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Robust epitaxial growth of two-dimensional heterostructures, multiheterostructures, and superlattices

Zhengwei Zhang,[1]* Peng Chen,[1,3]* Xidong Duan,[1]† Ketao Zang,[2] Jun Luo,[2] Xiangfeng Duan[1,3]†

[1]State Key Laboratory for Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China. [2]Center for Electron Microscopy, Institute for New Energy Materials and Low-Carbon Technologies, School of Materials, Tianjin University of Technology, Tianjin 300384, China. [3]Department of Chemistry and Biochemistry and California Nanosystems Institute, University of California, Los Angeles, CA 90095, USA.

*These authors contributed equally to this work.

†Corresponding author: E-mail: xidongduan@hnu.edu.cn; xduan@chem.ucla.edu

We report a general synthetic strategy for highly robust growth of diverse heterostructures, multi-heterostructures, and superlattices from two-dimensional (2D) atomic crystals. A reverse flow during the temperature swing stage in sequential vapor deposition growth process allowed us to cool the existing 2D crystals to prevent undesired thermal degradation and uncontrolled homogeneous nucleation, thus enabling highly robust block-by-block epitaxial growth. Raman and photoluminescence mapping studies showed that a wide range of 2D heterostructures (such as WS_2-WSe_2 and WS_2-$MoSe_2$), multihetero-structures (such as WS_2-WSe_2-MoS_2 and WS_2-$MoSe_2$-WSe_2), and superlattices (such as WS_2-WSe_2-WS_2-WSe_2-WS_2) were readily prepared with precisely controlled spatial-modulation. Transmission electron microscope studies show clear chemical modulation with atomically sharp interfaces. Electrical transport studies of WSe_2-WS_2 lateral junctions show well-defined diode characteristics with a rectification ratio up to 10^5.

The two-dimensional (2D) atomic crystals of transition metal dichalcogenides (TMDs) (*e.g.*, MoS_2, $MoSe_2$, WS_2 and WSe_2) have attracted intense recent interest (*1–11*). To explore the full potential of these 2D atomic crystals requires reliable synthesis of their heterostructures and superlattices with precisely defined spatial modulation of chemical compositions and electronic structures. Despite considerable efforts and some successful examples to date (*12–21*), the robust synthesis of the atomically thin 2D TMD heterostructures remains a significant challenge and the epitaxial growth of 2D superlattices with multiple alternating blocks has not been realized.

To date, diverse monolayer atomic crystals as well as their alloys have been successfully grown via chemical vapor deposition (CVD) or thermal CVD process by using various chemical vapor sources (*22–33*). With a similar crystal structure and comparable lattice constants among these 2D crystals, in-domain lateral heterostructures have also been successfully synthesized through a two-step epitaxial growth of a second material (*e.g.,* $MoSe_2$, WSe_2) at the edge of an existing domain of a first material (*e.g.*, MoS_2, WS_2) (*12–21*). In principle, such sequential growth process can be repeated multiple times for the block-by-block growth of multi-heterostructures (with multiple distinct material blocks) or superlattices (with multiple alternating blocks) by switching the chemical vapor source or modulating the exact growth conditions in each growth steps.

To rationally produce lateral heterostructures with multiple distinct material blocks requires sequential growth steps with different chemical supply, growth conditions, or both. The monolayer 2D crystals are usually too delicate to survive multiple sequential growth steps necessary for the formation of 2D heterostructures or superlattices. With just a single or a few atomic layers, the 2D crystals essentially have little tolerance for any thermal-induced degradation, and are more challenging to grow than other bulk or nanoscale heterostructures with more atomic layers. Additionally, the ill-controlled supply of chemical vapor sources during the temperature swing stage between the sequential growth steps often leads to undesired homogeneous nucleation. To experimentally realize robust step-by-step growth of atomically thin 2D heterostructures or superlattices, at least two key requirements must be satisfied. First, the nucleating block must be robust enough to survive the temperature or chemical environment swing between the sequential growth steps. Second, undesired homogeneous nucleation of the new crystal seeds must be minimized and ensure exclusive heterogeneous epitaxial growth at the edge of the existing 2D crystals.

Although the growth of 2D heterostructures has been demonstrated, the studies to date are largely limited to the simplest heterostructures with only two distinct material blocks for a few selected material combinations. The growth of multiheterostructures or superlattices with three or more distinct material blocks, which requires sequential growth with multiple back-and-forth swings between the less and

more aggressive synthetic conditions, making it inevitable that existing blocks are damaged when the subsequent growth step is carried out in a more aggressive condition (*e.g.*, higher temperature) than the prior step.

We designed a modified step-by-step thermal CVD process in which a selected source powder is heated and vaporized under a flow of argon carrier gas for each sequential step, and the heterostructures are formed by the continued lateral epitaxial growth at the edge of the first monolayer crystals placed at the downstream end of CVD furnace [See more details of modified growth process in the supplementary materials (*34*)]. In a typical sequential growth process, the excessive thermal degradation (fig. S1) or uncontrolled nucleation (fig. S2) during the temperature swing between sequential growth steps represents the key obstacles to reliable formation of monolayer heterostructures. To avoid such adverse effects, we used a reverse flow from the substrate to the source during the temperature swing between successive growth steps (Fig. 1A). A forward flow from chemical vapor source was only applied at the exact growth temperature. With such reverse flow, the existing monolayer materials on the growth substrate were continuously flushed by the cold argon gas during the temperature swing to reduce exposure to high temperature and minimize thermal degradation. The reverse flow from the substrate to the source during the temperature ramping-up stage could also prevent unintended supply of chemical vapor source at undesired temperature to eliminate uncontrolled homogeneous nucleation. With a high degree of controllability in each step, the integrity and quality of monolayer heterostructures can be well preserved after multiple sequential growth steps. This approach can thus offer a general and reliable strategy for the growth of a wide range of heterostructures, multiheterostructures and superlattices (Fig. 1B-E, fig. S3).

We used our approach initially for the general synthesis a wide range of 2D crystal heterostructures. Figure 2A$_1$ shows the optical microscope image of a synthesized triangular domain of WS_2-WSe_2 monolayer heterostructure on SiO_2/Si substrate, which exhibits two concentric regions with slightly different optical contrast. Atomic force microscope (AFM) studies show that the heterostructure domain exhibits a smooth surface with a single step-height of 0.75 nm (fig. S4), confirming the monolayer nature of the heterostructure domain. To probe the spatial modulation of the structural and optical properties in the resulting WS_2-WSe_2 heterostructures, we have conducted micro-Raman and micro-photoluminescence (micro-PL) studies using a confocal Raman microscope. The Raman spectra taken from the center and peripheral regions of the triangular domain clearly show distinct features. The Raman spectrum from the center region exhibit two prominent peak at 350 cm^{-1} and 419 cm^{-1} (pink line in Fig. 2A$_2$), corresponding to the E$'$ and A$_1'$ resonance modes of WS_2; while the Raman spectrum from the peripheral region display one prominent peak at 250 cm^{-1} (green line in Fig. 2A$_2$), in agreement of the A$_1'$ resonance modes of WSe_2, respectively (*35*, *36*). These micro-Raman studies demonstrate the co-existence of two distinct materials within the same triangular domain. The spatially resolved Raman mapping studies further reveals the spatial modulation within the triangular domain, with the center part consisting of a triangular domain of WS_2 and the peripheral region composed of WSe_2 (Fig. 2A$_3$)

Similarly, micro-PL studies also show highly distinct photoluminescence peaks at 630 nm for the center part and 760 nm for the peripheral part (Fig. 2A$_4$), consistent with the near band-edge emission from WS_2 and WSe_2, respectively (*36*, *37*). The PL mapping studies (Fig. 2A$_5$-2A$_6$) show features similar to those of Raman mapping studies, further confirming the formation of WS_2-WSe_2 lateral heterostructures. The PL spectra at the interface region display two distinct peaks (fig. S5A) with the peak positions displaying little deviation from those of the center region (WS_2) or the peripheral region (WSe_2). The simple overlap of the PL spectra at interface indicates rather sharp transition from WS_2 to WSe_2 at the interface of the synthesized lateral heterostructure (*13*), as will be further evidenced below. Using the same strategy, we synthesized a wide range of monolayer heterostructures including WSe_2-MoS_2 (Fig. 2B$_1$-B$_3$), WS_2-MoS_2 (Fig. 2C$_1$-C$_3$), WSe_2-$MoSe_2$ (Fig. 2D$_1$-D$_3$), and WS_2-$MoSe_2$ (Fig. 2E$_1$-E$_3$), which as shown by optical microscopy, Raman spectroscopy and PL mapping studies (fig. S6), formed lateral heterojunctions similar to the WS_2-WSe_2 heterostructures.

We also grew more complex compositionally modulated superlattices or multiheterostructures through a step-by-step growth process, in which the number of periods and repeating spacing can be readily varied during growth. The optical microscope image of a synthesized WS_2-WSe_2-WS_2-WSe_2 monolayer superlattice on SiO_2/Si substrate (Fig. 3A$_1$) exhibited four concentric regions with slightly different optical contrast. The spatially resolved Raman mapping at 350 cm^{-1} (E$'$ mode of WS_2) and 250 cm^{-1} (A$_1'$ mode of WSe_2) (Fig. 3A$_2$) revealed the spatial modulation of the triangular domain: with the first and third parts composed of WS_2 and the second and fourth parts composed of WSe_2. Thus, a seamless lateral superlattice structure formed within the same triangular domain. The PL mapping images at 630 nm (near band edge emission of WS_2; Fig. 3A$_3$) and 760 nm (near band edge emission band edge of WSe_2; Fig. 3A$_4$) also confirmed the formation of WS_2-WSe_2 monolayer lateral superlattice structure. In addition to the lateral superlattices, monolayer lateral multiheterostructures including WS_2-MoS_2-WS_2, WS_2-WSe_2-MoS_2 and WS_2-$MoSe_2$-WSe_2 were synthesized, and optical microscopy, Raman and PL characteri-

zations of these lateral multiheterostructures confirmed the formation of multiheterostructures with well-defined spatial modulation (Fig. $3B_1$-D_5).

The detailed atomic structure of the lateral heterostructure interface was revealed by high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) *Z*-contrast imaging. Figure 4A shows a Z-contrast image of the WS_2-WSe_2 lateral interface, where Se atoms exhibit higher image intensity than the S atoms. The atomically sharp interface can be clearly observed along the overall-straight "interline" in the WS_2-WSe_2 lateral junction. The WS_2 and WSe_2 domains connect seamlessly at the interface into a single hexagonal monolayer lattice and share the same crystal orientation. The corresponding atomic model, obtained via atom-by-atom image quantification indicates the seamless connection and atomically abrupt transition between the WS_2 and WSe_2 lattice. Figure 4B further showed the atomic structure of WS_2-$MoSe_2$ lateral junction, where an atomically sharp "interline" was also well resolved.

We further investigated the structural modulation across the WS_2-$MoSe_2$-WSe_2 multi-heterostructure using the low-magnification *Z*-contrast image. Three regions with slightly different contrast were observed, corresponding to the WS_2, $MoSe_2$ and WSe_2, respectively. The selected area electron diffraction (SAED) patterns are taken at the WS_2 region, $MoSe_2$ region and WSe_2 region, respectively (Fig. 4, D-F). The hexagonally arranged diffraction spots can be indexed to the hexagonal symmetry of the [001] zone plane of WS_2, $MoSe_2$ and WSe_2 lattice structures. A careful analysis of these diffraction peaks yields (100) lattice plane spacings of 2.70 Å, 2.77 Å and 2.81 Å, in agreement with the values for WS_2, $MoSe_2$ and WSe_2 (*12*, *38*). Figure 4G-I show the high-resolution STEM images of WS_2, $MoSe_2$ and WSe_2. Based on these images, we can also determine the (100) lattice plane spacings of WS_2, $MoSe_2$ and WSe_2 to be 2.70 Å, 2.79Å and 2.81 Å, consistent with the lattice plane spacings yielded from SAED studies. Together, these studies demonstrate the well-defined chemical/structural modulation in 2D crystal heterostructures and multi-heterostructures with atomically sharp interfaces.

With the atomically sharp interface, the width of heteroepitaxy can be controlled down to nanometer scale (fig. S7), which may enable the realization of ultrashort period superlattices or and open up a pathway to multi-quantum-well (or "quantum-line") structure in the 2D atomic crystals. To further characterize the electronic properties of the monolayer heterostructures, we have also fabricated the monolayer lateral p-n junction device from WSe_2-WS_2 lateral heterostructures by taking advantage of the intrinsically p-type characteristics of WSe_2 and the n-type characteristics of WS_2. The current versus voltage measurements showed a rectification ratio up to 10^5 (fig. S8), consistent with the presence of a monolayer lateral p-n junction. The robust synthesis of diverse 2D heterostructures and superlattices with atomically sharp interfaces creates an interesting material system for fundamental studies and novel device demonstrations at the limit of single atomic thickness, which will be an important topic for future studies. Furthermore, by using site specific nucleating blocks obtained from lithography patterning or patterned growth (*39*), a similar sequential epitaxial growth may be used for producing complex heterostructures with controlled location and orientation, which will be important for developing practical technologies from these atomically thin crystals.

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SUPPLEMENTARY MATERIALS

www.sciencemag.org/cgi/content/full/science.xxxxxxx/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S8
Table S1

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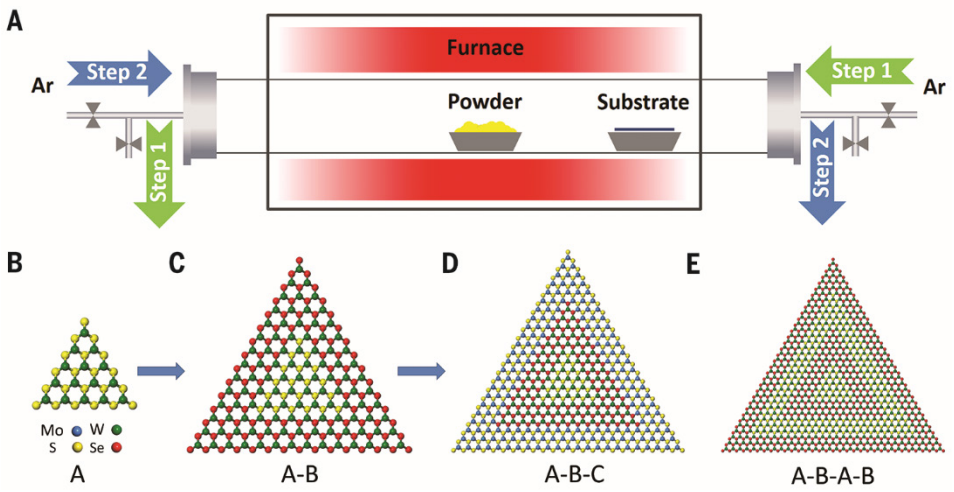

Fig. 1. Robust epitaxial growth of 2D monolayer heterostructures, multiheterostructures and superlattices with a modified CVD process. (**A**) Schematic illustration of a modified CVD system for the robust epitaxial growth of lateral heterostructures. The solid powders were directly used as the source material. Both sides of quartz tube are equipped with gas inlet and outlet. The direction of argon gas flow can be switched by using the angle-style valves at the two ends of quartz tube. A reverse flow from the substrate to the source is applied during the temperature ramping and stabilization stage to cool existing 2D crystal on substrate and prevent unintended supply of vapor source reactant or uncontrolled nucleation and growth (step 1). After reaching the desired growth temperature, a forward flow from the source to the substrate is applied to transport the vapor phase reactant onto the growth substrate for the epitaxial growth of the desired 2D crystals (step 2). The reverse flow can effectively prevent the unintended homogeneous nucleation and minimize the thermal degradation of the atomically thin 2D crystals to ensure highly robust sequential growth of (**B**) monolayer seed A, (**C**) A-B heterostructure, (**D**) A-B-C multiheterostructures, and (**E**) A-B-A-B superlattices.

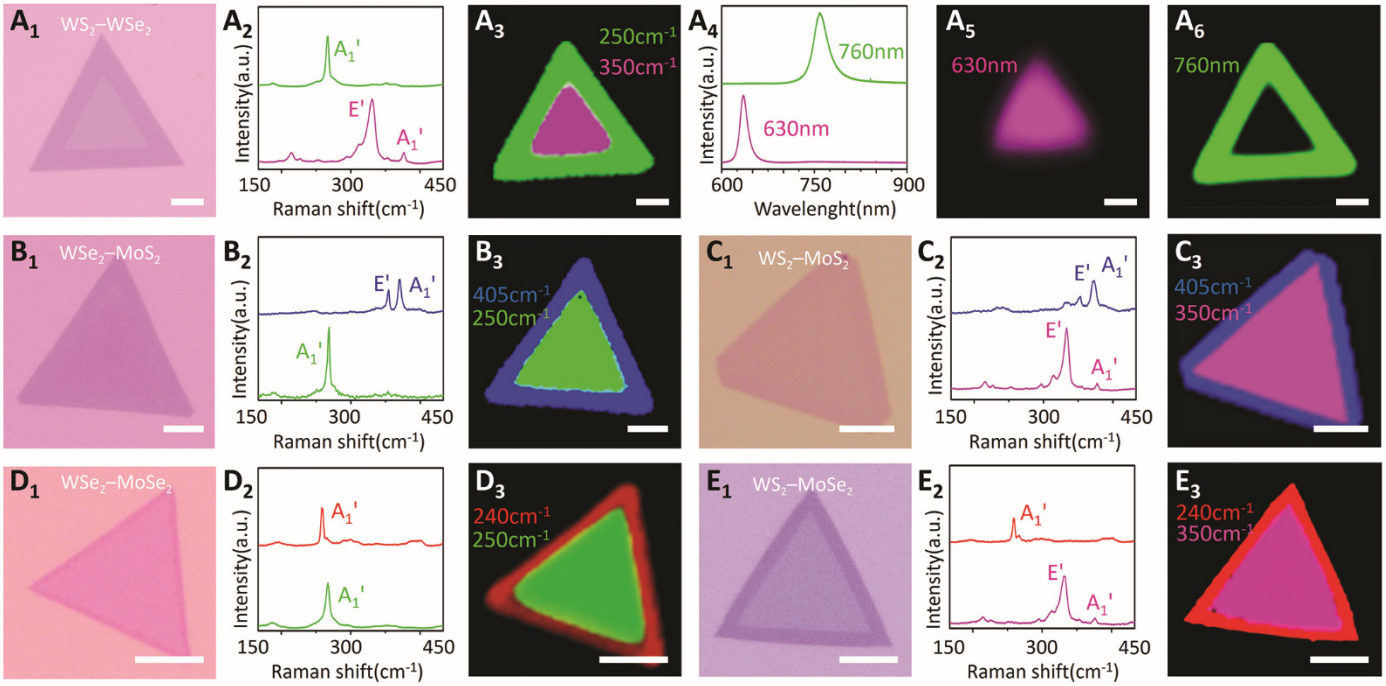

Fig. 2. General growth of diverse 2D lateral heterostructures. (**A_1**) Optical microscope image of a WS_2-WSe_2 heterostructure domain. (**A_2**) Raman spectra of the WS_2-WSe_2 heterostructure. The pink curve is obtained from the center region, showing the characteristic Raman peaks of WS_2; and the green curve is obtained from the peripheral region, showing the characteristic Raman peaks of WSe_2. (**A_3**) Spatially-resolved Raman mapping image shows clear lateral integration of the WS_2-WSe_2 heterostructure. (**A_4**) Photoluminescence (PL) spectra of the WS_2-WSe_2 heterostructure. The pink curve is obtained from the center region, showing the characteristic PL peak of WS_2; and the green curve is obtained from the peripheral region, showing the characteristic PL peak of WSe_2. (**A_5-A_6**) Spatially resolved PL mapping images at 630 nm and 760 nm, showing characteristic PL emission of WS_2 and WSe_2 in the center and peripheral regions of the triangular domain. (**B_1-B_3**) Optical microscope image, Raman spectra and mapping image of monolayer WSe_2-MoS_2 heterostructure. (**C_1-C_3**) Optical microscope image, Raman mapping spectra and image of monolayer WS_2-MoS_2 heterostructure. (**D_1-D_3**) Optical microscope image, Raman spectra and mapping image of monolayer WSe_2-$MoSe_2$ heterostructure. (**E_1-E_3**) Optical microscope image, Raman spectra and mapping image of monolayer WS_2-$MoSe_2$ heterostructure. All scale bars are 5 μm.

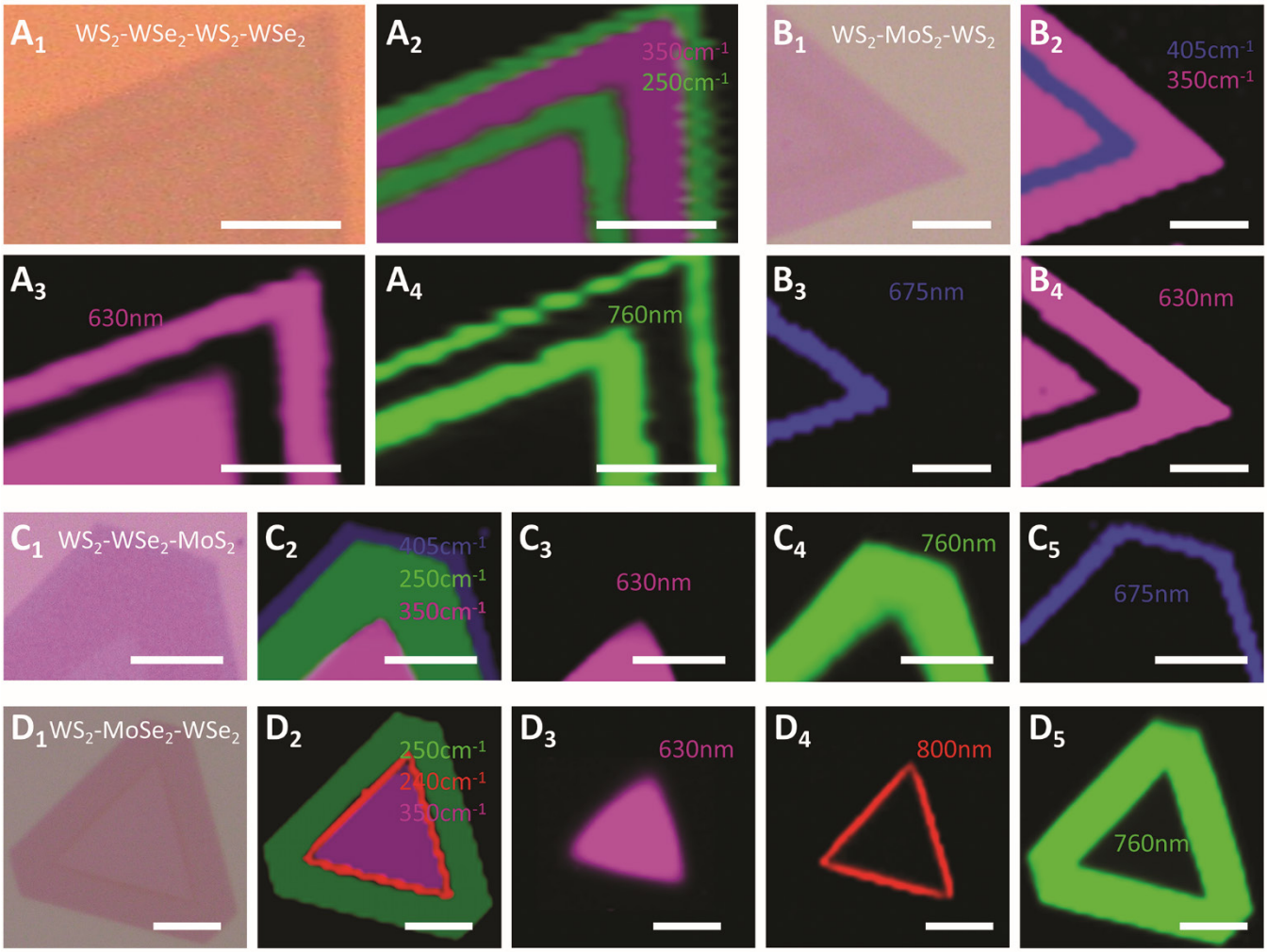

Fig. 3. Raman and photoluminescence characterizations of 2D superlattices and multiheterostructures. (**A_1**) Optical microscope image of WS_2-WSe_2-WS_2-WSe_2 superlattice on SiO_2/Si substrate. (**A_2**) Raman mapping image at 250 cm^{-1} and 350 cm^{-1} show clearly the WS_2-WSe_2 superlattice structure. (**A_3-A_4**) PL mapping images at 630 nm and 760 nm further confirm the WS_2-WSe_2 lateral superlattice structure. (**B_1-B_4**) Optical microscope image, Raman mapping and PL mapping images of the WS_2-MoS_2-WS_2 multiheterostructure on SiO_2/Si. Raman mapping at 405 cm^{-1} and 350 cm^{-1} show clearly the formation of WS_2-MoS_2-WS_2 multiheterostructure, which is confirmed by PL mapping images at 675 nm and 630 nm. (**C_1-C_5**) Optical microscope image, Raman mapping and PL mapping of the WS_2-WSe_2-MoS_2 multiheterostructure on SiO_2/Si. Raman mapping at 405 cm^{-1}, 250 cm^{-1} and 350 cm^{-1} show clearly the formation of WS_2-MoS_2-WS_2 multiheterostructure, which is confirmed by PL mapping images at 630 nm, 760 nm and 675 nm. (**D_1-D_5**) Optical microscope image, Raman mapping and PL mapping of the WS_2-$MoSe_2$-WSe_2 multiheterostructure on SiO_2/Si. Raman mapping at 250 cm^{-1}, 240 cm^{-1} and 350 cm^{-1} show clearly the formation of WS_2-MoS_2-WS_2 multiheterostructure, which is confirmed by PL mapping images at 630 nm, 800 nm and 760 nm. All scale bars correspond to 5 μm.

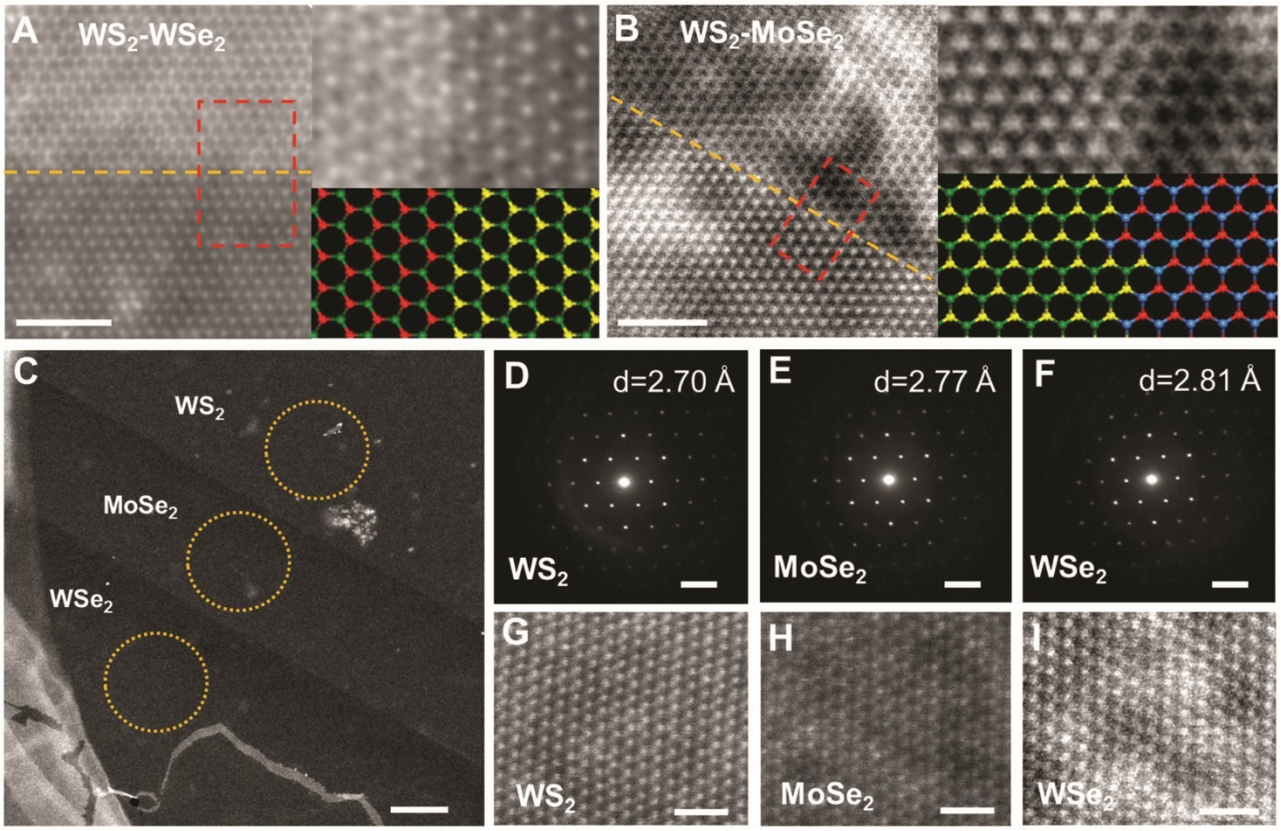

Fig. 4. Atomic structure of the lateral heterostructures and multiheterostructures. (**A**) Atomic-resolution *Z*-contrast STEM image taken from the WS_2-WSe_2 lateral heterostructure (left); Magnified STEM image of the doted red rectangle region (top right) and the corresponding atomic model (bottom right); The orange dashed lines highlight the atomically sharp interface ("interline"). Scale bar, 2 nm. (**B**) Atomic-resolution *Z*-contrast STEM image taken from the WS_2-$MoSe_2$ lateral heterostructure (left); Magnified STEM image of the doted red rectangle region (top right) and the corresponding atomic model (bottom right); The orange dashed lines highlight the atomically sharp "interline". Scale bar, 2 nm. (**C**) Low-magnification *Z*-contrast image of the lateral WS_2-$MoSe_2$-WSe_2 multiheterostructure. Scale bar, 100 nm. (**D, E, F**) Electron diffraction patterns taken from the yellow doted circles in (**C**), corresponding to WS_2 region (**D**), $MoSe_2$ region (**E**) and WSe_2 region (**F**). Scale bar, 5 nm^{-1}. (**G, H, I**) Atomic-resolution STEM image taken from the WS_2 region (**G**), $MoSe_2$ region (**H**) and WSe_2 region (**I**). Scale bar, 1 nm.