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‘Colorful’ Polyline Grain Boundaries in Two-dimensional Transition Metal Dichalcogenides

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Grain boundaries (GBs) are vital to crystal materials and their applications. Although the GBs in bulk and two-dimensional materials have been extensively studied, the polyline GBs prevalently forming in transition metal dichalcogenide monolayers by a sequence of folded segments remain a mystery. We visualize the large-area distribution of the polyline GBs in MoSe₂ monolayers by means of a strain mapping method and unravel their structural origin using *ab initio* calculations combined with high-resolution atomic characterizations. Unlike normal GBs in two-dimensional materials with one type of dislocation cores, the polyline GBs consist of two basic elements—4|8 and 4|4|8 cores, whose alloying results in structural diversity and distinctly high stability due to relieved stress fields nearby. The defective polygons can uniquely migrate along the polyline GBs via the movement of single molybdenum atoms, unobtrusively giving the GBs their chameleon-like ‘colorful’ appearances. Furthermore, the polyline GBs can achieve useful functionalities such as intrinsic magnetism and highly active electrocatalysis.

Crystal materials are typically polycrystalline, with distinct grains of varying orientation stitched by grain boundaries (GBs). The average grain size and microstructures of the GBs are critical to material properties. Elemental and alloyed metals can exhibit greatly enhanced yield strength by optimizing grain sizes and boundaries¹⁻³, while strong covalent crystals can be continuously hardened by decreasing grain sizes down to a few nanometers⁴⁻⁶. The GB effects become more significant in two-dimensional (2D) materials⁷⁻⁹, where the crystalline order is highly vulnerable to various types of disorder and can be directly disrupted by a line defect. These issues are of special significance in 2D transition metal dichalcogenides MX_2 ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{S}, \text{Se}, \text{etc.}$), a large family of three-atom-thick 2D materials that have attracted keen current interest¹⁰⁻¹³. The MX_2 monolayers can now be fabricated by chemical vapor deposition (CVD)^{11,14-17} on scales up to centimeters^{18,19}, such that GBs are almost unavoidable and even ubiquitous in these materials. GBs in MX_2 are unique for their extension into a third dimension, forming series-connected, dreidel-shaped polyhedra¹². They likewise present a fertile ground for exploring new phenomena²⁰⁻²⁴ through the fascinating interplay they afford between local chemistry and far-field mechanics.

GBs in graphene are mostly a string of pentagon-heptagon (5|7) dislocation cores, which have low elastic strain energy. These GBs generally follow straight or wiggle lines²⁵⁻²⁷. In contrast, the 5|7 cores in 2D MX_2 introduce extra chemical energy due to local nonstoichiometric compositions^{12,13,28}, such that square-octagon (4|8) cores, which meet the stoichiometry but have high strain energy, can be favored by high-angle GBs where the high linear density of dislocations alleviate stress fields^{12,29}. The rich mechanochemical coupling at dislocations in 2D MX_2 would cause distinct behaviors for the corresponding GBs. Indeed, experimentally observed GBs in 2D MX_2 often exhibit a fine-polyline topology with a sequence of alternately folded segments^{11,14,24}. Despite extensive study of GBs in the flatland, the polyline GBs (p-GBs) are yet to be understood, hampered by the fact that the characteristic size spans several orders of magnitude, from grains, via GB segments, to atoms. In this work, we perform a cross-scale study to unravel the structural origin of the p-GBs by combining a large-scale strain mapping method, atomistic computations and annular dark-field scanning transmission electron microscope (ADF-STEM) characterizations. The p-GBs are distinguished by their

‘colorful’ appearances due to exceptional variability of component dislocation cores and rich functionalities because of the diverse sequences of defects. The results may bridge the relatively monotone GB structures in truly planar graphene and *h*-BN and the rich ‘complexions’³⁰⁻³² and phase transformations³³ of GBs in bulk systems.

Results and discussion

We conduct the CVD growth of MoSe₂ monolayers by merging numerous grains. This results in rich GBs. To rapidly locate the GBs in the process of STEM characterization, we introduce the substitution reaction of Se by S atoms within the MoSe₂ matrix for a short time and at ~700 °C. The concentrated stress field along the GBs makes the nearby atomic sites more active than those in the perfect region, so that the substitution reaction preferentially starts from the GBs and then proceeds to extend the MoS₂ domains along the GBs. As a result, the short-time reaction generates hybrid MoS₂ channels within the MoSe₂ matrix that strictly follow the GB shapes. Our early work has verified that this substitution can well preserve the morphology of GBs in 2D MoSe₂²⁴. S and Se atoms show distinct brightness in the STEM images according to their sizes. This enables easy recognition of the hybrid channels and large-scale characterization of the microscopic structures of GBs.

The global GB morphology can be visualized by mapping the nominal lattice rotation with respect to the MoSe₂ lattice obtained from our geometric phase analysis (Fig. 1a and Supplementary Fig. S1). The distinguished intensity of rotation in the maps reveals a significant number of p-GBs in the same matrix. Compared with straight GBs as have been focused in previous reports^{12,34}, the p-GBs exhibit unexpected structural diversity, with a series of segments alternately folded at various angles θ_f . These segments differ in length l and angle θ_f . 96% of these segments are shorter than 15 nm, with a highest distribution of 33% in the range of 3-6 nm (Fig. 1b, right). The angle exhibits a wide range of distribution, from 79.1° to 149.1°. By distributing all the measured θ_f into a sequence of intervals spaced by 10°, we find θ_f exhibits an outstandingly high probability distribution of 58.2% in 107±5°, followed by a distribution of 19.4% in 117±5°, while the distributions in other intervals appear to be much lower (Fig. 1b, left).

Fig. 1 | STEM structural analysis of the p-GBs in MoSe₂ monolayers. **a**, Extracted rotation maps of lattices after the Se-to-S substitution reaction advancing along GBs clearly display a series of polyline GBs. Folding angles θ_f along GBs are marked with numbers. **b**, Statistical probability distribution of folding angles θ_f and segment length l in a set of ranges, incremented by 10° and 3 nm, respectively. **c**, ADF-STEM images of the GBs with $\theta_f = 110.1^\circ$ (left), 118.6° (middle) and 136.5° (right) unambiguously show atomic structures of dislocation cores along the GBs.

Atomic-resolution ADF imaging for the GB regions in the MoS₂ channels displays two grains stitched seamlessly by each p-GB, with the Mo atoms being brighter than the S atoms (Fig. 1c). The two grains are Mo-oriented toward each other so that all the p-GBs have a uniform tilt angle of $\theta_T = 60^\circ$. The GB segments are composed of a string of mixed squares and octagons, consistent with previous experiments on 2D MX₂^{11,13,28,29}. Yet, we find that the p-GBs of distinct θ_f differ significantly in polygon sequences, suggesting a correlation of their morphology with the defect structures. It has been deemed that the overall orientations of GBs are not determined by energy but by growth history³⁵. While this viewpoint may hold for straight GBs, the following analysis suggests distinction for the p-GBs.

To unravel the origin of polyline morphology and understand the structural diversity of p-GBs, we resort to first-principles calculations. Owing to the similarity in atomic structures and bonding characteristics in 2D MX_2 , we take MoSe_2 as an example. Two 60° tilted domains with inverse lattice orientations are stitched by either a straight GB or a p-GB denoted by the white band in Fig. 2a. Instead of only one type of dislocation core for building the GB, we here identify two types of cores as two basic elements from our experiments—the $4|8$ and $4|4|8$ dislocation cores^{11,12,24,29}, which can be mixed to fill the interstice between the two domains. According to the content of dislocation cores, the p-GBs can be expressed as A_xB_{1-x} , where $A = 4|8$, $B = 4|4|8$. The three-fold symmetry of the 2D MoSe_2 dictates that the octagons in A and B are either aligned or misoriented by 120° (right, Fig. 2a).

Fig.2 | Structures and energetics of p-GBs in 2D MoSe_2 . **a**, A schematic model of a 60° tilted GB stitching two inversely oriented domains, following a polyline shape as indicated by the white band. The GB is made of two basic elements— $4|8$ and $4|4|8$ cores which are slanted at different angles. The octagons in these dislocation cores can be either aligned or misoriented by 120° . **b**, In the aligned case, the $4|8$ and $4|4|8$ cores can be alloyed to form a set of relaxed p-GB structures, depicted as A_xB_{1-x} , where A and B denote the $4|8$ and $4|4|8$ cores, respectively. The octagons in A and B are aligned. A straight Mo-4|8 structure of GB is given on the rightmost for comparison. **c**, The relative energy of these p-GBs to the one with $x = 0.5'$ as a function of the chemical potential of Se, μ_{Se} . The shaded area indicates the range of μ_{Se} corresponding to our experiments. **d**, A set of relaxed p-GB structures, A_xB_{1-x} , in which octagons in two segments are misoriented by 120° . Calculated folding angles, θ_i , from the structures of distinct x are marked with numbers.

We first considered the aligned case. With a periodic boundary condition, we build a set

of p-GBs with varying x in A_xB_{1-x} (Fig. 2b). Note that the periodicity does not exist in practical GBs and is adopted here to facilitate computations. Calculated θ_f from fully relaxed structures of p-GBs for distinct x in A_xB_{1-x} is marked in Fig. 2b, showing an almost linear relationship with x . The p-GB with $x = 0$ has a minimum of $\theta_f = 98^\circ$, since each 4|4|8 core is slanted at an angle of $\sim 49^\circ$, whereas the p-GB with $x = 1$ has a maximal $\theta_f = 121^\circ$, enabled by a larger slant angle of $\sim 60.5^\circ$ of the 4|8 core (middle, Fig. 2a). All other p-GBs with mixed A and B cores have θ_f stayed in-between. Interestingly, when the A and B cores are mixed equally (i.e. $x = 0.5$), the p-GBs have a constant $\theta_f = 107^\circ$, regardless of the detailed arrangement of the two types of cores. For comparison, we also build a straight GB structure with densely packed 4|8 cores, ever reported to be one of the most favorable high-angle GB structures³⁴.

We then examine the relative stability of these p-GBs by their relative energies ΔE ,

$$\Delta E = (E_{\text{tar}} - E_{\text{ref}} - n_i \mu_i - T \Delta S_{\text{conf}}) / L$$

where E_{tar} and E_{ref} are the total energies of targeted and referenced p-GBs, respectively, n_i is the number of excessive Mo or Se atoms, μ_i is the corresponding chemical potential, and ΔS_{conf} is the configurational entropy difference, as detailed in the Methods section below. We take the structure $x = 0.5$ with equally mixed A and B cores as the point of reference. The energy unit is normalized by the GB length, L . μ_{Mo} and μ_{Se} satisfy $\mu_{\text{MoSe}_2} = \mu_{\text{Mo}} + 2\mu_{\text{Se}}$ at equilibrium, where μ_{MoSe_2} is the chemical potential of a MoSe₂ unit in a pristine sheet.

The calculated ΔE of p-GBs at $T = 973$ K as a function of μ_{Se} are summarized in Fig. 2c. The straight Mo-4|8 structure, albeit with a shorter length, has a much higher energy than the p-GBs across the whole range of μ_{Se} . This is attributed to the higher stress concentration caused by densely stacked 4|8 cores. In contrast, the dislocation cores in p-GBs are more linearly connected, which relieves the stress fields of dislocations to lower the energy. This contrast is supported by the calculated maps of stress distribution around the GBs (Supplementary Fig. S2). Under a Mo-rich condition, the GB with $\theta_f = 98^\circ$ is preferred, and its ΔE increases with θ_f . Relative stabilities of the p-GBs with different θ_f are blurred as μ_{Se} increases. Our experiment corresponds to a Se-rich condition, indicated by the shaded area in Fig. 2c, in which the p-GB with $\theta_f = 107^\circ$ is the most favorable. This energetic preference agrees with the experimental

abundance of the p-GBs in the interval of $107 \pm 5^\circ$ (Fig. 1b).

We next consider the case in which the octagons in two segments are misoriented by 120° . A set of A_xB_{1-x} with varying x can then be built as shown in Fig. 2d, where segments in p-GBs are joined by squares at the corner. This set of p-GBs exhibit apparently larger θ_f than those GBs with aligned octagons. Calculated θ_f from relaxed structures of these GBs decreases from 140° at $x=0$ to 118° at $x=1$. It is noteworthy that all these p-GBs are Se-oriented and are less stable than the straight counterpart composed of aligned rhombs (Supplementary Fig. S3)³⁴. These features may account for their relatively less frequency in our experimental observation (Fig. 1b). The stability ranking of p-GBs depends also on other factors such as temperature and lattice stress. For example, an applied tensile stress of 200 MPa decreases the free energy difference between the p-GBs with $x=0.5$ and 0.8 by 90% at $\mu_{\text{Se}} = -3.7$ eV. Hence, different p-GBs could stably coexist under given conditions, as observed in our experiments.

Aside from the standard combination of 4|8 and 4|4|8 cores, the p-GBs strike us more by unusual structural evolution. Scrutinizing STEM images of p-GBs shows strings of successive squares or octagons, such as the 4|4|4 and 8|8 motifs (Fig. 1c and Supplementary Fig. S4). These new dislocations can be rationalized by structural evolution of the p-GBs via polygon migrations, like the dislocation motions observed in MX_2 sheets³⁶. For example, the connected square and octagon in p-GBs may swap positions, turning a 4|4|8|4|4|8 segment into a 4|8|4|4|4|8 or a 4|8|4|8 segment into a 4|4|8|8, and further (Fig. 3a).

Fig. 3 | Structural evolution of the p-GBs in 2D MoSe₂. **a**, Proposed migrations of polygons along the p-GBs. **b**, Calculated minimum energy pathways for a Mo atom (as indicated by the red circle) migrating along GB segments composed of the 4|4|8 (black line) and 4|8 (red line) cores, respectively. The migrations result in distinct 4|4|4 and 8|8 cores, indicated by colored segments. **c-e**, The evolution of p-GBs with an initial θ_f of 98°, 115°, and 116° are demonstrated through a series of steps shown in the left panels. The light gray, dark gray, light blue, and dark blue segments represent the 4|4|8, 4|8, 4|4|4|8, and 4|4|8|8 cores, respectively. The folding angles of p-GBs in the initial and final steps are marked. Right panel images are experimental ADF images that verify the calculated structures and orientations. All the stick models are obtained from structures relaxed by first-principles calculations.

To deepen our understanding of the structural evolution, we calculate the minimum energy pathways in the process of polygon migrations. Surprisingly, the polygon migrations can be easily realized by merely moving one Mo atom shared by both a square and an octagon, as indicated by the red circle in Fig. 3b. Taking the p-GB composed of 4|4|8 cores for example, the migration starts from the break of a Se-Mo bond in the square, transforming the square-octagon into a paired heptagon-heptagon at the transition state. Finally, the Mo atom bonds to a Se atom on the opposite side of the second heptagon, transforming the original 4|4|8|4|4|8 sequence to 4|8|4|4|4|8 (black line, Fig. 3b). This migration mechanism does not require collective movement of multiple atoms, which is in sharp contrast to the glide of 6|8 cores in 2D WS₂ through concerted bond breaking and reconnection^{36,37}. This new mechanism can explain the structural evolution of other p-GBs, such as the p-GB composed of 4|8 cores whose evolution features 8|8 motifs (red line, Fig. 3b).

The energy barriers for moving the Mo atom to form the 4|4|4 and 8|8 motifs are 1.96 and 1.43 eV, respectively, both markedly lower than the barriers of 6-10 eV in graphene and 5.4 eV in *h*-BN^{37,38}. The Mo movement in the p-GBs locally increases the energies of the two GBs by only 0.23 and 0.31 eV, respectively. According to transition-state theory^{39,40}, we estimate the activating temperatures for the polygon migrations by $X \times \exp(-E_{\text{barrier}}/k_B T) \approx 1$ with X ranging from $\sim 10^{12}$ to 10^{15} . Estimated temperatures of 658-828 K and 480-600 K for forming the 4|4|4 and 8|8 motifs, respectively, are well below the experimental temperatures of ~ 973 K. The involved monatomic movement with relatively low energy barriers suggests a potential way to program the sequence of polygons: a STM tip scanning along the GBs. Distinct properties, then, can be anticipated from different polygon sequences.

The polygon migrations provide another degree of freedom for diversifying the morphology of p-GBs. Fig. 3c presents how the p-GB with $\theta_f = 98^\circ$ evolves via successive migrations of a Mo atom along it. The sequence of one of the GB segments can change from the original 4|4|8|4|4|8|4|4|8|4|4|8 via the 4|4|4|8|4|8|4|4|8|4|4|8 to the 4|4|4|8|4|8|4|4|4|8|4|8|, along with a reduction of θ_f to 95° . The energies of the corresponding GBs agree within 7 meV/Å. Thus, all the intermediate states are close to thermodynamic equilibrium and can be kinetically trapped during the materials growth. The evolved GB structure agrees with our ADF-STEM image of one GB in terms of the polygon sequence and folding angle (right, Fig. 3c). Fig. 3d presents a similar structural evolution of another p-GB with $\theta_f = 115^\circ$, where the polygon migrations occur in two segments of the elbow to form structures composed of 4|8, 4|4|4|8, and 4|4|8|8 cores. The successive change of the polygon sequence gradually reduces θ_f from 115° to 111° ; the evolved structure exactly reproduces the structure from our atomic-resolution ADF characterization (right, Fig. 3d).

In contrast to the migration of squares toward the folding point that sharpens the elbow, the accumulation of octagons at this point tends to increase θ_f . Fig. 3e shows how the θ_f of a GB increases from 116° to 119° via this sort of polygon migration, reaching a GB structure that closely resembles another experimental image. Similar polygon migrations can be analyzed in the p-GBs with misoriented octagons in two segments (Supplementary Fig. S5), reproducing the experimental image in the rightmost of Fig. 1c. These results strongly indicate that all the experimentally observed p-GBs can be restored back to one of the standard structures shown in Fig. 2, which are comprised of the 4|4|8 and 4|8 cores. Hence, our model based on mixed dislocations appears to be general for the description of structurally diverse p-GBs.

With this structural understanding of the p-GBs, we proceed to explore their possible properties. Fig. 4a shows the electronic density of states projected onto just the atoms in the intermediate vicinity of a p-GB with $\theta_f = 107^\circ$ compared with those of an ideal MoSe₂ sheet, shown in grey. The p-GB brings extra electronic states within the bulk bandgap, predominantly contributed by Mo 3d orbitals at the p-GB. An evolution of the p-GB into a 4|4|4|8|8 sequence leads to different mid-gap states (Supplementary Fig. S6). These defect states result in a weak ferromagnetic ground state for the p-GBs and evolved forms (inset, Fig. 4a), benefitting from

the semiconducting bulk state that localizes the defect states. Magnetism was also predicted in the GBs composed of 5|7 cores in 2D MX_2 ²⁹. However, experimental confirmation of such magnetism remains unavailable, probably due to the low areal density of spins and the high sensitivity to carrier concentrations in the samples.

Fig. 4 | Electronic and catalytic properties of p-GBs. **a**, Density of states (DOS) for the p-GB with $\theta_f = 107^\circ$. The gray shadow indicates DOS of a perfect MoSe_2 sheet. The inset shows an isosurface plot ($3 \times 10^{-3} \text{ e}/\text{\AA}^3$) of the magnetization density. **b**, Calculated Gibbs free energy ΔG as a function of d for two straight GBs composed solely of 4|8 and 4|4|8 cores, respectively. d denotes the distance of reaction sites from the GB line. The results for a perfect 2D MoSe_2 and the Mo-4|8 GB are also provided. **c**, A contour plot of ΔG around the p-GBs. **d**, Optical images of micro-electrochemical devices, where the HER process occurs at the exposed windows on the p-GBs in a MoSe_2 matrix as indicated by a dark frame. **e-f**, Polarization curves and Tafel plots of current density for catalytic devices based on the p-GBs, edges, and basal planes of MoSe_2 , respectively. The plot of Pt is also provided for comparison.

Since the p-GBs create rich states near the Fermi level in an otherwise semiconductor, they should be chemically active for catalysis. We use the hydrogen evolution reaction (HER) as a test to demonstrate this potential. We first take p-GB segments composed solely of 4|8 and 4|4|8, respectively, as model systems. The Gibbs free energy ΔG of hydrogen atoms is calculated by first-principles, scanning all possible adsorption sites. The results suggest high intrinsic per-site activity at the GBs, with $\Delta G = -0.15$ and -0.19 eV for the 4|8 and 4|4|8 cores, respectively, compared with 0.25 eV of the Mo-4|8 GB (Fig. 4b). Following the decay of the stress field, ΔG rises sharply as the reaction site moves away from the GB, until there is a convergence in the

bulk region. A contour plot of ΔG around a p-GB with $x=0.5$ shown in Fig. 4c displays a zigzag-like distribution of catalytic sites, offering a higher density of active sites than straight GBs. Notably, the sites over the hollow octagons of the folding corners in this p-GB have ΔG as small as 0.03 eV, nearly as perfect as that of Pt.

To verify the enhanced catalytic performance of the p-GBs experimentally, we manage to fabricate a micro-electrochemical device to selectively examine the HER on the p-GBs (Fig. 4d). Similar devices are also fabricated to examine HER on the edges and basal plane of a MoS₂ sheet (Supplementary Fig. S7). The polarization curves and corresponding Tafel slopes recorded with these devices in a 0.5 M H₂SO₄ solution are shown in Fig. 4e-f, where the result of Pt is also provided for comparison. Compared to previously focused MX₂ edges, the p-GBs exhibit a markedly higher catalytic performance, manifested as having a lower onset potential and a higher current density, in agreement with our calculations. While the activity of p-GBs remains inferior to that of Pt, which is due to the small fraction of GBs in our 2D system, it should be amenable to improvement if the areal density of GBs is increased.

Extensive calculations show that the thermodynamic stability and structural evolution of p-GBs are common within the family of 2D MX₂ (M = Mo, W; X = S, Se), as shown in Supplementary Fig. S8. Therefore, the ‘colorful complexions’ of p-GBs are a general behavior in this family of 2D materials, in contrast to relatively monotone GBs in graphene yet showing striking similarity to multiple ‘complexions’³⁰⁻³² and transitions³³ of GBs in bulk systems.

Conclusions

In conclusion, comprehensive analyses based on intensive experimental characterizations and *ab initio* calculations have deciphered the mystery of the GBs with polyline morphology that are commonly observed in a range of 2D MX₂. We have identified two types of basic dislocation cores for all the polyline GBs—the 4|8 and 4|4|8 cores, which can be well mixed at any ratio to make diverse polyline GBs with different shapes but similar energy. At the same time, they can also mutate to form more complex dislocations via a simple migration of M atoms, thereby further diversifying the GB morphologies. The residual stress and mis-coordinated atoms around the GBs create mid-gap states and promise intrinsic magnetism. We

further demonstrate the utility of p-GBs for catalyzing the hydrogen evolution reaction to an extent that outperforms previously concerned MX_2 edges. This atomic-level understanding and demonstrated utility are likely to inform on-going efforts to introduce polyline GBs in 2D metal dichalcogenides for achieving functionalities unavailable in pristine materials.

Methods

Synthesis procedure. A two-step CVD method was applied to synthesize the MoSe_2 - MoS_2 hybrid channel. The first step was the growth of MoSe_2 monolayers. Two quartz boats containing 20 mg MoO_3 and 0.5 g Se powder were placed in the middle and upstream of a quartz tube, respectively. The SiO_2/Si substrate was placed face-down onto the middle quartz boat. The growth was carried out under the mixed input gas of 5 sccm H_2 and 50 sccm Ar at atmospheric pressure, with a temperature ramping rate of $30\text{ }^\circ\text{C}/\text{min}$, and a duration time of 10 min at $720\text{ }^\circ\text{C}$. The second step was the growth of embedded MoS_2 channels. The substrate overlaid with the MoSe_2 monolayers was placed face-down onto another quartz boat and transferred to a new quartz tube. In this step, the growth was performed at 973 K for 5 min using 20 mg MoO_3 and 0.5 g S powder as the precursors and with the same gas flow as in the MoSe_2 case.

STEM characterization. The samples for STEM characterization were obtained using a general poly (methyl methacrylate) (PMMA) transfer method, which was performed on a JEOL ARM-200F (S)TEM equipped with a CEOS CESCOR aberration corrector, and operated at an 80 kV acceleration. The convergence semi-angle and acquisition semi-angle were set to 28-33 and 68-280 mrad, and the per pixel dwell time was 12-20 μs for the image acquisition. The obtained ADF images were deconvolution filtered to enhance the contrast.

Geometric phase analysis. GPA was used to extract the displacement fields and strain maps of the GB region. Specifically, two sets of nonparallel fast Fourier transformation (FFT) spots in reciprocal space containing both MoS_2 and MoSe_2 information were Gaussian masked. Subsequent calculations of these two sets of spots resulted in the corresponding strain and rotation maps in real space.

Fabrication of micro-electrochemical devices. The HER catalytic performance of MoS_2 was

measured by assembling them into micro-electrochemical devices. A set of Au electrodes were first patterned on standard SiO₂/Si substrates using photolithography. Then, high-quality graphene monolayers were transferred onto pre-patterned substrates with the aid of PMMA, followed by another transfer procedure of as-synthesized MoS₂ onto the graphene. After that, a further annealing at 200 °C in a high-vacuum environment (1×10^{-5} torr) was carried out to optimize their contact for better electron transport during reaction. Finally, a layer of PMMA (1 μ m) was deposited on the sample, and a reaction window on a target area (plane, edge or grain boundary) was opened by e-beam lithography to expose the reaction region of MoS₂. A four-electrode micro-electrochemical measurement system was applied in the electrocatalytic experiment. 0.5 M H₂SO₄ was used as the electrolyte solution, and the scan rate was set to 5 mv/step. During the measurements, only the exposed region of the sample (reaction window area) was available for HER. The electrocatalytic current (I_c) and conductance current (I_{ds}) could be simultaneously obtained for monitoring the electric conductivity of devices.

Theoretical Calculations. Density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP) code⁴¹, with the Perdew–Burke–Ernzerhof parametrization (PBE) of the generalized gradient approximation (GGA) and projector-augmented wave (PAW) potentials⁴². The model systems were built with sufficiently wide nanoribbons to isolate the grain boundaries from the edges. A kinetic energy cutoff was set to 300 eV for the plane-wave expansion, and a vacuum region of 15 Å was adopted to isolate neighboring periodic images. Structures were fully relaxed until the force on each atom was less than 0.01 eV/Å⁻¹. The Brillouin zone integration was sampled by five k-points along the GB direction. The minimum-energy paths of polygon migration for p-GBs were mapped out with the climbing image-nudged elastic-band method⁴³.

The configurational entropy S was included in calculating the GB energy by employing the Boltzmann's entropy formula $S_{conf} = k_B \cdot \ln W$. In p-GBs, the 4|8 and 4|4|8 cores intermix, and the number of possible configurations is $W = \frac{(N_{4|8} + N_{4|4|8})!}{N_{4|8}! \cdot N_{4|4|8}!}$, where $N_{4|8}$ and $N_{4|4|8}$ are the number of 4|8 and 4|4|8 cores, respectively. According to the Stirling approximation $\ln X! \approx X \cdot \ln X$, the configurational entropy of p-GBs with intermixed cores is $S_{conf} = k_B \cdot [(N_{4|8} + N_{4|4|8}) \cdot \ln(N_{4|8} + N_{4|4|8}) - N_{4|8} \cdot \ln N_{4|8} - N_{4|4|8} \cdot \ln N_{4|4|8}]$. Thus, the energy contributed by the configurational entropy reads

as $E_{\text{conf}} = -TS_{\text{conf}}$, with $T = 973$ K, according to our experiments.

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Author Contributions

M.Y. and C.Z. contributed equally to this work. Z.Z. conceived the project. Z.Z., W.G. and Z.L. supervised the research. M.Y. designed the polyline structures and performed the theoretical calculations. C.Z. performed the electron microscopy experiments and the electron microscopy data analysis. J.Z. synthesized the samples. Y.H. carried out the electrochemical experiments. Y.X. helped with theoretical data analysis. Z.Z. wrote the paper with input from all coauthors. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing financial interest.

References

1. Lu, K., Lu, L. & Suresh, S. Strengthening materials by engineering coherent internal boundaries at the nanoscale. *Science* **324**, 349-352 (2009).
2. Li, X., Jin, Z., Zhou, X. & Lu, K. Constrained minimal-interface structures in polycrystalline copper with extremely fine grains. *Science* **370**, 831-836 (2020).
3. Hu, J., Shi, Y., Sauvage, X., Sha, G. & Lu, K. Grain boundary stability governs hardening

- and softening in extremely fine nanograined metals. *Science* **355**, 1292-1296 (2017).
4. Gao, F., He, J., Wu, E., Liu, S., Yu, D., Li, D., Zhang, S. & Tian, Y. Hardness of covalent crystals. *Phys. Rev. Lett.* **91**, 015502 (2003).
 5. Huang, Q., Yu, D., Xu, B., Hu, W., Ma, Y., Wang, Y., Zhao, Z., Wen, B., He, J. & Liu, Z. Nanotwinned diamond with unprecedented hardness and stability. *Nature* **510**, 250-253 (2014).
 6. Tian, Y., Xu, B., Yu, D., Ma, Y., Wang, Y., Jiang, Y., Hu, W., Tang, C., Gao, Y. & Luo, K. Ultrahard nanotwinned cubic boron nitride. *Nature* **493**, 385-388 (2013).
 7. Tsen, A. W., Brown, L., Levendorf, M. P., Ghahari, F., Huang, P. Y., Havener, R. W., Ruiz-Vargas, C. S., Muller, D. A., Kim, P. & Park, J. Tailoring electrical transport across grain boundaries in polycrystalline graphene. *Science* **336**, 1143-1146 (2012).
 8. Yazyev, O. V. & Chen, Y. P. Polycrystalline graphene and other two-dimensional materials. *Nat. Nanotech.* **9**, 755-767 (2014).
 9. Grantab, R., Shenoy, V. B. & Ruoff, R. S. Anomalous strength characteristics of tilt grain boundaries in graphene. *Science* **330**, 946-948 (2010).
 10. Lin, Y.-C., Dumcenco, D. O., Huang, Y.-S. & Suenaga, K. Atomic mechanism of the semiconducting-to-metallic phase transition in single-layered MoS₂. *Nat. Nanotech.* **9**, 391-396 (2014).
 11. Van Der Zande, A. M., Huang, P. Y., Chenet, D. A., Berkelbach, T. C., You, Y., Lee, G.-H., Heinz, T. F., Reichman, D. R., Muller, D. A. & Hone, J. C. Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide. *Nat. Mater.* **12**, 554-561 (2013).
 12. Zou, X., Liu, Y. & Yakobson, B. I. Predicting dislocations and grain boundaries in two-dimensional metal-disulfides from the first principles. *Nano Lett.* **13**, 253-258 (2013).
 13. Zhou, W., Zou, X., Najmaei, S., Liu, Z., Shi, Y., Kong, J., Lou, J., Ajayan, P. M., Yakobson, B. I. & Idrobo, J.-C. Intrinsic structural defects in monolayer molybdenum disulfide. *Nano Lett.* **13**, 2615-2622 (2013).
 14. Zhang, Y., Zhang, Y., Ji, Q., Ju, J., Yuan, H., Shi, J., Gao, T., Ma, D., Liu, M. & Chen, Y. Controlled growth of high-quality monolayer WS₂ layers on sapphire and imaging its grain boundary. *ACS nano* **7**, 8963-8971 (2013).
 15. Tang, L., Li, T., Luo, Y., Feng, S., Cai, Z., Zhang, H., Liu, B. & Cheng, H.-M. Vertical chemical vapor deposition growth of highly uniform 2D transition metal dichalcogenides. *ACS nano* **14**, 4646-4653 (2020).
 16. Ly, T. H., Chiu, M.-H., Li, M.-Y., Zhao, J., Perello, D. J., Cichocka, M. O., Oh, H. M., Chae, S. H., Jeong, H. Y. & Yao, F. Observing grain boundaries in CVD-grown monolayer transition metal dichalcogenides. *ACS nano* **8**, 11401-11408 (2014).
 17. Cheng, J., Jiang, T., Ji, Q., Zhang, Y., Li, Z., Shan, Y., Zhang, Y., Gong, X., Liu, W. & Wu, S. Kinetic nature of grain boundary formation in As-grown MoS₂ monolayers. *Adv. Mater.* **27**, 4069-4074 (2015).
 18. Yang, P., Zhang, S., Pan, S., Tang, B., Liang, Y., Zhao, X., Zhang, Z., Shi, J., Huan, Y. & Shi, Y. Epitaxial growth of centimeter-scale single-crystal MoS₂ monolayer on Au (111). *ACS nano* **14**, 5036-5045 (2020).
 19. Tao, L., Chen, K., Chen, Z., Chen, W., Gui, X., Chen, H., Li, X. & Xu, J.-B. Centimeter-scale CVD growth of highly crystalline single-layer MoS₂ film with spatial homogeneity and the visualization of grain boundaries. *ACS Appl. Mater. Interfaces* **9**, 12073-12081

- (2017).
20. Mariano, R. G., McKelvey, K., White, H. S. & Kanan, M. W. Selective increase in CO₂ electroreduction activity at grain-boundary surface terminations. *Science* **358**, 1187-1192 (2017).
 21. Dai, M., Zheng, W., Zhang, X., Wang, S., Lin, J., Li, K., Hu, Y., Sun, E., Zhang, J. & Qiu, Y. Enhanced piezoelectric effect derived from grain boundary in MoS₂ monolayers. *Nano Lett.* **20**, 201-207 (2019).
 22. Zhu, J., Wang, Z.-C., Dai, H., Wang, Q., Yang, R., Yu, H., Liao, M., Zhang, J., Chen, W. & Wei, Z. Boundary activated hydrogen evolution reaction on monolayer MoS₂. *Nat. Commun.* **10**, 1-7 (2019).
 23. Sangwan, V. K., Jariwala, D., Kim, I. S., Chen, K.-S., Marks, T. J., Lauhon, L. J. & Hersam, M. C. Gate-tunable memristive phenomena mediated by grain boundaries in single-layer MoS₂. *Nat. Nanotech.* **10**, 403-406 (2015).
 24. Zhu, C., Yu, M., Zhou, J., He, Y., Zeng, Q., Deng, Y., Guo, S., Xu, M., Shi, J. & Zhou, W. Strain-driven growth of ultra-long two-dimensional nano-channels. *Nat. Commun.* **11**, 1-10 (2020).
 25. Wei, Y., Wu, J., Yin, H., Shi, X., Yang, R. & Dresselhaus, M. The nature of strength enhancement and weakening by pentagon–heptagon defects in graphene. *Nat. Mater.* **11**, 759-763 (2012).
 26. Zhang, Z., Yang, Y., Xu, F., Wang, L. & Yakobson, B. I. Unraveling the sinuous grain boundaries in graphene. *Adv. Funct. Mater.* **25**, 367-373 (2015).
 27. Li, Q., Zou, X., Liu, M., Sun, J., Gao, Y., Qi, Y., Zhou, X., Yakobson, B. I., Zhang, Y. & Liu, Z. Grain boundary structures and electronic properties of hexagonal boron nitride on Cu (111). *Nano Lett.* **15**, 5804-5810 (2015).
 28. Najmaei, S., Liu, Z., Zhou, W., Zou, X., Shi, G., Lei, S., Yakobson, B. I., Idrobo, J.-C., Ajayan, P. M. & Lou, J. Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers. *Nat. Mater.* **12**, 754-759 (2013).
 29. Zhang, Z., Zou, X., Crespi, V. H. & Yakobson, B. I. Intrinsic magnetism of grain boundaries in two-dimensional metal dichalcogenides. *ACS nano* **7**, 10475-10481 (2013).
 30. Yu, Z., Cantwell, P. R., Gao, Q., Yin, D., Zhang, Y., Zhou, N., Rohrer, G. S., Widom, M., Luo, J. & Harmer, M. P. Segregation-induced ordered superstructures at general grain boundaries in a nickel-bismuth alloy. *Science* **358**, 97-101 (2017).
 31. Tang, M., Carter, W. C. & Cannon, R. M. Grain boundary transitions in binary alloys. *Phys. Rev. Lett.* **97**, 075502 (2006).
 32. Zhou, N., Hu, T. & Luo, J. Grain boundary complexions in multicomponent alloys: Challenges and opportunities. *Curr. Opin. Solid State Mater. Sci.* **20**, 268-277 (2016).
 33. Meiners, T., Frolov, T., Rudd, R. E., Dehm, G. & Liebscher, C. H. Observations of grain-boundary phase transformations in an elemental metal. *Nature* **579**, 375-378 (2020).
 34. Zou, X. & Yakobson, B. I. Metallic high-angle grain boundaries in monolayer polycrystalline WS₂. *Small* **11**, 4503-4507 (2015).
 35. Yakobson, B. I. & Ding, F. Observational geology of graphene, at the nanoscale. *ACS nano* **5**, 1569-1574 (2011).
 36. Azizi, A., Zou, X., Ercius, P., Zhang, Z., Elías, A. L., Perea-López, N., Stone, G., Terrones, M., Yakobson, B. I. & Alem, N. Dislocation motion and grain boundary migration in two-

- dimensional tungsten disulphide. *Nat. Commun.* **5**, 1-7 (2014).
37. Zou, X., Liu, M., Shi, Z. & Yakobson, B. I. Environment-controlled dislocation migration and superplasticity in monolayer MoS₂. *Nano Lett.* **15**, 3495-3500 (2015).
 38. Banhart, F., Kotakoski, J. & Krasheninnikov, A. V. Structural defects in graphene. *ACS nano* **5**, 26-41 (2011).
 39. Xu, L., Mei, D. & Henkelman, G. Adaptive kinetic Monte Carlo simulation of methanol decomposition on Cu (100). *J. Chem. Phys.* **131**, 244520 (2009).
 40. Liu, L., Zhang, Z., Liu, X., Xuan, X., Yakobson, B. I., Hersam, M. C. & Guo, W. Borophene concentric superlattices via self-assembly of twin boundaries. *Nano Lett.* **20**, 1315-1321 (2020).
 41. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15-50 (1996).
 42. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
 43. Henkelman, G., Uberuaga, B. P. & Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **113**, 9901-9904 (2000).

Figures

Figure 1

STEM structural analysis of the p-GBs in MoSe₂ monolayers. a, Extracted rotation maps of lattices after the Se-to-S substitution reaction advancing along GBs clearly display a series of polyline GBs. Folding angles θ_f along GBs are marked with numbers. b, Statistical probability distribution of folding angles θ_f and segment length l in a set of ranges, incremented by 10° and 3 nm, respectively. c, ADF-STEM images of the GBs with $\theta_f = 110.1^\circ$ (left), 118.6° (middle) and 136.5° (right) unambiguously show atomic structures of dislocation cores along the GBs.

Figure 2

Structures and energetics of p-GBs in 2D MoSe₂. a, A schematic model of a 60° tilted GB stitching two inversely oriented domains, following a polyline shape as indicated by the white band. The GB is made of two basic elements—4|8 and 4|4|8 cores which are slanted at different angles. The octagons in these dislocation cores can be either aligned or misoriented by 120°. b, In the aligned case, the 4|8 and 4|4|8 cores can be alloyed to form a set of relaxed p-GB structures, depicted as A_xB_{1-x} , where A and B denote the 4|8 and 4|4|8 cores, respectively. The octagons in A and B are aligned. A straight Mo-4|8 structure of GB is given on the rightmost for comparison. c, The relative energy of these p-GBs to the one with $x = 0.5'$ as a function of the chemical potential of Se, μ_{Se} . The shaded area indicates the range of μ_{Se} corresponding to our experiments. d, A set of relaxed p-GB structures, A_xB_{1-x} , in which octagons in two segments are misoriented by 120°. Calculated folding angles, θ_f , from the structures of distinct x are marked with numbers.

Figure 3

Structural evolution of the p-GBs in 2D MoSe₂. a, Proposed migrations of polygons along the p-GBs. b, Calculated minimum energy pathways for a Mo atom (as indicated by the red circle) migrating along GB segments composed of the 4|4|8 (black line) and 4|8 (red line) cores, respectively. The migrations result in distinct 4|4|4 and 8|8 cores, indicated by colored segments. c-e, The evolution of p-GBs with an initial θ of 98°, 115°, and 116° are demonstrated through a series of steps shown in the left panels. The light gray, dark gray, light blue, and dark blue segments represent the 4|4|8, 4|8, 4|4|4|8, and 4|4|8|8 cores, respectively. The folding angles of p-GBs in the initial and final steps are marked. Right panel images are experimental ADF images that verify the calculated structures and orientations. All the stick models are obtained from structures relaxed by first-principles calculations.

Figure 4

Electronic and catalytic properties of p-GBs. a, Density of states (DOS) for the p-GB with $\theta_f = 107^\circ$. The gray shadow indicates DOS of a perfect MoSe₂ sheet. The inset shows an isosurface plot ($3 \times 10^{-3} \text{ e}/\text{\AA}^3$) of the magnetization density. b, Calculated Gibbs free energy ΔG as a function of d for two straight GBs composed solely of 4|8 and 4|4|8 cores, respectively. d denotes the distance of reaction sites from the GB line. The results for a perfect 2D MoSe₂ and the Mo-4|8 GB are also provided. c, A contour plot of ΔG around the p-GBs. d, Optical images of micro-electrochemical devices, where the HER process occurs at the exposed windows on the p-GBs in a MoSe₂ matrix as indicated by a dark frame. e-f, Polarization curves and Tafel plots of current density for catalytic devices based on the p-GBs, edges, and basal planes of MoS₂, respectively. The plot of Pt is also provided for comparison.

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