Edge Segregated Polymorphism in 2D Molybdenum Carbide

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Molybdenum carbide (Mo₂C), a class of unterminated MXene, is endowed with rich polymorph chemistry, but the growth conditions of the various polymorphs are not understood. Other than the most commonly observed 1T-phase Mo₂C, little is known about other phases. Here, Mo₂C crystals are successfully grown consisting of mixed polymorphs and polytypes via a diffusion-mediated mechanism, using liquid copper as the diffusion barrier between the elemental precursors of Mo and C. By controlling the thickness of the copper diffusion barrier layer, the crystal growth can be controlled between a highly uniform AA-stacked 1T-phase Mo₂C and a “wedding cake” like Mo₂C crystal with spatially delineated zone in which the Bernal-stacked Mo₂C predominate. The atomic structures, as well as the transformations between distinct stackings, are simulated and analyzed using density functional theory (DFT)-based calculations. Bernal-stacked Mo₂C has a d band closer to the Fermi energy, leading to a promising performance in catalysis as verified in hydrogen evolution reaction (HER).
dark field (STEM-ADF) imaging, a diverse range of polymorphs and stacking polytypes was identified along the edge regions. A full spectrum of intermediate states due to fractional intralayer or interlayer translation, in monolayer and multilayer Mo$_2$C, was revealed. The atomic structures at various stages of phase transformations were simulated and analyzed by using density functional theory (DFT). All phase transitions observed can be explained by the gliding of the Mo layer along the Mo-Armchair ($<10\bar{1}0>$) direction, this includes, for example, the 1T-Mo$_2$C to 1H-Mo$_2$C polymorph transition. Importantly, we found that Mo$_2$C crystals ring-fenced by Bernal-stacked (AB-stacked) Mo$_2$C in the edge region show a reduced onset potential for HER compared to conventional AA-stacked crystals.

An ambient pressure CVD system is used for the growth. A Cu foil, which serves as the catalyst as well as a diffusion barrier, is placed on the supporting Mo substrate and introduced into the quartz reactor.$^{[5,15]}$ At temperatures > 1100 °C, the Cu foil melts and wets the entire Mo substrate. The high reaction temperature results in the formation of a Cu-Mo alloy, through which surface segregation of Mo occurs. The segregated Mo further reacts with the carbon precursor to form Mo$_2$C crystals. The growth rate of the Mo$_2$C crystal is mediated by the thickness of the underlying Cu foil due to the variation of Mo diffusion rates. When the Cu foil thickness is reduced from 100 to 25 µm (see the Experimental Section for details), the Mo$_2$C crystals grow rapidly on the Cu surface and form a “wedding-cake” structure due to the fast diffusion of Mo atoms from the edge to center regions (Scheme 1), as revealed from the optical image (Figure 1a) and atomic force microscope (AFM) (Figure 1b). The height profile shown in the inset of Figure 1b reveals a gradual thickness reduction from the center toward the edge region. Under fast growth conditions, the growth is non-equilibrated leading to a mixture of metastable phases at the edge zone. The atomic structure of the as-grown Mo$_2$C crystals was

Scheme 1. Schematic illustration showing the controlled growth of a) hexagonal shape single crystals and b) “wedding cake” like Mo$_2$C crystals by tuning the thickness of the copper diffusion barrier. c) Atomic model of monolayer 1T-phase Mo$_2$C. The side view and perspective view are depicted in the lower and right panels, respectively.
revealed by atomic-resolution STEM-ADF imaging. Due to the huge atomic number disparity between carbon (Z = 6) and molybdenum (Z = 42) in Mo₂C, only molybdenum atoms are imaged and carbon atoms are almost invisible in the experimental and simulated STEM-ADF images (Figure S1a, Supporting Information). The carbon atoms can only be approximately visualized when sufficient coherent elastic scattered electrons are collected (Figure S1b,c, Supporting Information).

In the wedding cake-like crystal, we observe that metastable polymorphs and polytypes are spatially delineated at the edge zone with a lateral width of ≈100 nm. A typical STEM-ADF image showing a well-delineated edge region in a Mo₂C flake is depicted in Figure 1c. The interlayer stacking order reveals a gradual evolution (Figure 1d and Figure S2, Supporting Information) along the edge zone, in which the predominant stacking registry belongs to the Bernal type (region 1 in Figure 1d) and is distinct from the usual AA stacking registry (see the honeycomb structure shown in Figure S1, Supporting Information) in the bulk regions. The presence of a high density of step edges (Figure 1e and Figure S3, Supporting Information) further confirms the crystal growth is mediated by Mo atom diffusion. The fact that this is a diffusion-mediated process is proven by using a ≈100 µm thick Cu foil to slow down the diffusion of Mo. In this case, the entire flake is uniform in thickness and the stacking order belongs to the AA type throughout (Figure S4, Supporting Information). In contrast, the wedding cake-like crystal grown with a 25 µm thick Cu foil presents a gradient of thickness going from monolayer-thick edge to the thicker bulk crystal, this presents a unique opportunity to monitor the evolution in polymorphs and stacking polytypes.

Under the nonequilibrated growth conditions where edge zones are richer in Mo than C, various metastable polymorphs attributed to intralayer gliding were observed to coexist in the edge zones of monolayer Mo₂C crystals (Figure 2a and Figure S5, Supporting Information). These polymorphs were induced by the gliding of one Mo atomic plane along the Mo-Armchair direction. Due to the in-plane sixfold symmetry in 1T-Mo₂C, the crystallographic orientation could be classified into two degenerate directions, i.e., Mo-Armchair <1010>, and carbon-zigzag (C-ZZ) <1210> directions, as illustrated in Figure 2b. In monolayer Mo₂C, there are two thermodynamically stable phases, i.e., 1H and 1T, where two layers of Mo take aa (1H) or ab (1T) stacking orders, respectively; the prefix “a” or “b” refers to intralayer stacking order in a single unit cell of Mo₂C, while “A” or “B” refers to the interlayer stacking order between two unit cells of Mo₂C; both phases were observed to be present, as presented in Figure 2c.

To investigate the intralayer gliding behaviors in monolayer Mo₂C crystals, we carried out DFT calculations to investigate the mechanism of phase transitions and map the energy

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**Figure 1.** Diffusion-mediated CVD growth of Mo₂C crystals with graded thickness. a) Optical microscope image and b) AFM image showing variation in the thickness of the steps. The inset of (b) reveals the height profile along the red dashed line in the AFM image. c) STEM-ADF image showing delineated edge zones. d) Atomic-resolution STEM-ADF image showing the stacking registry evolution in the vicinity of the step edges. Right panels show atom-resolved stacking registry variations of two different locations; step edges are highlighted by the white dashed lines. e) Atomic structure of the step edge in the edge zone. Scale bars: 10 µm in (a), 4 µm in (b), 200 nm in (c), and 2 nm in (d) and (e).
landscapes driven by the translation of the Mo atomic plane along the Mo-Armchair and C-ZZ directions in the monolayer Mo₂C model. The calculated energy landscape for the gliding of the top Mo layer along the Mo-Armchair direction for one period δ (5.3 Å) is shown in Figure 2d (The same period δ also applies for gliding along the degenerate C-ZZ direction), where insets present atomic models of various intermediate states. Due to the strong Mo-C interactions, the gliding barrier in monolayer Mo₂C is ≈200 meV Å⁻², which is almost two times larger than that of the 1H to 1T phase transition in MoS₂.²² Besides the common 1T (Figure 2e) and 1H (Figure 2f and Figure S6, Supporting Information) phases located in the saddle points of the energy profiles, another stacking order in which the Mo atomic plane glides for 1/₆, denoted as 1T-ARM₁/₆ (Figure 2g), is commonly seen and marked in the energy landscape. The 1T-ARM₁/₆ stacking order is a metastable state. 1T-ARM₁/₆ (Figure 2g and Figure S7, Supporting Information) is symmetrically distinct from the 1H-phase Mo₂C, and it is composed of periodic single Mo stripes showing an in-plane symmetry reduction to 2-fold. The experimentally observed 1T-ARM₁/₆ strongly resembles the simulated image derived from the DFT optimized model. On the other hand, the calculated energy barriers for gliding the Mo atomic plane along the C-ZZ direction is larger than that along the Mo-Armchair direction (Figure S8, Supporting Information), and no metastable fractional translated states are found along the entire gliding path. Hence, the simulation results are consistent with the experimental results that all metastable states are likely induced by gliding along the Mo-Armchair direction.

Going from the monolayer edge to bilayer edges and thicker (Figure 3a), we observe stacking polytypes arising from interlayer sliding in bilayer Mo₂C films (Figure 3b). The energy barrier of interlayer sliding (≈150 meV Å⁻²) is lower than that of intralayer gliding (≈200 meV Å⁻²) as suggested by the DFT (Figure 3c). In a bilayer Mo₂C film, the gliding component is a unit cell of the Mo₂C layer, and the interlayer bonding is described by metallic Mo–Mo interaction. Despite a larger interlayer gliding barrier in bilayer Mo₂C compared to bilayer...
graphene\textsuperscript{23} and transition metal dichalcogenides,\textsuperscript{17} various fractional translated stacking orders, induced by a consecutive atomic-scale shift preferentially along the Mo-ZZ direction, were found in the edge zones (Figure S9, Supporting Information), including, e.g., AA-ARM\textsubscript{1/6} (Figure 3d and Figure S10, Supporting Information), Bernal (AA-ARM\textsubscript{1/3}) (Figure 3e and Figure S11, Supporting Information), and AA-ARM\textsubscript{1/2} (Figure 3f and Figure S12, Supporting Information), which are induced by interlayer fractional translation for \( \frac{1}{6} \delta \) (0.9 Å), \( \frac{1}{3} \delta \) (1.8 Å), and \( \frac{1}{2} \delta \) (2.7 Å) period, respectively. According to DFT calculations, the Bernal (AA-ARM\textsubscript{1/3}) stacking order is thermodynamically more stable by 15 and 45 meV unit\(^{-1}\), respectively, compared to AA-ARM\textsubscript{1/6} and AA-ARM\textsubscript{1/2} stacking order. DFT calculations show that local energy minima can be identified among all the metastable phases. Structurally, Bernal-stacked Mo\textsubscript{2}C reveals a similar interlayer structure with commonly encountered bilayer 3R-stacked MoS\textsubscript{2} or AB-stacked bilayer graphene,\textsuperscript{24,25} and is noncentrosymmetric.\textsuperscript{17}

Further away from the bilayer edges, we observed that Mo\textsubscript{2}C crystals undergo interlayer gliding in thicker regions and spotted a large amount of Bernal like stacking orders. In multilayer crystals, Bernal like Mo\textsubscript{2}C can be confirmed by the presence of additional atom blobs (highlighted by pink) in each honeycomb (Figure 4a,b). The additional atom blobs could be induced by Mo atomic plane gliding (intralayer) and/or Mo\textsubscript{2}C plane gliding (interlayer). The STEM-ADF image is incoherent and the contrast is varying approximately as \( Z^{1.6-1.7} \), where \( Z \) is the atomic number. Therefore, the ratio between the translated Mo layers versus the static Mo layers can be calculated by measuring the intensity ratio between the additional atom blobs (site c) and the atom blobs in the honeycomb (site a or b). Four different regions revealing different degrees of gliding (Figure 4a), along with their simulated images (Figure 4b) derived from “abc,” “abc\textsubscript{0.75},” “abc\textsubscript{0.5},” and “abc\textsubscript{0.25}” stacking orders, are depicted in the lower panels. The atomic model showing the deficiency at the “c” atom sites is depicted.
Figure 4. Electron microscopy study of the Bernal (abc, x = 0.25 to 1) stacking registry in multilayer Mo2C. a) Atomic resolution STEM-ADF images showing different degrees of gliding in few-layer Mo2C crystals. The gliding ratio x is defined by calculating the intensity ratio between the static Mo layer versus the gliding Mo layer. b) Corresponding simulated images of Bernal-stacked few layer Mo2C when the gliding ratio x = 1, 0.75, 0.5, and 0.25, respectively. Three atomic sites, a, b, and c, representing the density of a, b, and c components, respectively, in the unit cell are highlighted in (a) and (b). c) Atomic model of the Bernal-stacked Mo2C and the side view showing different layers of a, b, and c components. Averaged intensity of all atomic sites from d) experimental and e) simulated abc (x = 1, 0.75, 0.5, 0.25) images. Intensity line profiles of the averaged three representative atomic sites (a, b, and c) in f) experimental and g) simulation results. Scale bars: 0.5 nm.
in Figure 4c. To quantify the intensity ratio between different atom blobs, we integrate the intensity of all equivalent atom sites (Figure 4d,e) in the experimental images (see Methods) in order to reduce the local intensity fluctuations as the probability of forming a defect is equivalent at all atomic positions. The analysed intensity line profiles (Figure 4f,g) agree well with the simulation results, confirming different degrees of gliding in thick regions. Other structures induced by fractional translations are depicted in Figure S13, Supporting Information.

The activation barrier for Mo plane gliding can be reduced by the presence of vacancies. Point defects are abundant in the IT/1H phase boundary (Figure S14, Supporting Information) in monolayer and few layer films (Figure S15, Supporting Information). To understand the role of point defects in the formation of various intermediate states, we employed DFT and constructed a IT/1H lateral phase boundary in monolayer Mo2C nanoribbon as depicted in Figure S16 (Supporting Information). When the phase boundary contains diverse point defects, i.e., a Mo vacancy and Mo and C divacancy, they stabilize the formation of intermediate states. Hence, the presence of imperfections facilitates the formation of different phases as observed by STEM, which opens a door to manipulating the structures of MXenes and metallic 2D materials via defect engineering.

We now elucidate the stacking dependent properties of the Bernal-stacking polytype and compare with that of AA-stacked T phase Mo2C. The various stacking configurations and their energies are displayed in Figure S17 (Supporting Information). The bilayer Bernal stacking consists of an abac stacking sequence for four Mo atomic layers as opposed to the abab stacking sequence in AA stacking order. The density of states (DOS) shown in Figure 5a,b clearly indicates that both AA and Bernal stacked polytypes are metallic with Mo bands dominating the Fermi energy εF. In the orbital resolved DOS of AA-stacked Mo2C in Figure 5a, the DOS near εF is mainly due to the Mo-4d states. Between −4.8 and −7 eV, C-2p derived states hybridize with Mo states, and the valence band is dominated by the Mo(4d)-C(2p) hybridization. The upper and lower Mo2C layers in the AA stacking are similar because of the absence of gliding. εF is situated in a pseudogap, similar to bulk metal carbides and MXenes.[26,27] In the case of the Bernal-stacked Mo2C, gliding introduces stronger Mo(4d)-C(2p) hybridization in the DOS for both Mo atomic layers, and in fact the lower Mo2C layer is also perturbed due to the interlayer coupling. Furthermore, the pseudogap that was visible at about −5 eV in the AA-stacked Mo2C is eliminated in Bernal stacking and replaced by the tail states due to Mo(4d)-C(2p) hybridization. Around εF, the two-peak DOS in the AA stacking order has been modified and transformed to a multiple split-peak feature. Lastly, the electron localization function (ELF) (Figure 5c) and the line profile of the ELF (Figure S18, Supporting Information) indicates that Bernal stacked Mo2C exhibits stronger covalent bonding than the AA stacked counterpart, suggesting the gliding has induced partial ionic-covalent transformation.

The linear Brønsted–Evans–Polanyi relation and Hammer–Nørskov d-band models[28,29] for metals have been widely applied to rationalize activity trends in metal surface-catalyzed reactions. This “golden rule” is usually invoked to explain catalytic activity in multiple systems, including the Pt-WC(0001) surface[30] and Pt alloys.[31,32] The distance of the d band center to εF (εF−εb) reflects the activity for charge exchange. With the aid of the linearization energy resolved in the FP-LMTO method, the 4d band center of each Mo layer shown in Figure 5d can be quantitatively characterized. The εF−εb of the surface Mo layer in Bernal stacking Mo2C is smaller than that in the AA-stacked Mo2C. Moreover, the electron cloud of the surface Mo is more spread out and denser than that of AA stacked Mo2C, suggesting the former may have greater surface catalytic activity. Prompted by these predictions, we have tested the catalytic activity of wedding-cake crystals containing the Bernal-stacked Mo2C versus that of AA-stacked Mo2C in HER. From the linear sweep voltamograms (LSV, Figure 5e), it is seen that the wedding cake like Mo2C crystal has a lower onset overpotential (280 mV at 10 mA cm−2) and smaller Tafel slope (75 mV dec−1) as compared to single-crystal Mo2C (onset potential is 340 mV at 10 mA cm−2 and Tafel slope is 82 mV dec−1) (Figure S21, Supporting Information). As an electrocatalyst, Bernal-stacked Mo2C is highly stable and there is almost no discernible decay in the HER current after 1000 cycles (dashed curve in Figure 5e). In addition, the hydrogen adsorption Gibbs free energy (ΔGθH) of AA- and Bernal-stacked Mo2C, an indicator for the HER performance, was calculated. According to the calculations (Figure S22, Supporting Information), Bernal stacked Mo2C has a ΔGθH of −0.58 eV as compared to −0.62 eV for AA-stacked Mo2C. An optimal value of ΔG is ≥0 is obtained when the adsorption and desorption of H2 has low energy barriers, thus Bernal-stacked Mo2C has a lower onset potential for HER.

Our studies show that the use of melted copper as a diffusion barrier between the two elemental precursors (Mo and C) allows CVD growth to be operated under diffusion-limited, nonequilibrated conditions, whereby metastable polymorphs and polytypes can be generated at the edge zones of the crystals, thus affording a strategy to tune the electronic and catalytic properties of the crystals. Under nonequilibrated, fast growth conditions, metastable polymorphs (intraunit cell), and polytypes (interunit cell) dominate the edge regions in which Bernal (AB) stacking is abundant. All phase transitions observed can be explained by the gliding of the Mo layer along the Mo–Armchair <10̅10> direction, which are promoted by the presence of Mo vacancies. According to DFT calculations, the Bernal stacking order have their d bands closer to the Fermi energy than the AA stacked counterpart, thus affording enhanced catalytic reactivity observed in HER. The growth method demonstrated here allow metastable phases to be segregated at the edges of the crystal, which constitute as a new strategy for spatially segregated phase engineering; it can also be applied to other members of the MXene family and to other non-vdW 2D materials, thereby expanding the synthetic space for a wide class of polymorphs and polytypes.

**Experimental Section**

CVD Grown Mo2C crystals: The detailed growth method can be seen in the previous report.[33] Briefly, Cu foil was cut into 10 × 10 mm² pieces and placed onto a piece of Mo foil. The thickness of the Cu foil for growing wedding cake-like Mo2C was ~25 μm, and 100 μm thick Cu foil was used for growing uniformly thick Mo2C crystals. The Cu-on-Mo foils together were loaded into the quartz tube with an outer diameter of 25 mm, inner diameter of 22 mm, and a length of 1220 mm. The
substrate was heated to 1100 °C in a horizontal tube furnace under a constant flow of 200 sccm of H₂ gas. Subsequently, 0.6 sccm of CH₄ gas was introduced to the quartz tube at ambient pressure. The growth time was about 3 h. When the growth was complete, the Cu foil together with the Mo foil was quickly unloaded to ensure rapid cooling.

Mo₂C Crystals Sample Transfer: A bubbling assisted transfer method[33] was employed for transferring Mo₂C crystals grown on the Mo foil. First ≈50 nm poly(methyl methacrylate) (PMMA, 495 kDa molecular weight, 3 wt% in ethyl lactate) was spin coated (2000 r.p.m. for 2 min) onto the Mo foil. was subsequently cured at 170 °C for 5 min. The current density and the corresponding electrolytic voltage were set at ≈0.5 A cm⁻² and ≈10 V, respectively. Normally 5 min bubbling time is sufficient to detach the PMMA/Mo₂C film from the Cu surface. After detaching, the PMMA/Mo₂C film was placed onto TEM grids with

Figure 5. Electronic structure and chemical bonding analysis of AA and Bernal stacked polytypes. The atom and orbital projected DOS of upper and lower layers in a) AA-stacked Mo₂C and b) Bernal-stacked Mo₂C. The pink and brown curves present DOS of Mo-4d and C-2p orbitals in AA-stacked Mo₂C. The blue and brown curves present DOS of Mo-4d and C-2p orbitals in Bernal-stacked Mo₂C. c) The side view of electronic localization function (ELF) of the AA and Bernal-stacked Mo₂C with a color bar representing the degree of localization of electrons. d) the distance of the 4d-band center (ε_{4d} - ε_{f}) with respect to ε_{f} of each Mo layer. The pink and blue curves stand for the AA and Bernal stacking orders, respectively. e) First linear sweep voltammograms (LSV) scan (blue curve) and the LSV after 1000 cycles (blue dashed curve) for Bernal-stacked Mo₂C crystals, and LSV curve (pink curve) of AA-stacked Mo₂C crystals.
additional 10 min heating (100 °C) to enhance the binding between the Mo2C crystals with TEM grids. Next, PMMA/Mo2C/TEM grids were immersed in hot acetone (60 °C) for ~2 h to dissolve the PMMA residues. Finally, the Mo2C/TEM grids were rinsed in isopropyl alcohol (IPA) and acetone for a few times to remove all possible residues.

STEM-ADF Imaging, Processing, and Simulation: STEM-ADF imaging was performed on an aberration-corrected JEOL ARM-200F equipped with a cold field emission gun and ASCOR probe corrector. 80 kV was employed for analyzing edge regions to reduce beam damage, and 200 kV was applied for the interior bulk regions. The convergence semi-angle of the probe was set at ~30 mrad. ADF images were collected for a half-angle ranging from ~68 to 280 mrad. The dwell time was fixed at 19 μs pixel−1. STEM-ADF image processing was first convoluted by a series of Laplacian of Gaussians (LoG) filters, the positions of atomic columns were located by finding the local maxima of the filtered series. Subsequently, the intensity extracted from the same type of atom blobs were transferred onto a 3 mm diameter glassy carbon (GC) electrode using the bubbling assisted transfer method. The GC plate was polished by diamond slurries prior to transfer. All electrochemical measurements were done under ambient conditions using a three-electrode cell. Standard Ag/AgCl electrodes and a Pt foil were used as the reference and counter electrode, respectively. The LSV was recorded in 0.5 M H2SO4 electrolyte with a scan rate of 2 mV s−1 on an Autolab 302 N electrochemical workstation. The LSV curves were averaged over three different samples.

DFT Calculations: To derive structures and energies of various stacking modes, DFT calculations were carried out within the Vienna Ab-initio Simulation Package (VASP).[34–36] On the basis of the projector augmented-wave (PAW) method, the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)[39] was adopted. Within PAW, the 4d and 5s states were considered as the valence states for Mo with frozen semi-core states of 4s and 4p. The 2s and 2p states treated as the valence states for C. A cut-off energy of 580 eV was used in all calculations, and for Brillouin zone (BZ) integration a 15*15*1 Monkhorst-Pack k-point mesh in the first order approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) was applied. The relaxation time was set to a constant value of 5.52 fs. The relaxation of the Mo2C crystals with TEM grids. Next, PMMA/Mo2C/TEM grids were immersed in hot acetone (60 °C) to dissolve the PMMA. Additionally, the Mo2C/Mo2C/TM grids were integrated and normalized to obtain a relatively smoothed 2D point-spread function, which is used for quantitative image comparison. Image processing was carried out using Python scripts. HER Sample Preparation and Measurement: The as-grown Mo2C crystals were transferred onto a 3 mm diameter glassy carbon (GC) electrode using the bubbling assisted transfer method. The GC plate was polished by diamond slurries prior to transfer. All electrochemical measurements were done under ambient conditions using a three-electrode cell. Standard Ag/AgCl electrodes and a Pt foil were used as the reference and counter electrode, respectively. The LSV was recorded in 0.5 M H2SO4 electrolyte with a scan rate of 2 mV s−1 on an Autolab 302 N electrochemical workstation. The LSV curves were averaged over three different samples.

Conflict of Interest
The authors declare no conflict of interest.

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