

# One-pot growth of two-dimensional lateral heterostructures via sequential edge-epitaxy

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**Two-dimensional heterojunctions of transition-metal dichalcogenides<sup>1–15</sup> have great potential for application in low-power, high-performance and flexible electro-optical devices, such as tunnelling transistors<sup>5,6</sup>, light-emitting diodes<sup>2,3</sup>, photodetectors<sup>2,4</sup> and photovoltaic cells<sup>7,8</sup>. Although complex heterostructures have been fabricated via the van der Waals stacking of different two-dimensional materials<sup>2–4,14</sup>, the *in situ* fabrication of high-quality lateral heterostructures<sup>9–13,15</sup> with multiple junctions remains a challenge. Transition-metal-dichalcogenide lateral heterostructures have been synthesized via single-step<sup>9,11,12</sup>, two-step<sup>10,13</sup> or multi-step growth processes<sup>15</sup>. However, these methods lack the flexibility to control, *in situ*, the growth of individual domains. *In situ* synthesis of multi-junction lateral heterostructures does not require multiple exchanges of sources or reactors, a limitation in previous approaches<sup>9–13,15</sup> as it exposes the edges to ambient contamination, compromises the homogeneity of domain size in periodic structures, and results in long processing times. Here we report a one-pot synthetic approach, using a single heterogeneous solid source, for the continuous fabrication of lateral multi-junction heterostructures consisting of monolayers of transition-metal dichalcogenides. The sequential formation of heterojunctions is achieved solely by changing the composition of the reactive gas environment in the presence of water vapour. This enables selective control of the water-induced oxidation<sup>16</sup> and volatilization<sup>17</sup> of each transition-metal precursor, as well as its nucleation on the substrate, leading to sequential edge-epitaxy of distinct transition-metal dichalcogenides. Photoluminescence maps confirm the sequential spatial modulation of the bandgap, and atomic-resolution images reveal defect-free lateral connectivity between the different transition-metal-dichalcogenide domains within a single crystal structure. Electrical transport measurements revealed diode-like responses across the junctions. Our new approach offers greater flexibility and control than previous methods for continuous growth of transition-metal-dichalcogenide-based multi-junction lateral heterostructures. These findings could be extended to other families of two-dimensional materials, and establish a foundation for the development of complex and atomically thin in-plane superlattices, devices and integrated circuits<sup>18</sup>.**

Chemical vapour deposition can produce high quality transition-metal dichalcogenide (TMD) monolayers and heterostructures<sup>9–13</sup>. The one-pot synthesis strategy involves using a single solid source, composed of MoX<sub>2</sub> and WX<sub>2</sub> powders placed within the same boat at high temperatures. Implementing this strategy for the fabrication of TMD-based heterostructures requires regulating the relative amounts of precursors in the gaseous phase through controlled vaporization from the solid sources, and/or promoting the selective deposition of individual compounds onto the substrate held at lower temperatures. In general, MX<sub>2</sub> compounds (where M = W, Mo and X = S, Se) have high dissociation temperatures. However, the presence of water vapour at high temperatures promotes the formation of highly volatile species, including metal oxides and hydroxides<sup>16,17,19,20</sup>. Using a one-pot

strategy (Extended Data Fig. 1), we found that the selective growth of each TMD can be controlled independently, solely by switching the carrier gas (Extended Data Figs 2, 3): N<sub>2</sub> + H<sub>2</sub>O<sub>(g)</sub> promotes the growth of MoX<sub>2</sub>, whereas switching to Ar + H<sub>2</sub> (5%) stops the growth of MoX<sub>2</sub> and promotes the growth of WX<sub>2</sub>. When the carrier gas is cyclically switched back and forth, heterostructures consisting of a sequence of multi-junctions can be synthesized continuously (Fig. 1 and Extended Data Fig. 4). The growth mechanism can be summarized as follows (see Methods and Extended Data Fig. 5 for a detailed discussion): N<sub>2</sub> + H<sub>2</sub>O<sub>(g)</sub> (without H<sub>2</sub>) favours the evaporation of both the molybdenum and the tungsten precursors (oxides and hydroxides), but because gaseous tungsten precursors are mainly hydroxides—which are volatile at temperatures above 500 °C (ref. 17)—only molybdenum precursors are deposited on the substrate. A sudden switch of the carrier gas to Ar + H<sub>2</sub> depletes the supply of molybdenum precursors, while supplying tungsten precursors owing to the slower reduction rate of WO<sub>x</sub>. This vapour-phase modulation of the oxide species is the key driving force for the sequential growth of lateral heterojunctions.

Figure 1a–d shows optical images of a series of distinct multi-junction heterostructures, with alternating MoSe<sub>2</sub> (dark contrast) and WSe<sub>2</sub> (bright contrast) regions. The number of junctions is controlled by the number of gas-switching cycles, and the lateral size of each domain (width) is determined by the growth time of each individual cycle (Fig. 1b, c and Extended Data Fig. 2a–h). The growth rate of MoSe<sub>2</sub> and WSe<sub>2</sub> domains was found to be a function of the substrate temperature (Extended Data Figs 1c, 2i). The single-crystalline heterostructure islands, up to 285 μm in size (Fig. 1a), are among the longest reported so far<sup>10</sup>. Spatially resolved Raman and micro-photoluminescence spectroscopies confirmed the sequential distribution of the chemical composition as well as the local optical properties within the heterostructures. Raman spectra (Fig. 1e) collected from regions 1 and 3 (Fig. 1a, inset) in the heterostructure exhibit the A<sub>1g</sub> phonon mode (240 cm<sup>−1</sup>) and the E<sub>2g</sub><sup>2</sup> (M) shear mode (shoulder at 249 cm<sup>−1</sup>), corresponding to monolayer MoSe<sub>2</sub>, whereas regions 2 and 4 display the A<sub>1g</sub> (250 cm<sup>−1</sup>) and the 2LA(M) (260 cm<sup>−1</sup>) phonon modes of monolayer WSe<sub>2</sub> (refs 12, 21). Raman intensity maps at 240 cm<sup>−1</sup> and 250 cm<sup>−1</sup> further corroborated the spatial distribution of the MoSe<sub>2</sub> and WSe<sub>2</sub> domains, respectively (Extended Data Fig. 3c–f). The photoluminescence spectra (Fig. 1f) show a strong excitonic single peak at around 1.52 eV for MoSe<sub>2</sub> (regions 1 and 3) and 1.6 eV for WSe<sub>2</sub> (regions 2 and 4)<sup>12</sup>. The integrated photoluminescence intensity maps (Fig. 1g) and the corresponding composite map (Fig. 1h) of the heterostructures reveal the alternate formation of concentric triangular domains of MoSe<sub>2</sub> and WSe<sub>2</sub> monolayers (Extended Data Fig. 4a, c–e). The contour plots of the normalized photoluminescence intensity as a function of the position across three-junction (Fig. 1i) and five-junction (Fig. 1j) heterostructures clearly show the evolution of the distinct excitonic transitions within each domain. Across the first junction (marked 1), the MoSe<sub>2</sub> photoluminescence peak at 1.53 eV gradually shifts to higher energies until it reaches 1.60 eV, corresponding to the WSe<sub>2</sub> domain—a total shift of 70 meV. At the second and third junctions there is an abrupt

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