD parameters such as the gas flow rate (N2/H2: 600/15 sccm) and growth time (6 min) are fixed. At a growth condition of 750 °C and NaOH/ANO ratio of 2 (bottom left), the NbSe2 flakes are barely grown with remnant precursors. By increasing the partial concentration of NaOH, the triangular NbSe2 monolayers are dominantly grown (NaOH/ANO = 2.5) in the planar direction due to the promotion effect of NaOH. The NbSe2 flakes are further enlarged with shape evolution to the tripods and maple-like domains as the NaOH/ANO ratio increases (NaOH/ANO = 3). With the elevated growth temperatures (800 and 850 °C), the truncated hexagonal NbSe2 domains appear together with the triangular domains at low NaOH concentration ratio (NaOH/ANO = 2). A similar trend of morphology transitions is seen as the NaOH/ANO ratio increases, while intriguing dendritic fractals...
are preserved at high growth temperature and NaOH/ANO ratio (top right).

The morphology transitions observed for NbSe$_2$ are explained on the basis of the NaOH/ANO ratio (Figure 2b). NaOH promotes the lateral growth of a NbSe$_2$ flake by anchoring the Nb precursor, similar to other types of precursors such as Mo and W.\textsuperscript{15,44} The Nb-precursor concentration increases in proportion to the NaOH concentration and eventually overwhelms the Se precursor. Consequently, Se-terminated facets grow faster than Nb-terminated facets under Nb-rich conditions, and the NbSe$_2$ domain morphology evolves from hexagonal to triangular, tripod-like, and herringbone-like shapes.\textsuperscript{24} To investigate domain morphology preservation over repeated growth, experiments are conducted eight times under the same growth conditions. The domain morphologies of the NbSe$_2$ flakes are well preserved for up to eight growth cycles (red box in Figure 2a; see also Figures S4 and S5). Furthermore, the extracted edge lengths and coverages of the NbSe$_2$ flakes are found to be similar within small error ranges: the average edge length is determined to be 14.1 $\mu$m with a standard deviation of 1.8 $\mu$m, while coverage is retained at 40.3% with a standard deviation of 1.6%.

Coverage of the grown NbSe$_2$ flakes is studied at various liquid-precursor concentrations with the NaOH/ANO ratio fixed at 3 and the growth temperature fixed at 800 °C. Figure 3a shows optical images of NbSe$_2$ samples prepared at liquid-precursor concentrations that range from 100% (ANO 26 and NaOH 80 mM) to 200% (ANO 52 and NaOH 160 mM) in 20% increments. Tripod-like NbSe$_2$ flakes are clearly defined at low precursor concentrations (100% and 120%). Small branches of fractals appear further from the tripod-like NbSe$_2$ and eventually form herringbone-like fractals at higher precursor concentrations (140–200%). Figure 3b shows coverage as a function of liquid-precursor concentration. NbSe$_2$-flake coverage is proportional to the liquid-precursor concentration and becomes saturated at ~76% at precursor concentrations above 180% with enlarging the flake sizes, with a small portion of multilayers (~2%) (Figure S6).

The uniformity of the NbSe$_2$ sample is further analyzed along the gas flow direction at a liquid-precursor concentration of 100% (Figure 3c). Four representative optical images of the NbSe$_2$ sample are taken from the inlet to the outlet region. The domain morphologies and sizes are similar to each other and independent of the position and gas flow direction, indicative of a highly uniform NbSe$_2$ sample, which is attributable to the uniform liquid-precursor concentration distribution obtained by spin-coating onto the substrate (see Figure S1). The triangular NbSe$_2$ sample also shows high uniformity along the gas flow direction (Figure S7).

In addition to the reliable NbSe$_2$ monolayer growth and well-controlled domain morphology, a lateral W$_x$Nb$_{1-x}$Se$_2$ heterostructure is synthesized by mixing the liquid W precursor with the Nb precursor and applying the aforementioned CVD process (Figure 4a and see Methods for details). During the heterostructure growth, the inner W$_x$Nb$_{1-x}$Se$_2$ domain is formed first and NbSe$_2$ domain is synthesized later from the border of the W$_x$Nb$_{1-x}$Se$_2$ domain in a single step due to a relatively lower growth temperature of WSe$_2$ (~700 °C)\textsuperscript{45} than that of NbSe$_2$ (~800 °C).\textsuperscript{14} Inner polygonal W$_x$Nb$_{1-x}$Se$_2$ domains that are typically ~40 $\mu$m in size are clearly distinguished from outer branch sea-urchin-like NbSe$_2$ domains in the optical micrograph (Figure 4b and inset). The NbSe$_2$/W$_x$Nb$_{1-x}$Se$_2$ heterostructure is characterized by noncontact-mode AFM topography and phase image (Figure 4c and inset). The topographical image reveals a uniform monolayer thickness (~1 nm) that is preserved over the entire heterostructure region. On the contrary, the phase image shows clear phase contrast across the NbSe$_2$ and W$_x$Nb$_{1-x}$Se$_2$ domains, consistent with the formation of the 2D lateral heterostructure. The bright contrast observed for the needle-like NbSe$_2$ domain in the phase image is attributable to strong electrostatic interaction of the metallic NbSe$_2$ compared with the semiconducting WSe$_2$ domain and SiO$_2$ region (Figure S8).\textsuperscript{46}

The NbSe$_2$/W$_x$Nb$_{1-x}$Se$_2$ heterostructure is characterized by confocal Raman intensity mapping in the 245–250 cm$^{-1}$ range, which includes the mixed $E^{1g}_{2g}$+$A^{1g}_{1g}$ mode of WSe$_2$ (~249 cm$^{-1}$) and the $E^{1g}_{2g}$ mode of NbSe$_2$ (~248 cm$^{-1}$) (Figure 4d).\textsuperscript{47} The Raman intensity gradually decreases from the central to the outer region in the W$_x$Nb$_{1-x}$Se$_2$ domain (white dotted line), while no distinguishable signal appears in
the NbSe₂ region (yellow dotted line) due to the relatively low intensities of the Raman modes of NbSe₂ (Figure S9). Representative Raman spectra are extracted from the central (red spot) and outer (green spot) WₙNb₁₋ₓSe₂ domains (Figure 4e). The mixed WSe₂ mode in the central region is red-shifted by ∼2 cm⁻¹ (at ∼247 cm⁻¹) compared to that of pristine WSe₂ (∼249 cm⁻¹) and further red-shifted by ∼6 cm⁻¹ (at ∼243 cm⁻¹) in the outer region, with significantly reduced intensity (Figure S9). Such mixed-mode red-shifts are attributed to the p-doping effect associated with gradual Nb incorporation toward the outer WₙNb₁₋ₓSe₂ domain.¹⁶,⁴⁹

Nb-incorporation in the WSe₂(WₙNb₁₋ₓSe₂) domain is atomically resolved by annular dark-field scanning transmission electron microscopy (ADF-STEM) (Figure 4f). The Nb atom (yellow circle) with darker contrast is clearly observed together with bright W (green circle) and gray Se (red circle) atoms in 2H-phase WSe₂, which is consistent with the simulated image and its intensity profile (Figure 4g and h).⁴⁹ As is observed by confocal Raman mapping, the ADF-STEM image of the outer WₙNb₁₋ₓSe₂ region shows a relatively high Nb-doping concentration compared with that of the inner WₙNb₁₋ₓSe₂ region (Figure 4i). Nb-doping concentrations from six positions within the WSe₂ domain are extracted from the ADF-STEM image and plotted in Figure 4j (see also Figure S10). The outermost WSe₂ region, which is near to the NbSe₂-domain border (position 1), reveals a high Nb-doping concentration (∼9.1%), while the inner WₙNb₁₋ₓSe₂ region shows a low Nb-doping concentration (∼0.9%).

SiO₂ back-gated field-effect transistors (FETs) are fabricated to investigate the effect of Nb doping on the electronic properties of WSe₂ (Figure 4k). The source and drain electrodes (Cr/Au: 5 nm/50 nm) are deposited on both the
outer and the inner $W_{x}Nb_{1-x}Se_{2}$ with the same channel area ($1 \, \mu m \times 1 \, \mu m$). The Nb-deficient inner $W_{x}Nb_{1-x}Se_{2}$ FET (bottom) manifests dominant p-type ambipolar transfer characteristics with an on/off ratio of $\sim 10^3$. Meanwhile, the highly Nb-doped outer $W_{x}Nb_{1-x}Se_{2}$ FET exhibits heavily degenerate behavior with a negligible gate-voltage dependence within the $-60$ to $60 \, V$ range. $NbSe_2$ shows metallic behavior without gate-voltage dependence with high transmittance over $90\%$ at $550 \, nm$ and $97\%$ at $750 \, nm$ (Figure S11). Note that $NbSe_2$ is easily oxidized in the heterostructure; thus special care of this is needed (Figure S12).

Since growth temperature is a critical parameter that controls domain morphology and the degree of alloying in a heterostructure, the temperature-dependent heterostructure growth is investigated (Figure 5a). A large $NbSe_2$ area grows laterally from the edge of the $W_{x}Nb_{1-x}Se_{2}$ domain to form a lateral $NbSe_2/W_{x}Nb_{1-x}Se_{2}$ heterostructure with sea-urchin-like needles without $NbSe_2$ nucleation on the substrate at a low temperature ($750 \, ^\circ C$, Figure 5b). Within the $W_{x}Nb_{1-x}Se_{2}$ domain, strong phase segregation is observed between the Nb-rich outer region and the Nb-poor inner region due to dominant enthalpic contribution compared with the entropic contribution in Gibbs free energy. Meanwhile, Nb precursors are consumed by the $NbSe_2$ nucleation at high temperatures ($800$ and $850 \, ^\circ C$, Figure 5b), resulting in small $NbSe_2$ branches with protruded hexagonal forms at the border of the $W_{x}Nb_{1-x}Se_{2}$ domain. In the meantime, the Nb atoms are well-distributed in the entire $W_{x}Nb_{1-x}Se_{2}$ region due to prominent entropic contributions. At a low growth temperature of $700 \, ^\circ C$ with a NaOH/ANO ratio of 2.5, $NbSe_2/W_{x}Nb_{1-x}Se_{2}$ heterostructures are formed with a triangular shape, while at an elevated growth temperature of $825 \, ^\circ C$, the tripod shapes are abundant (Figure S13). By varying Se content via Se-zone temperature (400, 390, and 380 $^\circ C$) with other growth parameters fixed (growth temperature of $850 \, ^\circ C$ and NaOH/ANO ratio of 2.5), the hexagonal heterostructure at a high Se-zone temperature ($400 \, ^\circ C$) is transformed into enlarged tripod domains at a low Se-zone temperature ($380 \, ^\circ C$).
°C) (Figure S14). Under a Nb-rich precursor ratio (Nb:W = 4:1), tripod domains are abundant with a limited portion of polygonal hexagon shapes, while starfish-like hexagon shapes are constructed in Nb-poor conditions (Nb:W = 1:4) (Figure S15).

Raman spectroscopy is performed to investigate the phase segregation of the Nb atoms within the \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \) domain at different growth temperatures (Figure 5c), which reveals discrepancies between the Raman spectra acquired from the inner and outer \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \) regions, while the mixed \( A_{1g} + E_{2g} \) mode of the outer \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \) domain is more red-shifted than that from the inner \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \) domain. The difference of mixed mode (\( \Delta_{\text{mixed}} \)) between the inner and the outer \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \) regions is indicative of the degree of phase segregation and is plotted against growth temperature in Figure 5d. The 4.1 cm\(^{-1} \) of \( \Delta_{\text{mixed}} \) at 750 °C is observed to gradually decrease with increasing growth temperature to a value of 0.8 cm\(^{-1} \) at 850 °C, which clearly indicates that a high growth temperature minimizes the phase segregation of Nb atoms in the \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \) domain.

Photoluminescence (PL) spectra are taken to analyze the effect of Nb doping on the optical properties of \( W_{\text{Se}_{2}} \) (Figure 5e). While PL emissions are completely quenched in the highly Nb-doped outer \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \) regions because of strong charge (hole) screening,\(^{48} \) detectable PL emissions are observed from the inner lightly Nb-doped \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \) regions. The PL spectrum from the inner \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \) region of the sample grown at 750 °C exhibits an emission at ~780 nm, which is red-shifted compared with that of pure \( W_{\text{Se}_{2}} \) (~760 nm, black dashed line). Notably, the PL peak from the inner region is further red-shifted at higher growth temperature and eventually reaches 870 nm (850 °C). The Nb atom acts as the p-dopant to \( W_{\text{Se}_{2}} \) and generates the energy level near the valence band edge of \( W_{\text{Se}_{2}} \).\(^{51,52} \) Therefore, as the Nb-doping concentration increases, the PL emission becomes down-shifted due to the Nb acceptor states in the \( W_{\text{Se}_{2}} \) bandgap\(^{52} \) or band renormalization attributed to the screened-exchange contribution.\(^{53} \)

**CONCLUSION**

In conclusion, we demonstrate the domain morphology tailoring for the metallic \( \text{NbSe}_2 \) as well as its lateral heterostructure with semiconducting \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \) via the liquid-precursor CVD approach. The Nb-precursor and Na-promoter are mixed and uniformly spin-coated on the substrate, followed by selenization to form \( \text{NbSe}_2 \) with a few tens of \( \mu \text{m} \) flake size. The morphology of the \( \text{NbSe}_2 \) domain is precisely engineered by the NaOH/ANO ratio and growth temperature in various forms of triangles, hexagons, tripods, and herringbone-like domains. Furthermore, the \( \text{NbSe}_2/ W_{\text{Nb}_{1-x}\text{Se}_{2}} \) lateral heterostructure is easily synthesized by adding a W precursor into the liquid \( \text{NbSe}_2 \) precursor. The outer \( \text{NbSe}_2 \) is grown from the edges of the first-grown inner \( W_{\text{Se}_{2}} \) to form a lateral metal-semiconductor heterostructure. Nb atoms are doped in the \( W_{\text{Se}_{2}} \) domain, and the Nb-doping concentration gradually decreases from the outside to the inside of the \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \). The morphology of the heterostructure is efficiently modified by the growth temperature. Large areas of \( \text{NbSe}_2 \) with sea-urchin needle-like forms are produced in the heterostructure at a low growth temperature by suppressing \( \text{NbSe}_2 \) nucleation. Meanwhile, the Nb precursors are consumed by \( \text{NbSe}_2 \) nucleation at a high growth temperature, leading to small areas of \( \text{NbSe}_2 \) beside the inner \( W_{\text{Nb}_{1-x}\text{Se}_{2}} \).

**METHODS**

**Liquid-Precursor Preparation.** The precursor solution for \( \text{NbSe}_2 \) is prepared by mixing the following aqueous solutions: (A) 26 mM ammonium niobate oxalate \((\text{C}_4\text{H}_4\text{NNbO}_9\text{H}_2\text{O}, \text{Sigma-Aldrich})\), (B) 26 mM NaOH (Sigma-Aldrich), and (C) Optiprep density gradient medium (Jodixanol, Sigma-Aldrich). For example, solutions A, B, and C are mixed in a 2:5:1 ratio as the standard conditions for the growth of triangular \( \text{NbSe}_2 \) monolayers (red box in Figure 2a).

To grow the \( \text{NbSe}_2/W_{\text{Nb}_{1-x}\text{Se}_{2}} \) heterostructure, solution D (68 mM ammonium metatungstate hydrate \( ((\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}, \text{Sigma-Aldrich}) \)) is also injected into the \( \text{NbSe}_2 \) liquid precursor at an A:B:C:D ratio of 2:5:1:0.5.

**Growth of Monolayer \( \text{NbSe}_2 \) and the Heterostructure.** Monolayer \( \text{NbSe}_2 \) flakes are grown on a 300 nm SiO\(_2\)/Si substrate by CVD. The liquid precursor is dropped onto the SiO\(_2\)/Si substrate and then spin-coated at 3000 rpm for 30 s. The precursor-coated substrate and 0.1 g of selenium (Sigma-Aldrich) are separately introduced into the two-zone furnace. Growth proceeds at atmospheric pressure in a two-zone furnace. The Nb-doping concentration is regulated by the ratio of precursor and selenium. After 20 min of growth, both furnaces are opened and naturally cooled to room temperature. The \( \text{NbSe}_2/W_{\text{Nb}_{1-x}\text{Se}_{2}} \) lateral heterostructure is grown under the condition used to grow \( \text{NbSe}_2 \) with the exception that the temperature of the substrate zone is set to 750 °C.

**Characterization.** Raman and PL spectra are acquired with 532 nm laser excitation (RM1000, Renishaw). The edge lengths and coverages of the \( \text{NbSe}_2 \) flakes are extracted using freely available Gwyddion software. XPS is performed using a monochromatic Al Kα source (\( h\nu = 1486.6 \text{ eV} \) (ESCALAB 250, Thermo Scientific)), while AFM is conducted using an XE-7 microscope (Park Systems).

**STEM and Specimen Preparation.** ADF-STEM images are acquired using a probe aberration-corrected JEM ARM 200F microscope operating at 80 kV. The imaging time is set to 1 s in high-magnification STEM mode to prevent the beam from damaging the monolayer samples. Samples are transferred to the TEM grid by coating poly(methyl methacrylate) (PMMA C4, MicroChem) onto the \( \text{NbSe}_2 \) and \( \text{NbSe}_2/W_{\text{Nb}_{1-x}\text{Se}_{2}} \) samples on SiO\(_2\)/Si wafers, which are then immersed in diluted hydrofluoric acid to detach the samples from the wafer. The PMMA-supported sample is transferred to the TEM grid (PELCO, 200 mesh, copper, 1.2 \( \mu \text{m} \) holes), and then the PMMA is removed by dipping in acetone for 5 min. The grid is then annealed at 180 °C in a high-vacuum chamber at ~7.5 × 10\(^{-5} \) Torr for 12 h prior to TEM to avoid polymerization during STEM imaging.

**Device Fabrication and Measurements.** The \( \text{NbSe}_2 \) and heterostructure samples are transferred onto a highly p-doped silicon substrate with a 300 nm thick oxide. Metal electrodes for contact are patterned onto the samples by e-beam lithography followed by e-beam deposition of Cr/Au (5 nm/50 nm). All electrical experiments are performed in a high vacuum (~10\(^{-6} \) Torr) using a Keithley 4200 SCS system.

**ASSOCIATED CONTENT**

© Supporting Information

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Thickness of the liquid-precursor-coated substrate; survey XPS spectrum of \( \text{NbSe}_2 \); analysis of coverage and edge lengths of the \( \text{NbSe}_2 \) flakes; Raman spectra of the \( \text{NbSe}_2/W_{\text{Nb}_{1-x}\text{Se}_{2}} \) heterostructure; position-dependent ADF-STEM images of the \( W_{\text{Se}_{2}} \) domain in...
the heterostructure; electrical characteristics of the NbSe$_2$ FET device (PDF)

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S.P. and S.J.Y. developed the work. Y.I.K. and Y.-M.K. performed the annular dark field scanning tunneling microscopy. J.-H.K. conducted electrical measurements. K.K.K. and Y.H.L. guided the writing of the manuscript. All authors discussed the results and commented on the manuscript.

Notes
The authors declare no competing financial interest.

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