TOPICAL REVIEW

Recent advances in the properties and synthesis of bilayer graphene and transition metal dichalcogenides

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Abstract

In the past few years, considerable progress has been made on the controlled synthesis of bilayer van der Waals (vdW) materials such as graphene and transition metal dichalcogenides (TMDs), which are of interest due to their attractive optical and electronic properties. A variety of methods have been developed to synthesize bilayer vdW materials. This review is devoted to recent advances in the properties and synthesis of bilayer graphene (BLG) and TMDs. We emphasize the intriguing properties of BLG and TMDs, depending on their composition, stacking configurations, and twisting angles. The large-scale chemical vapor deposition (CVD) growth of BLG and TMDs with large domain size, high quality, and strong interlayer coupling is highlighted. We then expand the discussion to the current understanding of the growth mechanisms of BLG by CVD and synthetic methods of bilayer TMDs. Finally, the crucial challenges of BLG synthesis and our perspective of the future of bilayer TMDs will be laid out for potential applications of vdW materials.

1. Introduction

Two-dimensional (2D) van der Waals (vdW) materials fabricated by stacking of monolayer ‘building blocks’, such as graphene and transition metal dichalcogenides (TMDs) [1–6], are attracting increasing attention due to their intriguing electronic and optoelectronic properties that can lead to unprecedented advances in the performance of next-generation electronics [7, 8], sensors [9, 10], and optoelectronic devices [11]. These materials have strong in-plane covalent bonding but relatively weak layer-to-layer vdW interactions. For stacks of 2D vdW materials, the number of layers plays a crucial role in the ultimate physical properties [1, 12–14]. In particular, the change in properties from monolayer to bilayer is typically more significant than that resulting from additional layers [15–18]. For example, with one more graphene layer added, bilayer graphene (BLG) exhibits entirely different or an even more abundant array of properties, such as tunable bandgap [19, 20], topologically protected one-dimensional chiral states [21–23], coherent commensurate electronic states [24, 25], van Hove singularities [26–30], Moiré superlattice-induced superconducting, insulating states [31–35], atomic level reconstruction [36, 37], helical edge states [38] and quasicrystals [39, 40]. BLG has prompted significant interest in the fields of condensed matter physics and potential applications in future electronics [41–45]. This wide array of new properties originates from the interlayer coupling between the two graphene layers [31–33, 46], and BLG properties sensitively depend on the stacking configurations and relative twisting angles between the two graphene layers. Scanning tunneling spectroscopy [30, 47], Raman spectroscopy [28, 48, 49], and optical conductivity [50] studies of twisted BLG (tBLG) have provided evidence of intriguing twist angle-dependent electronic and optical properties. In fact, a twist angle as small as 0.1° is sufficient to create an entirely new electronic band structure as compared to its ground state [51].

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Beyond graphene, atomically thin TMDs have become the flagship 2D materials owing to their novel properties arising from their unique band structures [12, 52–54]. 2D TMDs are formed of a transition metal atoms layer sandwiched by two chalcogen atom layers, showing a general formula of MX$_2$ (M = Mo, W; X = S, Se, Te, etc.). The weak vDW interaction in bilayer TMDs keeps the monolayers stacked together while retaining their intrinsic properties. The atomic interaction between stacked single layers gives bilayer TMDs distinctive optical and electronic properties as well as unprecedented phenomena [14, 55–57]. Generally, there are two main types of TMD bilayers: (1) homogeneous bilayers which are composed of two monolayers with the same composition, and (2) heterogeneous bilayers that are formed by stacking two different monolayers, such as MoS$_2$/WS$_2$ vertical heterostructure. Compared to monolayers, homobilayer and multilayer TMDs have higher density of states, carrier mobility, and stability at room temperature, exhibiting superior performance in thin-film transistors, logic devices, and sensors [58–61]. For many TMDs, such as MoS$_2$ and WSe$_2$, the bandgap is direct for monolayer and indirect for the bilayer [62], which leads to a monolayer-bilayer heterojunction with unique optoelectronic properties for potential applications in light-emitting diodes, laser diodes, and solar cells [18, 63, 64]. In heterobilayer TMDs, the stacking of two different monolayers tends to type II band alignment heterostructures, with only a few exceptions forming type I heterostructures [62]. For type II band alignment, the conduction band minimum (CBM) and valence band maximum (VBM) are well retained in their respective layers. Thus, the electron-hole pairs with the lowest energy are spatially separated, rendering an ultrafast charge transfer in the heterobilayers, which is beneficial for the applications in solar energy conversion and optoelectronics [65, 66].

In addition to the compositions of TMDs, the stacking rotation or twist angle between two monolayers is also of great importance for the physical properties of ultimate bilayers. Raman and photoluminescence (PL) spectroscopy measurements of bilayer TMDs demonstrate their optical properties are significantly affected by the twist angles [56, 67]. Similar to BLG, flat bands were observed for small-angle twisted bilayer WSe$_2$ [68–70]. A correlated insulating state appears at half band filling that can be sensitively tuned with the out-of-plane displacement field. The evidence of superconductivity was also observed upon doping away from half-filling [69]. In small-angle twisted heterobilayer TMDs, the experimental evidence of moiré-trapped valley excitons has been widely demonstrated, suggesting their applications in nanophotonics and quantum information [57, 71–73].

To catalyze a wide range of studies of the unexplored physics and potential applications, it is of utmost importance to produce BLG and TMDs with a controllable twisting angle and stacking configurations. For BLG, among the various preparation methods, mechanical exfoliation [19, 20] produces BLG of the highest quality; however, the downside of exfoliation is its low yield that may not be suitable for the scalable production of the devices. Moreover, it often requires a multiple-step transfer process to yield tBLG with a precisely controlled twist angle and stacking order [74–76]. For bilayer TMDs, a variety of preparation approaches have also been developed, including mechanical exfoliation from the bulk [77], post-treatment methods [78], artificial stacking [15], molecular beam epitaxy (MBE) [79], and chemical vapor deposition (CVD) [16, 63]. Again, the direct mechanical exfoliation from the bulk accompanied by a well-developed artificial stacking process has been widely used to create high-quality bilayer TMDs either for fundamental research or for constructing conceptual devices [57, 71–73]. It also shows the strong capability to precisely control the stacking orientation and sequence. However, this method is not compatible with batch production. The trapped interfacial impurities or residue and mechanical damage during the transfer process may seriously modify the properties of the obtained bilayer TMD structures. For example, CVD-grown WS$_2$/MoS$_2$ heterobilayers showed a high mobility ranging from 15 to 34 cm$^2$/V·s, which is much higher than the average mobility of heterobilayers created by artificially stacking (0.51 cm$^2$/V·s$^{-1}$) [80]. This suggests that a clean interface between WS$_2$ and MoS$_2$ is crucial in achieving high-quality device performance. Scalable synthesis of high-quality BLG and TMDs with controlled stacking configuration is thus of critical importance for both academic research and practical applications.

For the past decades, extensive research has been carried out on the synthesis of high-quality graphene and TMD materials using CVD. For graphene, the most noticeable advance is the invention of Cu-based catalytic substrate for the scalable growth of monolayer graphene [81–89]. With a Cu substrate, the CVD process can be surface-mediated rather than the precipitation/segregation on a Ni substrate due to the negligible solubility of carbon in Cu (∼7.4 ± 0.5 at. ppm at 1020 °C [90]), yielding predominantly monolayer graphene with high crystallinity. Single-crystal graphene flakes with lateral dimensions of up to sub-centimeter have been achieved by controlling the nucleation density of graphene in the self-limiting surface-mediated reaction on Cu surfaces [91–93]. In this vein, researchers had modified the self-limiting growth conditions in CVD [94, 95], e.g. reducing cooling rates, increasing carbon supplies, creating Cu pockets, alloying Cu substrates, to yield double or multiple stacks of graphene layers. The as-grown CVD samples were then transferred onto h-BN or SiO$_2$ substrates for transport measurements [96, 97]. Progress has been made toward the growth of BLG in the Bernal-stacked form [98–101]; however, the synthesis of
BLG with controlled crystallinity and stacking configurations remains a significant experimental challenge [102, 103].

For TMDs, CVD has emerged as a reliable method because it not only provides high-quality and scalable bilayer TMDs but also can lead to cleaner interfaces between the layers and more intimate electronic coupling [52, 80]. Several strategies, including both one-step and two-step processes, have been developed to achieve the precise control over the layer number and stacking orientation of obtained TMDs [63, 80, 104, 105]. As a result, a large number of bilayer TMDs, both homo and hetero-bilayers as well as bilayer lateral heterostructures, etc., have been successfully obtained by CVD. Their interesting optical, electronic, as well as optoelectronic properties, have been extensively studied.

So far, a few reviews have appeared on the growth of graphene and TMDs and their applications [1, 13, 52, 53, 106]. However, a comprehensive review focusing on the bilayer form has yet to appear. This topical review endeavors to provide an up-to-date overview of recent progress in the properties and synthesis of BLG and bilayer TMDs. This review is organized to emphasize the intriguing properties of BLG and bilayer TMDs, which depend mostly on their stacking configurations and twisting angles. We will discuss the current understanding of the growth mechanisms of BLG by CVD. The synthetic methods of homo- and hetero-bilayer TMDs will also be discussed in detail. Furthermore, the crucial challenges of BLG synthesis and our perspective of the future of bilayer TMDs will be laid out with an emphasis on their potential applications.

2. Properties of BLG and TMDs

In BLG, two graphene monolayers can be stacked in the AB configuration (Bernal-stacked), the AA configuration (hexagonal on-top stacked), or a twisted configuration (tBLG). The different stacking configurations lead to interlayer hopping and hybridization of the bands that modify the low-energy band structures [107–109], featuring many intriguing emergent properties [110]. When stacked in the AA configuration, BLG displays a massless Dirac spectrum and gapless characteristics under external electric fields that are similar to monolayer graphene [111]. In contrast to monolayer graphene, which exhibits linear, massless dispersion at the Dirac point (figure 1(a)), AB-BLG displays a quadratic band dispersion (figure 1(b)) with massive chiral quasiparticles. The BLG band structure is sensitive to the lattice symmetry, which can be broken with respect to the c axis of AB-BLG [112]. If the individual graphene layers are rendered inequivalent (figure 1(c)), e.g. a perpendicular displacement field, the symmetry will be broken, leading to an energy gap between the low-energy bands. For BLG, an energy bandgap of up to 250–300 meV can be opened (and is tunable) through a perpendicular displacement field induced by doping or gating [19, 75, 76, 113–115]. Ohta et al [113] reported on a tunable bandgap of potassium doped AB-BLG with angle-resolved photoemission spectroscopy (ARPES, figures 1(d)–(f)). The tunable bandgap of AB-BLG was later confirmed with transport measurements, and infrared microspectroscopy (figures 1(g) and (h)) with a dual-gate structure to break the inversion symmetry of AB-BLG [19, 75, 76, 113]; the existence of tunable energy bandgap was evidenced by the increase in the on/off ratio as the strength of the displacement electric field was increased [19, 76].

Semiconducting monolayer TMDs possess a tunable direct bandgap from 80 meV to 2.3 eV, blooming a series of excellent optical, electronic, and optoelectronic properties [116]. The stacking of two monolayer TMDs together changes the bandgap transition from direct to indirect. Using density functional theory (DFT) calculations, it was found that when stacking two layers of the same TMDs, most of the resulting bilayer TMDs exhibit an indirect bandgap (figure 2) [62]. However, when layers of disulfides and diselenides are stacked together, a direct bandgap is possible for the heterobilayer (figures 2(d) and (h)). Liu et al experimentally demonstrated the indirect to direct bandgap transition when thinning the MoS2 crystals to monolayer using PL spectroscopy [67]. Later on, Zhao et al [117] reported differential reflectance and PL spectra of mono- to few-layer WS2 and WSe2 and demonstrated similar indirect-to-direct gap transition when these materials were thinned to monolayers. This bandgap transition behavior gives bilayer TMDs unique optical, electronic, and optoelectronic properties.

2.1. Optical properties

Raman, PL, and absorption spectra are optimum methods to characterize the optical properties of BLG and TMDs since these measurements are efficient, accurate, and nondestructive [28, 48–50, 65]. Ju et al [118] reported on the observation of two prominent excitonic resonances with narrow line widths that are tunable from the mid-infrared to the terahertz range in AB-BLG, allowing the studies of exciton physics with electrically tunable graphene systems. In TMDs, the Raman modes are sensitive to layer interactions. For example, as the layer thickness of MoS2 increases, the E2g mode downshifts and the A1g upshifts [119]. Exfoliated monolayer MoS2 exhibits a difference in mode frequency of $\Delta \omega = 19 \text{ cm}^{-1}$, which increases to...
Figure 1. Electronic structure of (a) monolayer, (b) symmetric bilayer (without doping), and (c) asymmetric bilayer graphene (doped by electric field) [113]. (d)–(f) Evolution of gap closing and reopening of AB-BLG by potassium doping, ARPES (left panel) and theoretical band structures (right panel) of as-prepared AB-BLG without doping (panel d) and with potassium doping (panel e and f). The number at the top of each panel are estimated doping electrons per unit cell. (g) Optical transitions between different sub-bands that are allowed in AB-BLG. Transition I is the tunable bandgap transition that accounts for the gate-induced spectral response at energies lower than 300 meV (see experimental data in panel h). Transitions II, III, IV, and V contribute to the spectral feature near 400 meV. (h) Direct observation of bandgap in AB-BLG with infrared microspectroscopy. Gate-induced absorption spectra of AB-BLG at charge-neutral points in different displacement fields. Absorption peaks associated with the transition I are apparent (dashed black lines) [19]. Reproduced with permission from Zhang et al [19]., copyright 2009, Nature Publishing Group. Reproduced with permission from [113], copyright 2006, American Association for the Advancement of Science.

Figure 2. Side and top view of atomic models showing the structure of (a) monolayer WS$_2$, (b) bilayer WS$_2$ with AA' stacking, (c) bilayer WS$_2$ with AB stacking, and (d) WS$_2$/WSe$_2$ heterobilayer with AA' stacking; Corresponding band structures of (e) monolayer WS$_2$, (f) bilayer WS$_2$ with AA' stacking, (g) bilayer WS$_2$ with AB stacking, and (h) WS$_2$/WSe$_2$ heterobilayer with AA' stacking. Reproduced with permission from Terrones and Terrones [62]., copyright 2013, Cambridge University Press.

20.5 cm$^{-1}$ in bilayers. Similar phenomena have been widely observed for many TMDs, and Raman has been used as an efficient method to distinguish bilayer TMDs from monolayers. PL spectroscopy is widely used to probe the interlayer coupling and charge transfer in bilayer TMDs. When two monolayer TMDs are stacked, a drastic PL quenching is observed due to the efficient interlayer charge transfer. Due to the bandgap transition, some interesting physical phenomena are observed at the 1L-2L interface in bilayer TMDs. Kim et al [120] conducted integrated PL mapping over the 1L and 2L MoS$_2$ regions and observed that the neutral exciton emission was significantly enhanced in the 1L region near the 1L/2L boundary, whereas the negative trion emission remained unchanged. Zhang et al [121] directly observed the type I band alignment for 1L-2L.
MoS₂ reported the ∼ of both femtosecond pump-probe and PL mapping spectroscopy, Hong efficient electron-hole separation resulted from the type II band alignment for heterobilayer TMDs leads to WS₂/WSe₂ stacked MoS₂ created a 1L-2L WSe₂ 1L-2L domains exhibited a diode-like rectification behavior with a rectification ratio of 81 band structure offsets at their interfaces rectification behavior due to the different build-in surface potentials of the monolayer and bilayer TMDs and on/off ratio of transport properties were also observed for heterobilayer TMDs compared to their constituents. Zhang on/off ratio were doubled for the bilayer WSe₂ FETs on both monolayer and bilayer regions from the same bilayer WSe₂ exhibited carrier mobility of field-effect transistors (FETs) based on monolayer and bilayer MoS₂ leads to higher on-current with the same gate bias. Besides, a smaller bandgap in bilayer TMDs creates lower Schottky barrier heights and sheet resistance, which First, bilayer TMDs are less sensitive to the ambient environment due to their less specific surface area. Bilayer TMDs usually shows superior electronic transport properties compared with the monolayer ones. For this 1L-2L WS₂ homojunction, the band offset value of CBM is larger than that of VB, indicating the electron transfer from monolayer to bilayer is more efficient than hole transfer. This charge transfer process makes the PL emission of bilayer WSe₂ from the 1L-2L junction area blue shift by ∼23 meV and ∼31 meV for direct and indirect bandgap emission, respectively, compared with bare WSe₂ bilayers [122].

Unlike the homobilayers, most heterobilayer TMDs tend to form a type II band alignment. Using microbeam x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy/spectroscopy (STM/STS), Chiu et al determined a type II band alignment between MoS₂ and WSe₂ with a valence band offset value of 0.83 eV and a conduction band offset of 0.76 eV [123]. The type II band alignment between MoS₂/WS₂ heterobilayers was also experimentally verified [124]. The unique band profiles and strong interlayer coupling between heterobilayer TMDs lead to optical and optoelectronic properties distinct from those of the component monolayers. Fang et al observed a distinguished PL peak at 1.55 eV for WSe₂/MoS₂ heterobilayers, which is lower than both the excitonic PL peaks at 1.87 and 1.64 eV for monolayer MoS₂ and WSe₂, respectively [125]. Moreover, the absorption spectrum of the heterobilayer material exhibited two absorption peaks at 1.91 and 1.65 eV in accordance with the absorption peaks of monolayer MoS₂ and WSe₂, respectively. A prominent shift of 0.10 meV was observed between the absorbance and PL peaks, which confirmed the type II band alignment [125]. Tongay et al [126] tuned the interlayer coupling between stacked MoS₂ and WS₂ by thermal annealing. During the annealing process, a new PL peak at 1.94 eV distinct from that of monolayer MoS₂ and WS₂ appeared and became stronger. The PL peaks for MoS₂ and WS₂ gradually decreased during the process and were barely observable after 12 h of annealing. The highly efficient electron-hole separation resulted from the type II band alignment for heterobilayer TMDs leads to an ultrafast interlayer charge transfer, which is beneficial for light harvesting and detecting. By employing both femtosecond pump-probe and PL mapping spectroscopy, Hong et al observed the ultrafast charge transfer in photo-excited MoS₂/WS₂ heterobilayers [66]. They determined a hole transfer time of 0.5 fs from MoS₂ to WS₂ layer, which results in dramatical quenching effect of PL spectrum at the heterojunction. A similar phenomenon was also observed for MoS₂/WSe₂ heterobilayers, in which the ultrafast electron transfer from WSe₂ to MoS₂ take place within 470 fs upon optical excitation [127]. By exploiting the ultrafast charge transfer process that creates resident holes in the WS₂ layer, Kim et al [128] observed a valley-polarized hole population lifetime of more than 1 ms and a valley depolarization lifetime of more than 40 ms at 10 K in WSe₂/MoS₂ heterobilayers.

2.2. Electronic properties

Bilayer TMDs usually shows superior electronic transport properties compared with the monolayer ones. First, bilayer TMDs are less sensitive to the ambient environment due to their less specific surface area. Besides, a smaller bandgap in bilayer TMDs creates lower Schottky barrier heights and sheet resistance, which leads to higher on-current with the same gate bias [129]. Fang et al compared the performance of back-gated field-effect transistors (FETs) based on monolayer and bilayer MoS₂ channels [129]. The bilayer MoS₂ FET exhibited carrier mobility of ∼21 cm² V⁻¹ S⁻¹ and an on-current of ∼22 μA μm⁻¹, much higher than that of ∼5 cm² V⁻¹ S⁻¹ and ∼5 μA μm⁻¹, respectively, for monolayer MoS₂ FET. Mandym et al [63] fabricated FETs on both monolayer and bilayer regions from the same bilayer WS₂ flake. Both the carrier mobility and on/off ratio were doubled for the bilayer WSe₂ compared to that of monolayer region. Superior electronic transport properties were also observed for heterobilayer TMDs compared to their constituents. Zhang et al characterize the transfer properties of a MoS₂/WS₂ heterobilayer at room temperature in vacuum [130]. An on/off ratio of 10³ and a mobility of ∼30 cm² V⁻¹ S⁻¹ were measured, which was about five times higher than the FET made on monolayer MoS₂ and much higher than bilayer MoS₂. Similar phenomena were also observed by the Ajayan group using heterobilayer WS₂/MoS₂ from a different synthesis method [80].

The 1L-2L TMD junctions have been widely reported to form p-n diodes with obvious current rectification behavior due to the different build-in surface potentials of the monolayer and bilayer TMDs and band structure offsets at their interfaces [18, 64, 131], In CVD-grown MoS₂ flakes, He et al found that the 1L-2L domains exhibited a diode-like rectification behavior with a rectification ratio of 81 [18]. Xu et al created a 1L-2L WSe₂ junction by Ar Plasma thinning method and demonstrated their ideal p-n type band diagrams, which afforded a rectifying behavior with ideality factors of ∼20 [131]. The Johnson group also reported the p-n diode-like behavior for 1L-2L WSe₂ junctions on CVD-grown bilayer WSe₂ flakes, which yielded a rectification ratio of 13.5. For heterobilayer TMDs, p-n diode junctions can be easily formed by stacking n- and p-type monolayer TMDs together [63]. Lee et al created a p-n interface by stacking n-type MoS₂ on p-type WSe₂ and observed gate tunable diode-like current rectification and a photovoltaic response [132]. The formation of p-n diode junctions in bilayer TMDs motivates their potential applications in
photodetectors and solar energy harvesting. For example, Xu et al reported a highly efficient photodetector based on the 1L–2L WSe$_2$ junction. The photoresponsivity of the device was over 32 000 times higher than that of 1L WSe$_2$ based device and 4 times higher than the bilayer-based device, which leads to a high external quantum efficiency of 256% due to the efficient carrier extraction [131].

In AB-BLG, the tunable energy bandgap has been confirmed experimentally by transport measurements [19, 75, 76, 113–115]. Moreover, one graphene layer can shift by an atomic spacing with respect to the other layer, resulting in multiple stacking domains separated by soliton-like structural boundaries also known as layer stacking domain walls. Such an AB-BA (AB-AC [133]) domain wall features one-dimensional valley-polarized conducting channels and topologically protected one-dimensional chiral states (figure 4(f)) [21, 22, 134–136] that can be identified by DFTEM [96, 133, 137, 138] (figures 3(a) and (b)) and infrared near field scanning microscopy (IR-SNOM) [21, 22, 139]. Unlike single-domain AB-BLG with the gapped insulating state under a perpendicular electrical field, AB-BA domain walls in BLG display one-dimensional ballistic conducting channels (figure 3(e)), which can open up a new path for the studies of tunable topological phases and valley physics in graphene [21, 23, 140].

2.3. Effect of twist angle

Equally fascinating effects can be obtained by stacking one layer of graphene or TMDs on top of another and rotating them by a relative angle [141–143]. For bilayer vdW materials with a twist angle, the different lattice vectors between the two monolayers can lead to the formation of the superlattice, and the electrons in the system will feel an additional potential known as the moiré periodic potential. The moiré periodic potential and enhanced interlayer electronic coupling not only tune the intrinsic behavior of the component layers, but also bring many novel physical properties appearing at the interface [144]. These two mechanisms provide us with a new approach to engineering the properties of 2D bilayer materials by tuning the interfacial twist angle. The resulting periodic moiré pattern (figure 4(a)) leads to localized electronic wave functions [145] and one-dimensional topological channels in gapped AB-BLG [146]. Near the magic angle $\theta \approx 1.05^\circ$, electron–electron interactions strongly modify the low-energy band of tBLG, and the bands become highly non-dispersive and flat [109, 147], displaying unconventional superconductivity and correlated insulating states (figures 4(b)–(g)) [31, 107, 109, 148–150].

The electronic properties of tBLG with large angles, i.e. $>20^\circ$, are often indistinguishable from that of monolayer graphene. However, Ahn et al [39] recently reported on the quasicrystal $30^\circ$ tBLG that can form a 12-fold order with relativistic Dirac fermions (figures 5(a)–(c)). The platform of $30^\circ$ tBLG is expected to catalyze studies of various unsolved issues in anomalous physical properties of quasicrystals [151–155]. However, to date, the interlayer coupling of the $30^\circ$ tBLG has not yet been confirmed experimentally in the transport measurements [156].

Liu et al found that the indirect bandgap size of bilayer MoS$_2$ varied with the stacking twist angle. It showed the most significant redshift for AA' ($60^\circ$ twist) and AB ($0^\circ$ twist) stacking and a significantly smaller but constant redshift for all other twist angles [67]. Huang et al probed the interlayer coupling of twisted bilayer MoS$_2$ using PL spectroscopy. It was found that the PL intensity ratio of the trion and exciton reached a maximum value for twist angle $0^\circ$ or $60^\circ$ and the minimum value was observed for twist angle $30^\circ$ [55]. In another report, the same group used low-frequency interlayer Raman modes to probe the interface of twisted bilayer MoS$_2$ [157]. They found the notable frequency and intensity changes of low-frequency modes upon twisting. The frequency variation can be up to 8 cm$^{-1}$ and the intensity can vary by a factor of $\sim 5$ for twisting angles near $0^\circ$ and $60^\circ$ due to the high-symmetry stacking patterns. For twisting angles between $20^\circ$ and $40^\circ$, the interlayer coupling is nearly constant because of the mismatched lattices. The shear mode disappears near $30^\circ$, as the in-plane shear motion leads to almost no restoring force from the mismatched stacking and its frequency is close to zero. Xia et al demonstrated the distinct Raman and PL properties for CVD grown AA' and AB stacked bilayer MoS$_2$ [56]. A noticeable peak at 395 cm$^{-1}$ appears in AA' stacked bilayer MoS$_2$ resonance Raman spectra but not in the AB stacked bilayer. For PL spectra, a blue shift of the peak around 1.5 eV for AA' stacked bilayer, which represents the indirect bandgap transition, by $0.056 \pm 0.017$ eV over that of AB stacked bilayer was observed (figures 6(a)–(c)). The different energy band structure for bilayer TMDs with different twist angles may result in some discrepancy in their electronic transport property. For example, measurements conducted by Zhang et al reveals that the AA' stacking bilayer MoS$_2$ exhibit high mobility values ranging from 38 to 75 cm$^2$ V$^{-1}$ s$^{-1}$. In contrast, the AB stacking ones show much lower mobility values in the range of 1–7 cm$^2$ V$^{-1}$ s$^{-1}$ [104].

Twist-angle dependent physical properties are also frequently observed for heterobilayer TMDs. Nayak et al investigated twist-angle-dependent interlayer exciton evolution in artificially stacked CVD-grown MoSe$_2$/WSe$_2$ heterobilayers by PL spectroscopy [158]. They observed the strongest interlayer excitonic emission for twist angles of $0^\circ$ and $60^\circ$, which weakens for angles close to $0^\circ$ and $60^\circ$ and disappears for intermediate angles ($10^\circ$–$50^\circ$) (figures 6(d)–(f)). The excitonic absorption in heterobilayer MoS$_2$/WSe$_2$ with
Figure 3. (a, b) DFTEM images of AB-BA domain wall taken over 35 min. The domain walls fluctuate by as much as 20 nm, as indicated by the arrows [137]. (c) AFM topography image of an exfoliated BLG on a SiO$_2$/Si substrate, showing no surface wrinkles or defects. (d) IR-SNOM image of the same BLG sample as in panel b. The bright lines are absent in the topography image, which arises from the AB-BA domain walls in BLG. (e) Resistances at charge neutral point as a function of displacement field for BLG with no domain wall (NDW, solid black squares) and for BLG with a domain wall (DW, red solid circles). The lower saturation of the resistance at the region of high displacement field is due to the 1D conducting channels at the domain wall of BLG [21]. (f) Propagating chiral boundary modes (red) near the K (Upper) and K’ (Lower) points [136]. Reproduced with permission from Ju et al [21]., copyright 2015, Nature Publishing. Reproduced with permission from Zhang et al [136] and Alden et al [137]., copyright 2013, National Academy of Sciences of the United States of America.

Figure 4. (a) TEM dark-field images showing moiré patterns of tBLG with a series of controlled twist angles. The triangle-shaped domains are associated with the antisymmetric shift of the lattice period in AB and BA domains [146]. Reproduced with permission from Yoo et al [146]., copyright 2019, Springer Nature. (b, c) Schematic of a tBLG device and moiré pattern of the tBLG with a twisted angle of $\theta$ [31]. Reproduced with permission from Cao et al [31]., copyright 2018, Springer Nature. (d) Electronic structure of the magic-angle tBLG with a flat band near the charge neutrality point [32]. (e) Conductance-carrier density characteristics of a magic-angle tBLG device ($\theta = 1.16^\circ$). The curves exhibit insulating states at the superlattice bandgaps (blue and red bars). Near a filling of $-2$ electrons per unit cell, there is considerable conductance enhancement at zero field that is suppressed in $B_{\perp} = 0.4$ T, indicating superconductivity. (f) Four-probe resistance $R_{xx}$-carrier density characteristics of tBLG sample with $\theta = 1.16^\circ$. There are two superconducting domes observed next to the half-filling state, which is labelled ‘Mott’. The remaining regions in the diagram are labelled as ‘metal’ owing to the metallic temperature dependence [32]. (g) tBLG device with $\theta = 1.05^\circ$ shows two asymmetric and overlapping superconducting domes [32]. Reproduced with permission Cao et al [32]., copyright 2018, Springer Nature.

varied twist angles was investigated by Gogoi et al using electron energy loss spectroscopy. The results
Z Gao

is the electron momentum across the K points.

and 60° tBLG. k_{32} to 5.1°71 moiré (a) The false-colored TEM image of 30° twist, the evidence of superconductivity is observed lifetime of many microseconds was measured, orders of magnitude longer than that and WSe_{2} to 4° twist angles than in the 30° point were magnified by 100 (white dash circle), and the intensity of the Dirac cone at the K point was reduced by half. (c) Energy-momentum dispersions of Dirac cones at the K points of the upper- and lower-layer graphene of the 30° tBLG. k_{y} is the electron momentum across the K points. Reproduced with permission from Ahn et al [39], copyright 2018, American Association for the Advancement of Science.

showed that the interlayer charge transfer rates can be an order of magnitude faster in heterobilayers with 0° and 60° twist angles than in the 30°-twisted samples [159].

It is interesting to notice that the flat band properties, similar to tBLG about a ‘magic angle’, are also observed in small-angle twisted bilayer TMDs. Wang et al first reported the flat band properties for twisted bilayer WSe_{2} [70]. Unlike tBLG, there is no ‘magic angle’ for bilayer WSe_{2}, but a continuum of angles spanning 4° to 5.1°. In this range, a correlated insulating state appears at half band filling that can be sensitively tuned with the displacement field. At 5.1° twist, the evidence of superconductivity is observed upon doping away from half-filling. Similar phenomena were also observed by the LeRoy and Wang groups, with a reported twist angles ranging from 1° to 4° [68, 69]. For WSe_{2}/WS_{2} heterobilayers, when the twist angle is near zero, a correlated insulating state at one hole per superlattice site and surprising insulating phases at 1/3 and 2/3 filling of the superlattice are detected [160]. In the correlated insulating state, a very long spin reconstruction lifetime of many microseconds was measured, orders of magnitude longer than that of charge excitations [160]. Similarly, Tang et al [161] reported on the observation of a correlated insulating state with antiferromagnetic Curie–Weiss behavior. At half-filling of the first hole WSe_{2}/WS_{2} moiré superlattice band. Above half-filling, a possible quantum phase transition from an antiferromagnetic to a weak ferromagnetic state at filling factors near 0.6 was demonstrated.

In small-angle twisted heterobilayer TMDs, the moiré periodic potential could also result in notable effects on optical excitations. Seyler et al reported experimental evidence of interlayer valley excitons trapped in a moiré potential in MoSe_{2}/WSe_{2} heterobilayers, when the twist angle approaching 0° and 60° [72]. Such moiré excitons are also widely observed in other heterobilayer TMDs with a small twist angle (<2°), including MoSe_{2}/WS_{2} and WSe_{2}/WS_{2} [57, 71, 73]. These moiré exciton states manifest as multiple emergent peaks around the original TMD A exciton resonance in the absorption spectra. They also exhibit gate dependences that are distinct from that of the A exciton in TMD monolayers and in heterobilayers with large twist angles. When the twist angles go even smaller (≤1°), significant atomic level reconstruction in heterobilayer TMDs, such as MoSe_{2}/WSe_{2} and MoS_{2}/WS_{2}. This leads to discrete commensurate domains divided by narrow domain walls rather than a smoothly varying rigid-lattice moiré pattern. Such atomic level reconstruction can be expected to have a significant impact on the band structure and properties of bilayer TMDs [162].

3. Synthesis of BLG

3.1. Artificial stacking

Mechanical exfoliation is the most reliable approach to produce high-quality BLG. BLG can be distinguished from monolayer graphene using optical characterization (figures 7(a) and (b)). Based on the exfoliated graphene, a ‘tear and stack’ technique (figure 7(c)) was developed with hBN substrates to create the twisted BLG, e.g. magic angle tBLG, which led to the discovery of unconventional superconductivity and correlated insulating states in tBLG superlattices that is one of the most significant discoveries since the first isolation of graphene [31, 32, 150, 163, 164].

Despite the high quality of the resulting BLG devices, the artificial stacking method based on exfoliated monolayer graphene is not scalable, thus limiting both scientific research and potential applications. To
obtain BLG in a large scale, Brown et al [165] developed a transfer and stacking method based on CVD graphene grown on a Cu (111) substrate. Nguyen et al [166] developed a stacking approach based on single-crystalline graphene grown on Cu (111) for the fabrication of wafer-scale AB-BLG devices. Manual stacking of two large-area graphene sheets is promising to achieve scalable production of BLG transistors, but often involves complicated processing and easily introduces undesirable charged impurities in between the graphene layers, which degrades the electronic performance.

3.2. CVD of BLG
The downside of mechanical exfoliation is the relatively low yield and the challenges to produce contamination-free BLG devices in a reliable and scalable way, which can catalyze a wide range of studies of the physics and applications of this material systems. Large-scale BLG has been synthesized by thermal graphitization of SiC substrate [167–172]. Although a rich array of physical properties such as rotational stacking faults [167], Shubnikov–de Hass oscillations [170], width-dependent edge disorders [171], and opening of the energy band gap [168] have been reported for SiC-grown BLG, the precise control of BLG layer number over large area was found to be challenging due to the presence of vicinal steps of the SiC substrate [173] and the non-self-limiting decomposition of SiC [172]. Moreover, the strong adhesion
between graphene and SiC poses significant challenges to transfer the as-grown BLG onto a dielectric substrate [173].

Extensive research has been carried out on CVD synthesis of high-quality BLG over metallic substrates (figure 8) [95, 98–101, 174–179], which is emerging as a promising technique for the synthesis of high-quality BLG and few-layer graphene on a large scale (table 1), such as Ni [176], Cu [81], Ir [180], and their alloys. Though progress has been made towards the growth of BLG, the synthesis of BLG with large crystalline domains remains a significant experimental challenge. To date, the growth of crystalline BLG is mainly based on two strategies: segregate/precipitation growth on Ni-based substrates and surface-mediated growth on Cu-based substrates. The following discussion covers the graphene growth on Cu, Ni, and their alloy substrates.

3.2.1. Ni-based substrates and precipitation growth mechanism
Ni is long known for its relatively high carbon solubility (\(\sim 2\) at.% at 1000 °C [197]) and has been used for the segregation growth of carbon nanotubes [198, 199]. With Ni thin films or Ni foils, carbon species first dissolve into the bulk metal at high temperature and precipitate out to form graphene crystals on Ni surface during the cooling process [176, 177, 200–202]. Yu et al. [203] reported that higher cooling rates benefited graphene growth, while no graphene growth was observed at a low cooling rate. However, it can be

Figure 7. Optical image of (a) monolayer graphene and (b) BLG on a SiO\(_2\)/Si substrate. The scale bars are 20 \(\mu\)m [27]. Reproduced with permission from Wang et al. [27], copyright 2008, American Association for the Advancement of Science. (c) Schematic showing the rotationally aligned tBLG realized by using a hemispherical handle substrate. (d–h) Schematics showing the hBN based ‘tear and stack’ technique for the production of tBLG devices. The red boxes are zoom-in views of the hemispherical handle substrate. (i–k) The corresponding optical images of successive stacking steps [27, 163]. Reproduced with permission from Kim et al. [163], copyright 2016, American Chemical Society.

Figure 8. (a) CVD furnace for BLG growth, (b) as-grown BLG flakes using CVD [181]. Reproduced with permission from Fang et al. [181], copyright 2014, American Chemical Society.
Table 1. BLG growth conditions.

| Carbon precursors | Growth substrates | Method | Temp. °C | Pressure | Flow ratio | Growth duration | Layer number | Ref. |
|-------------------|-------------------|--------|----------|----------|------------|----------------|--------------|------|
| CH₄               | Rhodium (1 1 1) foil Thickness = 25 µm | CVD     | 1000     | 1 atm    | Ar/H₂/CH₄ = 200/50/12 | 10 min | Multilayer     | [182]|
| C₂H₂              | Ni foil Thickness = 25 µm | TCVD    | 600      | 133.3 pa | C₂H₂/H₂ = 12/2 | Few layers | [183]|
| C₂H₂              | Cu foil Thickness = 25 µm | APCVD   | 1000     | 1 atm    | C₂H₂/H₂/Ar = 1/100/90 | 10 min | Bilayer       | [184]|
| C₂H₅OH            | Stainless steel Thickness = 0.1 mm size (1 x 1) cm | Direct TCVD | 850      | 1 atm    | H₂/Ar = 100/1000 | Bilayer     | [185]|
| C₂H₁₂             | Cu Thickness = 50 µm | APCVD   | 900      | 1 atm    | H₂/Ar = 10/1000 | 30 min | Mono, bi- and few layers | [186]|
| Refined cooking palm oil | Ni, thickness = 100 µm | CVD     | 900      | 1 atm    | H₂/Ar = 200/50 | 15 s   | Mono and bi-layer | [187]|
| PMMA, high impact polystyrene, ABS | Cu foil, thickness = 25 µm | APCVD   | 1000     | 1 atm    | CH₄/H₂ = 20-100/50-600 | Bilayer | [188]|
| Lotus, Hibiscus flower foil | Ni nanoparticle | CVD     | 1600     | Vacuum   |           | 30 min | Multilayer, monolayer graphene Ni decorated | [189]|
| Camphor           | Ni foil           | APCVD   | 1020     | 1 atm    |             |             | Mono, bilayer | [190]|
| CH₄               | Cu foil Thickness = 25 µm | LPCVD   | 1050     | 20 mTorr | CH₄/H₂ = 4/2666 | 10 min | Multilayer, AB-staked bilayer | [191]|
| Ethanol           | Cu foil           | ACCVD   | 1065     | 450 pa   |             | 20–22 h | Bilayer       | [192]|
| CH₄               | Cu foil           | APCVD   | 1080     |          |             | 40 min  | Bilayer       | [193]|
| CH₄               | Cu foil           | CVD     | 1050     |          | CH₄/H₂ = 1.5/50 | 1 h    | Bilayer       | [194]|
| CH₄               | Cu foil, Thickness = (2 x 2) inch | CVD     | 1035     | 5 x 10⁻² torr |             | 15 min | Single crystal bilayer | [195]|
| CH₄               | Cu foil, Thickness = 25 µm | LPCVD   | 1070     | 10 mTorr | H₂/CH₄ = 1320/8800 | 25 min | Bilayer and bilayer graphene | [196]|
| CH₄               | Cu foil, thickness = 100 µm | APCVD   | 1060     |          | H₂/CH₄/Ar = 50-350/1-90/1000 | 4 min | Bilayer, tri-layer, and multilayer graphene | [197]|
| CH₄               | Ni film, thickness = (200 x 200) µm | CVD     | 1000     |          | H₂/CH₄/Ar = 65/23/200 | 20 min | Bilayer       | [198]|
| CH₄               | Cu/Ni foil (3 x 5) cm² | CVD     | 1050     | ~0.3 Torr |             | 10–20 min | Bilayer and Trilayer | [199]|
| Coronene          | Cu foil, Thickness = 25 µm, (1 x 1) cm | APCVD   | 1000     |          |             | 30 min  | Bilayer and monolayer | [200]|
| Ethanol           | Cu foil, thickness = 10 µm | ACCVD   | 1000     | 50 pa    |             | 80 min  | Monolayer and bilayer | [201]|
challenging to control the layer number and crystallinity of the as-grown BLG with the precipitation growth mode. To that end, one natural scenario is to reduce the amount of carbon dissolved in the catalytic substrate. Considering the relatively low solubility of carbon in Cu, it is desirable to form a Ni-Cu alloy to assist the controlled growth of high-quality BLG [98–100, 178, 181, 204–206]. Recently, Huang et al [195] prepared a single-crystal Cu/Ni(111) alloy foils by plating Cu(111) foil with Ni, followed by annealing in furnace. By controlling the Ni contents, they were able to control the layer number of the as-grown graphene crystals, i.e. AB-BLG with a coverage of more than 95%, ABA-stacked trilayer graphene with more than 60% coverage (figure 9).

3.2.2. Cu and alloys based on Cu

Cu is one of the most used substrate materials in the CVD synthesis of monolayer graphene. The initial intention was to utilize a metallic substrate that is of lower solubility of carbon than the previously used Ni [177] to assist the surface catalyzed growth that is self-limiting and to prevent the formation of multilayer graphene [81]. Different from the precipitation growth of graphene on Ni [177], Cu leads to the surface-mediated growth of graphene confirmed by the carbon isotope labeling experiment [207], where most of the as-grown graphene was identified as a monolayer, i.e. >95%. Meanwhile, the formation of the bilayer and trilayer domains were also frequently observed with the Cu substrate [81], implying that a more complicated process was involved.

The attempts to understand the formation of these multilayer graphene have led to signification advance in the controlled growth of BLG. The underline mechanism can be rather complicated and largely depends
on the different growth conditions. The first question is whether the smaller graphene layers is buried below or stacked on top of the larger layers of the BLG flakes (figure 10). Most of the reports in the literature appear to be the bottom growth mode [97, 181, 207, 208], which has sparked a debate over whether the growth mechanism is surface-mediated or relies upon the back-diffusion process. For the surface-mediated growth of BLG, the decomposed carbon species diffuse underneath the edge of the first-layer graphene for the nucleation of the second-layer graphene [209]. In contrast, for back-diffusion growth, the top/first graphene layer forms first over one side of the substrate, and then bottom/second BLG layers grow beneath the top layer via carbon back-diffusion from the other side [96, 97, 181, 210]. Although the two mechanisms are not mutually exclusive, few reports studied the growth process by considering both. To date, a universal growth mechanism of BLG on copper is still lacking.

3.2.2.1. Top growth mode
Though simultaneous seeding and self-limiting growth of BLG has been reported [211], the majority of the literature is based on the layer-by-layer growth with different sizes for the two graphene layers. The location of the second graphene layer (usually the smaller flakes) has long been a controversial topic, and both top and bottom growth of crystalline graphene have been reported under typical laboratory conditions.

In the adoption of top-growth mode, Yan et al placed a piece of fresh copper foil upstream from the growth substrate to act as a catalyst to continuously decompose CH\textsubscript{4} and supply carbon radicals for the growth of the top layer of the BLG on the downstream substrate [179]. Liu et al implemented a high H\textsubscript{2}/CH\textsubscript{4} ratio in a low-pressure CVD process to create exposed Cu gaps on the upstream to continuously supply the carbon fragments for the growth of BLG on the downstream [175]. The as-grown BLG shown a high AB stacking ratio (up to 90%) and high coverage (up to 99%). By tuning the relative gas ratio of CH\textsubscript{4} to H\textsubscript{2} in atmospheric pressure, Ta et al [174] were able to switch between the top growth mode and bottom growth mode in CVD of BLG, implying the growth mode sensitively depends on the growth condition and the technique used.

To confirm the top-growth mode, Kalbac et al [212] and Wang et al [213] performed hydrogen etching on the as-grown BLG samples and found the removal of layers can proceed in a layer-by-layer manner. The smallest layer is the first to disappear in each stack, indicating those are the topmost layer but not the buried layers. It should be noted that the hydrogen etching is an indirect characterization approach. Direct observations of the top-growth mode through isotope labeling [207] TOF-SIMS mapping [207], and LEEM [97, 208] so far have not been reported yet.

3.2.2.2. Bottom growth mode
In contrast to the top-growth mode, several research groups have shown strong evidence of the bottom growth mode of BLG, where the top graphene layer forms on top of the bottom layer (the smaller flakes), which grows beneath it either by subsurface diffusion or back-diffusion of carbon species.

3.2.2.2.1. Subsurface diffusion mechanism
Li et al [207] use isotope-labeled methane as the carbon source for the CVD growth of BLG. With micro-Raman mapping and time-of-flight secondary ion mass spectrometry (TOF-SIMS), they showed strong evidence that the second/smaller layer of BLG formed beneath the top layer (figure 11(a)–(g)). Zhang et al [209] performed ab initio calculations for the detailed subsurface diffusion growth mode of BLG on Cu substrates. They found that the hydrogen-terminated graphene edge favors the subsurface diffusion of carbon species into the area beneath the first graphene layer to form the second BLG layers (figures 11(i)–(k)). Based on this mechanism, Gan et al [214] developed a surface oxidation method to suppress nucleation density and coverage of the first graphene layer to maximize the growth of the second layer of BLG. Due to the increased duration of absorption–diffusion–reaction, they were able to achieve BLG domains of sub-mm.

3.2.2.2.2. Back-diffusion growth mechanism
One argument of the subsurface diffusion growth (figure 11(g), path (ii)) over the back-diffusion growth (figure 11(g), path (i)) is the ultralow solubility of carbon in Cu, which prohibits the precipitation of carbon from the bulk phase of the Cu substrates. However, several reports revealed that the carbon source indeed diffuses through the bulk Cu for the growth of highly crystalline BLG (figure 12). Fang et al utilized a manually constructed Cu pocket to yield high BLG coverage (up to 100%) on the outside surface of the pocket. The underlying mechanism is that carbon can diffuse from the inside surface of the Cu pocket to its outside surface through the exposed copper regions on the inside surface (figures 12(a) and (b)) [181]. Hao et al [97] adopted the pocket structure for the synthesis of single-crystal BLG with large domains, i.e. half-mm. They found that the oxygen-activated CVD process is critical to promote the dehydrogenation of hydrocarbon molecules for the back-diffusion growth mode (figures 12(c) and (d)). Such a back-diffusion
Figure 11. (a–e) TOF-SIMS mapping of isotopically labeled multilayer graphene on a Cu foil (200 × 200 µm²), showing the $^{12}\text{C}$ isotope distribution images of graphene after different $\text{Cs}^+$ ion beam sputter time. The layer-by-layer removal of graphene by TOF-SIMS indicates a bottom growth mode of multilayer graphene. (f) Schematic showing the bottom growth of BLG by subsurface diffusion of active carbon species [207]. Reproduced with permission from Li et al [207]., copyright 2013, American Chemical Society. (g) Three potential transportation paths of the active carbon species for the growth of BLG. Schematic illustration of the graphene growth on a Cu (111) surface with (h) metal-passivated edge and (i) hydrogen-terminated edge [209]. Reproduced with permission from Zhang et al [209], copyright 2014, American Chemical Society.

Figure 12. (a, b) Schematics showing the back diffusion processes of carbon to form BLG on the outside surface of the Cu pocket underneath the first-grown monolayer graphene [181]. Reproduced with permission from Fang et al [181], copyright 2014, American Chemical Society. Schematics of the diffusion growth processes from the interior (c) to the exterior (d) surfaces of the Cu pocket [97]. Reproduced with permission from Hao et al [97], copyright 2016, Nature Publishing Group. (e) Schematic showing the back-diffusion growth of BLG with a Ni–Cu gradient alloy catalytic substrate [96]. (f–h) Control experiment validating the back-diffusion growth mechanism. Monolayer graphene was transferred onto the Ni-poor side of an optimized Ni–Cu gradient alloy substrate before CVD growth. Panel (f) is a picture of the Ni-poor side after CVD growth. The transferred monolayer graphene (indicated by the black arrow) has remained as a continuous film. Panel (g) is a photograph of the Ni-rich side of the substrate that is fully covered by graphene after CVD growth. The black box in panel (g) outlines the region that is opposite the black box in panel (f). (h) Optical micrograph of the region in the black box in panel (g) after transfer onto Si/SiO$_2$. The area opposite the transferred monolayer graphene is covered with the pure monolayer. In contrast, nearby areas that were not opposite the transferred monolayer show abundant formation of multilayer graphene. Reproduced with permission from Gao et al [96], copyright 2018, American Chemical Society.

The back-diffusion path was further evidenced by the reversed diffusion of carbon by placing a ‘carbon sink’ on the inside surface of the Cu pocket. Fang et al [216] employed a tungsten foil to control the carbon adsorption and back-diffusion path in this region. They found on the opposite side of the substrate, BLG formation was frustrated (figures 12(f)–(h)). Their experiment provided evidence that carbon back-diffusion is the majority component of carbon supplies for BLG formation. Besides the growth of BLG, back-diffusion growth is also valid for the synthesis of other 2D materials, such as hBN [215].
diffusion within Cu pockets and selectively remove bi-/multi-layer graphene that nucleates underneath the monolayer graphene to form pure monolayer graphene. Abidi et al [217] developed a Ni-based carbon ‘getter’ substrate on the backside of the Cu foil to mitigate the carbon diffusion to the top-surface to control the nucleation density and layer numbers of graphene. The above results unambiguous validate the back-diffusion path of carbon in BLG growth. Although the solubility of carbon in Cu is low, it is essential to consider the back-diffusion paths in the CVD process with Cu and Cu-based alloys. The trace amount of carbon in Cu may have a significant impact on the growth process of BLG, e.g. nucleation density [218].

Back-diffusion growth and subsurface diffusion growth modes both require the decomposition of hydrocarbon on exposed catalytic Cu surface, however few works in literature considered both modes in a single growth. It remains unclear that what fraction of the subsurface diffusion and back-diffusion are responsive to the CVD growth of BLG, and what are the key parameters to switch from one mode to another.

4. Synthesis of bilayer TMDs

The synthesis of bilayer TMDs with required composition, size, twist angle, and stacking sequence is prerequisite to explore their properties and potential applications. So far, numerous strategies have been developed to build bilayer TMDs, including both top-down and bottom-up methods. Among these, artificial stacking process shows the strongest capability to precisely control the stacking orientation and sequence and CVD is considered the most promising method to provide high-quality and scalable bilayer TMDs.

4.1. Synthesis of homobilayer TMDs

4.1.1. Top-down methods

The weak vdW interaction between TMD layers makes mechanical exfoliation from the bulk the most straightforward method to obtain homobilayer TMDs. It will provide bilayer TMDs with the best quality for fundamental scientific research [72, 73, 219]. However, it is hard to control the layer number and domain size by mechanical exfoliation. As a result, post-synthesis layer-by-layer thinning methods are widely developed to produce bilayer TMDs. One thinning method is to anneal the multilayer TMDs in an oxidative environment. However, this method typically requires temperature over 300 °C, which can result in a final sample with residue byproducts that impact the electrical and optical properties [78, 220]. Controllable laser-thinning method was developed for the thinning of multilayer TMDs down to bilayer and monolayers with few impurity byproducts [221]. By tuning the laser power and exposure time, precise control over the resulting TMD layer number is efficiently achieved [222]. Ar+ and O2 plasma are also used to achieve the layer-by-layer thinning of multilayer TMDs to produce bilayers [223, 224]. Similar to the laser-thinning method, the plasma etching also requires precise control on the thinning time and power and it is difficult to process without inducing damage. To solve this issue, atomic layer etching, which is a cyclic etching consisting of a radical-adsorption of Cl and a reacted-compound-desorption step via a low-energy Ar process without inducing damage. To solve this issue, atomic layer etching, which is a cyclic etching consisting of a radical-adsorption of Cl and a reacted-compound-desorption step via a low-energy Ar process without inducing damage.

4.1.2. Bottom-up methods

A variety of efficient bottom-up methods, such as CVD, have been widely developed to produce high-quality, large-scale monolayer TMDs. Artificial stacking of the same monolayer TMDs can generate large-scale homobilayer TMDs with varied twist angles, which provides an excellent platform to investigate the twist-angle-dependent properties for bilayer TMDs. For example, Puretzky et al used the typical poly(methyl methacrylate) (PMMA)-assisted wet-transfer method to transfer one film of monolayer MoSe2 flakes onto another one and obtained large-area twisted bilayer MoSe2 [15]. They further investigate the twist-angle-dependent interlayer coupling effect of this bilayer MoSe2 by low-frequency Raman spectroscopy. This wet-transfer method is scalable, but is not possible to control the twist angles and a weak interlayer coupling is always induced. The well-developed dry-transfer method shows the capability to precisely control the twist angle of obtained bilayer TMDs, but not scalable.

With the advantages of thickness control and the readily available surface characterization tools in site, the MBE has drawn increasing attention for the growth of TMDs with required layer numbers for surface and electronic studies. The growth of bilayer WSe2 by MBE has been achieved [79]. However, the high cost of MBE system, the limited grain size of the grown TMDs, and the requirement for specific growth substrates hinder the application of MBE in large-scale growth of bilayer TMDs.

So far, CVD is considered the most reliable method to synthesize bilayer TMDs in large scale with controlled morphology, clean interface, and strong interlayer coupling. However, the complex growth environment during CVD complicates precise control over the final TMD layer number. Recently, a multiscale model for the vertical growth of 2D TMDs was proposed, which indicated that temperature, vapor
adatom flux, as well as growth time are the primary parameters affecting the final TMD structures [17]. Guided by this model, the authors demonstrated preferential growth of bilayer TMDs, including MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$, MoTe$_2$, and WTe$_2$, at a higher temperature. The model can also be used to explain many of the current approaches, both one-step and two-step CVD processes, towards controlled growth of bilayer TMDs.

4.1.2.1. One-step CVD process

Precise control over the growth parameters can facilitate the direct growth homobilayer TMDs in a one-step CVD process. In most cases, prolonged the growth time always leads to the continuous growth of TMDs to form bilayers. Zhou et al reported the formation of large number of bilayer MoS$_2$ flakes after a 15 min growth while a 10 min growth mainly yielded monolayers [227]. This is because that as the TMD monolayer domains increase in size, the adatoms must diffuse a longer distance to reach the domain edges, therefore, they tend to contribute to bilayer growth instead of filling in the initial monolayer [228]. On the other hand, elevating the growth temperature would increase the vapor adatom flux, leading to the vertical growth of TMDs and the formation of bilayers. During the growth of WSe$_2$, Liu et al [229] found that high-quality monolayer WSe$_2$ was obtained at a growth temperature in the range of 850 °C–950 °C. However, the WSe$_2$ tended to form bilayer structure at a raised temperature >950 °C. He et al also reported that growth at 750 °C would yield dominating monolayer MoSe$_2$, while 825 °C and 900 °C can result in large quantity of bilayers [18]. At 850 °C, Xia et al achieved the preferential growth of bilayer MoS$_2$ with a selectivity of ~80%, which showed a mixed AA’ and AB stacking configuration [56]. In a later work carried out by Hao et al, dominating bilayer MoS$_2$ domains were obtained at 900 °C while the growth at 800 °C mainly generating monolayers. Furthermore, the elevated growth temperature of 900 °C led to strict identical AB stacking order [230]. The effect of high growth temperature was further confirmed Fang et al [231] during the WSe$_2$ growth (figure 13). The percentage of bilayer WSe$_2$ in the final structure increased from ~30% at 880 °C to ~60% at 900 °C and to ~80% at 940 °C. Moreover, the authors demonstrated that an AB stacking WSe$_2$ was directly nucleated and grown at the vertex of the bottom monolayer to form the 1L-2L homojunctions. After enough growth time, this WSe$_2$ homojunction evolved into a full triangular bilayer (figures 13(e)–(i)) [231].

A straightforward method to control the vapor adatom flux is to control the partial pressure of the precursors in the reaction system. In a typical thermal reduction-sulfurization method, the partial pressure of transition metal precursors can be easily controlled by tuning the thickness of metal oxide precursor films. Bilayer WS$_2$ films were obtained by sulfurizing 2 nm thick WO$_3$ films [232]. By controlling the partial pressure of MoCl$_5$ used in the experiments, precise control over the layer number of resulting MoS$_2$, including bilayers, has been widely achieved [16, 233]. Using MoO$_3$ precursor, Fang et al [129] systematically studied the effect of hydrogen flow on the as-grown MoS$_2$ layer number. They found that the layer number of MoS$_2$ increased with increasing H$_2$ flow rate and attributed it to the reduction of MoO$_3$ to MoO$_2$, which enhanced the partial pressure of Mo precursors. After the optimization, majority of bilayer MoS$_2$ flakes were obtained under the 10 sccm H$_2$ [129]. Instead of using solid precursor, Yan et al [234] used a H$_2$MoN$_2$O$_4$ solution precursor to render a better control over the vapor pressure of Mo precursors by tuning the amount of solution used. The results showed that a large number of bilayer MoS$_2$ were obtained when using 5 µl of the precursor solution, while monolayers were obtained for 4 µl and many multilayer flakes for 6 µl [234]. Not just transition metal precursors, the partial pressure of chalcogens also plays an important role in the vertical growth of TMDs. Efficiently controlled growth of bilayer MoS$_2$ was achieved by increasing the amount of S introduced in the reaction and bilayer WSe$_2$ was obtained by increasing the Se amount [235].

Modulating the substrate surface chemistry has also been demonstrated as an effective method to achieve controlled growth of bilayer TMDs based on the change in surface absorption energy of precursors. For example, layer-controlled growth of large-area 2D MoS$_2$ films was achieved by tuning the O$_2$ plasma treatment duration of SiO$_2$ substrate [236]. Controlled growth of centimeter-scale bilayer MoS$_2$ film was obtained after a 120 s treatment, while monolayer and trilayer films were obtained after 60 and 300 s treatment, respectively [236]. Mandyam et al demonstrated dense, selective growth of WSe$_2$ bilayer flakes by CVD with the use of a 1:10 molar mixture of sodium chloride (C$_{24}$H$_{20}$NaO$_3$) and sodium chloride (NaCl) as the growth promoter to control the local diffusion of W-containing species [63]. The cholate ions are expected to enhance the wettability of the substrate and lower the free energy for nucleation, promoting adsorption of transition metal oxide precursors on the substrate and thus growth of monolayer TMDs. In contrast, the Cl ions can form volatile oxalides, which promotes the escape of transition metal precursors into the vapor and facilitates the vertical growth of additional TMD layers. A suitable balance of these two competing mechanisms enables the tuning of the layer number of CVD-grown TMD flakes (figure 14). In this work, the 1:10 molar mixture of sodium cholate and sodium chloride yielded ~100% selectivity of bilayer WSe$_2$ flakes uniformly grown on a centimeter-scale SiO$_2$/Si substrate with >60% coverage.
4.1.2.2. Two-step CVD process
In a two-step CVD process, monolayer TMD was firstly grown on a substrate by a typical CVD process. Then the growth environment was switched to allow the epitaxial growth of another layer of TMD. Zhang et al proposed a potentially universal sequential two-step CVD process to produce high-quality TMD bilayer crystals, wherein a reverse hydrogen flow was introduced and the process temperature was adjusted during the growth swing stage for the second layer growth (figure 15) [104]. For example, after the growth of monolayer MoS\(_2\) at 700 °C under forward flowing N\(_2\), the growth temperature was increased to 750 °C or 800 °C for the growth of second layer. During the temperature swing stage, a reverse flow of N\(_2\)/H\(_2\) was introduced. This approach produced high-quality bilayer MoS\(_2\) with high yield, large size up to 300 \(\mu\)m, and high controllability. During the process, the reverse H\(_2\) flow is demonstrated to be beneficial in both reducing the undesired nucleation centers and promoting homogeneous epitaxy growth of the second layer from the activated nucleation centers of the monolayer. The higher growth temperature for the second step is beneficial for the vertical growth of second layer but is against to the continued lateral growth at the edge of the first monolayer crystals. It was found that the growth at 750 °C tended to form AA’ stacking bilayer MoS\(_2\) and AB stacking dominated the products when growing at 800 °C. This two-step reverse flow CVD process can also be applied to other TMDs. In addition to MoS\(_2\), and bilayer WS\(_2\), Mo\(_{1-x}\)W\(_x\)S\(_2\), Mo\(_{1-x}\)W\(_x\)S\(_2\)(1–y)Se\(_{2y}\) single crystals were all produced.

4.2. Synthesis of heterobilayer TMDs
4.2.1. Artificial stacking methods
Artificial stacking, which can selectively join 2D materials and create a 2D material assembly, is the most widely used method to fabricate 2D heterobilayer TMDs for researching the unique electrical and optical properties. Depending on the stacking method, it can be divided into dry transfer, wet transfer, and semi-dry transfer processes.
2D heterobilayer TMDs were originally obtained via mechanical exfoliation followed with a dry transfer process. For example, WSe$_2$ monolayer is mechanically exfoliated on a SiO$_2$-coated Si substrate. Separately, MoS$_2$ monolayer is exfoliated on a Si substrate coated with a polymer bilayer consisting of thin water-soluble polyvinyl acetate (PVA) and PMMA films. Then, the PMMA film with MoS$_2$ flakes is released from the substrate by dissolving the PVA in water and transferred the film onto a polydimethyl siloxane (PDMS) stamp. Finally, a micromanipulator is used to place the MoS$_2$ layer on top of the WSe$_2$ monolayer through an aligned transfer procedure [132]. In addition to the use of sacrificing water-soluble polymer, mechanical exfoliated hexagonal boron nitride (hBN) flakes on a poly-propylene carbonate (PPC)/PMMA stamp are widely used to directly pick up and stack the TMD monolayers in sequence to create heterobilayers through an all-dry transfer process [128, 132]. An all-dry viscoelastic stamping method is also well developed to construct heterobilayer TMDs layer by layer with no chemical in contact with the layers during transfer [237]. The dry transfer method, along with Polarization- and phase-resolved second-harmonic generation measurements allow precise control over the twist angle of the resulting heterobilayer TMDs to investigate twist-angle-dependent properties [57, 71–73, 160, 161].

Similar to the fabrication of homobilayer TMDs, the PMMA-assisted wet transfer process is widely used to create large-scale TMD heterobilayers with a series of twist angles using the CVD-grown TMD monolayers. Not just PMMA, other kinds of polymer, such as PDMS, are also widely used for the wet transfer process. A variety of TMD heterobilayers, including MoS$_2$/WS$_2$, MoS$_2$/WSe$_2$, WS$_2$/WSe$_2$, and MoSe$_2$/WSe$_2$, etc., are all produced in large scale using the wet-transfer process [66, 123, 158, 238]. In a semi-dry transfer process, PMMA-assisted wet transfer is used to peel monolayer TMDs off from the substrate. The floating PMMA/TMD film is then pick up by a stamp and the TMD monolayer is placed on top of another kind of monolayer TMD using a micromanipulator [239]. This process is easier and faster than the all-dry transfer and more controllable compared to the wet transfer process. However, impurities are introduced during the first wet-transfer step.

4.2.2. MBE growth
Dai et al successfully fabricated the MoSe$_2$/WSe$_2$ heterobilayer by MBE and investigated the behavior of heterointerface formation [240]. During the growth, a Se/Mo(W) flux ratio of $\sim$22:1 was adopted and the films were deposited at a constant temperature of 500 °C–550 °C. After the WSe$_2$ deposition, both the metal source and the power of e-cell were turned off while the Se flux was kept. Meanwhile, a 30 min annealing at
650 °C was adopted before the deposition of MoSe$_2$ monolayer to minimize residue metals. The growth sequence showed a dramatic effect on the interface morphology. When the WSe$_2$ growth preceded MoSe$_2$, a sharp heterointerface was obtained, but an alloy without apparent heterointerface formed if MoSe$_2$ grew first. By choosing proper deposition conditions and coverage, the authors obtained a vertical junction of MoSe$_2$/WSe$_2$ heterobilayers.

4.2.3. CVD growth
Both one-step and two-step CVD processes have been widely developed for the growth of heterobilayer TMDs. In the one-step synthesis, all precursors are simultaneously injected into the chamber and separately vaporized because of their different sublimation or reaction temperatures. As a result, various heterobilayer TMDs can be directly grown by the one-step growth without impurities at the junctions. However, the one-step method has limitations in the spatial and size control of the heterostructures. In comparison, the two-step method involves the epitaxial growth process and can avoid forming alloy compounds that significantly influence the properties of the interface. It also allows a good control of the size of each TMD layers.

4.2.3.1. One-step CVD process
Through tellurium-mediated sulfurization of MoO$_3$ and W, the Ajayan group firstly achieved the direct growth of WS$_2$/MoS$_2$ heterobilayer flakes in one pot [80]. The authors found that the vertically stacked bilayers were mainly obtained at a high temperature of 800 °C, while low-temperature (650 °C) growth created mostly lateral monolayer heterostructures. This effect of growth temperature is in good agreement with the homobilayer TMD growth. Zhang et al reported the successful synthesis of pristine MoS$_2$/WS$_2$ heterobilayers using core–shell WO$_{3-x}$/MoO$_{3-x}$ nanowires as the precursor, which ensured the sequential feeding of Mo and W to avoid the formation of alloys [130]. Yu et al obtained similar MoS$_2$/WS$_2$ heterobilayers by sulfurization of a mixed MoO$_3$/WO$_3$ (1:99 in mass) powder at 950 °C for 2 h [241].

During the growth of heterobilayer TMDs, competition exists between the vertical growth to form heterobilayers and lateral growth to form monolayer heterostructures. As mentioned above, the temperature plays an important role in this competition. Chen et al systematically studied the influence of growth temperature on the final structure of MoS$_2$/WS$_2$ heterostructures in a combination approach of magnetron sputtering and CVD process [242]. When the growth temperature increased from 750 °C–900 °C, a series of structures, including MoS$_2$ monolayer (750 °C), MoS$_2$/WS$_2$ heterobilayer (780 °C), WS$_2$-MoS$_2$/WS$_2$
heterobilayer (810 °C), Mo$_{1-x}$W$_x$S$_2$/WS$_2$ heterobilayer (840 °C), Mo$_{1-x}$W$_x$S$_2$ alloyed bilayer (870 °C), and WS$_2$ bilayer (900 °C), were obtained in sequence. This evolution of various 2D heterostructures was attributed to the competition between the adsorption and desorption of Mo atoms and the diffusion of W atoms under various growth temperatures. The same group also reported the growth of various 2D WS$_2$-based heterobilayers, including WS$_2$/MoS$_2$, WS$_2$/MoS$_2$-Mo$_{1-x}$W$_x$S$_2$, and WS$_2$/Mo$_{1-x}$W$_x$S$_2$ at different regions of the substrate around the sputtered Mo/W film precursor [243]. The growth mechanism was discussed based on the variation of metallic atoms along the gas flow direction. These results also reveal the challenge of avoiding alloy formation during the one-step CVD growth of heterobilayer TMDs. Compared to increasing the growth temperature, Chen et al demonstrated that increasing the concentration of sulfur vapors was also an effective method to achieve the controlled growth of heterobilayer MoS$_2$/MoSe$_2$ TMD [244].

In addition to the group VI TMDs, heterobilayer TMDs with other kinds of compositions have also been reported. For example, Li et al reported the direct growth of high-quality SnS$_2$/MoS$_2$ heterobilayers, which exhibited extremely large band offset and type II band alignment, by sulfurization of a mixture of SnO/MoO$_3$ at 630 °C [245]. Zhou et al reported the direct growth of PtSe$_2$/MoSe$_2$ heterobilayers using PtCl$_6$ and MoO$_3$ as the Pt and Mo source, respectively [246]. Zhang et al demonstrated twinned growth of heterobilayer ReS$_2$/WS$_2$ flakes using a W–Re alloy foil as a supply source of Re and W atoms, which was due to the difference in the adsorption energies of Re and W atoms on Au(111) [247]. The method can also be applied to fabricate MoS$_2$/WS$_2$ heterobilayers by using Mo–W alloy foils in the place of W-Re alloy foils.

4.2.3.2. Two-step CVD process

Since the CVD growth of monolayer TMDs has been well developed, the two-step CVD, which just needs epilayer growth of another TMD monolayer, is becoming the most efficient method to grow heterobilayer TMDs. The Ajayan group firstly reported the two-step CVD growth of WSe$_2$/MoSe$_2$ heterobilayer flakes with a size up to 169 µm [248]. The MoSe$_2$ was synthesized first and followed by an epilayer growth of WSe$_2$ on the edge and top of MoSe$_2$. Lin et al built MoS$_2$/WSe$_2$ and WSe$_2$/MoSe$_2$ heterobilayer structures directly on epitaxial graphene (e.g.) by employing a combination of oxide powder vaporization and metal-organic CVD (MOCVD) [249]. The first TMD layer of the heterostructures, WSe$_2$ or MoSe$_2$, was grown on at 950 °C and 750 °C for WSe$_2$ and MoSe$_2$, respectively. Subsequently, the MoS$_2$/WSe$_2$ heterobilayers was fabricated by a second growth of MoS$_2$ on WSe$_2$ at 750 °C. The same structure was also reported by Zhang et al using a similar growth method [250]. The WSe$_2$/MoSe$_2$ heterobilayers were obtained after growth of WSe$_2$ on MoS$_2$, during which a Se–S ion exchange occurred when MoS$_2$ was exposed to the Se vapor. Irisawa et al conducted the growth of WSe$_2$ directly on MoSe$_2$ grown in the first step and obtained WSe$_2$/MoSe$_2$-WSe$_2$ heterobilayer structures with a monolayer MoSe$_2$/WSe$_2$ lateral heterostructure as the bottom layer [251]. Zhang et al conducted the conventional CVD growth of WSe$_2$ first, followed by the epilayer growth of MoS$_2$, leading to a MoS$_2$/WSe$_2$ heterobilayer structures with multiple, small MoS$_2$ domains on a large WSe$_2$ flake with 0° and 60° relative twist angles [252]. Using WSe$_2$ powder as the precursor, Yang et al prepared large-size WSe$_2$ monolayers first, followed by sulfurization of SnO$_2$ powder as the second step. The authors successfully obtained millimeter-scale SnS$_2$/WSe$_2$ heterobilayer flakes [253].

Similar with the one-step process, the competition between vertical and lateral TMD growth also exists in the two-step CVD process. A higher growth temperature, again, would lead to the preferential vertical growth. Bilayer MoS$_2$/WS$_2$/WS$_2$ heterostructures composed of both lateral and vertical monolayer heterostructures were obtained through a two-step CVD process by adjusting the growing temperature [254]. During the two-step growth of WS$_2$/MoS$_2$ heterobilayers, Heo et al observed the transition from lateral to vertical growth mode when the growth temperature increased from 660 °C to 800 °C, which was ascribed to the nucleation kinetics controls [255]. In a different approach reported by Shi et al, vertical stacks of MoS$_2$/WS$_2$ and WS$_2$/MoS$_2$ were obtained at both 680 °C and 880 °C for the second step, regardless of the temperature change [256]. It was just because the bottom continuous TMD monolayer film provided no room for the lateral TMD growth. Besides growth temperature, Yoo et al declared the important of hydrogen in the vertical growth of WS$_2$/MoS$_2$ heterostructures. When H$_2$ was used as the carrier gas, the synthesized ultraclean MoS$_2$ monolayers in the first step enabled lateral heteropitaxial growth of monolayer WS$_2$ [257]. Without H$_2$, the obtained MoS$_2$ were decorated with small particles along the edge, inducing vertical heteropitaxial growth of monolayer WS$_2$ to form the heterobilayer structure.

To achieve a better understanding of the growth mechanism of TMD heterobilayers, Li et al carried out an in-depth study of the nucleation and growth kinetics of TMDs by both experimental and theoretical methods (figure 16) [105]. They demonstrated that active clusters with a high diffusion barrier would induce the nucleation on top of the TMDC templates to realize vertical heterostructures, which can be effectively controlled by tuning the metal/chalcogenide ratio in the vapor precursor. In this way, a family of TMD heterobilayer structures was successfully designed and obtained, including MoS$_2$/WSe$_2$, MoS$_2$/MoSe$_2$, 

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Figure 16. (a) The schematic atomic structures and corresponding optical images showing the evolution of the MoS$_2$/WSe$_2$ heterostructure morphology with increasing W/Se ratio during the second-step CVD growth. (b) The evolution trends of lateral ($L_L$) and vertical ($L_V$) growth length with W/Se ratio. (c) The relation of heterostructure type with the dosage of W precursor (WO$_3$) and Se precursor. (d) The statistics of lateral, hybrid, and vertical heterostructures at different W/Se ratios. Reproduced with permission from Li et al. [105], copyright 2019, Wiley-VCH.

MoS$_2$/WS$_2$, WSe$_2$/MoSe$_2$, WS$_2$/WSe$_2$, WS$_2$/MoSe$_2$, WS$_2$/NbS$_2$, and MoS$_2$/NbSe$_2$. The method is expected to be universal for the controlled growth of all kinds of bilayer TMDs.

4.3. Synthesis of bilayer TMD lateral heterostructures

Recently, the synthesis of bilayer TMD lateral heterostructures, which consisting of two monolayers of TMD lateral heterostructure, is reported. The fabrication of monolayer TMD lateral heterostructures has been widely reported, which already demonstrates impressive electronic and optoelectronic properties. However, studies on lateral heterostructures based on bilayer TMDs are scarce. Ye et al carried out a two-step CVD method to growth bilayer WS$_2$–MoS$_2$ lateral heterostructures [258]. The bilayer WS$_2$ flakes were first grown on a Si/SiO$_2$ substrate by sulfurization of WO$_3$ powder. Epitaxial growth of bilayer MoS$_2$ along the edge of bilayer WS$_2$ was achieved the direct deposition of MoS$_2$ powder, assisted by NaCl. The as-grown bilayer WS$_2$–MoS$_2$ lateral heterostructures process atomically sharp and seamless interfaces and exhibit outstanding performance as photodetectors. Using a water-assisted CVD approach with MX$_2$ (MoS$_2$ or MoSe$_2$) and WX$_2$ (WS$_2$ or WSe$_2$) as the precursors, Sahoo et al reported the controlled synthesis of multi-junction bilayer lateral heterostructures based on MoS$_2$–WS$_2$ and MoSe$_2$–WSe$_2$ (figure 17) [259]. The heterojunctions are created by sequential lateral edge-epitaxy that happens simultaneously in both the first and second layers. The growth mode with the self-limited thickness that happens within a certain window of growth conditions can be explained by a phenomenological mechanism. Interestingly, the bilayer lateral heterostructures yield nearly 1 order of magnitude higher rectification currents compared to their monolayer counterparts. A clear photovoltaic response, with short circuit currents $\sim 10^3$ times larger than those of corresponding monolayers, are extracted. The improved performance of bilayer TMD lateral heterostructures significantly expands their potential for electronic and optoelectronic applications.

5. Control over the twist angles and stacking sequence

As mentioned above, the properties of BLG and TMDs are significantly affected by the twist angle. In addition, for heterobilayer TMDs, the stacking sequence is another important factor that will influence their properties. For example, Hill et al demonstrated the different bandgap structures between MoS$_2$/WS$_2$ heterobilayer with MoS$_2$ on the top and that with WS$_2$ on the top [124]. By tuning the stacking sequence of MoS$_2$ and WS$_2$ on fluorine-doped tin oxide (FTO), Liu et al [260] demonstrated that the electron transport rate from FTO to the MoS$_2$ surface of FTO/WS$_2$/MoS$_2$ was higher than the rate from FTO to the WS$_2$ surface.
of FTO/MoS$_2$/WS$_2$, leading to a higher catalytic activity of FTO/WS$_2$/MoS$_2$. The MoS$_2$/WS$_2$ stacks were also found to possess higher photocatalytic activity in hydrogen evolution reaction (HER) compared to WS$_2$/MoS$_2$, due to the effective electron–hole separation and the fast electron transfer kinetics [256]. Therefore, it is important to achieve good control over both the twist angle and stacking sequence during the synthesis of BLG and TMDs.

The artificial stacking approach is considered to be the most efficient method to control the twist angle and stacking sequence, as the process can be precisely operated and controlled [161]. Due to the epitaxial growth mode, control over the twist angles by CVD methods is limited. For CVD-grown BLG, 0° (AB) and 30° (quasicrystal) are energetically stable states against other twisting angles [96, 261, 262], and their synthesis was reported to be controllable via optimization of CVD parameters [97] and engineering of the growth substrate [39]. However, the synthesis of tBLG with an arbitrary twisting angle remains a significant experimental challenge, and there is so far no pathway towards such a capability, e.g. controlled synthesis of magic-angle tBLG.

For CVD-grown bilayer TMDs, 0° (AB) and 60° (AA') twist angles are frequently observed as they have the lowest energy and are the most stable configurations [56, 63, 130, 252]. However, other twist angles, such as 15°, 20°, and 30°, are also possible [63, 130]. Mandyam et al [63] carried out a statistical analysis of the twist angles of bilayer WS$_2$ grown by CVD. It was found that the strong majority (~84%) of bilayer WS$_2$ flakes showed a twist angle of 0°/60°, with smaller fractions having a twist of 30° (12%) or 15° (4%). Other twist angles were not observed. This distribution of twist angles was in good agreement with the calculated stacking energy density, with the 0°/60° twist showing the lowest values. It should be noted that the 0° twist angle with the AA stacking configuration, the top layer Se atoms are put above bottom Se atoms, is also not observed due to its high stacking energy density [63]. The appearance of 20° twist angle in the CVD-grown WS$_2$/MoS$_2$ heterobilayers was reported by Zhang et al, although the products showed dominating 0° and 60° twist angles [130]. Tuning the growth temperature has been shown as an effective method to control the twist angle of CVD-grown bilayer TMDs. Zhang et al [104] found that growth of bilayer MoS$_2$ at 750 °C was suitable for AA' stacking while 800 °C was optimal for AB stacking. However, precise control over a wide range of twist angles for BLG and bilayer TMDs by the CVD method is still a great challenge.

The stacking sequence of CVD-grown heterobilayer TMDs can be well controlled through a two-step process. Shi et al [256] achieved the fabrication of WS$_2$/MoS$_2$ and MoS$_2$/WS$_2$ heterobilayers by sequentially
growing the two composite MX₂ monolayers on Au foils through two typical CVD routes. Few reports have been published on the control of stacking sequence of heterobilayer TMDs in the one-step CVD process. For WS₂/MoS₂ heterobilayers, the one-step CVD growth method always results in heterostructure with MoS₂ as the bottom layer [80, 241, 243]. The MoS₂/WS₂ heterobilayers with WS₂ as the bottom layer are only obtained by the two-step CVD process [252, 256]. A better understanding of the growth sequence of different monolayer TMDs in the one-step CVD process is desired. It is still a challenge to control the stacking sequence of heterobilayer TMDs by one-step CVD.

6. Summary and outlooks

During the past few years, considerable progress has been made on the controlled synthesis of BLG and bilayer TMDs and the understanding of their optical and electronic properties. Most importantly, the twist-angle-dependent interlayer coupling of these bilayer vdW materials leads to many unprecedented physical properties. A variety of methods have been developed to synthesis BLG and bilayer TMDs. Among them, mechanical exfoliation followed by artificial stacking techniques provide strong capability to precisely control the stacking sequence and orientation. CVD is becoming the most reliable method to produce large scale BLG and bilayer TMDs with large domain size, high quality, and strong interlayer coupling.

A few challenges remain regarding the controlled synthesis of large-area graphene and TMDs with different stacking configurations. For instance, the majority of the research focuses on the synthesis of AB-BLG. Although the synthesis of tBLG with random angles is previously reported [263–265], the synthesis of tBLG with a controllable twisting angle is still of great challenge [180, 266, 267]. Nevertheless, the nucleation mechanism of the bilayer and multilayer graphene at the atomic level remains unclear. Future work on the controlled synthesis of tBLG is highly desirable: (1) strategies to achieve uniform stacking order at the wafer level. (2) Strategies to grow twisted BLG with a controlled twisting angle.

For the growth of bilayer TMDs, the complex CVD environment makes it challenging to achieve the precise control of the bilayer TMD structures, such as twist angles and stacking sequence. Besides, the selectivity of bilayer TMDs by CVD is usually low. So far, most studies on bilayer TMDs are focused on group VI TMD flakes. Investigation on other kinds of bilayer TMDs and the controlled growth of bilayer TMD continuous films are to be explored. Furthermore, researches on bilayer TMD lateral heterostructures are still in their initial stage. More efforts are needed for their large-scale and controlled synthesis, as well as their underlying interesting physical properties.

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