Selective deposition of nanoparticles on polycrystalline monolayer ReS$_2$ is utilized to swiftly identify the overlapping grain boundaries (GBs) constructed between parallel grains in monolayer ReS$_2$ under microscopic observation. Atomic structures of GBs with different widths, orientations, and interlayer atomic registries are interpreted using annular dark-field scanning transmission electron microscopy. Density functional calculations indicate that the electronic band structures of overlapping GBs are strongly direction dependent.
SUMMARY
Grain boundaries (GBs) are significant microstructures that dominate properties of polycrystalline two-dimensional (2D) materials. Low-symmetry rhenium disulfide monolayers provide an ideal platform to investigate diverse configurations of GBs and their orientation-dependent characteristics. Here, we utilize the preferential deposition of platinum-based nanoparticles on grain edges to rapidly locate nanoscale-wide overlapping GBs during microscopic-scale observation. Atomic-resolution investigations by aberration-corrected annular dark-field scanning transmission electron microscopy reveal diverse overlapping GBs constructed by parallel grains with transversal displacement. They prefer to align along several primary lattice directions with different interlayer atomic registries. Calculations show that the electronic band structures of overlapping GBs are strongly direction dependent, suggesting their potential in tunable electronic and photonic devices. Incommensurate overlapping GBs formed by quasi-parallel grains with ultrasmall twist angles are also observed. These results unveil the rich polymorphism of GBs and new opportunities to tailor properties of anisotropic 2D materials via GB engineering.

INTRODUCTION
Monolayer transition metal dichalcogenides (TMDs) have attracted great attention due to their potential in applications of multifunctional nanodevices and energy harvesting. Recent interests have extended from high-symmetry TMDs (e.g., MoS$_2$, WS$_2$) to low-symmetry ones. Rhenium disulfide (ReS$_2$) is a typical example. It belongs to the triclinic system with the least symmetry of all Bravais lattices, adopting a distorted octahedral phase (1T’ phase) with Re atoms interlinking into diamond-shaped chains (Figure 1A), thus inducing exotic properties and prominent in-plane anisotropy. Therefore, low-symmetry ReS$_2$ monolayers serve as an ideal platform to investigate how the alignment of some typical microstructures, such as grain boundaries (GBs) and line defects, could tailor material properties, and to develop applications in anisotropic devices.

GBs, which are unavoidable due to the polycrystalline nature of 2D materials even with the best synthetic techniques, have a remarkable impact on the overall material properties. Adjacent grains can be connected via two ways. One is to form atomic bonds at the interface, leaving linear arrays of defects (Figure 1B). The other is to extend one sheet on top of another to form a bilayer boundary region coupled by van der Waals (vdW) forces, termed overlapping GBs (Figure 1C). Atomically
stitched GBs have been intensively investigated and were found to alter the mechanical strength, implant mid-gap states, and influence the electrical transport and photoluminescence (PL) emission in 2D materials. In contrast, overlapping GBs are much less studied. They are experimentally manifested to improve the electrical conductance of graphene by one order of magnitude compared with the pristine monolayer lattice. Overlapping GBs constructed by different 2D building blocks (GaSe/MoSe2) performed as p-n junctions and generated gate-tunable photovoltaic responses. Given the fact that 2D materials can be vertically assembled with free tuning of interlayer forces, one can envisage the discovery of more intriguing properties of overlapping GBs especially after the observation of unconventional superconductivity in twisted bilayer graphene.

Unveiling the structure of GBs is of key importance in understanding the microscopic and macroscopic impact of these non-periodic configurations on 2D material properties. Several approaches have been established, including optical microscopy, Raman spectroscopy, photoluminescence (PL) spectroscopy, and dark-field transmission electron microscopy (DF-TEM). Despite their superiority in the high-throughput mapping of the GB distribution in a large area, these methods are limited in providing the atomic information and differentiating grains that are aligned in parallel or adopt ultrasmall angular mismatch. Annular dark-field scanning transmission electron microscopy (ADF-STEM) has outstanding capability of characterizing GB structures at sub-angstrom resolution. Graphene GBs composed of alternating pentagon-heptagon chains, MoS2 antiphase boundaries with linearly arranged four-fold rings, and the overlapping GBs in hexagonal boron nitride (h-BN) have all been clearly revealed. However, ADF-STEM, together with other aberration-corrected imaging techniques, suffers from a relatively low characterization efficiency. It originates from nearly five-orders-of-magnitude difference on scale between micrometer-sized grains and nanometer-wide GBs, making the fast and simultaneous acquisition of both GB locations and atomic structures extremely challenging. Beyond these, there also exist two gaps of structural investigation of GBs in 2D materials. First, atomic-level studies of interfaces formed by parallel and quasi-parallel grains are lacking, since they are more difficult to detect compared with the interfaces generated by misoriented grains even with the

Figure 1. Schematic Illustrations of Monolayer ReS2 and Two Types of GBs
(A) Atomic model of monolayer ReS2. Both the top and side views are given. Blue and yellow spheres represent Re and S atoms, respectively. The diamond-shaped Re4 chain is highlighted by pink parallelograms in the projective view. Two primary lattice directions, denoted as a axis and b axis, are marked by black arrows. Inset is an ADF-STEM image of monolayer ReS2 with Re4 chains labeled by cyan lines. Only Re atoms can be imaged due to a large difference in the atomic number between Re and S elements. Scale bar, 0.5 nm. (B) Schematic illustration showing both the projective view and the side view of an atomically stitched GB of monolayer ReS2. The defect line at the interface is highlighted in green. Re atoms in different grains are in blue and pink, respectively. (C) Schematic illustration of an overlapping GB showing monolayer ReS2 on the right overgrowing on top of the ReS2 on the left, thus forming a narrow bilayer boundary region at the interface.
association of diffraction techniques. Second, investigation of overlapping GBs with well-organized, narrow, and clean interfaces remains scarce, hindering the progress of tailoring GB properties by engineering the interlayer atomic registry.

In this work, we make use of the selective adsorption of platinum (Pt)-based nanoparticles on grain edges to easily locate GBs in low-symmetry polycrystalline monolayer ReS$_2$ during microscopic-scale observation. Atomic structures of overlapping GBs between parallel grains with nanometer-scale width and various interlayer atomic registries are clearly resolved by performing aberration-corrected ADF-STEM. The effect of edge structures and interlayer coupling on the band structures of these parallel overlapping GBs is further studied by density functional theory (DFT) calculations. Besides, overlapping GBs generated by two quasi-parallel grains with an ultra-small twist angle of less than 1° have also been discovered, which display Moiré patterns with a long-range variation but lack translational symmetry due to structural incommensurability. Our results provide insights into the impact of polymorphism of overlapping GBs on material properties, thus helping establish a more comprehensive understanding between the macroscopic performance and the microscopic structure of 2D materials.

RESULTS AND DISCUSSION

Monolayer ReS$_2$ was synthesized by chemical vapor deposition (CVD) (inset of Figures 2A and S1) and transferred onto a holey silicon nitride TEM grid using a polymer-assisted approach. Subsequently, the grid was annealed at 300°C in a tubular furnace to thoroughly remove poly(methyl methacrylate) (PMMA) residuals. During this period, a small amount of Pt-TCPP (5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin platinum(II)) was vaporized and deposited on the grid (see Experimental Procedures). Interestingly, Pt-based nanoparticles selectively anchored along some lines, as indicated by the yellow and blue arrows in Figure 2A, endowing the suspended monolayer ReS$_2$ with an intricate pattern (Figure S2). Sites that nanoparticles attached to are overlapping GBs and edges of ReS$_2$ (Figures 2B and 2C), which could be ascribed to high chemical activity of unsaturated edge atoms, similar to the preferential seeding of nanoparticles at GB dislocations in other 2D materials. Since ADF-STEM provides Z-dependent contrast, nanoparticles containing heavy Pt atoms provide much higher brightness than monolayer ReS$_2$ lattice and perform as indicators of GBs. Therefore, the selective attachment of Pt-based nanoparticles on grain edges serves as a rapid strategy to display a general view of the location and distribution of GBs on a micrometer scale, which complements the nanometer-scale imaging of high-magnification ADF-STEM and provides a multiscale understanding of ReS$_2$ GBs (Figures S3–S5). Figures 2D and 2E are magnified views of the regions in yellow boxes of Figures 2B and 2C, respectively. Adjacent grains coalesce by forming overlapping GBs that rely on the interlayer vdW forces. Since the edges of ReS$_2$ grains lack atomic flatness, GBs display alternative appearance of overlapping regions (Figure 2D) and narrow gaps (Figure 2E). Figure 2D is a close-up view of overlapping GBs corresponding to the yellow boxed region in Figure 2B, where a specific Moiré pattern emerges due to the atomic registry at the bilayer boundary region. The atomically resolved image exhibits no angular misfit between grains on two sides of the overlapping GB (inset on the top right of Figure 2D). The inset on the bottom left of Figure 2D labels two principal lattice directions (a axis and b axis) of monolayer ReS$_2$ and the alignment of diamond-shaped Re4 chains, indicating that the two contiguous grains are interconnected along the b direction (Figure S6). Figure 2E displays a zoomed-in image of the gap between two grains, indicating the nanoscale roughness of grain edges. The inset of Figure 2E shows the fast Fourier
transform (FFT) of two neighboring ReS$_2$ grains, providing lattice information in the reciprocal space. Only one set of reflexes can be observed, further verifying the same crystal orientation of two grains. Figure 2F schematically illustrates the three-dimensional (3D) perspective view of the GB structure generated by two parallelly aligned grains. Stripes of bilayer regions with nanometer width (Figure 2G) intersected by small unstitched gaps (Figure 2H) due to unsmooth grain boundaries.
We investigated the overlapping GBs generated by parallel grains from unconnected regions to overlapping bilayer boundaries to uncover how the edge of one grain approaches and grows over the top of a neighboring grain rather than forming atomic bonds at the interface. Figure 3A shows a typical ADF-STEM image of an unconnected segment in the overlapping GB. The inset displays an atomic model of monolayer ReS$_2$ with S atoms filtered to highlight the atomic arrangement of Re framework, facilitating the crystallographic analysis of ADF-STEM image, in which only Re atoms are visible. Figures 3B and 3C are FFT images of the left and right grains in Figure 3A, respectively, both of which display quasi-hexagonal patterns and adopt the same crystal orientation. Crystal planes of (100), (110), and (010) in the first ring of the reflexes are labeled, which correspond to the lattice planes marked by green, orange, and pink dashed lines in the inset of Figure 3A. Intensity line profiles were taken along three dashed boxes in Figure 3B (named as lines a, b, and c) to compare the intensity of reflexes from different lattice planes. It was found that the reflection spot from the (100) plane, which is parallel to the b lattice direction, exhibits the highest brightness, while the spot from the (010) plane, which is
parallel to the a direction, is the dimmest. The intensity variation of reflexes corresponding to different crystal planes can help accurately discriminate a and b axes of monolayer ReS\(_2\) without perturbing the close interplane spacing between a and b directions and the potential aberration-induced image distortion (Figure S8), which is of key significance to study the in-plane anisotropic performance of ReS\(_2\). Figure 3F shows a magnified view of the yellow boxed region in Figure 3A. The edges of two grains are both oriented along the b direction, but the two neighboring grains are shifted by approximately half of the side length of the Re4 diamond, as marked by cyan and yellow dashed lines, which is ~1.5 Å. Such horizontal displacement may result in the failure of the atomic stitching between domains, leading the formation of overlapping interfaces to be more energetically advantageous. The unconnected regions generated between two grain edges oriented along [110] and [100] lattice directions were also observed, where two neighboring grains are displaced by around a side length of the Re4 diamond (Figure S9). A minority of interdomain gaps seems to be atomically stitched but more regions are unconnected or associated by overlaps, indicating the thermodynamic disadvantage of the atomically bonded GB under this condition (Figure S9A). Figure 3F exhibits a typical edge structure along the b direction, showing nanometer-scale roughness, although the GBs appear straight at the micrometer scale (Figure 2A). DFT calculations show that S-terminated edges are more thermodynamically favorable than Re-terminated ones (Figure S10). The edge formation energies of S-terminated edges along three primary lattice directions ([100] (a direction), [010] (b direction), and [110]) are plotted in Figure 3G, in which edge along the [010] lattice orientation is the most energetically preferred case. This agrees well with the experimental results that edges along the b direction are most commonly observed and are smoother than those aligning along the a direction, which will be further discussed in Figures 5A and 5F.

Figure 4 illustrates the initial stage of the overlapping GB formation when only the outermost atom rows of the neighboring grain edges are stacked with various atomic registries between the vdW layers. As shown in Figure 4A, two parallel grains with edges oriented along the diamond-shaped chains (b direction) approach each other, constructing discrete atomically thin overlapping interfaces, as highlighted by the pink box and arrow. Two grains show transversal mismatch, as indicated by the yellow and cyan lines. Figure 4B is the zoomed-in ADF-STEM image showing the overlapping GB in the pink box of Figure 4A, while Figure 4C labels the Re atoms corresponding to the upper and lower grains by yellow and cyan circles, respectively. It can be seen that two adjacent grains are displaced by about half of the side length of the Re4 diamond along the b axis, generating a zigzag Re chain at the GB interface, as highlighted by the red dashed line in the atomic model of Figure 4D. Figure 4E reveals another scenario of the overlapping interface with grain edges still lying along the b direction. Yet the transversal shift between two grains increases to approximately one side length of the Re4 diamond, as indicated by the yellow and cyan lines in Figure 4E, leading to the overlap of Re atoms between two layers at the GB interface. Figure 4F magnifies the overlapping interface in the white dashed box in Figure 4E with Re4 diamond chains corresponding to the upper and lower grains highlighted by cyan and yellow circles, respectively, and the corresponding atomic model displaying the overlapping GB configuration is shown in Figure 4G.

The overlap of Re atoms from two grains not only induces extremely high brightness of the atomic columns at the interface but also gives rise to prominent lattice distortion of the diamond-shaped chains at GBs. Figure 4H is the histogram quantifying the alteration of the Re interatomic spacings in the diamond-shaped chain along
Figure 4. Atomic Configuration of Overlapping GBs with Subnanometer Width between Two Parallel Grains

(A) ADF-STEM image showing the initial formation stage of an overlapping GB with only the outermost edge atoms of one grain overgrowing the edge of another grain.

(B and C) Zoomed-in images of the pink boxed region in (A), with (C) and without (B) atomic models overlaid. Re atoms from the upper and lower grains are represented by yellow and cyan circles, respectively, in (C). Scale bar, 0.5 nm.

(D) Atomic model corresponding to the overlapping interface in (B). Re and S atoms in the top grain are represented by blue and orange spheres, respectively, while Re and S atoms in the bottom grain are represented by pink and yellow spheres, respectively.

(E) ADF-STEM image showing another scenario of the atomically narrow overlapping interface lying along the b axis constructed by two parallel grains.

(F) Zoomed-in images of the white boxed region in (E). Diamond-shaped Re4 chains of the top and bottom grains are represented by cyan and yellow parallelograms, respectively. Scale bar, 0.5 nm.

(G) Atomic model of the overlapping GB in (F).

(H) Histogram showing the variation of the Re atomic spacings between the pristine lattice and the overlapping interface in (F). "Yellow edge" denoted in the horizontal axis indicates the Re atoms in the fully overlapped atomic line corresponding to the bottom grain marked by yellow parallelograms in (F), while "blue edge" represents the Re atoms in the fully overlapped atomic line corresponding to the top grain labeled by blue parallelograms in (F).

(I) Line profiles comparing the difference in the column intensity and the Re interatomic spacing between the pristine monolayer lattice and the overlapping interface in (F).
the b axis at overlapping GBs, as represented by the schematic illustration of the inset. The data were extracted from the intensity line profiles taken along the overlapping edges and the pristine lattice, respectively (Figures 4I and S11). For the bottom grain marked by yellow parallelograms in Figure 4F, the Re interatomic spacing 1 shrinks by ~6.7%, while the spacing 2 enhances by ~3.0% compared with that of the pristine lattice, leading to an increased inequality of the Re intervals at the interface (Figure 4H). For the top grain highlighted by blue parallelograms, the Re spacings 1 and 2 exhibit even more pronounced discrepancy compared with the pristine lattice, showing a 21.2% increase and a 20.8% decrease, respectively. The obvious lattice deformation at the subnanometer-wide overlapping interface might be triggered by both the freedom of the edge atoms and an increased level of interlayer coupling in this scenario, since Re atoms in disparate layers are vertically overlapped, distinct from the staggered arrangement of Re atoms in Figure 4A.

Figure 5 shows two typical structures of nanometer-width overlapping GBs constructed by parallel ReS$_2$ crystals with different interlayer atomic registries, thus exhibiting distinct Moiré patterns. As shown in Figure 5A, two grains with edges aligning along the b direction form an atomically smooth stripe of bilayer boundary region that can extend several hundreds of nanometers (Figure S12). Re atoms are assembled into distorted hexagonal rings from the projective view (Figure 5B). Figure 5C is the magnified ADF-STEM image of the yellow boxed region in Figure 5A. The Re4 parallelograms from the top and bottom grains are marked in cyan and pink, respectively, which exhibit an interpenetrating pattern. Such a type of overlapping GB can be constructed by interlayer gliding along the red arrows between two grains, as highlighted in Figure 5D, leading to displacement of around half of the side length of the Re4 diamond along the b axis between the two neighboring grains. The image simulation (Figure 5E) corresponding to the atomic model in Figure 5D is consistent with the experimental ADF-STEM image in Figure 5C, confirming the validity of the interlayer stacking manner at the overlapping GB. Figure 5F illustrates another scenario, whereby the overlapping GB is oriented along the a direction. Distinct from the boundary with atomic flatness shown in Figure 5A, the overlapping interface appears rugged at the nanometer scale, which is triggered by the inferior stability of edges along the a axis compared with edges in the b direction, as verified by the formation energy variation by DFT calculations in Figure 3G. The Moiré pattern induced by such a type of interlayer atomic registry (Figure 5G) deviates from the first scenario. Figure 5H is the zoomed-in image of the yellow boxed region in Figure 5F with diamond-shaped chains from two grains overlaid in cyan and pink, respectively. In this case, two neighboring grains are shifted by about a side length of the Re diamond along both the [010] and [110] lattice directions, analog to the interlayer atomic registry at the bilayer boundary region shown in Figure 4F. Figure 5I displays the atomic model corresponding to Figure 5H with the image simulation shown...
in Figure 5J, which agrees well with the experimental observation, thus validating the structural interpretation of the overlapping GB. Moreover, the overlapping GBs extending along the [110] lattice direction between parallel grains were also observed (Figure S13). These preferential configurations unfold the polymorphism of overlapping GBs in monolayer ReS$_2$ when two parallel grains approach each other along various lattice orientations, which may motivate distinct electronic characteristics.

DFT calculations were then carried out to explore the effects of overlapping GBs on the electronic properties of ReS$_2$ (see Experimental Procedures). Figures 6A and 6B show the crystal structure and first Brillouin zone of the ReS$_2$ monolayer. The calculated band structure in Figure 6C shows that the ReS$_2$ monolayer is a semiconductor with an indirect band gap of 1.41 eV, which is consistent with other calculations. However, whether the band gap is indirect or direct remains a controversial issue in experimental reports. One key reason is that the energy difference between indirect and direct band gaps is only 0.032 eV, which is comparable with the thermal
energy at room temperature. For convenience, the conduction band minimum and valence band maximum in Figure 6C are denoted as C0 and V0. Figures 6D–6F show the calculated band structures of overlapping GBs extending along the [100], [010], and [110] directions, respectively. These band structures exhibit distinctly different features. GB extending along the [100] direction remains a semiconductor, but with a much reduced indirect band gap of 0.20 eV compared with bulk phase, while GB extending along the [010] direction changes into a direct band-gap semiconductor with a gap of 0.92 eV. More interestingly, GB extending along the [110] direction shows metallic features with Fermi level crossing in-gap bands. These characteristic electronic properties of GBs mainly come from the emerging in-gap states between C0 and V0, and these states are represented by partial charge-density distributions as shown in the right panels of Figures 6D–6F.

We can see that these states are mainly contributed by edges, so the electronic properties of overlapping GBs depend largely on the edge structures of boundaries. Furthermore, the variation of band structures for GBs with different overlapping widths is also studied, as shown in Figure S14. The calculation results show that the overlapping width has small effects on the band structures of GBs, so the electronic properties of overlapping GBs depend weakly on the interlayer coupling.

Apart from the Moiré patterns shown in Figure 5 that adopt a long-range period, surprisingly we also observed the Moiré superlattice with a continuous variation, as shown in Figure 7A. The discovery of this configuration is intriguing because recent studies indicate that even a small interlayer twist could strongly modulate the electronic structure of 2D materials, giving rise to the emergence of diverse exotic properties, such as superconductivity and optical chirality. Contrary to the overlap between two parallelly aligned grains, the GB in Figure 7A was constructed by two neighboring grains with an ultrasmall twist angle, which was measured to be ~0.5°. The existence of the angular mismatch between two grains can be verified by the FFT image of Figure 7A, where the reflex corresponding to the crystal plane of (110) split into two spots (inset of Figure 7F). The Moiré pattern displays a gradual evolution along the overlapping GBs. Figures 7B–7E show the zoomed-in ADF-STEM images of some typical Moiré patterns from left to right. No translational symmetry can be detected for the overlapping interface. Figure 7G is the established atomic model corresponding to the GB structure in Figure 7A. Re atoms from the top and bottom grains are represented by blue and pink spheres, respectively. S atoms are hidden in this model in order to highlight the atomic registry of Re, which makes the primary contribution to the ADF-STEM image contrast. Figure 7H is the image simulation of Figure 7G, agreeing well with the experimental image in Figure 7A. The overlapping GB in Figure 7A was formed by the stack of two grain edges oriented along the b axis. Moreover, we also found a bilayer Moiré superlattice without long-range period generated by the stacking of grain edges along the a axis (Figure S15). The misorientation between two grains is ~1.5°. The smoothness of the overlapping GB constructed by quasi-parallel grains along the a direction is severely inferior to that along the b direction, similar to the circumstances discussed in Figure 5. We conducted calculations to explore the commensurability of twisted bilayer ReS2 and found that only incommensurate superlattice can be obtained when the twist angle is between 0° and 180° (Figure S16), indicating that the Moiré patterns generated by bilayer ReS2, including the example shown in Figure 7A, lack a long-range translational symmetry in real space. This structural characteristic is in stark contrast to many other 2D materials, such as twisted bilayer graphene and MoS2, and originates from the low symmetry of ReS2, which belongs to the triclinic Bravais lattice with unequal lengths of three primitive vectors and different axial angles. The incommensurability of twisted bilayer ReS2 may...
trigger exotic properties and inspire potential applications in the field of structural superlubricity. 53–55

**Conclusions**

In summary, we combine atomic-resolution ADF-STEM and DFT calculations to investigate well-organized overlapping GBs in low-symmetry ReS$_2$ monolayers. Preferential nucleation of Pt-based nanoparticles on GBs facilitates the quick identification of overlapping GBs without intergrain misorientation or with ultrasmall twist angles at microscopic scale. The ability to accurately resolve the configuration of

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**Figure 7. Overlapping GBs Generated by Two Grains with an Ultrasmall Twist Angle**

(A) ADF-STEM image showing an overlapping GB with a long-range Moiré period generated by two quasi-parallel grains. The cyan arrow on the top grain and the yellow arrow on the bottom grain both extend along the b direction. The yellow arrow on the top was obtained by translating the yellow arrow in the bottom grain upward. Therefore, the angular misorientation between two grains can be achieved by measuring the intersection angle between the yellow and cyan arrows on the top, yielding ~0.5° in this example.

(B–E) Zoomed-in images exhibiting typical Moiré patterns of the overlapping GB from left to right in (A), indicating a gradual evolution of the interlayer atomic registry.

(F) FFT image of (A) where two spots corresponding to the (110) lattice plane can be observed, indicating the existence of an ultrasmall twist angle between two neighboring grains. Inset is the zoomed-in image of the cyan boxed region.

(G) Atomic model generated based on the bilayer boundary region in (A). Sulfur atoms are hidden in this model to highlight the stacking manner of Re atoms in two layers.

(H) Image simulation based on the atomic model in (G).
overlapping GBs with different widths, orientations, and interlayer atomic registries by ADF-STEM enables precise models to be constructed for theoretical calculations. DFT predicts that different alignments of GBs could lead to distinct band structures. Some remain as an indirect band-gap semiconductor but with a strong reduction in the band gap, while some other alignments could lead to a semiconductor with a direct infrared band gap or result in metallic properties. These results unveil the polymorphism of overlapping GBs, which have a broad impact on understanding the role of overlapping GBs in low-symmetry 2D materials. They also provide opportunities for constructing one-dimensional channels with various electronic properties in 2D semiconducting membranes and for patterning lateral junctions with sharp interfaces and nanometer-scale width through GB engineering, which paves the way for future electronic and photonic devices.

EXPERIMENTAL PROCEDURES
Resource Availability
Lead Contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Jin Zhang (jinzhang@pku.edu.cn).

Materials Availability
This study did not generate new unique reagents.

Data and Code Availability
All data are reported in the paper or Supplemental Information.

Synthesis and Transfer of Monolayer ReS2
Single-layer ReS2 was grown by a hydrogen-free CVD method with rhenium trioxide (ReO3, 99.9%, Sigma-Aldrich) and sulfur (S, 99.5%, Sigma-Aldrich) powder used as precursors, as previously reported.56,57 Freshly cleaved mica was applied as the substrate, which was loaded at the center of a crucible containing ReO3 powder. Some crushed molecular sieves were spread uniformly over ReO3 to ensure its uniform volatilization. Sulfur powder was placed upstream of the furnace, where the heating temperature was maintained at 200°C, while the crucible containing ReO3 was located at the furnace center. The furnace was heated to the growth temperature of 600°C–800°C at a rate of 25°C min⁻¹ with argon used as the carrier gas, then kept at the growth temperature for 10 min. After growth, the furnace was naturally cooled to room temperature. Monolayer ReS2 was then transferred to a SiO2/Si substrate for the optical imaging and the subsequent STEM sample preparation. A thin film of PMMA was first spin-coated on the ReS2/SiO2/Si substrate surface. Subsequently, the sample was floated on a 1 mol L⁻¹ potassium hydroxide (KOH) solution to etch SiO2 away. As soon as the PMMA/ReS2 film detached from the Si substrate, the film was transferred to the deionized water several times to thoroughly remove residuals left by the etchant. Thereafter, the PMMA/ReS2 film was scooped up by a holey silicon nitride (SiNₓ) TEM grid, allowed to dry in the air naturally, and baked at 180°C for 15 min. The PMMA scaffold was finally removed by submerging the TEM grid in acetone for 8 h.

Sample Preparation of Nanoparticle-Decorated Monolayer ReS2
A drop of Pt-TCPP-chloroform solution (10⁻³ mol L⁻¹) was deposited on an empty TEM grid. The grid was naturally dried in air. The silicon nitride TEM grid covered by monolayer ReS2 was loaded into a quartz tube and heated to 300°C for 1 h with Ar used as the carrier gas, and maintained at this temperature for another hour in a flow of mixed H₂ and Ar to thoroughly remove the PMMA residual and
adsorbates from the air before imaging. The empty grid deposited by Pt-TCPP was placed beside the ReS$_2$ STEM specimen in the quartz tube to gently transport a small quantity of vaporized Pt-TCPP onto the ReS$_2$ surface, thus facilitating preferential adsorption of Pt-TCPP to GBs and edges of ReS$_2$. After annealing, the sample was slowly cooled to room temperature under argon atmosphere. The cooling process took about 40 min.

**Scanning Transmission Electron Microscopy and Image Processing**

ADF-STEM imaging was conducted at room temperature on an aberration-corrected Titan Cubed Themis G2 300. STEM operated under an accelerating voltage of 300 kV. Dwell time of a single frame was 2 μs per pixel. A pixel size of 0.012 nm px$^{-1}$ as well as a beam current of 8 pA were used for imaging. Conditions were a condenser lens aperture of 50 μm, convergence semi-angle of 21.3 mrad, and collection angle of 39–200 mrad. It is noteworthy that the electron dose applied in our system is around two orders of magnitude smaller than those used in the low accelerating voltage STEM systems, which partially balanced the irradiation effect from the high accelerating voltage. Therefore, we did not observe obvious damage to the ReS$_2$ lattice due to the e-beam illumination under this imaging recipe. Images were processed using ImageJ software. Two types of false color look-up tables, fire and orange hot, were applied to grayscale images for the enhancement of the visual effect of overlapping GBs. A Gaussian blur filter (~2–4 pixels) was used on high-magnification ADF-STEM images for smoothing. Atomic models were constructed using the software of Accelrys Discovery Studio Visualizer. ADF-STEM image simulations based on corresponding atomic models were generated using COMPUTEM software with a proper parameter adjustment according to the ADF-STEM experimental conditions.

**Calculation Methods**

All the DFT calculations were carried out by the Vienna Ab Initio Simulation Package. The generalized gradient approximation with the Perdew-Burke-Ernzerhof method was used to deal with the exchange and correlation functional. The vdW interactions were considered by the optB86b-vdW functional. The crystal structures were fully relaxed with energy cutoff set as 400 eV and force convergence criteria set as 0.05 eV Å$^{-1}$. The lattice parameters along out-of-plane direction were larger than 20 Å to eliminate the interactions between periodic slabs. The edges of GBs were generated by nanoribbon models, and the widths of nanoribbons were larger than 25 Å to separate the interaction between two edges. The isovalue of charge density was set to 0.01 e Å$^{-3}$.

**SUPPLEMENTAL INFORMATION**

Supplemental Information can be found online at https://doi.org/10.1016/j.matt.2020.09.015.

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AUTHOR CONTRIBUTIONS

J.Z. and S.W. initiated the project and generated the experimental protocols. Y.Y. and S.W. fabricated the STEM sample and conducted the ADF-STEM imaging of 2D ReS$_2$. Shuqing Zhang and X.Z. performed DFT calculations. H.X. provided CVD-grown monolayer ReS$_2$ samples. Shishu Zhang transferred samples to SiO$_2$/Si to take optical images. S.W., Y.Y., and Shuqing Zhang analyzed the data. S.W., Y.Y., Shuqing Zhang, and J.Z. wrote the manuscript. All authors contributed to the discussion and revision of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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