

Designing artificial two-dimensional landscapes via atomic-layer substitution

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Technology advancements in history have often been propelled by material innovations. In recent years, two-dimensional (2D) materials have attracted substantial interest as an ideal platform to construct atomic-level material architectures. In this work, we design a reaction pathway steered in a very different energy landscape, in contrast to typical thermal chemical vapor deposition method in high temperature, to enable room-temperature atomic-layer substitution (RT-ALS). First-principle calculations elucidate how the RT-ALS process is overall exothermic in energy and only has a small reaction barrier, facilitating the reaction to occur at room temperature. As a result, a variety of Janus monolayer transition metal dichalcogenides with vertical dipole could be universally realized. In particular, the RT-ALS strategy can be combined with lithography and flip-transfer to enable programmable in-plane multiheterostructures with different out-of-plane crystal symmetry and electric polarization. Various characterizations have confirmed the fidelity of the precise single atomic layer conversion. Our approach for designing an artificial 2D landscape at selective locations of a single layer of atoms can lead to unique electronic, photonic, and mechanical properties previously not found in nature. This opens a new paradigm for future material design, enabling structures and properties for unexplored territories.

2D materials | Janus transition-metal dichalcogenides | atomic-layer substitution | room temperature | heterostructures

The wide and rich physics of two-dimensional (2D) materials have led to the fabrication of heterostructures (1–5), superlattices (6–8), and twisted structures (9–11) with breakthrough discoveries and applications. During the past 3 y, a new class of atomic layer structures, in which the top layer chalcogen atoms within the three-atom-thick transition-metal dichalcogenides (TMDs) are replaced by a different type of chalcogen atoms, has been developed, resulting in a Janus monolayer with broken out-of-plane symmetry, inherit strain, and a variety of attractive properties (12–16). However, such a transition has been subjected to thermal energy input because the top chalcogen–metal bonds need to be broken in order for the substitution to occur. Previous strategies (12, 15, 16) usually break off the original chalcogen atoms by purely harsh energetic means and then form new bonds with the incoming replacements. Since the displacement energies of these chalcogen atoms in 2D TMDs range from 5 to 7 eV (17, 18), the process requires either knocking off the top chalcogens via the kinetic energy of atoms in a hydrogen (12) or Se plasma (16) or purely high temperature (to form sulfur vacancies) (15) to happen.

It is well known that thermal energy has been widely used to enable chemical reactions. However, high reaction temperatures

incur severe limitations (for example, the types of substrate on which materials can be synthesized) and undesirable energy consumptions. There has been a continuing pursuit to reduce material synthesis temperatures while maintaining the quality of as-synthesized material (19–21). Recently, a room-temperature method to synthesis monolayer Janus WSe₂ and MoSe₂ by sulfurization from monolayer WSe₂ and MoSe₂ was reported (14). Nevertheless, the mechanism for such conversion was only hypothesized and has not been completely understood.

This paper reports our concurrent work for room-temperature atomic-layer substitution (RT-ALS), including the conversion of WSe₂ and MoSe₂ (2H phase) being sulfurized into Janus WSeS and MoSeS, WS₂ and MoS₂ (2H phase) being selenized into Janus WSSe and MoSSe, and the conversion of 1T' MoS₂ being selenized into Janus 1T' MoSSe. Using density functional theory

Significance

Manipulating materials with atomic-scale precision is essential for the development of a next-generation material design toolbox. Tremendous efforts have been made to advance the compositional, structural, and spatial accuracy of material deposition and patterning. Here, we presented a new reaction pathway to implement the conversions of two-dimensional materials within the atomic-layer thickness at room temperature for electrical dipole manipulation. Not only could various Janus monolayer transition metal dichalcogenides with vertical dipole be realized, but also some heterostructures, including the dipole-nondipole heterostructures (MoS₂–MoSSe) and multiheterostructures (MoS₂–MoSSe–MoSeS–MoSe₂) within the same monolayer host structure are developed, in which the dipoles can be selectively patterned to be zero (MoS₂, MoSe₂), positive (MoSSe), and negative (MoSeS).

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(DFT) calculations, we were able to elucidate the evolution of free energies in each reaction step and present a clear understanding of why such a reaction can occur at room temperature. More significantly, by combining RT-ALS with lithography patterning and flip 2transfer, a completely new class of monolayer lateral heterostructures and multiheterostructures are designed and fabricated.

Fig. 1A illustrates our RT-ALS process. The presence of hydrogen radicals (22) produced by a remote plasma strip the chalcogenide atoms on the top layer in a gentle and chemical way. Meanwhile, the low-pressure system facilitates the supply of vaporized chalcogen substitutes (here illustrated with Se) to take the place of missing atoms, resulting in an asymmetric Janus structure of MXY (M = Mo or W, X = S or Se, and Y = Se or S) at room temperature.

Results and Discussion

In sharp contrast to previous severe strategies (12, 15, 16), the RT-ALS steers the reaction via a different pathway. We use DFT (within the generalized gradient approximation, including van der Waals corrections [PBE-D2] on a supercell containing 4 MoS₂ unit cells [larger supercells are included in the *SI Appendix*]) to examine two reaction pathways to illustrate the difference, as shown in Fig. 1B–D and *SI Appendix*, Fig. S1D. One pathway is the conventional high-temperature substitution (replacing S by Se via thermal activation), and the other is our RT-ALS process. Due to the active roles of H radicals in the RT-ALS process, the energy barrier becomes much lower, and the process is overall exothermic. Fig. 1B exhibits that H radicals firstly adsorb on the upper surface of monolayer MoS₂ with adsorption energy of ~0.5 eV/H (which further increases with the H coverage, as shown in *SI Appendix*, Fig. S1A). As the H coverage increases, two H atoms form bonds with one S atom (*SI Appendix*, Fig. S1B), and the H₂S desorbs, leaving an S vacancy. Surprisingly, this desorption process only involves a small activation barrier <0.5 eV (i.e., 12 kcal/mol), an order of magnitude smaller than the total bond energies of 3 Mo–S bonds (~6 eV). In such a scenario, the removal of S is unlikely to be caused by collisions with hydrogen radicals because

the kinetic energy of an H radical in the remote hydrogen plasma is about two orders of magnitude smaller than the displacement energy of a chalcogen atom (16), and the masses are very different between H and S atoms. The S vacancy is then occupied by a nearby Se atom. In contrast, the high-temperature pathway (*SI Appendix*, Fig. S1D) involves Se adsorption on surface, Mo–S bond breaking, and Mo–Se bond reforming, requiring an energy barrier of ~2.5 eV that occurs when the Mo–S bond breaks (Fig. 1D). This calculated energy barrier matches well with the experimental findings, wherein the high-temperature substitution happens at ~1,000 K (23). Such a calculation comparison clearly reveals that RT-ALS is made possible via reducing the reaction energy barrier, and the reaction kinetics is controlled by the active H radicals.

For RT-ALS experiments, we start with chemical vapor deposition (CVD)-synthesized monolayer MoS₂ and perform selenization for the top sulfur layer to obtain MoSSe. Afterward, we use flip-transfer to expose the bottom surface and perform RT-ALS a second time to achieve MoSSe conversion to MoSe₂ (*SI Appendix*, Fig. S2). From the optical microscopy (OM) images (*SI Appendix*, Fig. S2B–D), the optical contrast of the MoS₂, MoSSe, and converted MoSe₂ triangular single crystals remain uniform and intact after RT-ALS, suggesting the process makes negligible disruption to the 2D lattice. This is also confirmed by atomic force microscopy (AFM) images (*SI Appendix*, Fig. S2E–G), as their surfaces remain pristine and flat after each RT-ALS step. In addition, it is straightforward to extend the single/double-sided conversions to continuous large-area films (*SI Appendix*, Fig. S2H–J). From a material synthesis perspective, here MoSe₂ is obtained from a MoS₂ template by room-temperature reaction, without the need of high-temperature conversions as in contrast to earlier approaches (21, 24), and thus avoids subsequent lattice or substrate damage. This provides an alternative route to obtain Se-based TMDs at room temperature. More importantly, this could be used to synthesize TMD materials that are hard to be directly grown by CVD or other methods.

To confirm the substitution of the top chalcogenide layer, measurements on Raman and photoluminescence (PL) spectroscopy

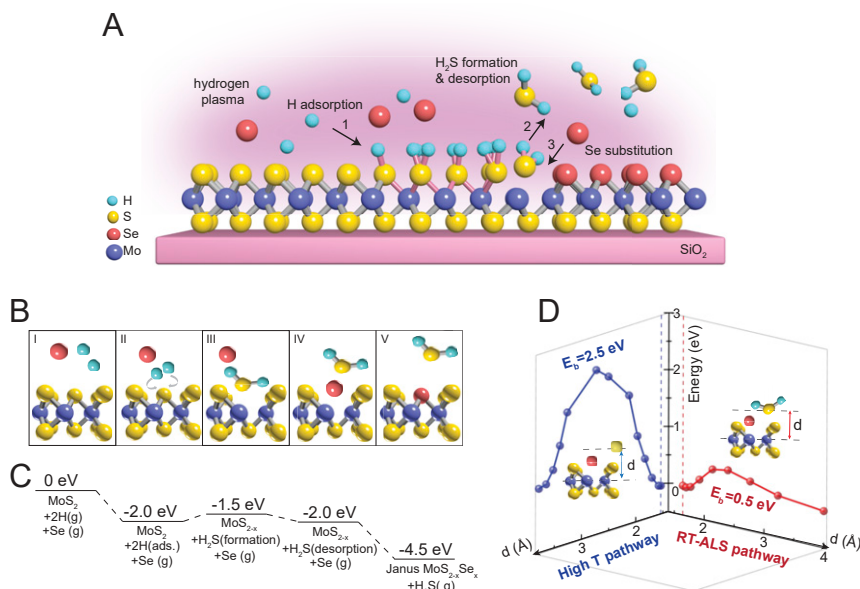


Fig. 1. RT-ALS with DFT calculation and comparison. (A) Schematic illustration of the RT-ALS process from monolayer MoS₂. (B) Schematics of the five key reaction steps for RT-ALS process (cartons from left to right): before H adsorption, 2 H adsorption and diffusion to the same S, formation of H₂S, desorption of H₂S, and Se occupation of the S vacancy. Purple, yellow, red, and green balls are Mo, S, Se, and H atoms, respectively. (C) Free energy of each step in B, relative to that of the first step. (D) Comparison of activation energy barrier between the RT-ALS strategy (red) and the conventional high-temperature substitution (blue). The axes of the two pathways correspond to distances (d) between the substituted S atom to Mo plane in each case. The vertical dashed lines (blue and red) indicate equilibrium S to Mo plane distances (1.54 Å for high T pathway, 1.64 Å for RT-ALS pathway). In RT-ALS process, the largest energy barrier occurs at a critical distance where H₂S starts to form. In the high-temperature pathway, the largest energy barrier corresponds to when S and Se are both disconnect with Mo.

are performed due to their sensitivity to the crystal structure. For TMDs, the A_{1g} and E_{2g} mode correspond to the out-of-plane and in-plane lattice vibrations, respectively. Therefore, changing the top layer of chalcogens produces different phonon frequencies for the same type of lattice vibrations. As shown in Fig. 2A, the MoS_2 A_{1g} (404 cm^{-1}) and E_{2g} (383 cm^{-1}) modes shift to 288 cm^{-1} and 355 cm^{-1} , respectively, in Janus $MoSSe^{12}$ due to the change of atomic mass and the broken symmetry in the vertical direction (12). Further flip-transfer and RT-ALS on the other sulfur layer yield full selenization, with a sharp peak at $\sim 239\text{ cm}^{-1}$ and a broad one at $\sim 284\text{ cm}^{-1}$, which are consistent with the A_{1g} and E_{2g} modes in monolayer $MoSe_2$ (25). These conversions are further evidenced by the strong PL emission shown in Fig. 2B, in which the PL peak energy shifts from 1.85 eV (pristine MoS_2) to 1.72 eV (Janus $MoSSe$) and then to 1.60 eV (converted $MoSe_2$). All the observed PL peak energies are consistent with reported values of previous literature (12, 25). Besides, Raman mappings (SI Appendix, Fig. S3 A–C) and PL intensity mappings (Fig. 2B, Insets) also confirm that crystals produced by RT-ALS have high spatial homogeneity.

This RT-ALS is found to be a general strategy to obtain various Janus materials (including different transition metal atoms, chalcogen atoms, for converting only top layer or both top and bottom layers, and different crystal phases) through our experimental investigations. The conversions from WS_2 to Janus $WSSe$ and then to WSe_2 were successfully obtained (SI Appendix, Figs. S2 K–M and S3 G–I), with the corresponding PL emissions shift

from 2.01 eV (WS_2) to 1.83 eV ($WSSe$) and to 1.63 eV (WSe_2) (Fig. 2D). Compared with $MoSSe$, the larger elastic modulus and smaller carrier effective mass of $WSSe$ may give rise to higher carrier mobility, especially for holes, due to the stronger spin-orbit coupling and overall cleaner optical signatures of W (16, 26). In addition, the conversion from monolayer MSe_2 ($M = Mo$ and W) to Janus $MSeS$ and then to MS_2 are realized by sulfuration (Fig. 2C and SI Appendix, Fig. S3 D–F) as well as the conversion from $1T'$ MoS_2 to Janus $1T'$ $MoSSe$ (SI Appendix, Fig. S3 J and K). The evolutions of Raman peaks are all in consistent with literature (12, 16, 27) and our theoretical predictions, suggesting the universality of RT-ALS strategy.

In order to verify the atomic structure of Janus $MoSSe$, we used annular dark-field scanning transmission electron microscopy (ADF-STEM) to obtain the tilted images of $MoSSe$. The image was obtained by rotating the $MoSSe$ sample 10° from the $[001]$ crystallographic orientation to a new orientation that resulted in the Mo, Se, and S atoms projected in a straight line. In that way, the Mo, Se, and S atoms can be individually identified. As shown in Fig. 2E, the tilted ADF-STEM image enables to separate the Se and S atoms. The results show that the Se atoms are located on one side of the monolayer $MoSSe$, and S atoms on the opposite side, which is direct evidence of the Janus structure. The corresponding intensity profile in Fig. 2F clearly show the individual Mo, Se and S atoms with their total peak intensities proportional to their atomic numbers.

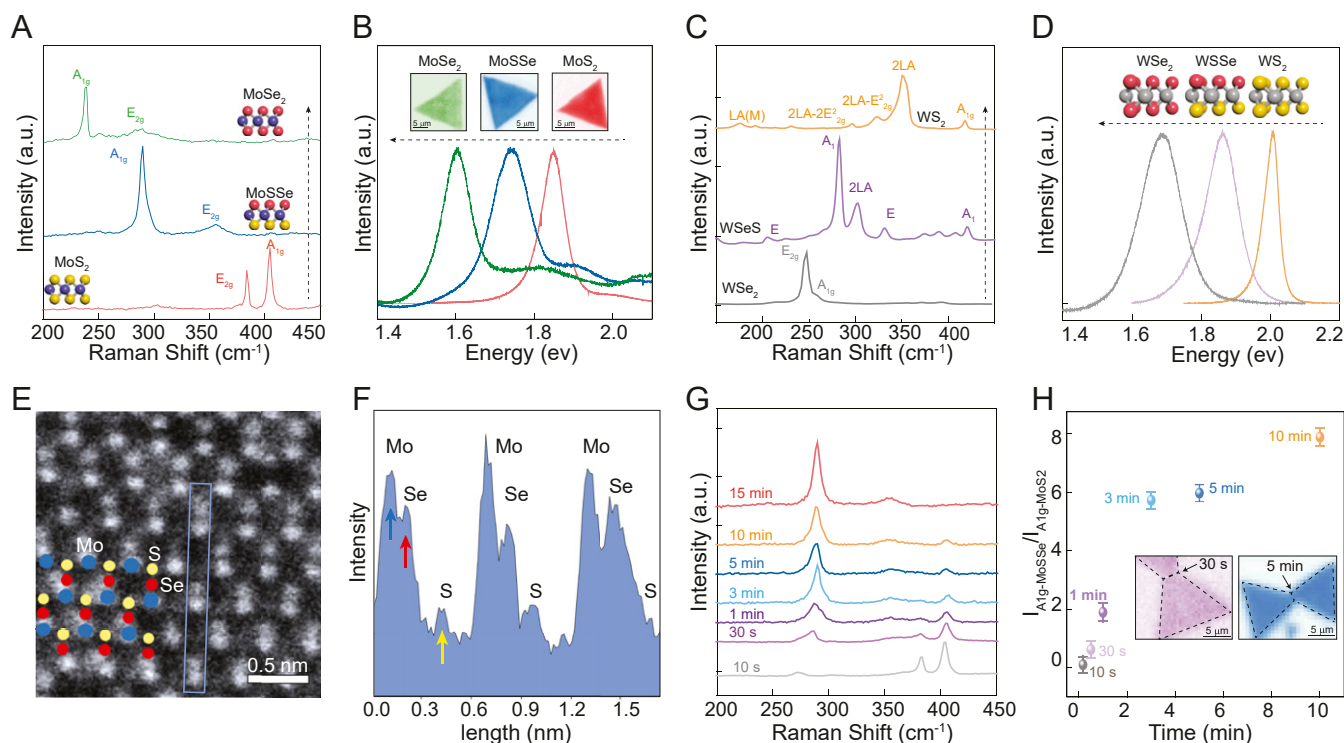


Fig. 2. Characterizations of the monolayer (Janus) TMDs converted using RT-ALS and the conversion process. (A) Raman spectra of starting monolayer MoS_2 , Janus $MoSSe$, and converted $MoSe_2$. (Insets) Crystal structures of MoS_2 , Janus $MoSSe$, and $MoSe_2$, respectively. (B) PL spectra of starting monolayer MoS_2 , Janus $MoSSe$, and converted $MoSe_2$. (Insets) Spatially resolved PL mappings of MoS_2 , Janus $MoSSe$, and converted $MoSe_2$ flakes at 1.85 eV, 1.72 eV, and 1.60 eV, respectively. (C) Raman spectra of starting monolayer WS_2 , Janus $WSSe$, and converted WSe_2 . (D) PL spectra of starting monolayer WS_2 , Janus $WSSe$, and converted WSe_2 . (Insets) Crystal structures of WS_2 , Janus $WSSe$, and WSe_2 , respectively. (E) Tilted ADF-STEM image of a $MoSSe$ sample to visualize the asymmetric atom structure in the vertical direction. The corresponding Mo, Se, and S atoms are schematically shown with blue, red, and yellow circles, respectively. (F) Intensity profile for the atomic chain highlighted in blue in E shows the intensity of individual Mo, Se, and S atoms. (G) Raman spectra collected at several monolayer Janus $MoSSe$ samples treated with hydrogen plasma for 10 s, 30 s, 1 min, 3 min, 5 min, 10 min, and 15 min, respectively. (H) The relationship between the conversion time (10 s, 30 s, 1 min, 3 min, 5 min, and 10 min, respectively) and the corresponding intensity $I_{A_{1g}(MoSSe)}/I_{A_{1g}(MoS_2)}$ ratio over the conversion process. (Inset) Spatially resolved Raman mappings of two coalesced Janus $MoSSe$ flakes converted within 30 s and 5 min, respectively, which show uniform Raman intensity over the whole $MoSSe$ regions.

To achieve a better understanding of the conversion process, we investigated the evolution of the Raman peaks during the synthesis. The results indicated in Fig. 2 *G* and *H*, and *SI Appendix*, Fig. S4A show that within 10 s, the A_{1g} peak of Janus MoSSe begins to emerge [at a frequency $\sim 10\text{ cm}^{-1}$ lower than the final point, most likely due to the modulation of phonon frequency from the local phonon vibrations at the reaction onset (26)]. The intensity of the Janus MoSSe A_{1g} mode increases with longer conversion time; meanwhile, the intensity of the MoS_2 A_{1g} peak decreases and eventually vanishes in 15 min. Based on the variation of Raman peaks at different time, the conversion yield (roughly defined by $Y\% = \text{Intensity } A_{1g} \text{ of MoSSe} / [\text{Intensity } A_{1g} \text{ of MoSSe} + \text{Intensity } A_{1g} \text{ of MoS}_2]$) from S to Se after RT-ALS treatment are estimated (*SI Appendix*, Fig. S4B). For material conversion through high-temperature substitution, previous reports (21) showed that the atomic replacement begins at energetically favorable sites (crystal edges, defect sites, and grain boundaries) and gradually progresses to the other regions

of the flakes, indicating it is controlled by thermodynamics. In contrast, the room temperature operation here suggests it is a kinetic process, in which the energy needed for the atomic substitution is supplied by the highly reactive hydrogen radicals. This leads to the spatially homogeneous substitution of atoms over the whole flake since the reaction onset (Fig. 2*H*, Insets and *SI Appendix*, Fig. S4C) and a fast progression of the reaction with a time scale as short as 30 s (Fig. 2*G* and *SI Appendix*, Fig. S4A).

Taking advantage of the room temperature procedure of the whole process, the programmable design in monolayer TMD can be realized using lithography combined with flip-transfer techniques, as illustrated in Fig. 3 *A–C*. Arbitrary patterns in a 2D plane can be implemented by using a physical mask (here, lithographic patterns is just an example), enabling locally programmed out-of-plane atomic structures (Fig. 3*A*, where electron-beam lithography [EBL] can define arbitrary patterns using a polymethyl methacrylate [PMMA] mask). RT-ALS will convert the exposed areas to MSSe, allowing the formation of lateral heterostructure between MS_2 and Janus

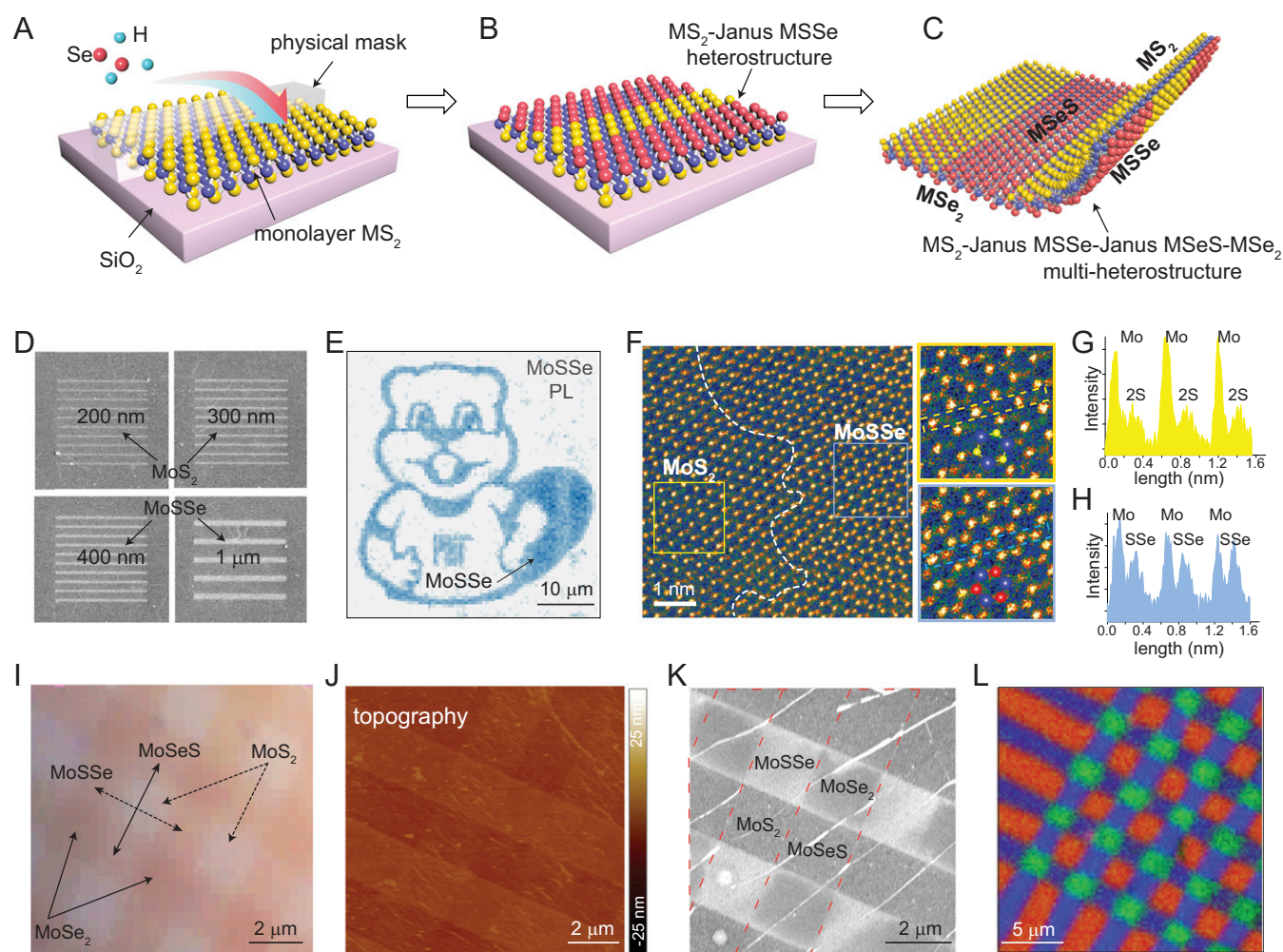


Fig. 3. RT-ALS with programmable design in dipole/nondipole lateral heterostructures and multiheterostructure. (A) Schematic representation of programmable ALS process by lithography patterning and ALS process. (B) Programmed monolayer MoS_2 -Janus MoSSe heterostructure on SiO_2/Si substrate. (C) A multiheterostructure composed of monolayer MoS_2 -Janus MoSSe-Janus MoSeS- MoSe_2 regions. (D) SEM images of monolayer Janus MoSSe- MoS_2 stripe patterns with different widths. (E) Spatially resolved PL mapping for a Massachusetts Institute of Technology mascot "Tim the beaver" pattern (Janus MoSSe) on a monolayer MoS_2 canvas. (F) Pseudocolor ADF-STEM image of a MoS_2 -MoSSe interface (Left), the zoomed-in views of a MoS_2 region (Right Top, highlighted in yellow) and a Janus MoSSe region (Right Bottom, highlighted in blue), and their respective intensity profiles in G and H. (I) OM image of monolayer multijunction composed with MoS_2 -Janus MoSSe-Janus MoSeS- MoSe_2 . (J) AFM topography image for the monolayer multiheterostructure of MoS_2 -Janus MoSSe-Janus MoSeS- MoSe_2 . (K) SEM image of monolayer multiheterostructure composed with MoS_2 -Janus MoSSe-Janus MoSeS- MoSe_2 . (L) Spatially resolved Raman mapping for A_{1g} mode intensity of monolayer multiheterostructures based on MoS_2 -Janus MoSSe-Janus MoSeS- MoSe_2 . The red area represents MoS_2 region, the blue area represents Janus region, and the green area represents MoSe_2 region.

MSSe within the same host monolayer (Fig. 3B). Furthermore, the chalcogen on the other side can be replaced by using a flip-over transfer (*Methods*) and another selective RT-ALS conversion, resulting in lateral multiheterostructures of $\text{MS}_2\text{-MSSe-MSeS-MSe}_2$ (Fig. 3C) with tailored functionalities. Fig. 3D shows the scanning electron microscopy (SEM) image of monolayer Janus MoSSe-MoS_2 stripe patterns with different widths. Even though both MoSSe and MoS_2 are semiconductors with comparable bandgaps, MoSSe is brighter than MoS_2 , possibly due to the intrinsic vertical dipole in the monolayer. Fig. 3E shows the spatially resolved PL mapping of Janus MoSSe with the pattern of the Massachusetts Institute of Technology mascot “Tim the beaver” made on a continuous monolayer CVD- MoS_2 canvas (RT-ALS converted the exposed regions to Janus MoSSe , while the masked regions remained as pristine MoS_2). The same pattern was characterized using various methods: OM image (*SI Appendix, Fig. S5A*), SEM image (*SI Appendix, Fig. S5B*), and Raman and PL mappings (*SI Appendix, Fig. S5C and D*), which all clearly verify that MoS_2 and MoSSe are well-located as designed. ADF-STEM is used to characterize the junction, which shows that the $\text{MoS}_2\text{-MoSSe}$ interface is seamlessly connected at the boundary defined by lithography (Fig. 3F and *SI*

Appendix, Fig. S6A). Elemental diffusion (2, 4) is not anticipated for the RT-ALS strategy, as the substitution occurs at room temperature within a short time. As ADF-STEM intensity scales with the atomic number, the MoS_2 region with weaker intensity from the S-S column on the left side of Fig. 3F is clearly distinguished from the stronger intensity from the S-Se column of MoSSe on the right. Additionally, the different structures of MoS_2 and MoSSe are further verified by the intensity profile of electron scattering, where the atomic positions of Mo, S/Se, and 2S are corresponding to their gradually decreased intensities (Fig. 3G and H). The energy-dispersive X-ray spectroscopy results (*SI Appendix, Fig. S6C-H*) indicate that Se and S atoms are well-confined in the selective regions. As the selected area electron diffraction patterns show nonseparable patterns from these two lattices (*SI Appendix, Fig. S7A-D*), real space strain mappings were further performed (*SI Appendix, Fig. S7G and H*), in which the slight lattice difference in the MoSSe region can be observed compared to the reference MoS_2 region.

Flipping over the $\text{MoS}_2\text{-MoSSe}$ heterostructures and repeating selective RT-ALS on the other side yielded lateral multiheterostructures with MoS_2 , Janus MoSSe and MoSeS , and MoSe_2 (Fig. 3I-L and *SI Appendix, Fig. S8*). From the OM image in Fig. 3I,

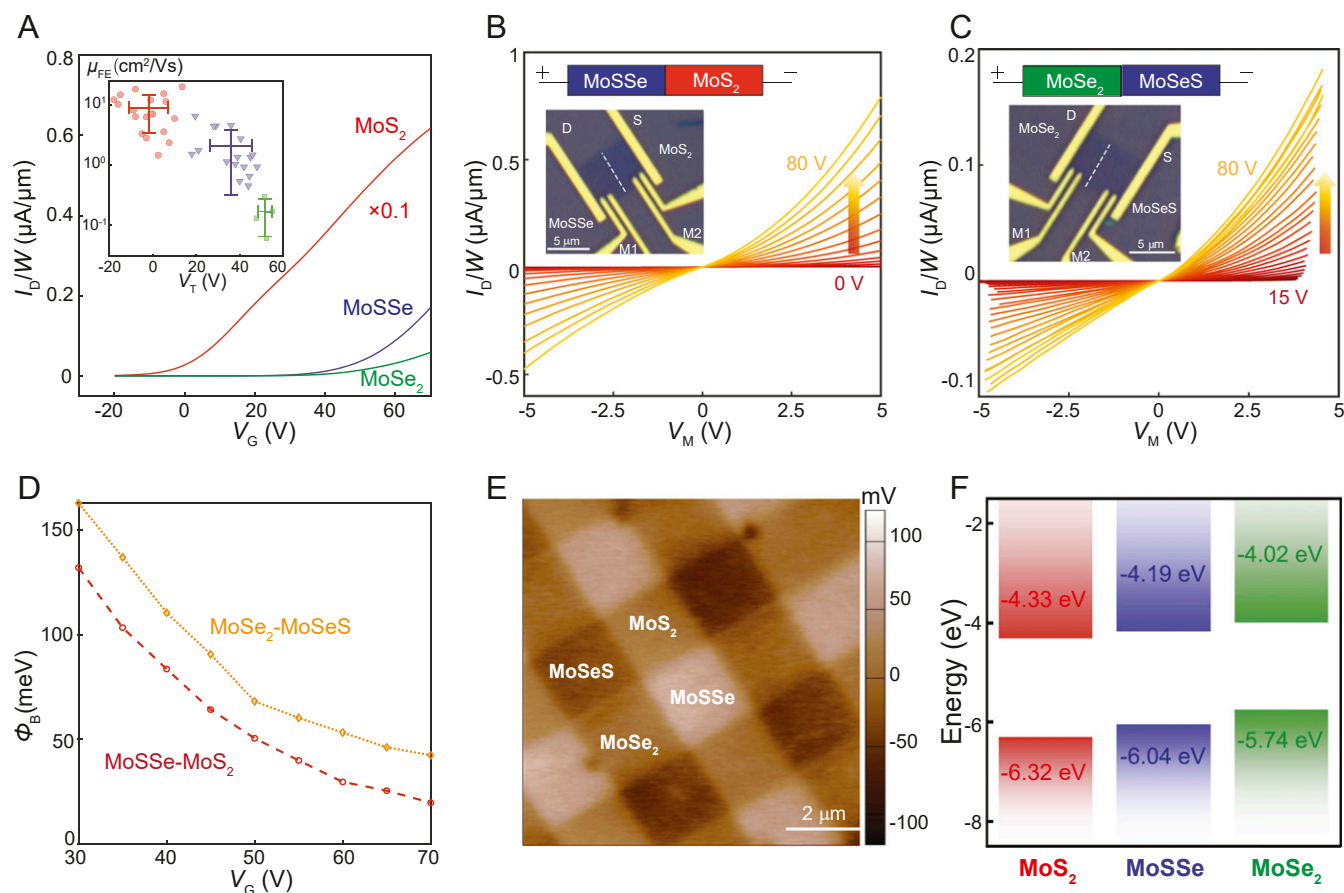


Fig. 4. Electrical properties of MoS_2 , Janus MoSSe , MoSe_2 , and their lateral heterostructures produced by ALS. (A) Transfer characteristics (current density I_D/W versus back-gate voltage V_G , $V_D = 1$ V) of typical MoS_2 , single-side-converted Janus MoSSe , and double-side-converted MoSe_2 . (Inset) Field effect mobility μ_{FE} versus threshold voltage V_T for tens of devices. The average mobility values for MoS_2 , Janus MoSSe , and MoSe_2 are 8.94, 2.11, and 0.17 cm^2/Vs , and the average V_T for them are -1.9 , 36.0 , and 51.6 V, respectively. (B and C) Four-probe output characteristics (current density I_D/W versus bias voltage V_M with various back-gate voltage V_G) for (A) MoSSe-MoS_2 and (B) MoSeS-MoSe_2 lateral heterojunctions. (Insets) Diagrams and OM images of these devices. (D) Barrier height Φ_B as a function of V_G for the MoSSe-MoS_2 (red) and the MoSeS-MoSe_2 (orange) lateral heterojunctions. (E) Kelvin probe force microscope image of the $\text{MoS}_2\text{-MoSSe-MoSeS-MoSe}_2$ multiheterostructure. The Janus MoSSe region with the Se layer on top and the MoSeS region with the S layer on top display the highest and the lowest surface potential, respectively, whereas the surface potentials for the MoS_2 and MoSe_2 regions are in between. (F) Conduction band minima and valence band maxima energies of MoS_2 , Janus MoSSe , and MoSe_2 relative to vacuum, obtained from DFT calculations. For Janus MoSSe , the vacuum energy levels from upper and lower planes are averaged.

it can be seen that Janus MoSSe and Janus MoSeS has very similar optical contrast, while the AFM image Fig. 3J indicates the slight height increase after each RT-ALS step, consistent with the observation from *SI Appendix, Fig. S2 E–G*. Fig. 3K shows the SEM of the multiheterostructure regions. The two types of Janus regions (MoSSe [having vertical dipole pointing up] and MoSeS [having vertical dipole point down]) demonstrates clear intriguing contrast under SEM. These two types of regions should have very similar properties (e.g., material composition, bandgap, etc.) except the dipole direction, such observation indicates the role played by the dipole moment in material functionalities. In Fig. 3L, spatially resolved Raman mapping for A_{1g} mode intensity of such monolayer multiheterostructures is presented, with the red region being MoS₂, blue region being Janus (either MoSSe or MoSeS), and green region being converted MoSe₂.

In principle, the minimum feature size of RT-ALS should be determined by the resolution of lithography (Fig. 3D and *SI Appendix, Fig. S5 E–H*). With current EBL, features of hundreds of nanometers can be achieved, with potential for scaling down to tens of nanometers using extreme ultraviolet, helium-beam, or AFM-based lithography (28). The interface revealed by ADF-STEM (Fig. 3F) indicates edge roughness due to EBL limitations. However, sharp edges are anticipated if atomically sharp physical masks such as aligned carbon nanotubes (29, 30) can be used in the future. Nevertheless, even with the current EBL, many new device structures with unusual physical properties and potential applications can already be envisioned. For example, periodic arrays of these planar heterostructures with 100-nm-scale pitch can be defined as an atomically thin optical grating, and metasurfaces for efficient modulation or steering of visible/near-infrared light can be designed. In these structures, the extremely strong light-matter interactions in 2D materials and the optical nonlinearity in Janus TMD (31, 32) could play critical roles in expanding the design space of these atomically thin optical metasurfaces with unprecedented efficiencies or novel functionalities. The ability to create these artificial TMD multiheterostructures within a continuous atomic-layer “canvas” has never been achieved before and presents extremely exciting potentials.

A major application of 2D materials and their heterostructures lies in novel electronic or optoelectronic devices. With RT-ALS, we found that high-quality materials are obtained, and the energy misalignment of band edges exist at both the MoSSe-MoS₂ and MoSe₂-MoSeS lateral heterojunctions with a type-II band alignment. Multiple back-gate transistors with long and short electrodes were fabricated and four-probe measurements were used to eliminate the contact resistance (OM images in Fig. 4 B and C, Insets). Typical transfer characteristics (channel current I_D versus back-gate voltage V_G) are plotted in Fig. 4A and used to extract the threshold voltage V_T , defined as the intersection of the linear fit of the on-current and the x-axis, and the field effect mobility μ_{FE} , defined as $\mu_{FE} = (L/W)g_m/(V_D C_{ox})$, where L and W are the channel length and channel width, g_m is the transconductance, V_D is the source-drain voltage (bias across the channel), and $C_{ox} = 12.1 \text{ nF/cm}^2$ (capacitance of the 285 nm SiO₂ gate oxide). The V_T and μ_{FE} of tens of devices were measured for the starting CVD MoS₂, single-side-converted Janus MoSSe, as well as double-side-converted MoSe₂, summarized in Fig. 4A, Inset. Average μ_{FE} for MoS₂, Janus MoSSe, and ALS MoSe₂ are 8.94 cm²/Vs, 2.11 cm²/Vs, and 0.17 cm²/Vs, respectively. Average V_T for them are −1.9 V, 36.0 V, and 51.6 V, respectively. The gradual degradation of mobility from MoS₂ to MoSe₂ may arise from the introduction of defects through the RT-ALS or transfer processes. Note that the mobility value measured in our Janus MoSSe devices is two orders of magnitude higher than through the route of conventional high-temperature substitution (15), which is indicative of the high quality of materials from RT-ALS. Furthermore, the increasing of V_T values indicates that MoS₂ is the most *n*-type doped,

whereas Janus MoSSe and MoSe₂ are decreasingly *n*-doped, in agreement with DFT calculated band alignment (Fig. 4F). This band alignment configuration further determines the electrical polarity of Janus MoSSe-MoS₂ and MoSe₂-Janus MoSeS lateral heterojunctions. The Janus MoSSe and the converted MoSe₂ regions are the anodes of these two *n*-*n*⁺ junctions, respectively, and confirmed with output characteristics (I_D versus V_M with different V_G , where V_M is the voltage drop across the two inner short electrodes [M1 and M2] as I_D is applied across the two long electrodes [D and S]), as shown in Fig. 4 B and C. The weak rectification behaviors observed on both lateral junctions suggest that the barrier heights (denoted as Φ_B) at the lateral heterojunctions are very low. We performed temperature-dependent four-probe transport measurement and used the thermionic emission model to extract the gate-dependent barrier heights (see *Methods* for details, and *SI Appendix, Figs. S9 and S10*), plotted in Fig. 4D, for $\Phi_B = 30 \text{ meV}$ and 50 meV for MoSSe-MoS₂ and MoSe₂-MoSeS lateral heterojunctions, respectively, when the channels are turned on completely ($V_G > 50 \text{ V}$).

More uniquely, our RT-ALS approach brings about a programmable control of the out-of-plane electrical dipole in TMD materials (induced by the electronegativity difference between S and Se atoms in Janus MoSSe). We performed Kelvin probe force microscope measurements on the MoS₂-MoSSe-MoSeS-MoSe₂ grid samples (Fig. 4E) to observe clear surface potential differences among these four distinct materials. As expected, the Janus MoSSe region with the Se layers on top and the flipped MoSeS region with the S layers on top display the highest and the lowest surface potentials, respectively, whereas the surface potentials for the MoS₂ and MoSe₂ regions are in between. The measured potential difference between the top Se layer of the MoSSe region and the top S layer of the MoSeS region is around 100 meV. Such potential difference is even larger than that between the MoSe₂ and MoS₂ regions (which is around 15 meV), suggesting that the Janus MoSSe (or MoSeS) holds a large intrinsic dipole that is locked to the 2D surface normal. Note that this dipole can be selectively patterned to be zero (MoS₂, MoSe₂), positive (MoSSe), and negative (MoSeS) on such a 2D material “canvas,” which would enable many nanostructures and devices with intriguing electrical and optoelectronic properties. For example, with proper choice of physical masks, such as e-beam resist, or carbon nanotubes (28, 29) with atomically sharp edges, it is possible to make in-plane quantum wells, superlattices, or photonic devices by generating periodic arrays of such dipole/non-dipole lateral heterostructures with 1- to 100-nm periodicity. Not only can the transport and optical properties of these MoXY multiheterostructures be altered, any materials in close vicinity would also be modulated by such an electrostatic “canvas.” Unusual physical properties and unprecedented functionality may be possible on such a platform, ranging from nonlinear optics, electronic band engineering, and nanoscale origami to electrochemical catalysis, all of which can be modulated by different electrostatic forces.

In summary, the RT-ALS combined with patterning and flip transfer present a powerful yet universal strategy to program material properties at the atomic-layer limit. It allows for creating diverse artificial low-symmetry 2D materials and their heterostructures. Such a process generates seamless, high-quality interfaces between different structures and can complement existing vdW heterostructure fabrication techniques by adding another intriguing class of materials (Janus and lateral Janus heterostructures and multiheterostructures). Furthermore, by designing these heterostructure patterns and surface charge distributions, great potential is anticipated in new physical discoveries and future applications.

Methods

Synthesis of MoS₂. A target SiO₂ substrate was suspended between two other SiO₂/Si substrates with predeposited perylene-3, 4, 9, 10-tetracarboxylic acid tetrapotassium solution. All of these substrates were placed facedown on a crucible containing MoO₃ precursor in a 1-inch quartz tube. This crucible was placed in the middle of the heating zone with another sulfur crucible on the upstream. Before heating, the whole CVD system was purged with 1,000 sccm Ar (99.999% purity) for 3 min. Then, 20 sccm Ar was introduced into the system as a carrier gas. The growth system was heated to 625 °C for 15 min. The MoS₂ growth was carried out around 620 to 630 °C for 3 min under atmospheric pressure. After growth, the whole system was naturally cooled down to room temperature.

Plasma-Assisted ALS. We use a remote commercial inductively coupled plasma system to substitute the top-layer sulfur atoms of monolayer MS₂ (M = Mo, W) with selenium. The CVD grown monolayer MoS₂/WS₂ were placed in the middle of a quartz tube. The plasma coil made by a cylindrical copper tube placed at the upstream of CVD furnace. The distance between the sample and the plasma coil is around 8 to 10 cm, with the selenium powder placed around 5 cm away from the plasma generator on the other side. Whenever masks were needed, the sample was covered with PMMA patterns defined by EBL. At the beginning of the process, the whole system was pumped down to a low pressure to remove air in the chamber. Then, hydrogen was introduced into the system and the plasma generator was ignited. The hydrogen atoms assist the removal of the sulfur atoms on the top layer of MoS₂. At the same time, the vaporized selenium filled in the vacancy of the sulfur atoms, resulting in the asymmetric Janus structure of MoSSe. The whole process was performed at room temperature. After the reaction, the whole system was purged with Ar gas (99.999% purity) to remove the residual reaction gas, and the pressure was recovered to atmospheric.

Transfer. For normal transfer, the samples were spin-coated with PMMA as a supporting layer. Then, they were put in the KOH solution and the PMMA/2D material was detached from the growth substrate and was floated on the surface of KOH solution. Afterward, it was taken to a deionized (DI) water bath by a glass slide and washed several times and then picked up with the target substrate. After baking on a hot plate at 100 °C for 15 min, the PMMA layer was removed with acetone and isopropanol (IPA). For flip-over transfer, the premade MoSSe sample was picked up by a polydimethylsiloxane stamp

and then was released onto an intermediate substrate. Then, the MoSSe was released through etching the SiO₂ in a KOH solution. The film was washed with DI water for several times and then put upside-down on the target SiO₂/Si substrate, with the bottom-layer selenium atoms touching the substrate. At last, the PMMA film was removed by acetone and IPA.

Data Availability. All study data are included in the article and/or *SI Appendix*. All materials are available upon request to J.K.

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