

Temperature-dependent polymorph evolution of NbSe₂ on WSe₂ via van der Waals epitaxy

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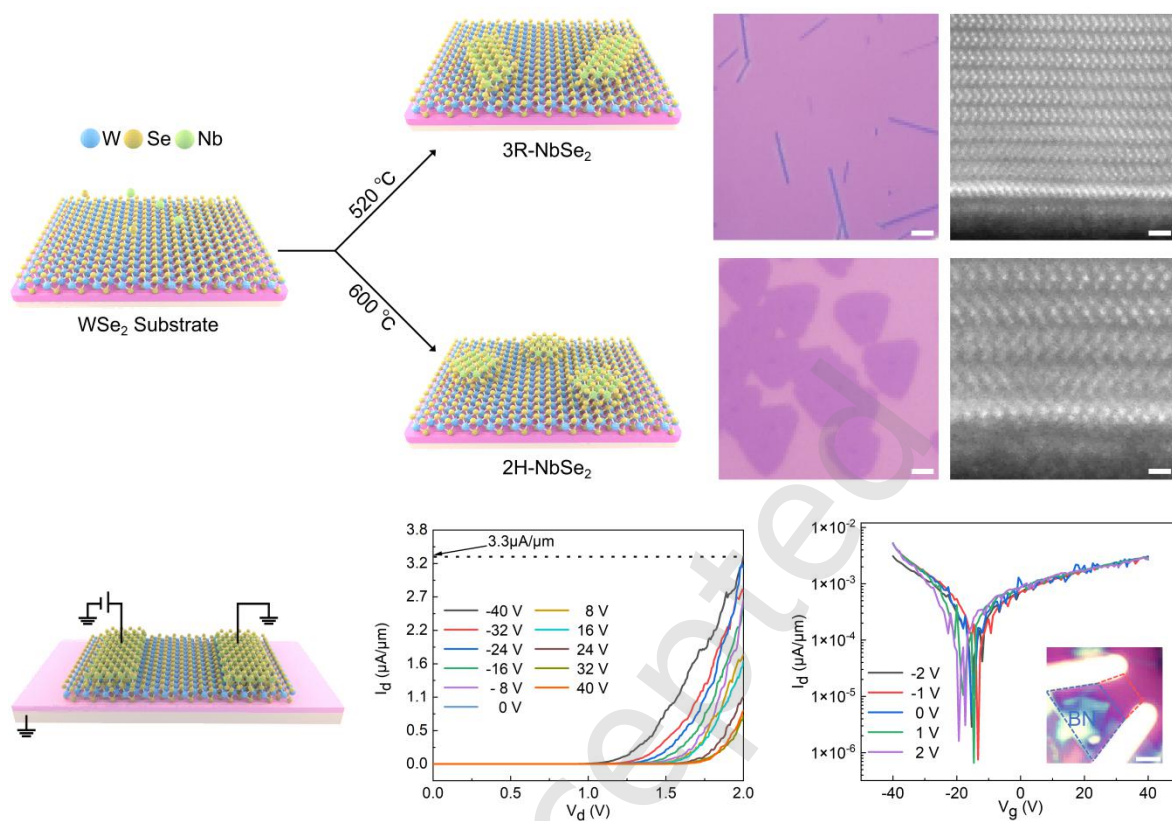
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A temperature-mediated van der Waals epitaxy strategy is developed to selectively synthesize distinct NbSe₂ polymorphs on a WSe₂ template. This work establishes a controllable route for phase engineering of two-dimensional materials and demonstrates the potential of NbSe₂/WSe₂ heterostructures for electronic applications.

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ABSTRACT: Polymorph engineering in two-dimensional transition metal dichalcogenides provides an effective route for tuning structure-dependent electronic properties, yet controllable phase-selective growth remains challenging because polymorph stability is highly sensitive to growth conditions. In particular, achieving reliable phase selectivity in chemical vapor deposition (CVD) without modifying precursor chemistry or introducing external perturbations remains difficult. Here, we report a temperature-dependent CVD growth strategy for phase-selective synthesis of NbSe₂ on atomically flat WSe₂ substrates. By tuning the growth temperature, rhombohedral 3R-NbSe₂ and hexagonal 2H-NbSe₂ can be selectively obtained within distinct temperature windows, with a coexistence region observed at intermediate conditions. Structural and spectroscopic characterizations reveal clear differences in morphology, stacking configuration, and vibrational properties between the two polymorphs, while atomic-resolution microscopy confirms the formation of atomically sharp and chemically abrupt interfaces. The observed temperature-dependent phase evolution suggests that surface diffusion and nucleation behavior may play important roles during growth. In addition, metallic NbSe₂ exhibits improved carrier injection as a contact electrode, highlighting its potential for device integration. This work demonstrates a feasible approach for temperature-dependent phase-selective growth in CVD-grown two-dimensional heterostructures.

KEYWORDS: polymorph engineering, van der Waals epitaxy, phase-selective growth, two-dimensional heterostructures, temperature-programmable synthesis, transition metal dichalcogenides

1 Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have attracted extensive attention owing to their atomic-scale thickness, tunable electronic structures, strong light-matter interactions, and excellent mechanical flexibility, making them promising candidates for next-generation electronic and optoelectronic devices.[1-6] Among them, NbSe₂ is a representative layered TMDC that exhibits rich polymorphic behavior and strongly structure-dependent electronic properties.[7-9] The most commonly studied NbSe₂ polymorphs are the hexagonal 2H phase and the rhombohedral 3R phase. Importantly, these two phases share the same intralayer Se-Nb-Se atomic framework and similar local coordination environment within each individual layer. Therefore, their essential structural difference does not originate from chemical composition or intralayer bonding, but from the stacking order of adjacent NbSe₂ layers.[7] In 2H-NbSe₂, adjacent layers follow an ABAB-type stacking sequence with alternating layer

orientations, resulting in a hexagonal structure with two-layer periodicity along the out-of-plane direction. In contrast, 3R-NbSe₂ adopts an ABCABC-type stacking sequence, in which neighboring layers are laterally translated relative to each other, giving rise to a rhombohedral structure with three-layer periodicity. Such stacking differences directly modify the crystallographic symmetry, interlayer coupling, and electronic band structure of NbSe₂, thereby leading to distinct electronic and transport-related behaviors. For example, 2H-NbSe₂ has been widely studied as a metallic layered superconductor, in which superconductivity and charge-density-wave-related phenomena are closely associated with its layered electronic structure.[9] By comparison, 3R-NbSe₂, owing to its rhombohedral and non-centrosymmetric stacking configuration, can exhibit different semimetallic transport characteristics, carrier-density-related behavior, and superconducting responses.[10-11] Therefore, although 2H-NbSe₂ and 3R-NbSe₂ consist of the same NbSe₂ layers, their different stacking sequences provide an effective structural degree of freedom for

modulating interlayer coupling, semimetallicity, and transport behavior.[12] This makes NbSe₂ an attractive platform for exploring stacking-dependent structure–property relationships and phase-engineered functionalities in two-dimensional systems. Achieving selective growth of distinct NbSe₂ polymorphs is therefore of considerable importance for both fundamental studies and device integration. However, precise control over polymorph formation in TMDC systems remains challenging because the relative stability of different phases is highly sensitive to growth conditions, including temperature, precursor concentration, and substrate interactions. In addition, uncontrollable nucleation behavior, defect formation, and interfacial disorder during growth can significantly affect the structural uniformity and electronic properties of the resulting materials. Therefore, developing controllable synthesis strategies for phase-selective growth of NbSe₂ remains an important issue in two-dimensional materials research.

Chemical vapor deposition (CVD) provides an effective route for the controllable growth of two-dimensional materials and heterostructures.[13–14] WSe₂ serves as an ideal growth template with its atomically flat basal plane and hexagonal symmetry.[15] The weakly coupled interface formed via van der Waals (vdW) interactions with NbSe₂ relaxes lattice constraints and preserves its intrinsic stacking configuration. The stability of different polymorphs is highly sensitive to growth temperature, precursor flux, and substrate interactions, hindering precise phase selectivity and control.[16–18] In addition, point defects, grain boundaries, and interfacial defects are prevalent, introducing localized states and degrading electronic and optical properties. These issues limit the implementation of 2D materials in high-performance devices and scalable applications.[19–20]

Here, we report a temperature-dependent vdW epitaxy strategy for phase-selective growth of NbSe₂ on WSe₂ substrates. By tuning the growth temperature within a controlled range, the selective formation of 3R-NbSe₂ and 2H-NbSe₂ phases, as well as their coexistence in an intermediate regime, can be achieved on the same vdW template. Structural and spectroscopic characterizations reveal distinct differences in morphology, stacking configuration, and vibrational properties between the two polymorphs. Atomic-resolution scanning transmission electron microscopy (STEM) measurements further demonstrate the formation of atomically sharp and chemically abrupt interfaces in both heterostructures. The observed phase evolution and morphology transition suggest that temperature-dependent growth behavior plays an important role in polymorph formation. In addition, NbSe₂-based heterostructures exhibit improved electrical contact behavior, highlighting their potential for future phase-engineered electronic devices.

2 Experimental

2.1 Synthesis of TMDCs Thin Films

NbSe₂/WSe₂ heterostructures were synthesized via a CVD method, and a schematic illustration of the reaction setup is shown in **Figure S1**. NbCl₅ powder, serving as the Nb precursor, was placed in a ceramic boat positioned at the center of a tube furnace. SiO₂/Si or other substrates were placed approximately 2 cm above the precursor with the polished side facing downward. Selenium powder was located in the upstream region of the quartz tube, where the temperature was maintained in the range

of 280–420°C during growth. Prior to the reaction, a mixed Ar/H₂ gas flow of 100 sccm was introduced to establish a stable growth atmosphere. The furnace was then heated for 6 minutes, during which an external heating coil was simultaneously activated to heat the Se precursor. Subsequently, the temperature was further increased over 4 minutes to reach the target growth temperature (520–600°C), followed by a growth period of 10 minutes. After growth, the heating system was turned off and the samples were naturally cooled to room temperature under the carrier gas flow, yielding NbSe₂/WSe₂ heterostructures on the substrates.

2.2 Preparation of STEM Sample

To prepare the STEM samples, the substrate containing the sample was first cut into approximately 1 cm × 1 cm pieces. A layer of poly(methyl methacrylate) (PMMA) was then spin-coated onto the surface of the substrate. The sample was baked at 100°C for 10 minutes to ensure the PMMA layer was fully cured and to enhance its mechanical stability. Following this, the PMMA-coated sample was immersed in sodium hydroxide (NaOH) solution for the etching of the SiO₂ layer, allowing the PMMA film to be separated from the silicon substrate. After detaching the PMMA film, the sample was repeatedly rinsed in fresh deionized water to remove any residual contaminants. The PMMA-covered sample was then transferred to a copper mesh with a microgrid supporting carbon film for further handling. Before immersing the sample in acetone to dissolve the PMMA coating, it was air-dried at room temperature to ensure the PMMA film was tightly bonded to the copper mesh. The sample was then soaked in acetone for 2 hours to completely remove the PMMA layer. To prevent unintended hydrocarbon contamination, all STEM samples were subjected to a bakeout process at 150°C for 2 hours prior to use.

2.3 Material Characterization

The samples were characterized using OM and SEM. Raman spectroscopy measurements were performed with a Renishaw confocal Raman system (488 nm laser, room temperature). EDS was conducted using a JEOL JEM-2100F at 200 kV. XPS was carried out with an AXIS SUPRA+ system, and STEM was performed using a Titan Themis G2 300 microscope at 300 kV.

2.4 Device Fabrication and Characterization

Gold electrodes were first defined and subsequently transferred onto the surface of the target material using a water-free dry-transfer technique, which effectively avoids interfacial contamination and ensures intimate electrical contact between both electrode terminals and the two-dimensional material.

3 Results and Discussion

Figure 1a schematically illustrates the crystal structure of NbSe₂ and its temperature-dependent phase evolution, showing that distinct polymorphs can be stabilized within a specific temperature range. At a relatively low growth temperature of 520°C, NbSe₂ predominantly crystallizes in the rhombohedral 3R phase, whereas increasing the temperature to 600°C results in the formation of the hexagonal 2H phase. Within an intermediate temperature regime, the coexistence of both polymorphs is observed, suggesting the presence of a temperature-dependent

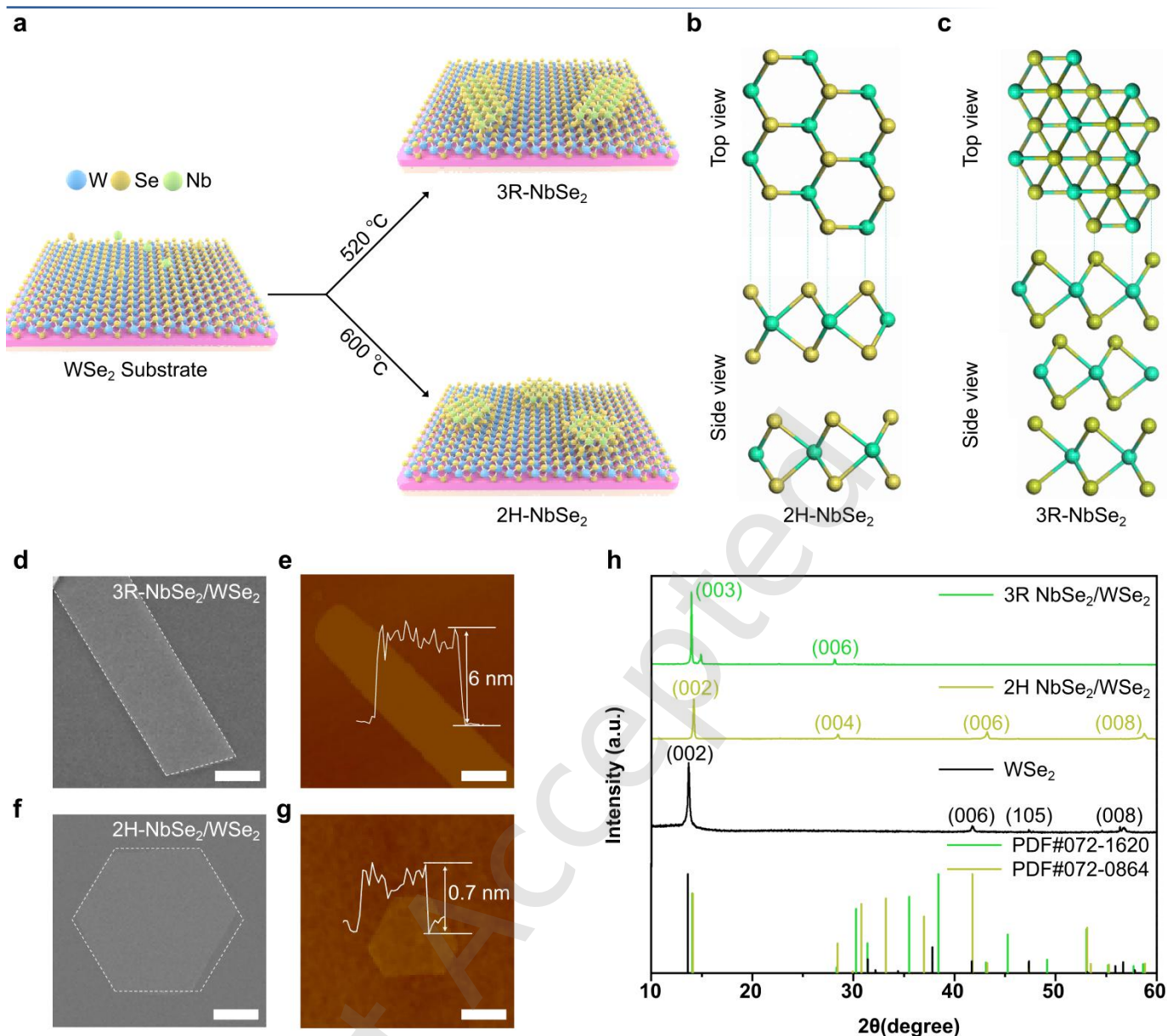


Figure 1. Schematic of temperature-programmable phase-selective CVD growth of NbSe₂ on WSe₂. (a) Schematic illustration of phase-selective epitaxial growth of NbSe₂ on WSe₂ by temperature regulation. Side and top views of the atomic model of (b) 2H-NbSe₂ and (c) 3R-NbSe₂. (d) SEM images of epitaxially grown 3R-NbSe₂ on WSe₂. (e) AFM images of 3R-NbSe₂ on WSe₂. (f) SEM images of epitaxially grown 2H-NbSe₂ on WSe₂. (g) AFM images of 2H-NbSe₂ on WSe₂. (h) X-ray diffraction patterns of 3R-NbSe₂/WSe₂, 2H-NbSe₂/WSe₂ heterostructures, and WSe₂ substrate. Scale bars are (d), (f) 2 μ m, (e), (g) 5 μ m.

phase transition region (Figure S2).[21-23] The structural distinctions between the two polymorphs are reflected in their atomic stacking configurations (Figure 1b, c). The 2H phase adopts an AB-type stacking sequence with alternating atomic alignment along the out-of-plane direction, resulting in higher crystallographic symmetry. In contrast, the 3R phase exhibits an ABC-type stacking configuration, characterized by an in-plane translational shift between adjacent layers. These different stacking configurations correspond to distinct crystallographic symmetries and growth morphologies. Temperature-dependent phase evolution is also evident in the macroscopic crystal morphology observed by scanning electron microscopy (SEM) (Figure 1d, f). The 3R-NbSe₂ phase forms elongated ribbon-like domains with pronounced anisotropy which may be related to anisotropic growth behavior and preferential edge expansion.[12,24] By comparison, the 2H phase develops into compact hexagonal platelets with well-defined edges, indicative of isotropic growth behavior and the stabilization of thermodynamically favored facets.[25-26] The morphological transition from anisotropic ribbons to symmetric platelets with

increasing temperature highlights the role of thermal conditions in modulating growth anisotropy. Atomic force microscopy (AFM) measurements (Figure 1e, g) show that the 3R phase exhibits a thickness of approximately 6 nm, while the representative 2H phase shown in Figure 1g is a monolayer with a thickness of ~0.7 nm. It should be noted that the formation of 2H-NbSe₂ is not limited to the monolayer regime; thicker 2H-NbSe₂ domains can also be obtained by adjusting the growth conditions (Figure S3), indicating that the phase selectivity and thickness evolution can be regulated independently to some extent. The successful growth of monolayer 2H-NbSe₂ further demonstrates the capability of the present CVD strategy for producing atomically thin 2H-phase domains. The observed differences in thickness and morphology suggest that growth temperature plays an important role in regulating lateral and vertical growth behavior. At elevated temperatures, enhanced adatom mobility may facilitate lateral domain expansion, whereas lower temperatures are more likely to favor localized nucleation and multilayer formation. Similar temperature-dependent growth behavior has been widely reported in CVD-

grown TMDC systems.[27-29] X-ray diffraction (XRD) patterns (**Figure 1h**) confirm the crystallographic differences between the two phases. The 3R-NbSe₂ exhibits characteristic reflections corresponding to rhombohedral stacking, including the (003) and (006) peaks, whereas the 2H phase displays the typical hexagonal reflections at (002), (004), and (006). The agreement with reference patterns confirms the crystallographic characteristics and high crystallinity of the synthesized samples.

Figure 2 illustrates the influence of substrate properties on the growth behavior of NbSe₂. As shown in **Figure 2a** and **2b**, NbSe₂ exhibits distinct morphologies on SiO₂ and WSe₂ substrates. On amorphous SiO₂, the material predominantly forms vertically stacked or randomly oriented structures with limited lateral expansion, whereas on atomically flat WSe₂, it tends to develop well-defined two-dimensional domains with larger lateral dimensions. These substrate-dependent differences can be clearly observed in the scanning electron microscopy (SEM) images, suggesting that the surface characteristics of the substrate play an important role in determining the overall growth morphology. For the 3R phase, NbSe₂ forms densely distributed nanoscale clusters on SiO₂ (**Figure 2c**), whereas on

WSe₂, it develops elongated ribbon-like domains with larger lateral dimensions (**Figure 2d**). The corresponding size statistics (**Figure 2e**) indicate an increase in domain size on WSe₂. A similar substrate-dependent trend is observed for the 2H phase, where dispersed granular structures on SiO₂ (**Figure 2f**) evolve into continuous and well-defined domains on WSe₂ (**Figure 2g**), as reflected by the statistical analysis (**Figure 2h**). Such substrate-dependent growth behavior is commonly associated with interfacial interactions and surface diffusion processes.[18,30] In the CVD growth of two-dimensional materials, crystal morphology and domain evolution are widely recognized to be governed by the surface diffusion of adatoms.[31-32] Temperature also affects the phase structure and domain morphology (**Figure S4**), with ribbon-like 3R domains gradually transitioning to regular hexagonal 2H domains as the precursor temperature increases. Within an intermediate temperature range, both morphologies coexist, reflecting a gradual change in growth behavior. These results are consistent with previous reports on substrate-dependent and temperature-dependent growth in CVD-synthesized two-dimensional materials.[33]

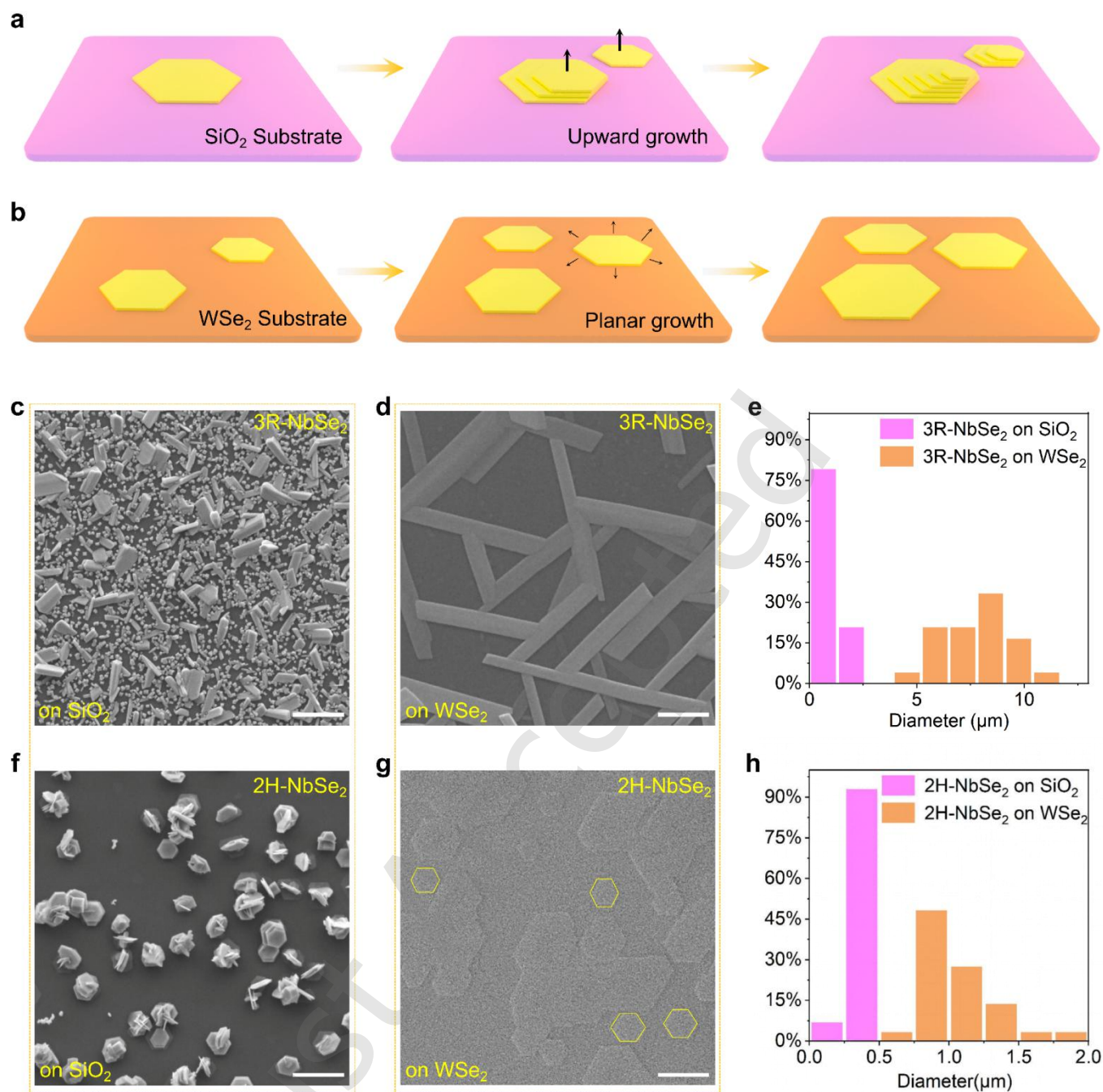


Figure 2. Growth Modes and Size Distribution of NbSe₂ on Different Substrates. Schematic illustration of the growth modes of (a) NbSe₂ on a SiO_2 substrate and (b) NbSe₂ on a WSe_2 substrate. (c) SEM image of 3R-NbSe₂ on SiO_2 . (d) SEM image of 3R-NbSe₂ on WSe_2 . (e) Size distribution of 3R-NbSe₂ on SiO_2 and WSe_2 . (f) SEM image of 2H-NbSe₂ on SiO_2 . (g) SEM image of 2H-NbSe₂ on WSe_2 . (h) Size distribution of 2H-NbSe₂ on SiO_2 and WSe_2 . All scale bars are 5 μm .

Optical microscopy images (**Figure 3a, d**) provide a direct overview of the phase-dependent morphology at the microscale. The 3R-NbSe₂ domains exhibit elongated ribbon-like morphologies with well-defined edges. In contrast, the 2H-NbSe₂ domains display compact hexagonal geometries with high symmetry and uniform size distribution. Optical microscopy images further reveal the large-area spatial distribution of different morphologies. Compared to the

localized morphological analysis presented in **Figure 1**, the optical images demonstrate the spatial separation of domains with distinct morphologies across the sample, suggesting reproducible morphology evolution under different growth conditions. These observations provide structural information for subsequent spectroscopic and interfacial characterization.

Raman

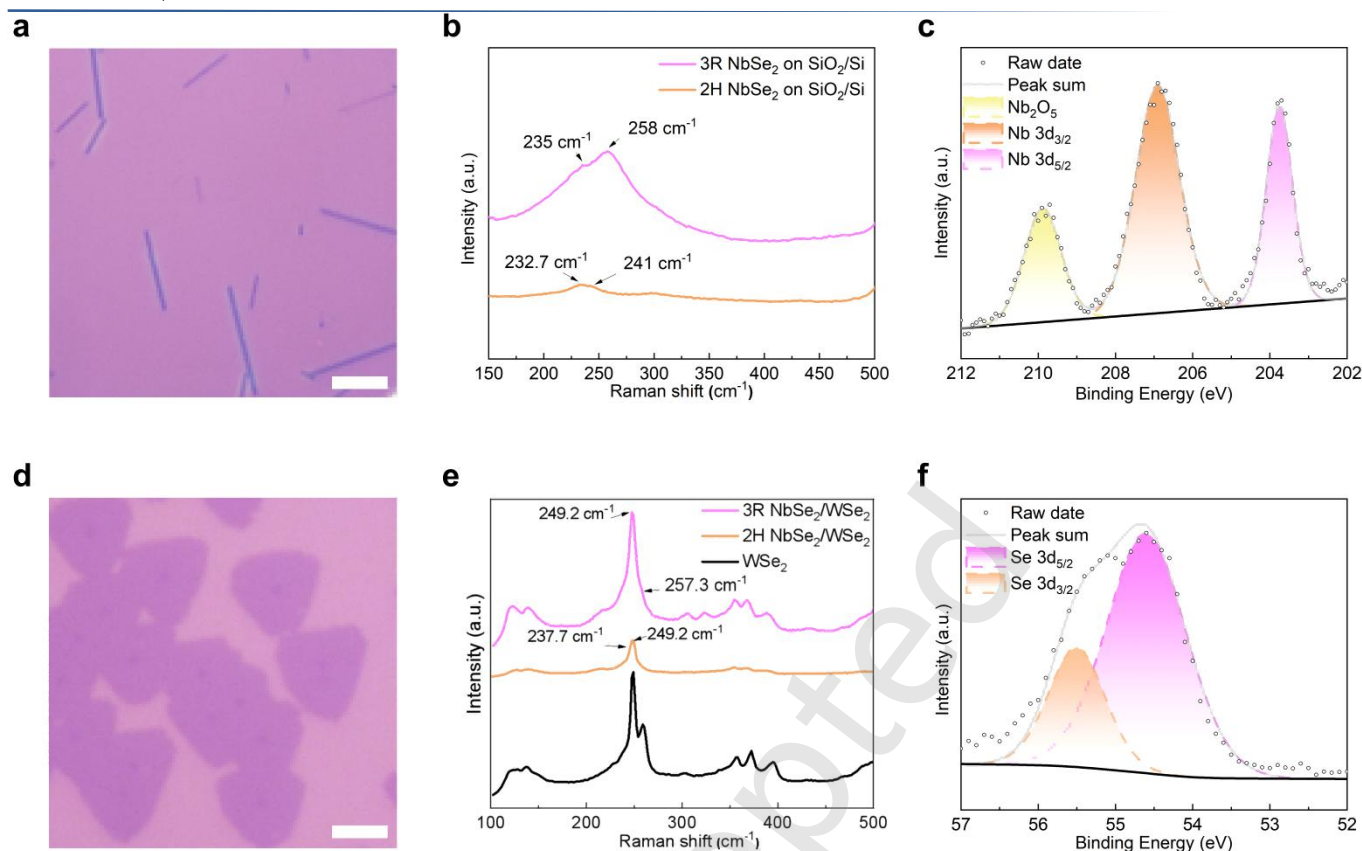


Figure 3. Structural and Chemical Characterization of 3R-NbSe₂ and 2H-NbSe₂ on Different Substrates. (a) Optical image of 3R-NbSe₂ on WSe₂. (b) Raman spectra of 3R-NbSe₂ and 2H-NbSe₂ on SiO₂/Si. (c) XPS spectra of the Nb 3d peaks from NbSe₂ crystals deposited on WSe₂ substrate. (d) Optical image of 2H-NbSe₂ on WSe₂. (e) Raman spectra of 3R-NbSe₂ and 2H-NbSe₂ on WSe₂. (f) XPS spectra of the Se 3d peaks from NbSe₂ crystals deposited on WSe₂ substrate. All scale bars are 10 μm.

spectroscopy was further employed to probe the lattice vibrational characteristics and confirm the phase identity. As shown in **Figure 3b**, NbSe₂ grown on SiO₂/Si exhibits distinct phase-dependent Raman features, where the 3R phase displays characteristic modes at approximately 235 and 258 cm⁻¹, while the 2H phase shows peaks at around 232.7 and 241 cm⁻¹. These differences originate from the distinct lattice symmetries and stacking configurations of the two polymorphs. **Figure 3e** presents the Raman spectra of NbSe₂ grown on WSe₂ substrates. Since the Raman modes of NbSe₂ and WSe₂ partially overlap in the 200–300 cm⁻¹ region, peak fitting after baseline correction was performed to identify the contributions from different vibrational modes (**Figure S5**). For the 3R-NbSe₂/WSe₂ heterostructure, the fitted peak around 235 cm⁻¹ is assigned to a 3R-NbSe₂-related vibrational mode, while the peak near 249 cm⁻¹ corresponds to the E' mode of WSe₂. The peak around 260 cm⁻¹

¹ is attributed to the overlapping contribution of NbSe₂- and WSe₂-related modes, including the WSe₂ 2LA(M) mode. For the 2H-NbSe₂/WSe₂ heterostructure, the fitted peaks are attributed to the characteristic A_{1g} and E_{2g} modes of NbSe₂ and the Raman modes of WSe₂. These results confirm the coexistence of characteristic Raman features from NbSe₂ and WSe₂ in the heterostructures, further supporting the successful formation of NbSe₂/WSe₂ heterostructures. X-ray photoelectron spectroscopy (XPS) was conducted to examine the chemical composition and bonding environment (**Figure 3c, f**). The Nb 3d spectrum exhibits two dominant peaks at 203.9 eV and 206.9 eV, corresponding to Nb 3d_{5/2} and Nb 3d_{3/2}, respectively, confirming the formation of Nb-Se bonds. A weak component at higher binding energies is attributed to slight surface oxidation.[34] The Se 3d spectrum further confirms the expected stoichiometry, with well-defined Se 3d_{5/2} and Se 3d_{3/2} peaks. No impurity-

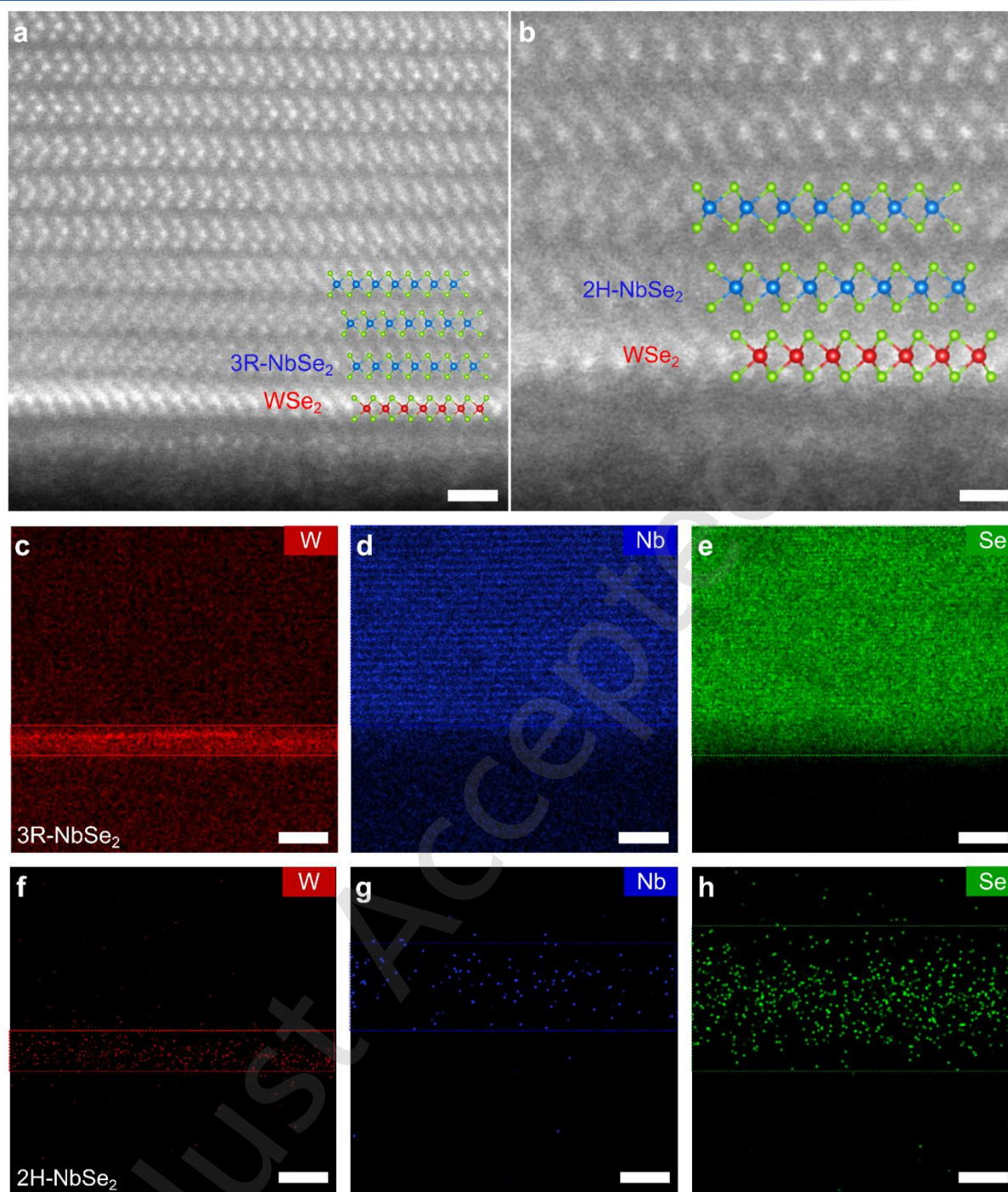


Figure 4. High-resolution STEM and elemental mapping of the NbSe₂/WSe₂ heterostructure. (a) STEM image of the 3R-NbSe₂/WSe₂ interface. (b) STEM image of the 2H-NbSe₂/WSe₂ interface. Corresponding EDS elemental mapping image of 3R-NbSe₂/WSe₂ for (c) W, (d) Nb, (e) Se. Corresponding EDS elemental mapping image of 2H-NbSe₂/WSe₂ for (f) W, (g) Nb, (h) Se. All scale bars are 5 nm.

related signals were detected, indicating high chemical purity and minimal contamination. To further confirm the phase assignment from the perspective of crystal symmetry, second harmonic generation (SHG) measurements were performed on representative NbSe₂ domains. SHG is highly sensitive to crystal symmetry and inversion-symmetry breaking, and therefore can serve as an effective probe for distinguishing different stacking

polymorphs in layered materials. As shown in **Figure S6**, the 3R-NbSe₂ domain exhibits a pronounced SHG signal, indicating the non-centrosymmetric nature of its rhombohedral stacking configuration. In contrast, the SHG signal from the 2H-NbSe₂ domain is close to the background level, suggesting that no obvious second harmonic response is observed under the present measurement conditions,

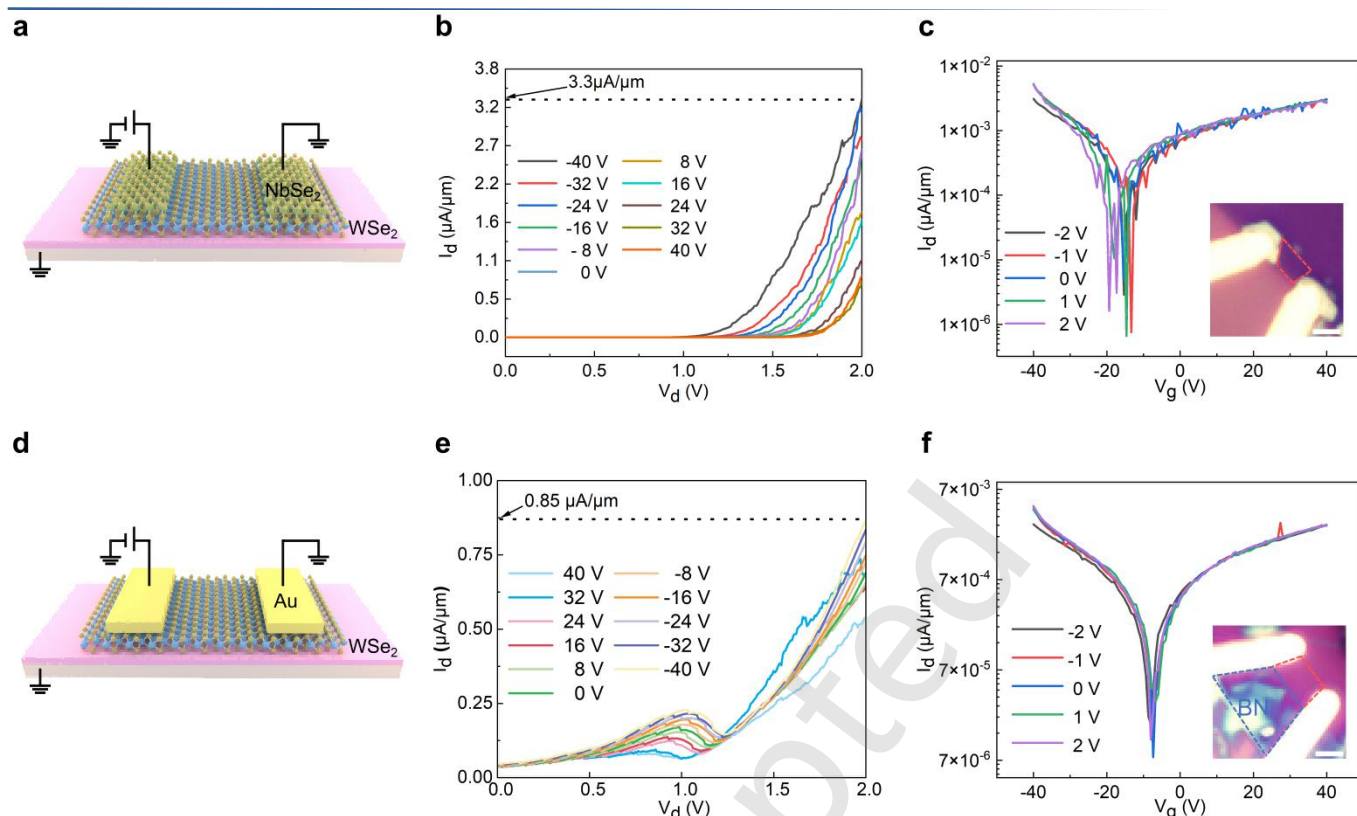


Figure 5. Demonstration of NbSe₂ as an efficient electrode material for WSe₂ field-effect transistors. (a) Schematic illustration of a WSe₂ device contacted with 2H-NbSe₂ electrodes. (b) Output characteristics of the NbSe₂-contacted WSe₂ device measured under different gate voltages. (c) Transfer characteristics of the NbSe₂-contacted device measured at various drain biases; inset: optical image of the representative device. (d) Schematic illustration of a control WSe₂ device with conventional Au electrodes. (e) Output characteristics of the Au-contacted WSe₂ device under different gate voltages. (f) Transfer characteristics of the Au-contacted device measured at various drain biases; inset: optical image of the representative device. All scale bars are 10 μm .

which is consistent with the relatively centrosymmetric stacking configuration of the 2H phase. Together, these structural and spectroscopic characterizations reveal clear differences between the two NbSe₂ polymorphs in terms of morphology, vibrational features, and stacking-related structural characteristics.

After establishing the phase assignment through Raman spectroscopy, XRD, SHG measurements, and large-area morphology observations, cross-sectional atomic-resolution STEM was further employed to directly confirm the stacking sequences at the atomic scale. As shown in **Figure 4a** and **4b**, both the 3R-NbSe₂ and 2H-NbSe₂ phases form atomically sharp and well-defined interfaces with the underlying WSe₂ substrate. The layered structures remain continuous across the interface without observable dislocations, lattice distortions, or amorphous interlayers, demonstrating high structural quality. Despite the distinct stacking configurations of the two polymorphs, no significant difference in interfacial quality is observed, suggesting that the interface does not impose strong structural constraints on phase formation. The stacking configurations resolved from STEM imaging further highlight the intrinsic structural differences between the two polymorphs. The 3R phase exhibits an ABC-type stacking sequence, characterized by a systematic in-plane translation between adjacent layers, whereas the 2H phase follows an AB-type stacking with alternating atomic alignment along the out-of-plane direction. These stacking differences correspond to the intrinsic crystallographic symmetry of each phase. The well-defined stacking sequence observed across the interface suggests that the polymorph structure is established during growth. **Figure 4c-h** presents the energy-dispersive X-ray spectroscopy (EDS) elemental mapping of Nb, W, and Se. As clearly observed, Se is uniformly distributed across the entire imaging area,

whereas W is confined to the substrate and Nb is located above it, exhibiting a spatially well-separated distribution. A sharp compositional boundary is observed at the interface, with no noticeable elemental interdiffusion. These results indicate that the interface is chemically abrupt and that the growth process does not involve alloying or interfacial reactions.[35] These observations highlight the coexistence of atomically sharp interfaces and distinct stacking sequences, providing insights into the structural characteristics of different NbSe₂ polymorphs.[26]

To evaluate the potential of phase-controlled NbSe₂ as a contact electrode for WSe₂-based devices, field-effect transistors were fabricated using directly grown 2H-NbSe₂ as van der Waals contacts, with conventional Au-contacted WSe₂ devices serving as controls. The 2H-NbSe₂ contacts were grown in situ on WSe₂ through the same CVD process described above, rather than being mechanically transferred from another substrate. According to the temperature-dependent growth window and the structural characterizations discussed above, the NbSe₂ domains used as contact electrodes are assigned to the 2H phase. This directly grown 2H-NbSe₂/WSe₂ configuration provides a clean van der Waals contact interface and avoids additional transfer-induced contamination at the metal/semiconductor junction. The device configurations are illustrated in **Figure 5a** and **Figure 5d**. To enable a fair comparison between the 2H-NbSe₂-contacted and Au-contacted WSe₂ devices, a comparable device geometry and effective channel area were maintained in both configurations. In this design, hBN was introduced only as a structural spacer/geometrical defining layer to ensure comparable channel dimensions, rather than as an encapsulation layer or an intentionally introduced dielectric screening layer. Therefore, the comparison mainly reflects the difference between directly grown 2H-NbSe₂ van der Waals contacts and

conventional Au metal contacts. As shown in **Figure 5b** and **Figure 5e**, the 2H-NbSe₂-contacted WSe₂ device exhibits a higher output current than the Au-contacted counterpart over the measured gate-voltage range. Under comparable bias conditions, the current density reaches approximately 3.3 $\mu\text{A}/\mu\text{m}$ for the 2H-NbSe₂-contacted device, nearly four times higher than that of the Au-contacted device ($\sim 0.85 \mu\text{A}/\mu\text{m}$). The transfer characteristics shown in **Figure 5c** and **Figure 5f** further suggest effective gate modulation in the 2H-NbSe₂-contacted WSe₂ device. In addition, the time-dependent photoresponse characteristics further demonstrate the advantage of directly grown 2H-NbSe₂ contacts. As shown in **Figure S7**, the 2H-NbSe₂-contacted WSe₂ device exhibits a rapid increase in photocurrent upon light illumination and a fast decay after the light is turned off, whereas the Au-contacted control device shows a much weaker response under the same measurement conditions. This result suggests that the directly grown 2H-NbSe₂/WSe₂ contact configuration facilitates more efficient photogenerated carrier collection.

4. Conclusion

In summary, a temperature-dependent CVD strategy is developed to enable selective formation of NbSe₂ polymorphs on WSe₂ substrates. By tuning the growth temperature, 3R and 2H phases, as well as their coexistence within an intermediate temperature range, can be selectively obtained without changing precursor chemistry or growth configuration. Characterization results indicate high crystallinity, clear stacking sequences, and well-defined interfaces of the synthesized heterostructures. The observations suggest that growth temperature and substrate properties play important roles in determining polymorph formation. Temperature and substrate effects appear to influence domain morphology and stacking behavior during growth.

The atomically sharp and chemically abrupt interfaces, with minimal interfacial mixing, highlight that the observed stacking sequences are preserved during growth. NbSe₂ can serve as a contact material in device configurations, showing enhanced current response in heterostructure devices compared to substrate-supported controls. These results demonstrate the potential of temperature-controlled growth for exploring polymorph-dependent properties and device applications. Overall, this study presents a temperature-controlled CVD approach to investigate polymorph evolution in two-dimensional NbSe₂ and provides insights into how growth temperature and substrate properties affect morphology and stacking behavior. This approach may guide future design of phase-engineered heterostructures for electronic and optoelectronic applications.

Electronic Supplementary Material: Supplementary material (please provide the brief detail of the ESM) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909064>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

W. T. L.: Investigation, visualization, writing original draft, writing review & editing. A. Z. K.: Investigation. B. H. Z.: Project administration. D. Y.: Investigation. J. N. X.: Investigation. L. Y. W.: Investigation. W. K. W.: Investigation. Y. H. C.: Funding acquisition. Q. L. X.: Funding acquisition. Z. W. Z.: Funding acquisition, supervision, resources, methodology, project administration. All the authors have approved the final manuscript."

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None.

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Electronic Supplementary Material

Temperature-dependent polymorph evolution of NbSe₂ on WSe₂ via van der Waals epitaxy

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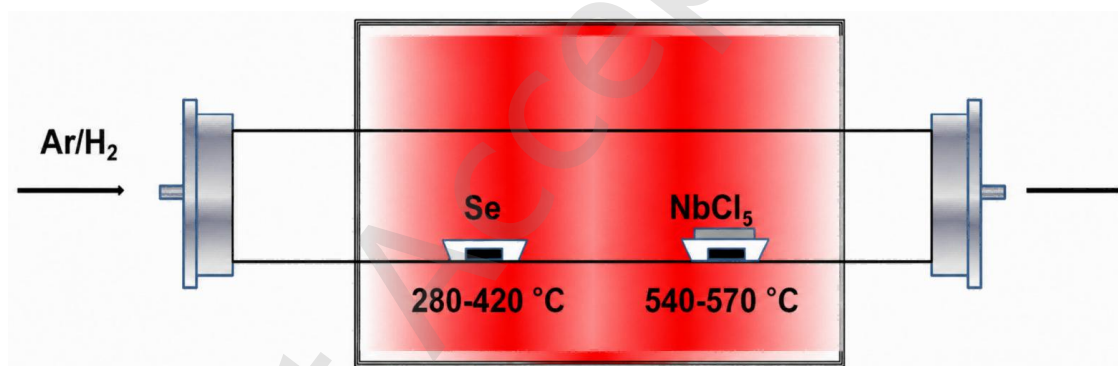


Figure S1. Schematic illustration of the chemical vapor deposition (CVD) system for NbSe₂ growth. Se and NbCl₅ powders were used as precursors and heated to 280–420°C and 520–600°C, respectively. The precursor vapors were carried by an Ar/H₂ gas flow to the substrate surface, where NbSe₂ crystals were deposited through vapor-phase reactions.

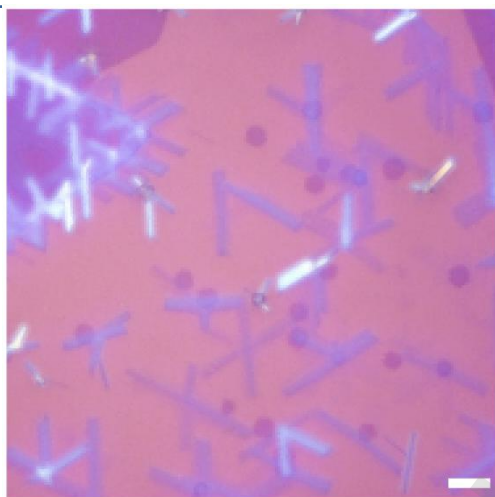


Figure S2. Optical microscopy image of the mixed 2H and 3R phases of NbSe₂. Scale bar is 10 μ m.

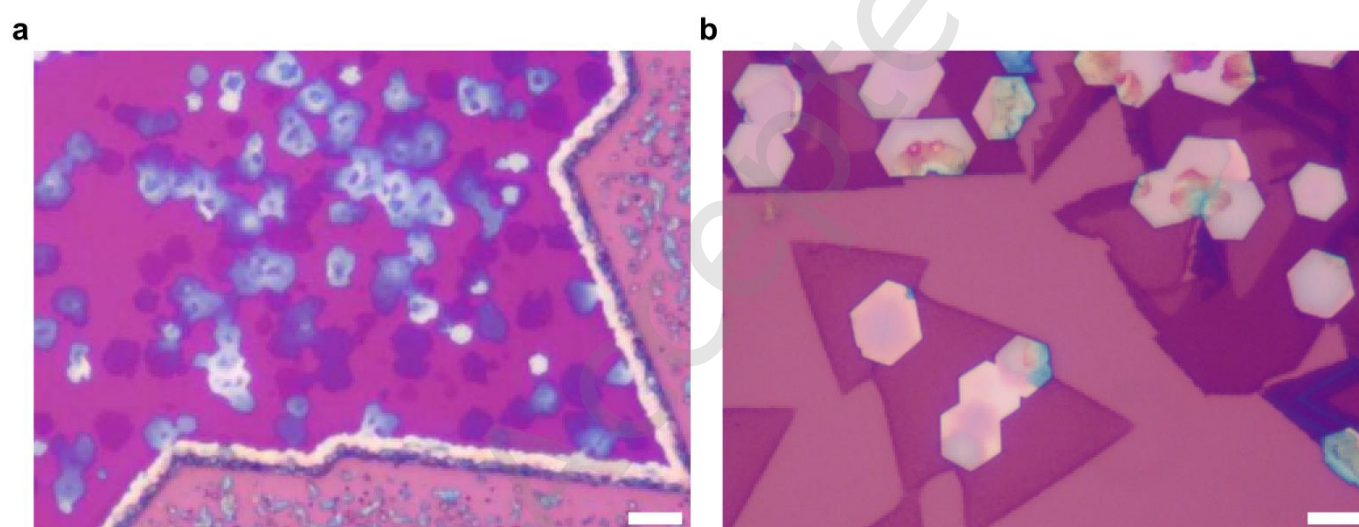


Figure S3. Optical microscopy image of the multilayer 2H-NbSe₂. Scale bar is 10 μ m.

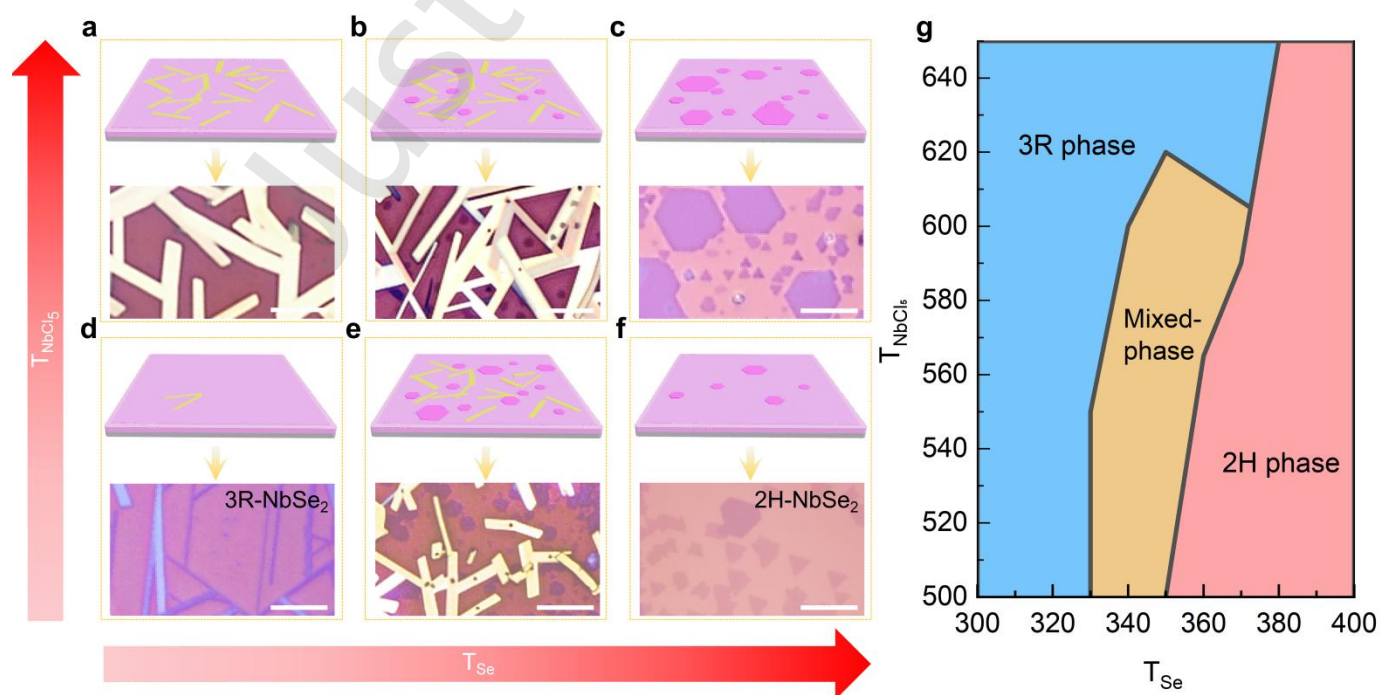


Figure S4. Temperature-dependent polymorph evolution and growth phase diagram of NbSe₂ on WSe₂. a-f) Schematic illustrations and corresponding optical microscopy images showing the morphology and phase evolution of NbSe₂ under different Se precursor temperatures (T_{Se}) and NbCl₅ precursor temperatures (T_{NbCl_5}). The growth evolves from ribbon-like 3R-NbSe₂ to mixed-phase domains and finally to hexagonal 2H-NbSe₂ with increasing precursor temperature. g) Schematic phase diagram summarizing the growth windows of the 3R phase, mixed phase, and 2H phase as a function of T_{Se} and T_{NbCl_5} , revealing the temperature-dependent polymorph selection during van der Waals epitaxy. Scale bar is 10 μm .

Table S1. Growth parameters corresponding to the optical images in Figure S3.

Panel	$T_{\text{NbCl}_5} / ^\circ\text{C}$	$T_{\text{Se}} / ^\circ\text{C}$	Growth time / min	Carrier gas	Dominant product
Figure S _{2a}	600	300	10	Ar/H ₂ , 60 sccm	3R
Figure S _{2b}	600	350	10	Ar/H ₂ , 60 sccm	mixed
Figure S _{2c}	600	400	10	Ar/H ₂ , 60 sccm	2H
Figure S _{2d}	500	300	10	Ar/H ₂ , 60 sccm	3R
Figure S _{2e}	500	350	10	Ar/H ₂ , 60 sccm	mixed
Figure S _{2f}	500	400	10	Ar/H ₂ , 60 sccm	2H

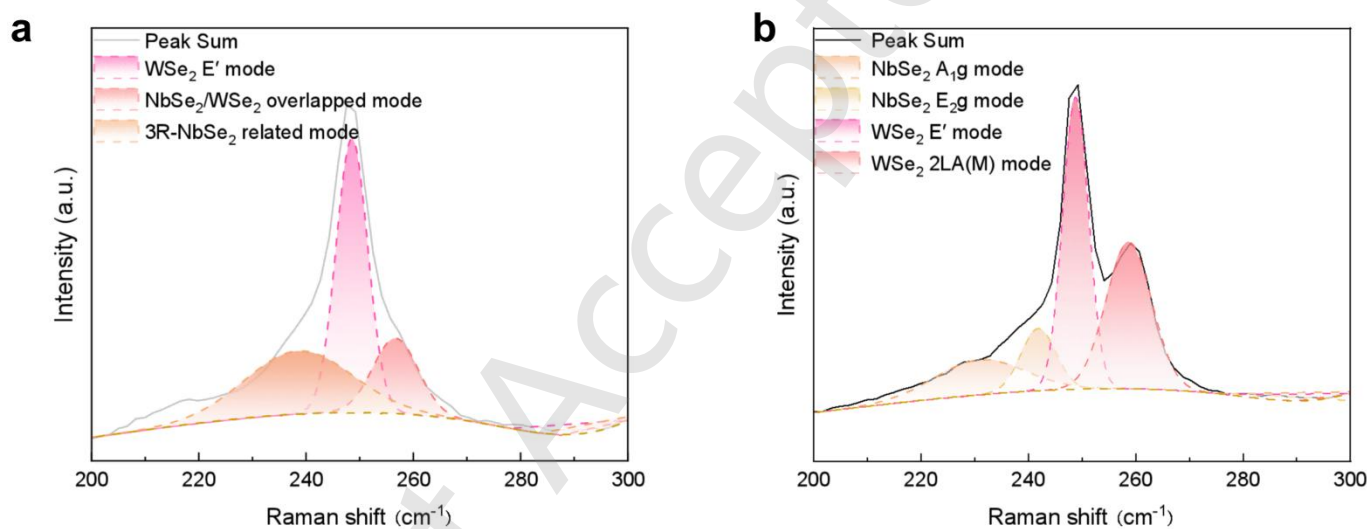


Figure S5. Peak fitting of Raman spectra for NbSe₂/WSe₂ heterostructures. (a) Peak deconvolution of the 3R-NbSe₂/WSe₂ spectrum. (b) Peak deconvolution of the 2H-NbSe₂/WSe₂ spectrum.

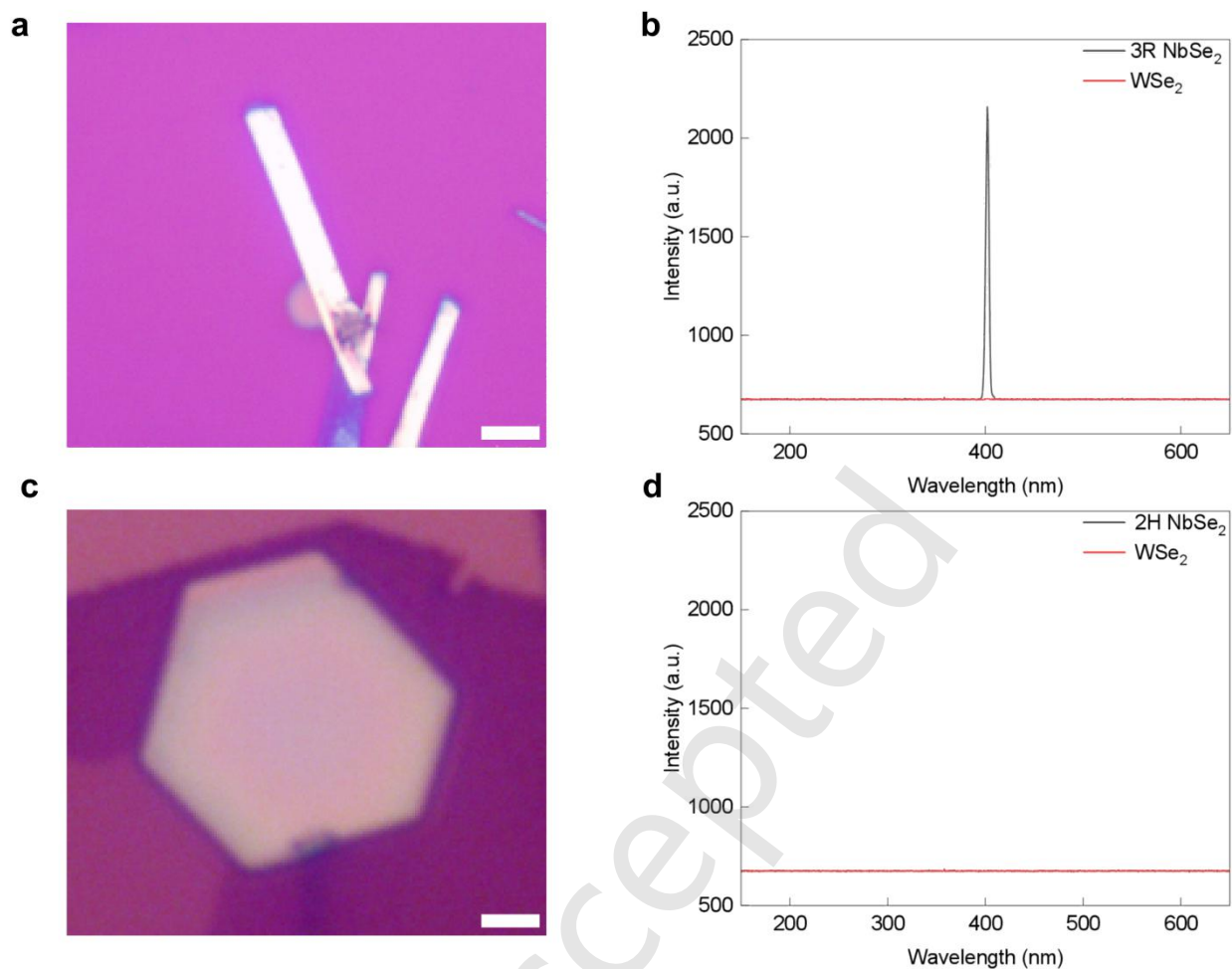


Figure S6. Optical images and SHG spectra of 3R-NbSe₂ and 2H-NbSe₂ domains. (a), (c) Representative optical microscopy images of 3R-NbSe₂ and 2H-NbSe₂ domains grown on WSe₂, respectively. (b), (d) Corresponding SHG spectra of the 3R-NbSe₂ and 2H-NbSe₂ domains measured under an excitation power of 10 mW, with WSe₂ used as the reference. Scale bar is 10 μ m.

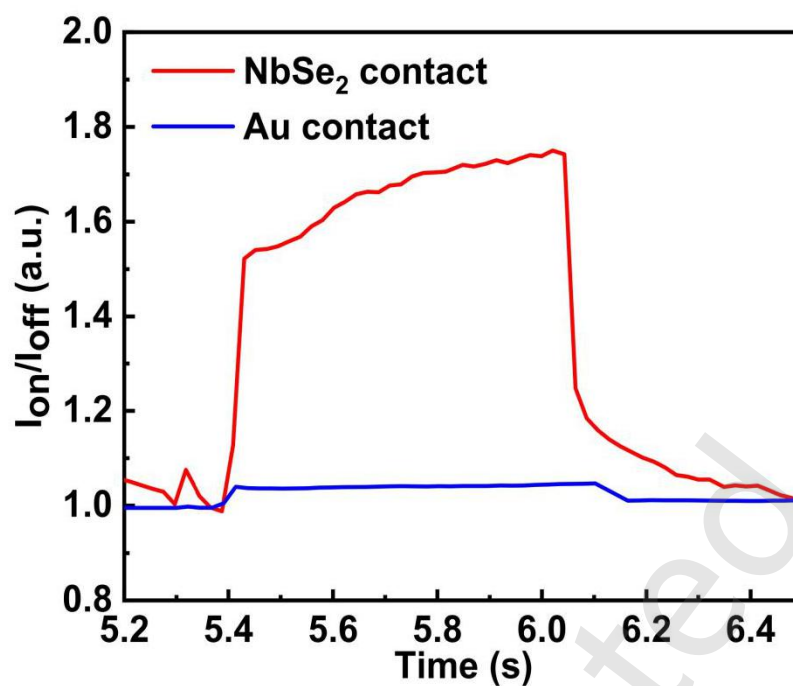


Figure S7. Photocurrent response of the NbSe₂/WSe₂ heterostructure under light illumination. Time-dependent current measurements show a rapid increase in current upon illumination (red curve) and a quick decay when the light is turned off, indicating fast photoresponse. The blue curve corresponds to the dark current measured under the same bias, demonstrating negligible background contribution. These results confirm the efficient photogeneration and collection of carriers in the heterostructure.