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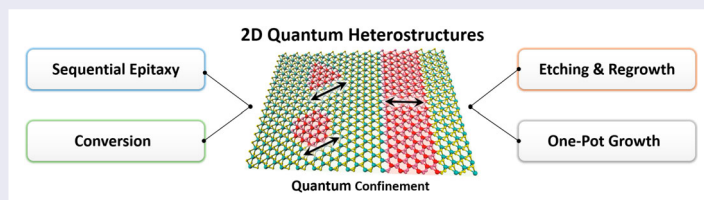
Spatially controlled two-dimensional quantum heterostructures

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ABSTRACT

Two-dimensional (2D) heterostructures have recently attracted interest as candidate materials for classical optoelectronics and in quantum information technology. Despite significant research, realizing deterministic, in-plane quantum confinement in synthetic 2D heterostructures at the nanoscale remains challenging. In this brief overview, we summarize recent advances in approaches for the growth of spatially controllable 2D quantum heterostructures. These growth methods enable the achievement of various 2D lateral/vertical heterostructures with controlled positions and dimensions while minimizing defects across the heterointerfaces. In addition, we provide an outlook on the future direction of developments and applications of 2D quantum-confined heterostructures.



IMPACT STATEMENT

Two-dimensional (2D) heterostructures have been investigated for optoelectronics and quantum engineering. This review provides critical analysis and perspective into the realization of spatially controlled 2D quantum heterostructures and their applications.

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KEYWORDS

2D materials; low dimensional materials; heterostructures; epitaxial growth; chemical vapor deposition

1. Introduction

Numerous studies on van der Waals (vdW) two-dimensional (2D) materials-based heterostructures have been demonstrated experimentally. The available material properties of the 2D heterostructures vary and are limitless due to the numerous combinations of the spatially controlled structures and different 2D materials available, such as semi-metallic graphene, insulating hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMDs) with metallic and semi-conducting properties. This provides versatile opportunities to advance various electronic and optical components in conventional devices and enable quantum-confined effects in atomically thin layers. Achieving spatial control of 2D materials with a nanometer-scale resolution and periodicity also opens new avenues in band-structure engineering and in creating isolated quantum states [1–6].

Quantum confinement is the spatial confinement of electrons and holes in a dimension within a material, and their electron energy levels are discrete. This effect occurs as the dimension potential approaches the de Broglie wavelength of the electron because the electronic wave function is confined to the physical dimensions of the materials. For this reason, confinement is much more significant in zero-dimensional (0D) quantum dots with a size of 10 nm or less, which are confined in all three dimensions by the size effect. In the case of 2D materials, the electrons in 2D materials are already quantized in one direction, namely, out-of-plane, but not in-plane. More lateral dimensional reduction is thus necessary for further quantum confinement in 2D materials, to induce and explore 0D-like behavior. In this respect, the Bohr radius, diffusion length of excitons, and the mean free path of free electrons of 2D materials must be addressed to achieve additional quantum confinement (Figure 1).

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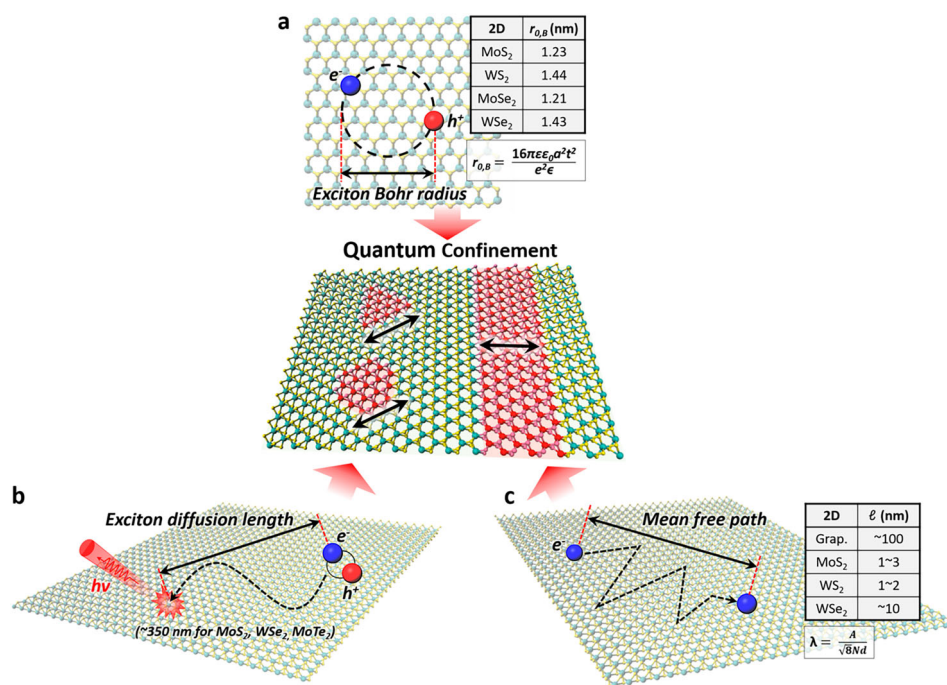


Figure 1. Quantum confinement in 2D materials. Schematics showing (a) the exciton Bohr radius [7] and (b) the diffusion length [12, 13, 14], and (c) the mean free path of free electrons [15, 21]. They are three factors to be considered for designing and engineering the quantum confinement effects in 2D materials.

For excited electronic states in semiconductors quantum confinement is induced by confining excitons within a dimension that approaches a critical quantum limit called the Bohr exciton radius, which is an average physical separation between the electron and hole. As shown in Figure 1a, the Bohr radius of the typical 2D TMD materials is ~ 1.2 – 1.5 nm [7]. In general, the physical dimensions of the material can tailor the confinement effects in the weak confinement regime with a size bigger than the exciton Bohr radius. For example, even in MoS₂ quantum dots with a size of 2–25 nm, blue shifting of the exciton has been shown as the size of the dots decreased [8–11]. In contrast, the strong confinement with a size smaller than the Bohr radius enables discrete energy levels and fermionic exciton behavior useful for quantum devices. This strong confinement regime requires the following conditions: First, the Coulomb interaction between the electron and holes should be small enough to trigger a perturbation. Second, the electrons and holes should behave independently with the small Coulomb interaction. Under these conditions, electrons and holes can be positioned as independent particles in discrete-size quantized levels. On the other hand, the exciton diffusion length of the 2D TMD materials is ~ 350 nm [12–14] (Figure 1b), which is much larger than the exciton Bohr radius. Consequently, without considering the exciton diffusion length, the quantum confinement effect in TMDs could be anticipated only with the Bohr radius.

Electrical quantum confinement occurs when the particle size is less than or equal to the electron mean free path (Figure 1c), which is the effective length of the wave function of the delocalized electron. Despite quantum size effects being anticipated to occur when the crystal size is less than 10 nm, simply considering the Bohr radius, quantum confinement can thus be discovered in materials with sizes of several tens of nanometers as a result of the impact of the electron mean free path. In this regard, graphene is very suitable for observing quantum transport for two reasons: First, the wavelength of electrons at the Fermi energy can be tuned up to hundreds of nanometers. Second, the mobility of the graphene monolayer can approach $\sim 10,000$ cm²V^{−1}s^{−1}, which corresponds to an electron mean free path of ~ 100 nm [15]. Therefore, the lithographic technology using e-beam allows the fabrication of graphene devices much smaller than the mean free path, enabling its ballistic transport. In addition, the device dimensions comparable to the electron wavelength also result in quantum confinement. For example, the quantized conductance steps in 0D or 1D graphene layers with sub-50-nm size (e.g. graphene constrictions, quantum dots, and nanoribbons) demonstrated quantum confinement in-plane [16–20]. In the case of MoS₂, although its mean free path is 1–3 nm [21], a signature of ballistic transport was observed in the tunneling transistor with a width of 50–100 nm [22]. Even though the channel size of TMD monolayers

is much larger than the mean free path of electrons, conductance quantization can occur due to the charge localization introduced by the defect states in the substrate; hence, the confined quantum devices can be fabricated using the same lithographic approach as graphene devices [23–25].

This Brief Overview reviews recent developments in the spatially controlled growth of quantum-confined heterostructures based on 2D materials. Four types of growth approaches are discussed: (i) sequential epitaxial growth, (ii) etching and regrowth, (iii) post-synthetic conversion, and (iv) one-pot synthesis, which are summarized in Figure 2 and Table 1. We thoroughly review examples of such heterostructures and present a forward-looking outlook on their potential applications. In addition, we discuss promises and strategies for designing quantum devices based on 2D heterostructures with spatial control.

2. Spatially controlled growth of 2D quantum heterostructures

2.1. Sequential epitaxial growth

The growth of 2D heterostructures has been successfully reported in numerous reports, using various chemical vapor deposition (CVD)-based methods. The gas-phase CVD with solid-powder precursors or the metal-organic CVD (MOCVD) with all vapor phase precursors allows a large degree of freedom to control the growth of various 2D materials, further offering a scalable growth scheme. In particular, the selective and sequential supply of precursors is critical to achieving spatially controlled heterostructures via ‘sequential growth’. In addition to precursor control, for controlled spatial dimensions of crystal regions in the growth, it is also critical to regulate the nucleation (both density and location) to further select between lateral vs vertical growth processes. In this regard, a recent report has explained the preferred nucleation sites and kinetics of the vertical and lateral growth during the two-step CVD of 2D heterostructure based on MoS₂ and WSe₂ (Figure 3a) [26]. The most critical factor determining the growth aspect is the diffusion barrier of gas-phase W₁Se_x clusters, enabling the growth of WSe₂ either on the basal plane or edge of the prepared MoS₂ (Figure 3b). Depending on the ratio between the transition metal and chalcogen flux (i.e. W/Se ratio), two types of W₁Se₁ and W₁Se₃ clusters can co-exist on the MoS₂ surface in the vapor precursors. As shown in Figure 3a, W₁Se₁ active clusters with a high diffusion barrier (1.2 eV) are dominantly formed for a high W/Se ratio, which can induce the nucleation on top of the MoS₂ basal plane to obtain vertical WSe₂/MoS₂ heterostructure. On

the other hand, for the low W ratio, W₁Se₃ clusters are formed which have a relatively lower diffusion barrier (0.4 eV) and tend to diffuse towards the edge of MoS₂, forming a lateral WSe₂-MoS₂ heterostructure. Similarly, the ratio between transition metal and chalcogen flux dictates lateral or vertical growth mode for various 2D heterostructures such as WS₂/WSe₂ [26,27], GaSe/MoS₂ [28], and MoSe₂/WSe₂ [29]. In addition, the growth temperature affects the lateral vs vertical growth of 2D heterostructures [36,48,58]. High-temperature (> 850 °C, roughly) growth promotes the extensive nucleation and growth of 2D crystals, resulting in a thermodynamic preference for vertical heterostructures. On the contrary, lower growth temperature favours a kinetic mechanism over a thermodynamic mechanism that stimulates lateral growth. Moreover, the defectiveness of the pre-formed crystal also determines the growth direction of the subsequent 2D structure [36,45]. If defects such as chalcogen vacancies exist in the 2D basal plane, the adsorption probability of precursors on the surface increases while promoting vertical growth rather than edge-mediated lateral growth [36,45].

Based on the aforementioned growth mechanisms, spatial-controllable lateral vs vertical 2D heterostructures can be obtained utilizing consecutively supplied gas-phase precursors during CVD. In this regard, this section handles two sequential epitaxial growth approaches for multi-heterojunction structures and superlattices: (i) the edge-mediated epitaxy process forming laterally covalent bonds between two different 2D materials and (ii) the vdW epitaxy process for vertical stacking of 2D materials by vdW interactions.

2.1.1. Lateral edge-mediated epitaxy

The selective evaporation of different precursors during powder-based CVD successfully induces sequential growth mode for lateral 2D heterostructures [26–29,33–35]. However, vacancy or alloy formation may occur along the pre-formed 2D crystal because of thermal decomposition and undesired chemical reactions at high temperatures during a thermal CVD process for heterostructures [31,36]. Furthermore, the nucleation of new crystals can be initiated from the growth template (sapphire, SiO₂, or even on pre-grown crystals) rather than the edge of the existing 2D crystal. These issues, i.e. the thermal stability of the growth template and nucleation control at the desired position, represent a major obstacle in the delicate fabrication of single-layer-lateral heterostructures and superlattices. To address these issues, a novel method has been reported for achieving diverse lateral superlattices (Figure 3c) by using a modified thermal CVD process with a reverse flow of additional Ar gas from the substrate to the sources [31].

Table 1. Summary of the spatially controlled growth of 2D lateral and vertical heterostructures. Lateral and vertical heterostructures are denoted by A-B and A/B, respectively.

Growth method	Heterostructures	Growth direction	Minimum feature size	Resultant crystal structures	Device applications or quantum phenomena	Refs
Sequential epitaxy	MoS ₂ -WSe ₂	Lateral /Vertical	~ 10 μm	Controllable lateral/vertical growth aspects		[26]
	GaSe-MoS ₂	Lateral	~ 1 μm	Lateral heteroepitaxy Lateral superlattices of quantum well	Photodetectors	[27]
	MoSe ₂ -WSe ₂		~ 3 μm			[28]
	Graphene-hBN		~ 3 μm			[29]
	WS ₂ -WSe ₂ ,		80 nm			[30]
	WSe ₂ -MoS ₂ ,		~ 200 nm			[31]
	WSe ₂ -MoSe ₂		~ 15 nm		Strain engineering of band structure	[32]
	MoSe ₂ -WSe ₂		~ 10 nm	Lateral heterostructure flake	Self-powered photodetector	[33]
	WSe ₂ -MoS ₂	~ 150 nm	A few μm	Self-aligned heterojunction	Light-emitting diodes	[34]
				Lateral heterostructure flake	Strain-induced type I band alignment	[35]
	PtTe ₂ -MoS ₂		~ 10 μm	Position-controlled heterostructure arrays	Transistors with low contact resistance and sub-1-nm transfer length	[36]
	MoS ₂ /WS ₂	Vertical	Monolayer	Vertical superlattices	Valley-polarized interlayer excitation	[37]
	WSe ₂ /Bi ₂ Se ₃		3.2 nm	Vertically stacked heterostructure	Self-powered broadband photodetector	[38]
	SnS ₂ /WSe ₂ , NbSe ₂ /MoSe ₂ , SnS ₂ /MoS ₂ /WSe ₂		Monolayer	Roll-up superlattices	1D magneto-transport	[39]
	Graphene/MoS ₂		N/A	Lattice aligned MoS ₂ on graphene	Band gap narrowing of MoS ₂	[40]
	Etching and regrowth	WS ₂ -WSe ₂ , WSe ₂ -MoS ₂ , WSe ₂ -MoS ₂	Lateral	~ 3 μm	Mosaic heterostructure	
Graphene-hBN			15 nm	Graphene nanoribbon	Carrier mobility of 20000 cm ² /Vs	[42]

(continued)

Table 1. Continued.

Growth method	Heterostructures	Growth direction	Minimum feature size	Resultant crystal structures	Device applications or quantum phenomena	Refs
Post-synthetic conversion	Graphene-hBN	Vertical	6 nm	Graphene nanoribbon	Bandgap with on/off ratios $> 10^4$	[43]
	Graphene-hBN		5 nm	Controllable edge topologies	Band gap opening and magnetic conductance	[44]
	VSe ₂ /WSe ₂ , NiTe ₂ /WSe ₂ , CoTe ₂ /WSe ₂ , NbTe ₂ /WSe ₂ , VS ₂ /WSe ₂ , VSe ₂ /MoS ₂ , VSe ₂ /WS ₂		N/A	Arrays of vertical heterostructure	High ON-current density transistors	[45]
	Graphene/hBN			Heterostructure with a vertically overlapped MSJ (2–200 nm)	Transistors with low contact resistance	[46]
	Graphene/MoS ₂					[47]
	MoS ₂ -MoSe ₂	[48] Lateral	$\sim 3 \mu\text{m}$	Arrays of lateral heterostructure	Type-I <i>n-n</i> junction	[49]
	MoS ₂ -Mo ₂ C		$\sim 25 \text{ nm}$		Transistor with low contact resistance	[50]
	Graphene-hBN		$\sim 1 \mu\text{m}$	Band splitting of 80–160 meV	Graphene transistors with an on/off ratio of $\sim 10^3$	[51]
		$\sim 25 \mu\text{m}$ $\sim 7 \text{ nm}$				[52]
						[53]
Simultaneous one-pot synthesis	MoS ₂ -WSe ₂	Lateral	Blue emission at the interface $\sim 2 \text{ nm}$	Sub-nm-wide 1D MoS ₂ channels	[54]	[55]
	1T'-MoTe ₂ -2H-MoTe ₂	Lateral	A few μm	Patternable lateral heterostructure	Transistor with low contact resistance	[56]
	MoS ₂ -WS ₂		$\sim 3 \mu\text{m}$	Monolayer lateral heterostructure	Self-powered photodetector	[57]
	WS ₂ /MoS ₂	Lateral/Vertical	$\sim 5 \mu\text{m}$	Controllable lateral/vertical growth aspects	<i>p-n</i> junction and photovoltaic effect	[58]
	Mo ₂ C/Graphene	Vertical	Monolayer	Controlled growth of graphene depending on carbon flux	Hydrogen evolution reaction	[59]

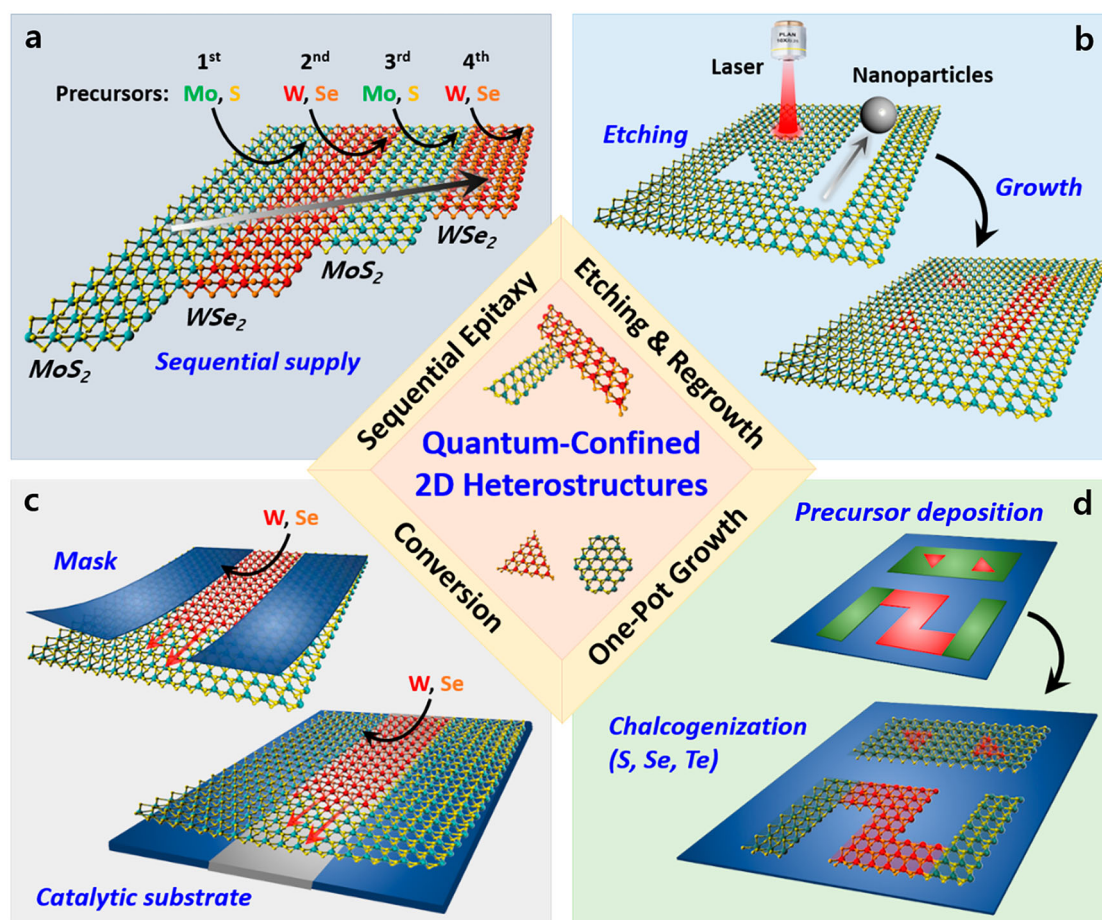


Figure 2. Approaches for spatially controlled growth of 2D quantum heterostructures. (a) Schematic of ‘Sequential epitaxy’ process, in which a new 2D layer is formed either vertically or laterally onto the pre-deposited 2D material by sequentially supplying sources. (b) Schematic of ‘Etching and regrowth’ process, in which a part of a 2D material is etched and then filled with another material via a chemical reaction. (c) Schematic of ‘Conversion’ technique for converting a preformed crystal into another crystal by a source supply during the thermal CVD. (d) Schematic of ‘One-pot growth’ process, showing a growth method that simultaneous growth of 2D heterostructure with different precursors in the same reactor.

By continuously flowing reverse Ar gas during the temperature change process, the high-temperature exposure of the existing monolayer grown on the substrate and the unintentional supply of chemical vapor precursors was minimized. Therefore, this approach allows the realization of lateral heterostructures with spatially-controlled interfaces without interfacial ternary or quaternary alloy regions (Figure 3d). In addition, supplying the source for a few seconds allows the width of the epitaxially grown 2D structure to be controlled on the nanometer scale (Figure 3e), showing the potential to fabricate laterally confined quantum wells or wires (QWs). In addition to the reverse flow scheme, thermally stable growth templates (e.g. multilayer PtTe_2 up to 750°C) can be employed to avoid both thermal decomposition and alloying of preformed 2D crystals, resulting in the growth of high-quality lateral 2D heterostructures [36].

However, modulating the width in the nanoscale range is still challenging because the growth rate is generally

fast and cannot be tuned delicately in the CVD process using powder-precursor vaporization [31]. Therefore, a fine-tunable injection of vapor-phase precursors has been recommended. This has been recently demonstrated for lateral 2D WS_2 - WSe_2 superlattices with coherent hetero-interfaces by utilizing metal-organic (MO) sources [32]. Quantum-confined WSe_2 monolayers down to 15 nm width with a relatively slow growth rate (i.e. 20 nm/min) was achieved and attributed to the significantly reduced flow rate of MO precursors. These advances highlight progress toward applying exceptional control over crystal growth and present a path toward realizing more complex and functional 2D quantum heterostructures.

2.1.2. Vertical vdW epitaxy

As mentioned above, in 2D vertical heterostructures, different atomic layers can be reassembled by vdW interactions with a minimized interfacial chemical bond

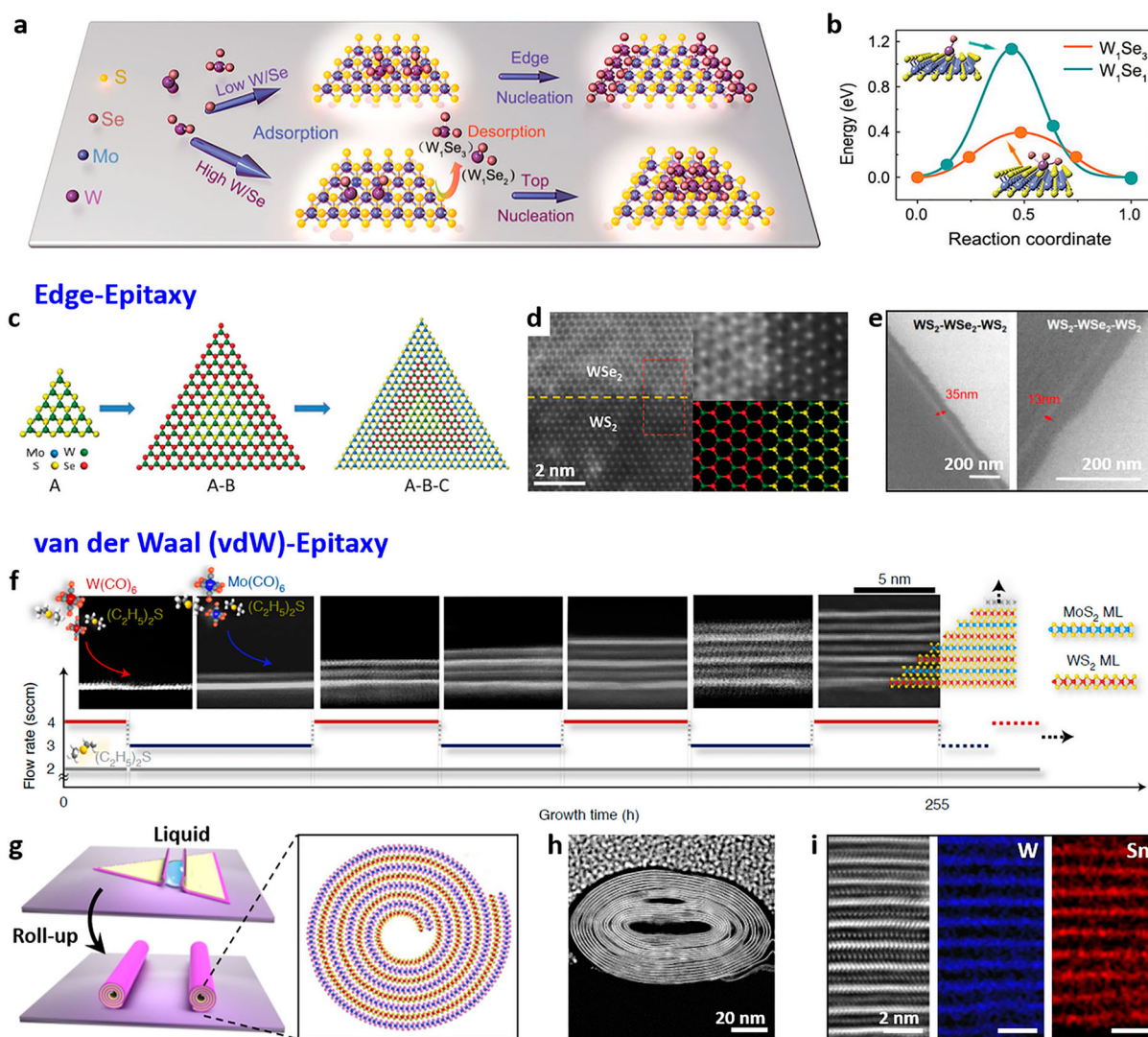


Figure 3. Sequential epitaxial growth of vertical/lateral 2D heterostructures. (a, b) Determination of lateral/vertical growth aspects by the W/Se ratio during the two-step CVD [26]. (a) Schematic of controllable lateral edge-mediated growth and vertical vdW epitaxy of heterostructures composed of MoS_2 and WSe_2 depending on the adsorption of various active clusters of W_1Se_x . (b) The diffusion barriers of W_1Se_3 and W_1Se_1 clusters on the edge/basal surface of the MoS_2 layer. (c-e) Edge-mediated epitaxy of lateral WS_2 - WSe_2 - WS_2 heterostructure [31]. (c) Schematic of the edge-mediated epitaxy of lateral heterostructures. (d) High-resolution scanning transmission electron microscopy (STEM) image of the WS_2 - WSe_2 lateral heterostructure (left). Magnified STEM image of the dashed red rectangle region (top right) and the corresponding atomic model (bottom right). (e) Scanning electron microscopy (SEM) images of the lateral WS_2 - WSe_2 - WS_2 multi-heterojunction with ultra-narrow WSe_2 width (~ 35 and 13 nm) with different growth times (10 and 5 s). (f) vdW epitaxy of vertical MoS_2 / WS_2 heterostructures [37]. Flow-rate modulations of the metal-organic precursors for the growth of (top) and a series of cross-sectional high-angle annular dark field (HAADF)-STEM images of the heterostructures depending on the flow rate (bottom) are shown. (g-i) Capillary force-driven rolling-up strategy for the fabrication of vdW superlattice [39]. (g) Schematic illustration of the fabrication process of roll-up vdW superlattices. (h) STEM image of a rolled-up SnS_2 / WSe_2 heterostructure. (i) STEM image (left) and corresponding energy-dispersive spectroscopy (EDS) mapping images (center: W, right: Sn) of the SnS_2 / WSe_2 vdW superlattice.

between neighboring layers. Therefore, these are often called vdW heterostructures. vdW epitaxial growth mode allows obtaining not only the simple vdW heterostructure with two different 2D materials [26–29,38] but also the multi-heterojunctions by periodic repetition of source supplying during the CVD [37]. Recently, an MOCVD-based growth method using MO precursors ($\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, and $(\text{C}_2\text{H}_5)_2\text{S}$) as precursors has

been reported to fabricate vdW MoS_2 / WS_2 heterostructures (Figure 3f) [37]. They epitaxially grew alternating MoS_2 and WS_2 monolayers on their respective surfaces by individually supplying the MO sources ($\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$) with $(\text{C}_2\text{H}_5)_2\text{S}$ background flow after reaching the growth temperature. The growth order and the number of atomic layers were determined by the corresponding transition metal or chalcogen supply and

the growth time. In addition, the vdW epitaxial growth was possible at a relatively low growth temperature (550 °C) due to the high vapor pressure of MO precursors. Other than MoS₂/WS₂ combination, this scheme can be expanded to TMD heterostructures with a graphene layer (WSe₂/Graphene/WS₂) as well as WS₂/WSe₂ and WSe₂/MoS₂/WS₂ superlattices by selectively injecting other vapor sources [37].

However, the MO precursor for MOCVD typically contains carbon atoms as part of precursor molecules that can cause carbon contamination, resulting in low quality and small domain size of the resulting crystal [60]. Moreover, although the slow growth rate of the MOCVD method is effectively applied to the previously introduced lateral edge-epitaxy growth, the vdW epitaxy growth requires a long time to fill the surface with a large-area monolayer [61]. Alternatively, a capillary force-driven rolling-up strategy has been proposed for producing vdW superlattices using pre-formed vertical vdW heterostructures with two different atomic layers (Figure 3 g) [39]. With this approach, two atomic layers can be stacked vertically at once into vdW superlattices with a more significant number of alternating layers (Figure 3 h, i), extending into heterogeneous structures composed of different types of 2D atomic layers [39]. In addition, 1D vdW heterostructures (or hybrid nanotubes) have recently been realized by the CVD method using single-walled carbon nanotubes (CNT) as a template [62]. This resulted in the epitaxial growth of boron nitride or MoS₂ shells around the CNT core, thus allowing the formation of single-crystalline boron nitride nanotubes and MoS₂ nanotubes. This CVD-based epitaxy can expand the vast experimental space by combining other TMDs, nitrides, and oxides with CNTs [63].

2.2. Etching and regrowth

As the previous section introduced, lateral or vertical heterostructures have been well established with sequential epitaxy growth. However, the production of high-density arrays of the 2D heterostructures with desired positions and dimensions is more practical and desirable for the design of quantum heterostructures. For example, to realize and control the quantum confinement effect within lateral heterostructures, we need to modulate the dimensions of the 2D semiconductors and the spacing between them as desired. Furthermore, the channel and contact dimensions should be scalable for 2D metal–semiconductor heterojunctions for realizing scaled atomically-thin circuits. Therefore, controlling the nucleation site for the second material growth in a two-step CVD technique is critical for the scalable production of quantum-confined heterostructures.

The partial etching of pre-deposited 2D materials followed by the growth of another 2D material (namely, the ‘Etching and Regrowth’ process) is the most widely used technique for the position-selective growth of 2D heterostructures (Figure 4) [64,65]. The key to this method is to etch desirable spots on a prefabricated 2D thin film and then regrowth of different 2D materials from the treated local regions. The nucleation location (i.e. either on the basal or edge surface) can be controlled depending on the growth conditions, such as source concentration and growth temperature. Moreover, the adsorption energy of the precursors on the specific point can be engineered by the etching and surface treatment process on the pre-deposited 2D materials, resulting in lateral [41,44,66] or vertical heterostructures [45,46]. For example, the standard lithography process [64,65] can unintentionally leave significant resist residue on the 2D substrates, becoming random nucleation centers leading to vertical growth. Therefore, residue-free treatments using laser [41,45], focused ion beam (FIB) [46,66], and metal particles [44] have been suggested. In this section, we introduce the approaches for desired growth of heterostructures with an ultraclean interface.

A laser-patterning and an anisotropic thermal etching process have been effectively demonstrated to create periodic monolayer lateral heterostructures [41]. The CVD-grown WS₂ single crystal was first obtained, and then laser irradiations were used to make periodic arrays of point defects. Thermal annealing of the laser-patterned WS₂ produced anisotropic thermal etching, resulting in WS₂ with triangular hole arrays. After that, the holey WS₂ template was employed as an epitaxial template to construct WS₂-WSe₂ mosaic heterostructures (Figure 4a). The preparation of atomically clean edges without residue to decrease random defects for unintentional nucleation is crucial to establishing a clean hetero-interface, which was made feasible by the laser treatment and thermal annealing procedure by preventing random etching. As a result, the monolayer WS₂-WSe₂ mosaic heterostructure array had a uniform, darker contrast in the optical image (Figure 4b), implying that the whole opening region of the triangular holes was filled. This strategy can be expanded to the growth of different heterostructures consisting of WS₂-WSe₂, WS₂-MoS₂, and WSe₂-MoS₂. Although this approach could produce triangular TMD islands at the desired position by laser patterning, the island dimensions were only on a micron scale rather than a nanometer scale, which is not small enough to exhibit quantum confinement of excitons or electrons.

In lateral 2D heterostructures, quantum-confined structures with nanoscale lateral dimensions have been

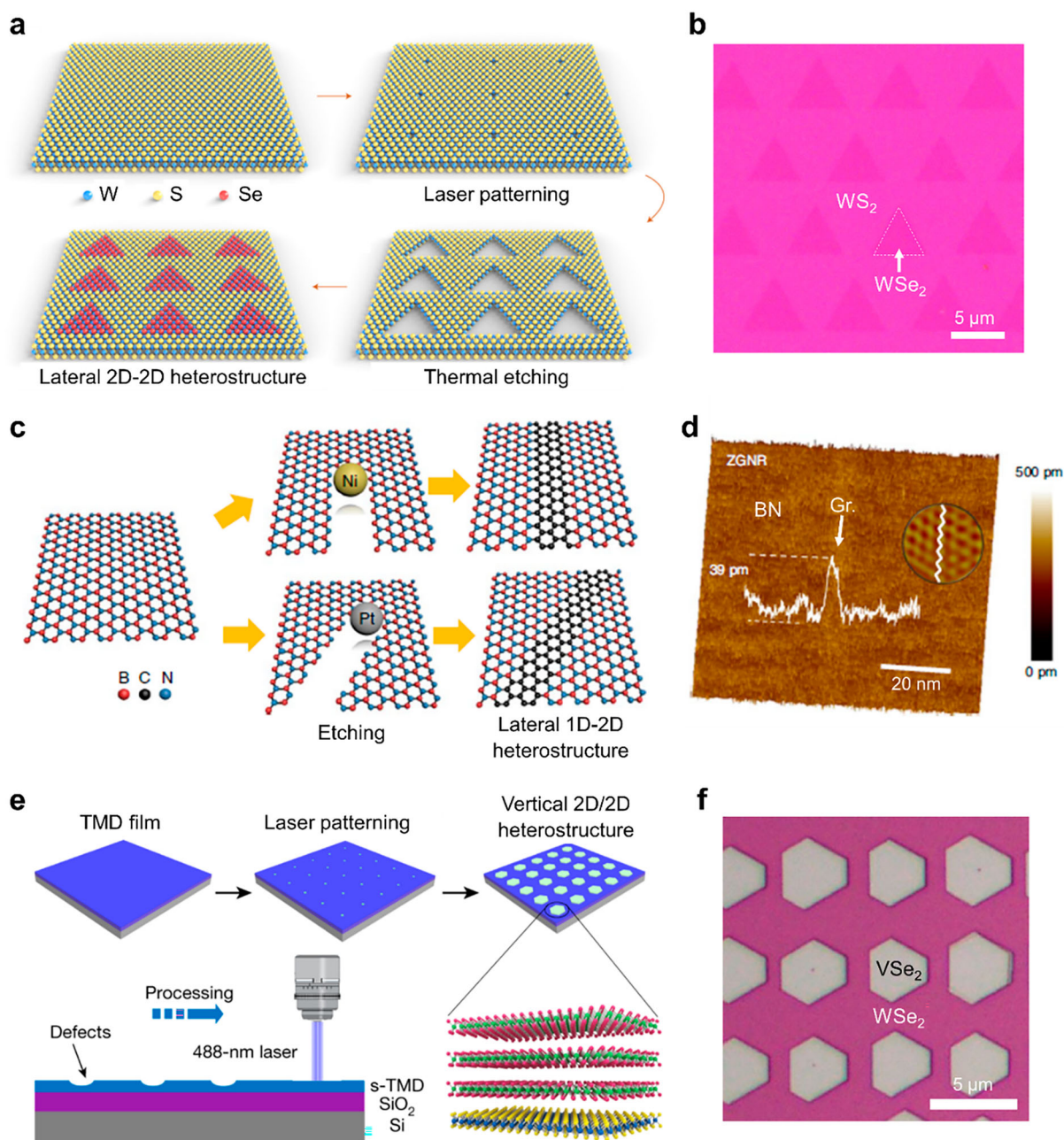


Figure 4. Etching and regrowth process for the production of vertical/lateral 2D heterostructures. (a, b) Synthesis of periodic monolayer 2D heterostructures by laser-patterning and thermal etching process [41]. (a) Schematic illustration of the growth process consists of laser patterning and thermal etching of the pre-deposited WS_2 matrix followed by the growth of WSe_2 . (b) Optical microscopy (OM) image of a lateral heterostructure with WSe_2 crystals embedded in a monolayer WS_2 matrix. (c, d) Synthesis of chirality-controlled graphene nanoribbons (GNR) embedded in hBN [44]. (c) Schematic showing the strategy to prepare GNRs with crystallographic edge orientations. Different particles of Ni or Pt etch nano-trenches with different edge topologies (Ni: zigzag, Pt: armchair) in an hBN layer. (d) AFM image of 1D GNR with zigzag terminations embedded in 2D hBN. (e, f) Vertical growth of VSe_2 on WSe_2 by incomplete etching of the WSe_2 [45]. (e) Schematic of the vertical growth process by laser irradiation. (f) OM image of periodic arrangements of VSe_2 / WSe_2 heterostructure arrays.

realized for the first time by a metal nanoparticle (NP)-catalyzed cutting process [44]. With this approach, chirality-controlled graphene nanoribbons (GNR) embedded in h-BN have been grown successfully using CVD within predefined zigzag or armchair

trenches from metal NP etching in various reports [42,43,44]. For instance, the Ni and Pt particles produced zigzag- and armchair-oriented nano-trenches in the hBN film (Figure 4c) [44]. A subsequent CVD process creates in-plane heterostructures with lattice coherence, that

is, the zigzag- and armchair-edge GNRs embedded in a continuous hBN sheet (Figure 4d). Together with the reduced dimensionality of GNR, its edges are passivated by hBN providing a robust platform to investigate their electrical transport [44]. For example, depending on the zigzag and the armchair edge of GNRs, one can modulate the bandgap opening behaviors as well as their magnetic conductance. Hence, this integration scheme can provide the possibility to design heterostructures consisting of semiconducting GNRs passivated by high-quality insulating substrates for 2D circuits.

In addition to lateral 2D heterostructures, vertical heterostructures can also be formed using the etching and regrowth approach. The incomplete etching of the pre-formed 2D surface to produce defect sites like vacancy clusters, rather than the complete etching of the layers, is the critical factor in inducing vertical layer-by-layer synthesis of 2D materials at the partially etched positions on the 2D substrate. The use of focused ion beam (FIB) processing [46] and laser irradiation [45] have been suggested to control the preferential nucleation sites of 2D domains that are vertically grown, as shown in Figure 4e. In particular, the position-selective nucleation and growth of VSe_2 crystals on large area WSe_2 was successful at the periodically patterned defects array introduced by laser irradiation [45]. The crystal size of VSe_2 can be controlled by adjusting the reaction time, suggesting the controllability of the dimensions of the resultant heterostructure. Furthermore, this method is a universal strategy with the feasibility of fabricating other large-area TMDs heterostructure arrays, such as NiTe_2 , CoTe_2 , NbTe_2 , and VS_2 on WSe_2 as well as VSe_2 on MoS_2 [45].

However, many of the heterostructures formed by ‘etching and regrowth’ have spatially confined features with at least a few micrometers rather than a few nanometers in dimensions [21,25–28]. Therefore, more precise patterning work is still required to reduce the size of heterostructures to realize a quantum-confinement effect. Furthermore, during the ‘etching and regrowth’ process, the large lattice mismatch or unintended polymer-based impurities on the 2D crystal can additionally trigger the vertical growth of the heterostructure [40,47,48]. The graphene and MoS_2 have a large lattice mismatch ($> 28\%$) [40], and the wet transfer process of graphene produces polymer impurities [47,48], which results in the nucleation of MoS_2 on the graphene basal plane. Therefore, the resulting heterostructure possesses vertically overlapped junctions ($\sim 2\text{--}200\text{ nm}$ in width) instead of a pure edge-to-edge connected structure. Recently, the direct preparation of a growth template (e.g. PtTe_2) with a small lattice mismatch with MoS_2 ($< 3\%$) on an arbitrary substrate and without a transfer process [36] has been

suggested for the production of an edge-contact lateral heterostructure of 2D MoS_2 - PtTe_2 with one-monolayer-thick lateral junction interface.

2.3. Post-synthetic conversion

The etching and regrowth approach described above has the benefit of enabling growth of desired 2D heterostructures at a chosen site. However, a delicate treatment for defect formation on the surface of the prepared 2D template is required to regulate the vertical or lateral growth direction. The ‘post-synthetic conversion process’ is a straightforward approach that induces atomic substitution based on the difference in thermal and chemical instability of 2D materials at high temperatures ($> 700^\circ\text{C}$). Several factors can modulate the relative thermodynamic instability, i.e. oxide masking layer [49–51], catalytic substrates [52,53], the thickness of 2D homo-junction [67], and the existence of atomic dislocations [55].

Patterning using a mask laser is a facile process to prepare heterostructures with desired patterns and is almost similar to the lithography process for conventional semiconductor production. After depositing an oxide (e.g. SiO_2 , Al_2O_3) mask layer over the 2D films, the supply of gaseous precursors at elevated temperatures can generate lateral 2D heterostructures in a scalable and controllable way (Figure 5a,b). [49–51]. The exposed regions in the gas precursors are selectively converted to different 2D materials at high temperatures, and in this way, 2D lateral heterostructures such as MoS_2 - MoSe_2 [49], MoS_2 - Mo_2C [50], and graphene-hBN [51] have been fabricated. However, several points must be considered from the thermodynamic perspective in this process. First, since sulfurization occurs at a lower temperature than the selenization, MoSe_2 can be easily converted to MoS_2 , but the reverse reaction is not energetically favorable. In addition, the chemical reaction for the replacement of transition metal is not straightforward because of the high activation energy for the conversion.

In the case of the graphene-hBN heterostructures, the spatially controlled conversion process can be achieved not only on samples with a patterned SiO_2 masking layer [51] but also via a catalytic Pt substrate (Figure 5c) [52,53]. The Pt metal substrate allows the catalytic conversion of hBN to graphene under the CH_4 atmosphere at 1000°C . The high-temperature process triggers the decomposition of CH_4 into carbon and hydrogen, followed by the simultaneous etching of hBN and the growth of graphene. This mask-free approach is beneficial to controlling the heterojunction more strictly because using the SiO_2 mask layer cannot prevent the unintended atomic diffusion underneath the masking

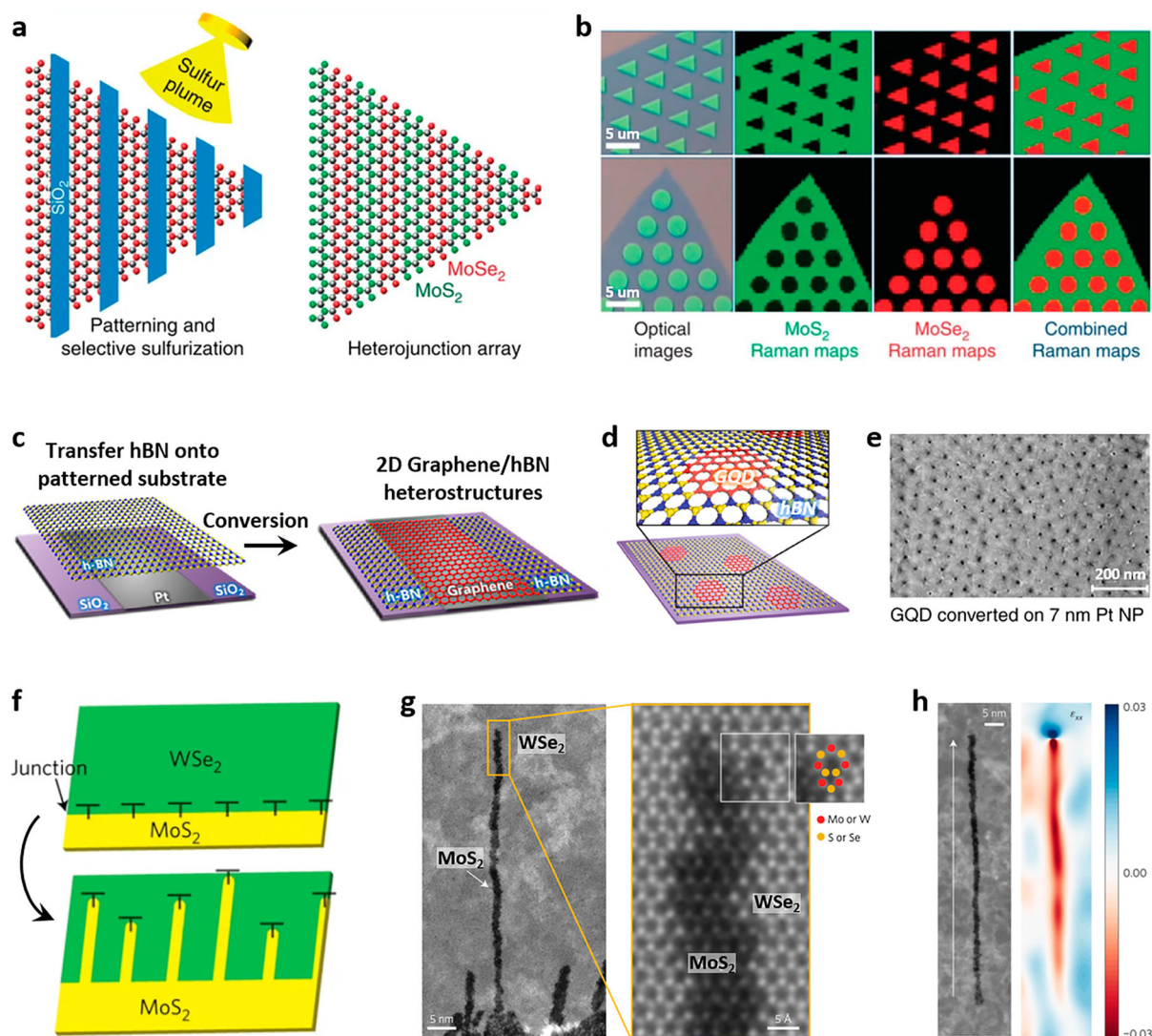


Figure 5. Post-synthetic conversion process to achieve lateral 2D heterostructures. (a, b) Position-controlled conversion of 2D materials for the growth of lateral MoS₂-MoSe₂ heterostructures [49]. (a) Patterning and selective conversion of 2D materials using SiO₂ masking layers for MoSe₂-MoS₂ heterostructures. (b) Raman mappings of MoS₂-MoSe₂ lateral heterojunction arrays formed within monolayer crystals by patterning and selective conversion processes. (c-e) Spatially controlled conversion process from hBN to graphene [52, 53]. (c) Schematic illustrations for the conversion process of hBN on Pt substrate to produce 2D lateral heterostructure of graphene-hBN [52]. (d, e) Schematic (d) and SEM image (e) of graphene quantum dots embedded in the hBN matrix, grown by the selective conversion on an array of the Pt nanoparticles. [53]. (f) Schematic of the patterning process guided by misfit dislocations (marked as 'T') at the MoS₂-WSe₂ lateral heterojunction. (g) STEM images of MoS₂ 1D channels embedded within WSe₂. (h) STEM image (left) and strain map (right) of a MoS₂ 1D channel formed from an intrinsic 5/7 dislocation in WSe₂ [55].

layer during the high-temperature process [52]. Taking advantage of the spatially controllable technique using a catalytic substrate pattern, the same research group recently realized a lateral heterostructure composed of 0D graphene quantum dots embedded in a 2D hBN monolayer utilizing an array of Pt nanoparticles (Figure 5d) [53,54]. The spatial locations and dimensions of graphene quantum dots arrays are determined by the size (7-13 nm) and position of Pt nanoparticles (Figure 5e). Further, the hBN matrix passivates graphene edges to minimize unintentionally formed localized

states, permitting preservation of pristine quantum confinement effects. Further, blue PL emission was also reported in their GQDs/hBN heterostructures, which was observed in samples fabricated under different conditions [54].

Another interesting example of a self-driven conversion reaction is a dislocation-catalyzed approach has been introduced to epitaxially grow 1D nanoribbons of MoS₂ embedded in a 2D WSe₂ matrix [55]. In this process, their lattice mismatch at lateral interfaces introduces misfit dislocations (marked as "T" in Figure 5f), where the

dislocation core exhibits high reactivity to growth precursors. This enables narrow nanoribbons to form behind an advancing dislocation core in the presence of a growth precursor. Although it requires the presence of a significant lattice mismatch at the interface to catalyze the formation of 1D nanoribbons, this method can produce very narrow nanoribbons with a width of a few nanometers or less. Controlling the dislocation spacing allows periodically spaced quantum-confined nanoribbons to be formed as 2D analogs to multilayer superlattices.

2.4. One-pot synthesis approach

This section introduces the one-pot synthesis approach for synthesis of vertical or lateral 2D heterostructures through precursor controls. The simultaneous growth process has the advantage of preventing unintended impurities or poisoning by exposure to the ambient atmosphere that may occur in the two-step CVD methods introduced in the previous sections. The different precursors for two different 2D materials in heterostructures are used for the delicate design of the target crystals. For example, simultaneous integration of metallic 1T'-MoTe₂ and semiconducting 2H-MoTe₂ has been reported by the conversion of two different precursors to MoTe₂ with 2H or 1T' phases during the tellurization process (Figure 6a) [56]. This one-pot synthesis of two different polymorphs allowed the simultaneous construction and the distinctive hexagonal and monoclinic structures of the 2H and 1T' phases at the atomic scale (Figure 6b). The lateral growth of 2D heterostructure is also possible by typical horizontal powder-based CVD, where two different transition-metal-based precursors are used under an S atmosphere for in-plane MoS₂-WS₂ *p-n* junction [57,58]. Probably due to the high vapor pressure of the Mo-based precursor [68], MoS₂ is preferentially formed, followed by the growth of WS₂ [57,58]. In addition, the vertical heterostructures of Mo₂C/graphene can be simultaneously prepared in the molten copper-catalyzed CVD process (Figure 6c) [59]. Using a Mo-Cu alloy catalyst in a CH₄ atmosphere allows the creation of high-quality Mo₂C layers on a graphene monolayer (Figure 6d). Graphene functions as a diffusion barrier to the phase-segregated Mo within the vertical heterostructure, allowing the growth of ultrathin Mo₂C on graphene. This approach is a promising strategy for obtaining superior transport characteristics through the ultraclean heterojunction of 2D vertical or lateral heterostructures. In comparison to the two-step growth procedure, this process requires more effort to be improved, especially concerning the scalability of the process. However, the delicate control of solid/vapor-phase precursors, growth

template, and temperature may facilitate the production of novel 2D quantum heterostructures via this approach.

3. Potential optoelectronic applications

3.1. Light-emitting diodes (LEDs)

The realization of lateral and vertical 2D heterostructures can provide versatile optoelectronic device applications that traditional heterostructures based on bulk materials may not allow with similar functionality. One such application is the LED, which can provide an effective way to probe excitonic optical responses by controlling carrier recombination [69]. Similar to the conventional LED using III-V compound semiconductors of In_xGa_yN, the QW structure fabricated by employing various 2D materials in the vertical heterostructure can perform as LED (Figure 7a) [70]. Multiple 2D materials, e.g. metallic graphene, insulating hBN, and semiconducting monolayer MoS₂, are stacked together for the superlattice of the QW. Due to the strong Coulomb interaction in monolayer MoS₂, the recombination of excitons leads to light emission efficiently at a wavelength from 600 to 700 nm. The hBN inserted between the luminescent MoS₂ and graphene electrodes minimizes the light emission quenching, suggesting that the delicate design of 2D vertical heterostructures will further enhance quantum emission efficiency. Also, appropriate selection of 2D semiconductors in the QW can allow control in the emission wavelength and enhance the emission intensity of the fabricated devices. For further improvement, multiple QW structure can be introduced by vertical vdW epitaxy growth.

Regarding lateral heterostructures, the in-plane *p-n* diode using WSe₂-MoS₂ heterojunction [34,35] with type-I band alignment can also be applied to function as an LED. The strain induced by lattice mismatch causes changes in the band structures of both WSe₂ and MoS₂. Under the misfit strain, the conduction band minimum (CBM) of WSe₂ exhibits downward band bending, whereas that of MoS₂ undergoes upward band bending, while also upshifting the valence band maximum (VBM) of MoS₂ at the heterointerface [15]. Hence, the misfit strain at the heterointerface leads to the conversion of type II to type I band alignment for the light emission, indicating that synthetically obtained heterostructure can modulate the band distributions/alignments [35,69]. Comparably, the localized disorder states can exhibit peculiar electroluminescence in an LED operation, which has been reported at in-plane hBN-graphene heterointerface [54]. Although the practical use of 2D quantum heterostructures in LEDs is still limited for the time being due to their low emission efficiency, the

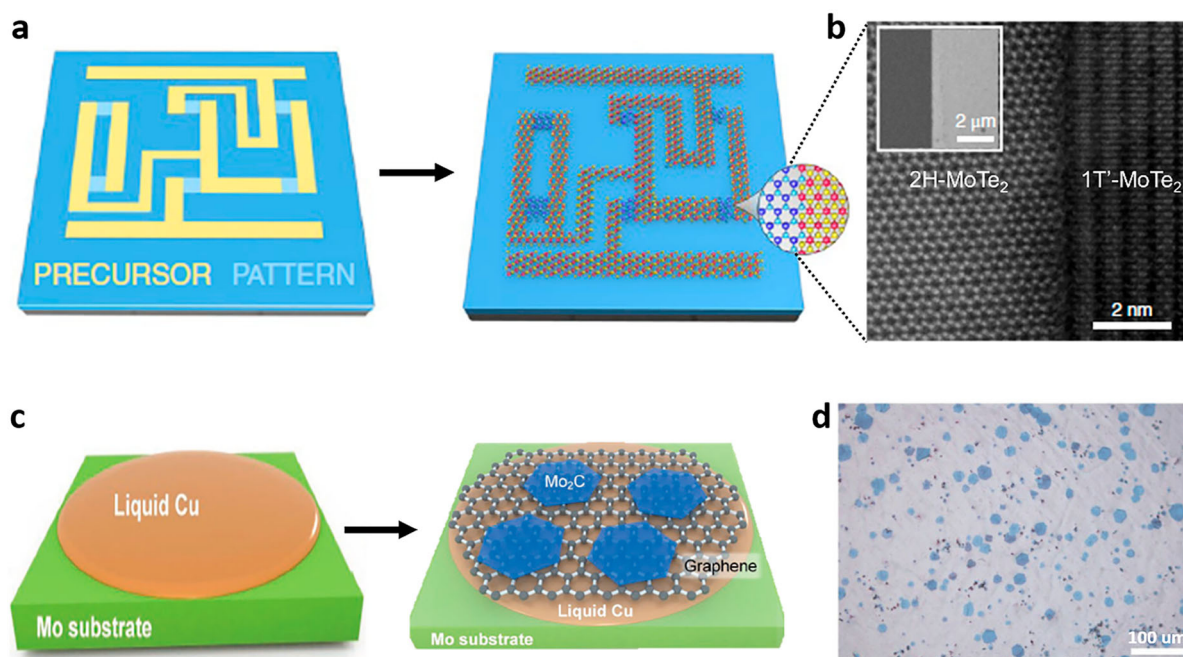


Figure 6. Simultaneous, one-pot synthesis of vertical or lateral 2D heterostructures. (a, b) Simultaneous integration of metallic 1T'-MoTe₂ and semiconducting 2H-MoTe₂ by tellurization of patterned precursors of MoO₃ and MoO_{3-x} [56]. (a) Schematic for the growth of lateral heterostructure of 1T'-2H MoTe₂ heterojunction. (b) STEM image of the heterojunction (inset: SEM image). (c, d) Direct synthesis of vertical 2D Mo₂C/graphene heterostructure using molten Mo-Cu alloy catalyst and high CH₄ concentration during the CVD [59]. (c) Schematic of the growth process, and (d) OM image of Mo₂C crystals on a graphene monolayer.

use of various heterostructures and materials will allow the fabrication of devices with desired properties in the future.

3.2. Photodetectors

Photodetection over a wide range of the electromagnetic spectrum, from UV to IR, has also been achieved in 2D materials based photodetectors with various active layers with different band gaps [38,71]. Specifically, the 2D material-based heterostructures, e.g. 2D *p-n* diodes, can act as a self-powered broadband photodetector because of the effective and fast separation of photo-excited carriers owing to the built-in potential [38]. The CVD-grown 2D vertical heterostructure further allows the enhanced performance of photodetectors because of intense coupling between the two 2D layers and the prevention of contaminants at the heterointerface as compared to their counterparts fabricated by mechanical exfoliation [71]. For example, self-powered broadband photodetectors have been demonstrated based on epitaxially grown vertical WSe₂/Bi₂Te₃ *p-n* heterojunction (Figure 7c) [38]. The synthetic heterojunction-based photodetector also has a low dark current with broadband responsivity, which is promising for highly sensitive photodetection (Figure 7d). Similarly, lateral heterostructures of WS₂-MoS₂ [57] and WSe₂-MoSe₂

[29,33] also offer novel potential for *p-n* junction-based photodetectors.

3.3. Single electron tunneling transistors

Because graphene is a zero-bandgap material, its band gap opening must be performed to fabricate a graphene transistor with a high on-to-off current ratio. Many attempts have been conducted to introduce the bandgap into graphene by tailoring it into quantum structures with lower dimensions (e.g. nanoribbon, constriction, and quantum dots) [16–20]. In addition, based on the low dimensional structures and vdW integration of graphene, the single electron tunneling (SET) transistor can also be realized [72,73].

These SET transistors have also been expanded in TMD materials. Unlike graphene, the inversion symmetry is broken in the semiconducting TMD monolayers. The monolayers with individual valleys in momentum space at points K and K' in the Brillouin region, together with the presence of time-reversal symmetry, facilitates the momentum state of electrons to be used for novel qubit architectures [74–76]. Some theoretical studies have suggested that the spin and valley states of gate-defined quantum dots can be used as quantum bits in 2D TMDs [77,78]. More recently, several groups have experimentally shown the possibilities of realizing SET

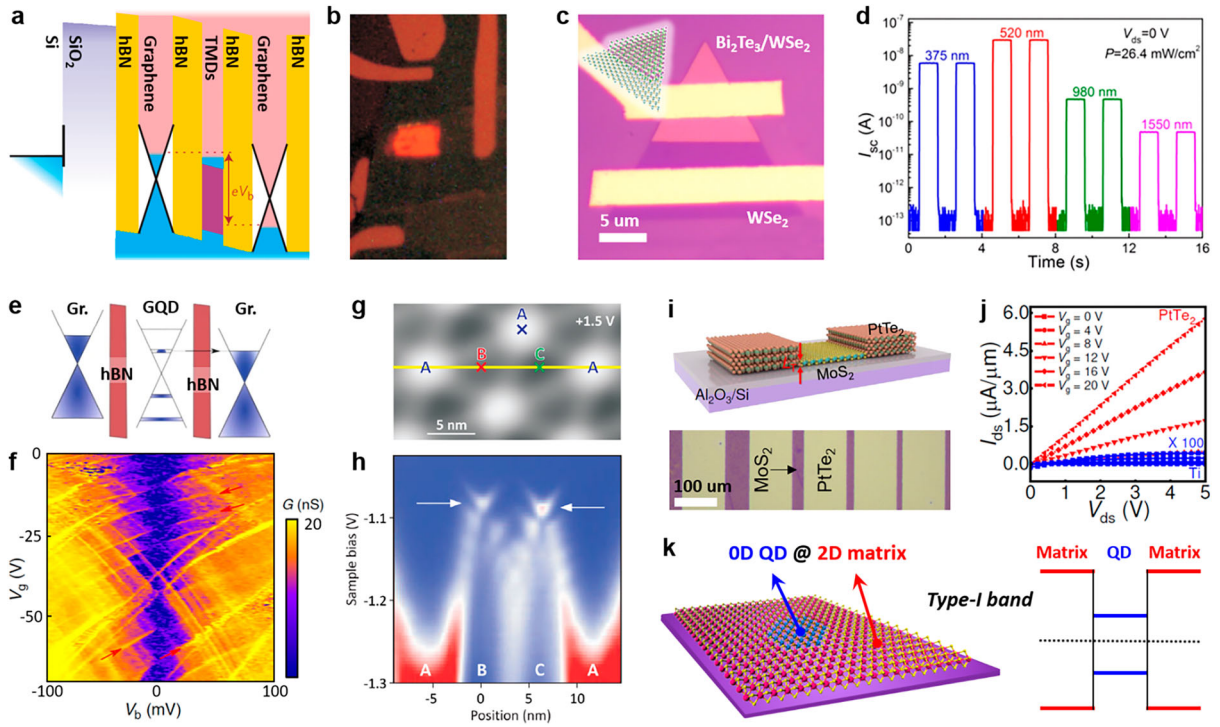


Figure 7. Promising applications of vertical or lateral 2D heterostructures. (a, b) Light-emitting diode (LED) based on vertical heterostructures composed of hBN, graphene, and TMD layers [70]. (a) Schematic of band alignments, and (b) OM image showing the red-light emission from the LED of vdW heterostructure. (c, d) Self-powered photodetector fabricated using *p-n* Bi₂Te₃-WSe₂ heterostructure [38]. (c) OM image of the photodetector, and (d) photoresponse of the corresponding junction device with different light wavelengths (375, 520, 980, and 1550 nm). (e, f) Tunneling transistor application realized by using graphene quantum dots (GQD) embedded in hBN layers [53]. (e) Modeling of the single-electron charging effect. (f) Conductance (G) as a function of V_g and V_b for a device with 10 nm-sized graphene quantum dots (QDs) measured at $T = 0.25$ K. (g, h) Quantum-confined electronic states in MoS₂/WSe₂ heterobilayers [82]. (g) STM image and (h) conductance map taken along the yellow line in (g) for voltages in the valence band-edge region. (i, j) Lateral metal-semiconductor junction (MSJ) comprised of MoS₂ and PtTe₂ synthesized by two-step growth [36]. (i) Schematic (top) and OM image (bottom) of the heterostructure. (j) Output electrical characteristics of MSJ transistor where the carriers are injected from PtTe₂ (red) and Ti (blue). (k) The proposed quantum-confined heterostructure based on 0D QDs and 2D matrix with type-I band alignment, (left) the atomic schematic, and (right) the band structure.

transistors by stacking exfoliated flakes [23–25]. However, studies using 2D monolayers and heterostructures grown over large areas have remained to be conducted, and the large-scale integration is obviously challenging compared with conventional 3D semiconductors.

Recently, research on the SET transistors has been reported, where the device was fabricated using the layer of graphene quantum dots (GQDs) arrays incorporated into a CVD-grown hBN monolayer matrix. The quantum dot array grown by conversion of hBN (discussed in section 2.3) was used as a channel, combined with hBN tunneling barriers and graphene electrodes. In this tunneling transistor, at a small bias voltage between the source and drain was applied, electrons can tunnel through quantum-confined states to create the current flow where the charge can be detected, as shown in Figure 7e. Interestingly, the fabricated GQDs have chemical bonds with insulating hBN, allowing the reduction

of the number of localized states along the quantum dot edge. Such edge-passivated GQDs/hBN heterostructures may open further opportunities for designing lateral QW structures.

The utilization of the quantum-confined states in vdW heterostructures is particularly interesting. The vertical combination of two 2D monolayers can generate new electronic states due to the hybridization of electronic states between the layers. Rotational misalignment between lattices of the same monolayers or lattice mismatch between different monolayers leads to moiré patterns when forming bilayers. Starting with twist graphene bilayers, these patterns have been studied not only in homogeneous hBN and TMD bilayers but also in heterobilayers made with other monolayer combinations, such as graphene/hBN and various TMD/TMD combinations. Quantum-confined electronic states have also been reported in the moiré patterns of MoS₂/WSe₂

heterobilayers on graphene synthesized by CVD. The potential variation in the moiré structures arising from lattice mismatch (3.7%) gives rise to confined states with discrete energy levels that could be studied by scanning tunneling spectroscopy at liquid helium (5 K) temperature. Figure 7 h shows a conductance map along the yellow line (A-B-C-A) across such a moiré unit cell (as indicated in Figure 7 g). Discrete confined states are observed at the AB stacking location (B: AB_W, C: AB_{Se} labeled in Figure 7 g). The significant modulation of band edge positions observed in these 2D heterogeneous bilayers can be utilized as a platform for quantum simulation or forming qubits. However, observing confined states at room temperature is very challenging. More sophisticated work is needed to determine the effects of band-edge shifts and concomitant band-edge states in device applications.

3.4. 2d semimetal-based source/drain in transistors

The conventional preparation of 2D metal-semiconductor junction (MSJ) by deposition of 3D metals (e.g. Ti/Au) on 2D semiconductors typically results in a defect-rich interface because 2D TMDs are vulnerable to the high-energy process that may form glassy layers, vacancies, and voids [45,79]. The defect-induced gap states also pin the Fermi level of MSJ at the shifted charge neutrality; hence, the Schottky barrier height at the MSJ interface cannot be effectively modulated by the selection of 3D metals with different work functions [79]. In contrast, the 2D heterostructures based on 2D (semi-)metal and 2D semiconductors can provide an ultraclean, sharp 2D MSJ interface compared to the conventional 3D/2D MSJ [36,45,47,48,50,56].

In particular, vertically produced 2D/2D heterostructures with metallic VSe₂ and semiconducting WSe₂ allow WSe₂ transistors to have a high current density (Figure 3e, f) [45]. In addition, the lateral MSJ heterostructure consisting of metallic PtTe₂ and semiconducting MoS₂ monolayer can have a sub-1 nm transfer length (L_T) due to its edge-to-edge connected atomically thin interface (Figure 7i) [36]. The reduced dimensionality with fewer interfacial defects can weaken the Fermi-level pinning effect, enabling the reduced Schottky barrier dimensions for high-performance 2D transistors, as indicated by the higher current density of 2D-2D PtTe₂-MoS₂ MSJ higher than that using Ti contact electrodes (Figure 7j) [36]. The synthesized edge-contact MSJ of 1T'-2H MoTe₂ also offers a novel strategy for constructing high-performance transistors. The reported field-effect transistor with edge contact showed higher mobility than that of the MSJ with 3D metal contacts [56].

Furthermore, the use of Dirac material, i.e. graphene, as a source in the 2D transistor has also enabled realization of subthreshold swing values smaller than the thermionic limit (< 60 mV/dec at room temperature), which is known as Dirac-source field-effect transistor [80,81]. The Fermi level of Dirac material can be changed depending on the gate voltages while shifting the contact barrier height between 2D semiconductor (e.g. MoS₂) and Dirac-source (i.e. graphene). Since the transport is still relies on the thermionic emission process, a high on-state current density is possible in the transistor, which promises an innovative approach for low-power and high-performance vdW electronics.

4. Challenges and future outlooks

Spatially controlled 2D heterostructures with new and unique physical properties have been synthesized through various developments in materials engineering, as we presented in the previous sections. The lattice and interlayer spacing mismatch between 2D materials shown in Figure 8 is one of the obstacles in the epitaxial growth of monolithic 2D vertical and lateral heterostructures. Despite different lattice constants and spacings, a strong chemical bond can form a heterojunction between the two materials. However, the large lattice or spacing mismatch leads to numerous mismatch-related defects, such as mismatch dislocations, strain, and interfacial disturbances at the heterointerface. Therefore, one should consider the unit cell sizes of 2D materials for designing defect-free 2D heterostructures.

For more novel fabrication of 2D heterostructures, we also suggest introducing the following strategies or structures. First, for a universal and reproducible production of laterally stitched TMD heterostructures, finding a reliable and compatible processing option is recommended for uniform nucleation. The random nucleation of TMD flakes, typically by a horizontal powder-based CVD approach [83], results in relatively small grain growth of semiconducting layers. The limited nucleation at the edge of TMDs followed by lateral growth may lead to forming of a full-grown coplanar heterostructure with larger grains. In this respect, MOCVD with a minimal growth rate in a vertical reactor [84,85] can be a favorable choice to promote uniform nucleation and layer-by-layer growth for the 2D heterostructures.

Second, finding a way to minimize thermal damage is important during the production of heterostructures in the case of sequential epitaxial growth. During synthesizing the second material by two-step CVD, the pre-deposited 2D material could be degraded thermally, especially under the reducing atmosphere containing H₂, producing a large density of vacancies along

→ Lattice mismatch (%)

Interlayer spacing mismatch (%)

	2D	Gra.	hBN	MoS ₂	MoSe ₂	MoTe ₂	WS ₂	WSe ₂	WTe ₂	PtS ₂	PtSe ₂	PtTe ₂	NbS ₂	NbSe ₂	VS ₂	VSe ₂	HfS ₂	HfSe ₂	ZrS ₂	ZrSe ₂
Gra.		2.46 3.35	1.6	21.9	25.2	30.3	21.9	25.0	29.3	31.3	34.4	39.1	25.9	28.5	23.6	25.9	32.4	34.4	32.8	34.7
hBN		0.4	2.50 3.33	20.6	24.0	29.2	20.6	23.8	28.2	30.2	33.3	28.1	24.7	27.3	22.4	24.7	31.3	33.3	31.7	33.7
MoS ₂		46.5	46.7	3.15 6.25	4.3	10.8	0.2	4.0	9.5	12.0	16.0	22.0	5.1	8.4	2.2	5.1	13.5	16.0	13.9	16.4
MoSe ₂		48.8	49.0	4.3	3.29 6.53	6.8	4.3	0.3	5.5	8.1	12.3	18.6	0.9	4.4	2.1	0.9	9.6	12.3	10.1	12.7
MoTe ₂		52.2	52.4	10.7	6.7	3.53 7.00	10.8	7.1	1.4	1.4	5.9	12.6	5.9	2.5	8.8	5.9	3.0	5.9	3.6	6.4
WS ₂		45.9	46.1	1.1	5.3	11.7	3.15 6.18	4.0	9.5	12.0	16.0	22.0	5.1	8.4	2.2	5.1	13.5	16.0	13.9	16.4
WSe ₂		48.2	48.4	3.2	1.1	7.7	4.3	3.28 6.46	5.7	8.4	12.5	18.8	1.2	4.7	1.8	1.2	9.9	12.5	10.4	13.0
WTe ₂		52.4	52.6	11.1	7.1	0.4	12.1	8.1	3.48 7.03	2.8	7.2	13.9	4.6	1.1	7.5	4.6	4.4	7.2	4.9	7.7
PtS ₂		33.6	33.9	19.4	22.8	28.0	18.4	22.0	28.3	3.58 5.04	4.5	11.4	7.3	3.9	10.1	7.3	1.6	4.5	2.2	5.0
PtSe ₂		34.2	34.4	18.7	22.2	27.4	17.8	21.3	27.7	0.8	3.75 5.08	7.2	11.5	8.3	14.1	11.5	2.9	0.1	2.4	0.5
PtTe ₂		35.9	36.1	16.5	20.1	25.4	15.5	19.2	25.7	3.4	2.7	4.04 5.22	17.8	14.9	20.3	17.8	9.9	7.2	9.4	6.7
NbS ₂		44.3	44.5	4.0	8.1	14.3	2.9	7.1	14.7	16.0	15.3	13.0	3.32 6.0	3.5	3.0	0.3	8.8	11.5	9.3	11.9
NbSe ₂		45.2	45.4	2.4	6.6	12.9	1.3	5.5	13.2	17.4	16.7	14.4	1.6	3.44 6.10	6.4	3.5	5.5	8.3	6.0	8.8
VS ₂		42.3	42.5	7.2	11.2	17.1	6.2	10.2	17.5	13.1	12.4	10.0	3.3	4.9	3.22 5.80	3.0	11.5	14.1	12.0	14.6
VSe ₂		46.0	46.2	0.8	5.1	11.4	0.3	4.0	11.8	18.7	18.1	15.8	3.2	1.6	6.5	3.32 6.20	8.8	11.5	9.3	11.9
HfS ₂		42.7	42.9	6.6	10.6	16.6	5.6	9.6	17.0	13.7	13.0	10.6	2.7	4.3	0.6	5.9	3.64 5.84	2.9	0.5	3.4
HfSe ₂		45.7	45.9	1.5	5.7	12.0	0.4	4.6	12.4	18.2	17.5	15.2	2.6	1.0	5.8	0.7	5.2	3.75 6.16	2.4	0.5
ZrS ₂		42.5	42.7	7.0	11.0	17.0	6.0	10.0	17.3	13.3	12.6	10.2	3.1	4.7	0.2	6.2	0.4	5.6	3.66 5.81	2.9
ZrSe ₂		45.5	45.7	1.8	6.0	12.3	0.7	5.0	12.7	17.9	17.2	15.0	2.2	0.6	5.5	1.0	4.9	0.3	5.3	3.77 6.14

Figure 8. Lattice and interlayer spacing mismatch between TMDs. The values in yellow boxes on the central diagonal represent the lattice constant (top, blue) and interlayer spacing (bottom, red) of the TMDs, respectively. The values in the lower right (blue) and upper left boxes (red) are the lattice and spacing mismatch between each TMD, of which values less than 3% are highlighted. The lattice mismatch was calculated by simply considering the in-plane lattice distances of each unit cell of two materials.

the growth template. Furthermore, this may also lead to the creation of atomically mixed alloys by introducing different atomic species in the second growth step instead of compositionally distinct heterostructures [86]. Considering that thermal degradation typically produces chalcogen vacancies rather than transition-metal vacancies in 2D TMDs [87,88], the growth of TMDs with the same chalcogen atom is better for reducing any chances of forming chalcogen alloys during the two-step CVD (e.g. MoS₂-WS₂ instead of MoS₂-MoSe₂ heterostructures). In addition, single-crystalline 2D materials rather than polycrystalline are more beneficial as a growth template, given their higher thermal stability [87,89].

Third, the minimization of device variability and realization of high-yield processes are much desired to afford a practical technological option. Owing to the ultrathin body of vdW TMDs, even minor mechanical stress during the transfer process can induce various defects, such

as cracks, wrinkles, and ripples at the layer [90,91]. The handling by the polymeric support layer also degrades the TMD layer by leaving behind polymer residues [92]. Additionally, numerous TMDs [93,94] show structural vulnerability against air exposure because humidity and oxygen can readily oxidize their surface. Hence, optimizing the fully automated transfer and device fabrication process under air-free conditions should be adapted for the devices using the quantum heterostructures.

Finally, we would like to note that the type-I lateral heterostructures with quantum-confined superlattice or QW structure have not yet been achieved by CVD methods. Recently, quantum confinement in 2D TMD materials has been investigated for single photon emission based on naturally or artificially occurring defects [95–98]. However, it is necessary to realize deterministic nanoscale exciton confinement in planar structures for better compatibility with microdevices. We propose that 0D TMD quantum confined structures distributed

in a distinct 2D TMD layer can be a viable solution for achieving quantum confinement of excitons in lateral heterostructures, as shown in Figure 7k. To realize quantum confinement of 2D excitons at the nanoscale, the following requirements should be satisfied; (i) precise and deterministic control of quantum dot position and bandgap, (ii) proper band alignment (type-I) between matrixes and quantum dots (Figure 7k, right), and (iii) seamless and defect-free interfaces between quantum dots and matrix material. This heterostructure will provide opportunities for integrating quantum-confined TMDs with conventional optical and optoelectronic devices, such as LEDs, micro-resonators, and high Q cavities. We believe these new approaches will significantly contribute to a breakthrough in quantum photonic technologies for quantum cryptography and communications.

5. Conclusions

This paper reviews the recent advances in spatially-controlled growth of 2D vertical/lateral heterostructures for quantum optoelectronic applications. We first cover the ‘sequential epitaxial growth’ of 2D heterostructures, where the vertical and lateral growth direction of subsequently grown 2D materials may be dominantly determined by the chalcogen-to-metal ratio, growth temperature and defect densities at the preformed 2D crystal. The ‘etching and regrowth’ and ‘post-synthetic conversion’ processes are established for selective control of the nucleation sites for the patterned heterostructures arrays or 1D-like confined heterostructures. The ‘one-pot synthesis’ of 2D heterostructures is possible by using different precursors during the growth at the same time. The spatially controlled 2D lateral/vertical heterostructures can be used in different optical and electrical applications by using their novel physical phenomena or band alignments. In particular, the strain induced by the lattice mismatch could result in the band edge shift, enabling its type-I band alignments of *p-n* diodes for LED. The increased coupling between 2D materials and the ultra-clean interface allows the fabrication of highly efficient photodetectors and low-series resistances at 2D MSJ in transistors. In addition, the confined nanostructures of QW or QDs across the 2D matrix and the lateral heterointerfaces result in new electronic states in these synthetic heterostructures, which may be useful for potential tunneling transistors or quantum photonic applications.

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Disclosure statement

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