Structure, Preparation, and Applications of 2D Material-Based Metal–Semiconductor Heterostructures

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Two-dimensional (2D) materials’ family with its many members and different properties has recently drawn great attention. Thanks to their atomic thickness and smooth surface, 2D materials can be constructed into heterostructures or homostructures in the fashion of out-of-plane perpendicular stacking or in-plane lateral stitching, resulting in unexpected physical and chemical properties and applications in many areas. In particular, 2D metal–semiconductor heterostructures or homostructures (MSHSs) which integrate 2D metals and 2D semiconductors, have shown great promise in future integrated electronics and energy-related applications. Herein, MSHSs with different structures and dimensionalities are first introduced, followed by several ways for their preparation. Their applications in electronics and optoelectronics, energy storage and conversion, and their use as platforms to exploit new physics are then discussed. Finally, the perspectives about the challenges and future research directions in this emerging field are given.

1. Introduction

Since Novoselov et al. isolated graphene from graphite in 2004,[1] the family of two-dimensional (2D) materials has been extended to thousands of members with a variety of electronic properties[2,5] ranging from insulators (hexagonal boron nitride [h-BN], mica), to semiconductors (MoS2, black phosphorus, TiO2), and to metals (graphene). Compared with bulk materials, they exhibit many unique physical and chemical properties, which are related to the electron and phonon confinement effect in the 2D limit.[4,5]

Another advantage of 2D materials is their ability to be integrated into heterostructures. In bulk materials, heterostructures obtained by epitaxial growth play key roles in semiconductor industry, although strict requirements on the matching of lattice symmetry and lattice constant limit the choices of materials.[6] As a result, only a few combinations such as III-V compound-based heterostructures can be epitaxially grown as bulk materials and sophisticated procedures are needed to obtain a sharp interface with minimum strain and few defects. In contrast, because of their atomic thickness, 2D material-based heterostructures with surfaces free of dangling bonds, and weak van der Waals (vdW) forces between adjacent layers, combinations of 2D components are less limited and they can be constructed into lateral heterostructures by in-plane stitching or vertical heterostructures by placing the layers on top of each other.[7–9] In the past few years, 2D material-based metal–insulator heterostructures and semiconductor–semiconductor heterostructures have been widely investigated in both theory and experiments. There are several review articles focusing on these two categories of heterostructures,[10–14] because they not only exhibit new physical phenomena (e.g., self-similar Hofstadter butterfly states in graphene/h-BN heterostructures[15] and ultrafast charge transfer in MoS2/WS2 heterostructures[16]), but also show good performance in electronic and optoelectronic applications (e.g., field effect transistors [FETs][17,18] photodetectors[19,20] and light-emitting diodes [LEDs][21,22]).

Recently, as a promising electrical contact in 2D electronics, the experimental realization of 2D material-based metal–semiconductor heterostructures or homostructures (denoted as MSHSs in this article) have sparked considerable research interest. Although currently, there are some reports of MSHSs, most of which focus on graphene-based MSHSs due to limited numbers of 2D metallic materials, increasing investigations on metallic transition metal dichalcogenides (TMDCs)[23] and metal carbides/nitrides (MXenes)[24] provide opportunities for creating new types of MSHSs. MSHSs can integrate the properties of 2D metals and 2D semiconductors in a single structure, and also produce transport[25] and magnetic[26] properties that are absent in the individual components, giving the materials a wide range of properties. For example, MSHSs are seen as candidates for future integrated 2D electronics, in which the metallic components with a high electrical conductivity serve as electrodes and connect with semiconductors with a high-quality interface, leading to a much reduced contact resistance.[27–29]
In addition, constructing MSHs opens a new way of modifying the electronic states and catalytic properties of 2D materials\[30,31\]. In particular, some metallic 2D materials like VS\textsubscript{2} have a high conductivity as well as electrochemical activity\[32\] so the heterostructures based on these materials are promising for energy-related applications. As examples of the new physics, some properties of metallic TMDCs, like 2D superconductivity\[33\] and charge density wave (CDW) states\[34\] can be tuned through interlayer coupling in MSHs. Therefore, MSHs will become an important topic in 2D materials and more studies are needed for both fundamental research and practical applications.

In this Review, we aim to present the latest research progress in the structure, preparation, and applications of 2D material-based MSHs. A classification based on structure is first given, and we then summarize methods to fabricate both lateral and vertical MSHs, including direct growth by chemical vapor deposition (CVD), post-synthesis chemical and phase engineering, and vdW stacking. We also discuss the uses of MSHs in electronic and optoelectronic devices, energy storage and conversion, and as platforms to explore new physics. Finally, challenges and future prospects are suggested to motivate more effort in this emerging research area.

2. Categories of 2D Material MSHs

Due to the versatile compositions of 2D materials and the few requirements to fabricate MSHs, in theory 2D-material based MSHs comprise a big family with many different combinations. From structural and dimensional points of view, MSHs are categorized into two types, i.e., all 2D MSHs and xD/2D hybrid MSHs (here x is 0, 1, or 3, Figure 1). The contact behavior is always a critical issue for the metal–semiconductor junctions, and forming ohmic contact is preferred for most electronics. The structural diversity of 2D material-based MSHs provides more routes to moderate the contact, from the Schottky contact to the ohmic one, which will be discussed later.

2.1. All 2D MSHs

Lateral and vertical heterostructures are the most common configurations for all-2D MSHs. For lateral MSHs, 2D semiconductors are stitched with 2D metals within the same atomic plane. In this case, different 2D components are connected with each other by covalent bonds formed at the one-dimensional interface. A sharp interface is the key feature of lateral MSHs, which may lead to unique optical and electrical transport properties. Due to lattice matching constraints, the lattice constant difference between the metallic and semiconducting components must be considered carefully to avoid large stresses or defects occurring at the interface. Limited by current CVD or post-treatment preparation approaches, only a few 2D components can be integrated into lateral MSHs, including graphene-semiconducting TMDC (e.g., graphene–MoS\textsubscript{2}\textsuperscript{35,36}), metallic TMDC-semiconducting TMDC (e.g., MoTe\textsubscript{2}–MoS\textsubscript{2}\textsuperscript{37}), and MXene-semiconducting TMDC (e.g., Mo\textsubscript{2}C–MoS\textsubscript{2}\textsuperscript{38}).

Different from lateral MSHs, 2D metallic flakes and 2D semiconducting flakes can be stacked together with fewer requirements for lattice matching by weak vdW forces, forming vertical MSHs\[7\]. Without lattice matching requirements, almost all metallic flakes and semiconducting flakes can be integrated, and the stacking process can be repeated many times to construct superlattices by layer-by-layer stacking\[39\]. For vertical MSHs, their electrical, optical, and magnetic properties not only depend on the components, but also are influenced by interlayer interactions, and this broadens their applications. In this article, lateral MSHs and vertical MSHs, which are made up of components A and B, are denoted as A–B and A/B, respectively.

2.2. xD/2D Hybrid MSHs

In addition to integrating different 2D materials, integrating them with other dimensional (0D, 1D, or 3D) materials can form xD/2D hybrid MSHs, which expands the existing 2D-material

Figure 1. Schematics of the different structures of 2D-material based MSHs. All-2D MSHs include a) lateral and b) vertical structures. Here, xD/2D MSHs include c) 0D/2D, d) 1D/2D, and e) 3D/2D combinations.
based MSHS family. For 0D/2D MSHSs, the most common examples are graphene quantum dots (QDs)\[^{40}\] or metal nanoparticles\[^{41,42}\] located on 2D semiconducting TMDCs. Taking the Ag nanoparticle/MoS\(_2\) system as an example, the coupling between the two components within the MSHS can be utilized to tune the photonic behavior of 2D semiconductors by changing light–matter interactions.\[^{41}\] For 1D/2D MSHSs, a combination of metallic carbon nanotubes (CNTs) and semiconducting TMDCs has been realized by either transfer\[^{43}\] or CVD growth\[^{44}\] methods. A FET based on 1D/2D CNTs/TMDC MSHSs, where the CNTs and TMDC are respectively used as gate electrodes and the channel material, scales down the lateral size of the heterostructure area to nanometer scale and has a great potential for use in nanoelectronics.\[^{45,46}\] 3D/2D MSHSs, combining a 2D semiconductor with 3D metallic materials, are very common and have been studied in several devices.\[^{47–49}\] In addition, the integration of graphene and a 3D semiconductor like GaN is another type of 3D/2D MSHS,\[^{50}\] which shows good stability at elevated temperatures due to the high thermal stability of graphene.

### 3. Preparation of 2D MSHSs

Integrating materials with different properties is an important strategy to build novel platforms for fundamental research and applications, as has been witnessed in the semiconductor industry. In the following section, we will introduce recent progress in the development of preparation methods of lateral MSHSs, including CVD growth and postsynthesis treatment methods, as well as vertical MSHSs, including vdW stacking, CVD growth, and some other methods.

#### 3.1. Lateral MSHSs

For lateral MSHSs, due to the chemical bond formed between the metallic and semiconducting components, it is difficult or even impossible to build such structures by aligned transfer or solution assembly methods. CVD growth or similar bottom-up synthesis approaches are the main methods to prepare high-quality 2D materials and have been proven to be able to integrate 2D semiconducting and metallic materials during the growth process to prepare lateral heterostructures. Recently, postsynthesis treatment has also been shown to be a path to obtain lateral MSHSs by a phase transition or chemical reaction. In the following section, the fabrication of lateral MSHSs by CVD growth and postsynthesis treatment methods will be discussed (Table 1).

#### 3.1.1. CVD Growth

CVD can grow individual 2D materials as well as lateral heterostructures of two different 2D materials. Since the first construction of a graphene/h-BN lateral heterostructure by CVD,\[^{51}\] a wide range of 2D lateral heterostructures has been produced by this approach.\[^{35,36,52–63}\] However, most research has focused on joining different 2D semiconductors, including 2H–2H phase TMDCs like MoS\(_2–\)WS\(_2\),\[^{54,55}\] MoSe\(_2–\)WSe\(_2\),\[^{56,57}\] MoS\(_2–\)MoSe\(_2\),\[^{58}\] MoS\(_2–\)WSe\(_2\),\[^{59,60}\] 1T–1T’ phase ReS\(_2–\)ReSe\(_2\),\[^{61}\] and even 2H–1T’ phase WS\(_2–\)ReS\(_2\).\[^{62}\]

CVD also offers an effective way to fabricate 2D lateral MSHSs. As one early representative, graphene was chosen as the metallic component to integrate with semiconducting TMDCs, forming graphene–TMDC lateral heterostructures.\[^{63}\]

As shown in Figure 2a, CVD-grown graphene was first transferred onto a SiO\(_2\) substrate, followed by patterning by photolithography and oxygen plasma etching. Later, MoS\(_2\) nucleated at the exposed edge sites of graphene and expanded into a continuous film filling the bare channels on the substrate, forming graphene-MoS\(_2\) lateral MSHSs.\[^{64}\] As these exposed edges are random and contain abundant defects, MoS\(_2\) prefers to grow along these edges and is polycrystalline, as shown by the false-color dark field transmission electron microscope (TEM) image in Figure 2b. Other methods of growing graphene–TMDC lateral heterostructures have been developed, in which patterning is a critical step for the nucleation of the TMDCs.\[^{35,65–67}\] So far, whether covalent bonds are formed between graphene and the TMDC is still unclear. Note that, monolayer TMDC consists of three atom layers, in which the metal atom layer is sandwiched between two layers of chalcogens

| Preparation methods | Materials | Notes | Ref. |
|---------------------|-----------|-------|------|
| CVD                 | Graphene–MoS\(_2\) | Millimeter scale; Overlapped junction area rather than seamless stitching | [64] |
|                     | VS\(_2–\)MoS\(_2\) | Two-step CVD; Multilayer core–monolayer shell structure | [75] |
|                     | 1T’–2H MoTe\(_2\) | One-step CVD; Multilayer thickness structure | [78] |
| Postsynthesis treatment | 1T–2H MoS\(_2\) | Phase transition via Li ion intercalation; Monolayer structure | [103] |
|                     | 1T–2H MoS\(_2\) | Phase transition via Ar plasma; Inevitable formation of S vacancies | [113] |
|                     | 1D MoSe\(_2–\)2D MoSe\(_2\) | Phase transition via electron beam irradiation; Electrical test in TEM | [108] |
|                     | Mo\(_x\)C–MoS\(_2\) | Chemical reactions via CH\(_4\) treatment; Centimeter-scale size | [126] |
atoms, while the graphene is composed of only one layer of carbon atoms. Therefore, in theory, it is difficult to connect these two components seamlessly by chemical bonds. As shown in Figure 2c, a cross-sectional TEM image of the interface indicates that some TMDC grows into the confined space between the graphene and the growth substrate, forming an overlapping junction rather than an atomically sharp junction.[65] This phenomenon is consistent with the previous report,[64] although the interface seems to be seamless under an optical microscope (OM).

In addition to the aforementioned graphene–TMDC, another type of lateral MSHS is metallic-semiconducting TMDCs. To prepare such a structure, the synthesis of the metallic TMDC is a prerequisite and is challenging. This is because a high temperature is needed to evaporate the metal precursor, whereas metallic TMDCs are not usually stable at such temperatures. The recent molten-salt-assisted CVD growth process has significantly enhanced the controllability and reproducibility of the growth of metallic TMDCs, by moderating the growth kinetics and reducing the temperature by the addition of salt.[68,69] The choice of growth procedure is also critical to prepare lateral MSHSs, which can be divided into one-step or two-step methods. For a direct one-step CVD method, different 2D components are synthesized and stitched together in a single growth procedure. Although this has been commonly used for synthesizing a MoS2–WS2 lateral heterostructure,[70,71] there is still no report for growing MSHSs by a one-step method. In addition, avoiding the alloying of the two components during growth must be carefully considered.[72] For a typical two-step growth method, the TMDC with the higher synthesis temperature was prepared first. Then, under mild growth conditions, the second TMDC would nucleate and extend from the edge of the first, forming lateral heterostructures. For example, a monolayer 1T–2H MoTe2–MoS2 lateral MSHS was synthesized by adjusting the supply sequence of the chalcogens.[37] The scanning transmission electron microscope high-angle annular dark-field (STEM-HAADF) image in Figure 2d shows the atomically sharp interface of the as-prepared heterostructure. Although there is a non-negligible lattice mismatch of >7% between MoS2 (b = 3.183 Å) and MoTe2 (b = 3.455 Å), the wrinkles in the MoS2 region caused by Te substitution release the strain and avoid the formation of misfit dislocations at the interface. However, as shown in the OM image in Figure 2e, the domain size of 1T–MoTe2, which would serve as the contact area for the FETs, is still small and needs to be increased. To date, only a few 2D lateral MSHSs have been reported, such as NbS2–WS2,[73,74] and VS2–WS2.[75] Unlike what has been reported in semiconducting MoS2–WS2 lateral heterostructures,[34] all these lateral MSHSs have a thicker shell–core structure and a relatively small lateral size, which inevitably hinders their availability for forming
contacts. It is believed that synthesizing a range of 2D lateral MSHSs of large size and high quality will be an important topic for CVD research in the following years. Furthermore, some superior design and experimental setups for growing a 2D lateral semiconductor superlattice, including reverse-flow CVD[76] and one-pot growth,[77] may offer a potential solution for modifying the growth of MSHSs.

Phase engineering during CVD growth is another way to prepare lateral 2D MSHSs. It is known that for Mo-based and W-based TMDCs, the 2H phase is semiconducting, whereas the 1T/1T‘ phase is metallic. Most reported CVD-grown 1T‘-2H TMDC homouni crystal structures are based on MoTe2,[78–82] due to the small energy difference between its 2H and 1T‘ phases (345 meV per unit cell).[83] For example, a 1T‘–2H MoTe2 lateral MSHS was synthesized using one-step epitaxial growth (Figure 2f–h) and it was found that temperature plays a key role in controlling the phase of MoTe2. At 670 °C, the reaction products are mainly the 2H phase, whereas the 1T‘ phase dominates at 710 °C. Therefore, some 1T‘–2H MoTe2 mixtures form between 670 and 710 °C. Figure 2i shows a homouni crystal possessing a clean and sharp interface without obvious defects. Tellurizing the predeposited Mo oxide film with different Mo/O stoichiometric ratios is another method to obtain 1T‘ MoTe2 lateral MSHSs with a large size.[84] This method provides a scalable way to integrate 2D material-based channels, electrodes, and interconnects into circuits in a single step.

In addition to MoTe2, some other TMDCs like VS2 and TaS2 also have small energy differences between their metallic and semiconducting phases,[85] and the CVD growth of 1T and 2H phases of VS2[86–87] or TaS2[88–89] has been realized. One could obtain lateral MSHSs if both phases were synthesized during one single growth process. However, for some TMDCs like MoS2, it is much more difficult to obtain their corresponding lateral MSHSs because of the large formation energy difference between the metastable metallic and stable semiconducting phases.[90] Specifically, MoS2 tends to form the 2H phase during CVD growth.[91–94] Recently, both a gas–solid reaction[94] and a K ion-assisted CVD method[95] have been reported to produce 1T‘–MoS2. However, synthesizing a 1T‘–2H MoS2 lateral heterouni crystal structures remains challenging. It worth mentioning that a 1T–2H WS2 lateral heterouni crystal was grown with the aid of synergistic catalysts (Fe3O4 and NaCl, Figure 2j)[96] but the following photoluminescence and exciton adsorption spectra indicate a direct bandgap semiconducting nature of 1T–WS2, which is inconsistent with present theory.[97] Further investigations on the properties of TMDC polymorphic phases are needed to ascertain their electrical properties.

### 3.1.2. Postsynthesis Treatment

In addition to the above CVD growth of lateral MSHSs, postsynthesis treatment is another approach to obtain lateral MSHSs. This involves inducing a phase change in certain areas or chemically modifying them. Both approaches could convert a selected area of a semiconducting TMDC into a metallic one, or the reverse, forming a lateral MSHS. Compared to the complicated in situ CVD growth of a lateral MSHS, such methods are more convenient and will be discussed in the following sections.

**Postsynthesis Treatment-Induced Phase Transitions**: To realize a phase transition of TMDCs, ion intercalation, external irradiation, and annealing are commonly used. As early as the 1980s, the ion intercalated metallic 1T or 1T‘ phase MoS2 nanosheets were obtained using Li ions during the chemical exfoliation process.[98] The mechanism was explained by the electron transfer from alkali metal to MoS2 increasing the stability of the metallic phase of MoS2, and also significantly decreasing the kinetic energy barrier for the phase transition.[99] By precisely controlling the intercalation process, metallic-semiconducting 1T (or 1T‘)–2H MoS2,[100–101] and 2H–1T TaS2,[102] heterouni crystal structures were prepared by chemically exfoliating the corresponding bulk materials. To enhance the spatial controllability of the ion intercalation process, it could be directly conducted on 2D flakes located on substrates (like the CVD samples), combined with patterning techniques like e-beam lithography. Based on this process, a 1T–2H MoS2 lateral MSHSs (Figure 3a)[103] and a complicated 2H–1T–2H–1T–2H WS2 superlatticet[104] were made. This lithiation process also depends on the thickness of the TMDC, requiring the concentration of the Li reactant to increase with decreasing number of TMDC layers. As a result a MoS2 flake with uneven thickness formed heterouni crystal structures in which the thicker part was converted to the 1T‘ phase while the monolayer retained the original 2H phase.[105] Apart from alkali metals, zero valent metals can also be intercalated into TMDCs and lead to a change of their electrical properties. For example, Gong et al. intercalated Cu or Co into the vdW gap of bilayer SnS2, converting it from n-type to p-type (Co-SnS2) and even to a metallic (Co-SnS2) state. Based on this conversion, different patterned SnS2-based MSHSs were obtained with the aid of lithography and, for the first time, 2D metal and n- and p-type semiconductors were stitched together in the same atomic plane as shown in Figure 3b.[106]

External irradiation like an electron beam and plasma can also convert semiconducting 2D materials into those with metallic states. Under the electron beam in the TEM, the irradiated MoS2 region undergoes a phase transition from the hexagonal 2H phase to the metallic octahedral 1T phase, and by spatially moving the electron beam, the 1T–2H interface moved, leading to an expansion of the metallic phase area.[107] Lin et al. directly sculpted 2D semiconductor MoSe2 into metallic MoSe nanoribbons by manipulating a focused electron beam (Figure 3c), which suggested a new way to fabricate metal interconnects for future 2D electronics.[108] A plasma, which is a useful tool for defect engineering[109,110] and reducing the thickness[111,112] of layer materials, can also be used to modulate the phase transition.[113,114] Unlike an electron beam, a plasma is always generated in the whole reaction chamber and cannot achieve selected-area etching.[115] Using a prepatterned mask, a large area of 1T–2H MoS2 MSHSs pattern has been realized under an Ar plasma.[116]

In addition, some experiments have shown that heat treatment leads to the structural rearrangement of TMDCs to lower the energy.[116–118] Unlike the recurring transformation between 2H and 1T phases, 2H–MoTe2 shows a unique phase transition under vacuum annealing.[119] As shown in Figure 3d, a parallel bundle of metallic Mo4Te6 nanowires was formed and stitched to pristine 2H–MoTe2, forming lateral MSHSs.
Postsynthesis Treatment-Induced Chemical Reactions: Although there is a sharp interface in the lateral MSHSs prepared through phase transitions, the obtained metallic phase is usually metastable, which hinders their applications in ambient conditions. By contrast, for the lateral MSHSs prepared through chemical reactions, the as-formed metallic components can be stable. MXenes are promising 2D metals due to their excellent stability and electrical conductivity. Most research has been limited to etching the ceramic MAX phase (M$_{n+1}$AX$_n$, where M is an early transition metal, A is a group A element such as Al or Si, and X is C and/or N, $n = 1–3$) in solution, so the exfoliated MXenes inevitably contain surface functional groups and defects, which degrade their intrinsic properties. Recently, chemical conversion between layer materials and nonlayer materials has become a hot topic. High-quality MXenes with no surface groups can be obtained by annealing a TMDC in CH$_4$ or NH$_3$, providing a new method for constructing 2D MSHSs. For example, Choi et al. patterned a CVD-grown MoS$_2$ film with a mask and in subsequent CH$_4$ treatment the exposed area was converted to metallic Mo$_2$C, while the protected MoS$_2$ area remained unchanged (Figure 3e). The size of the formed lateral MSHS array reached hundreds of micrometers. In a similar way, under NH$_4$ treatment, Mo$_2$S$_2$ was converted to metallic Mo$_3$N$_6$, and MoS$_2$–Mo$_2$S$_2$ lateral MSHSs were made by controlling the reaction time. Compared with growth methods like CVD, post-treatment such as mentioned above does not need rigorous growth conditions. This topic would be one basis of heterostructure preparation processes, which can greatly increase the number of existing MSHSs.

3.2. Vertical MSHSs

Due to the smooth surface and absence of dangling bonds, isolated 2D materials, e.g., 2D metals and 2D semiconductors, can be directly stacked. CVD is a powerful tool and has the potential to fabricate an array of vertical MSHSs. Furthermore, there are some other preparation approaches, including solution assembly, wet chemistry synthesis, and post-treatment methods, which can also build MSHSs (Table 2).

3.2.1. vdW Stacking

Typically, vdW stacking (aligned transfer) consists of two steps. 2D materials are first disassembled from the bulk and are then stacked in the desired sequence by operating a micromanipulator under OM. Since Scotch-tape-based mechanical exfoliation was used to isolate graphene from a graphite crystal, it has become a universal approach to produce a wide range of 2D materials. In the past decade, many efforts have been made to exfoliate high-quality single crystals with a large domain size. However, it is difficult to obtain bulk crystals of wafer-scale to exfoliate into 2D flakes. CVD or molecular beam epitaxy (MBE) synthesized 2D continuous films with a few-layer thickness are also a choice as materials for monolayer production. For example, Shim et al. developed a layer-resolved splitting technique based on Ni stickers, that produced a 5 cm-diameter monolayer TMDC on a host wafer from a few-layer sample (Figure 4a). Such an improved exfoliation method is a prerequisite for stacking wafer-scale 2D flakes as vertical MSHSs.
Maintaining clean surfaces during stacking is essential for the integration of 2D materials into high-quality vertical heterostructures. Neither dry nor wet transfer can avoid absorbed contamination or residual polymer because of air, water, and amorphous carbon contamination in the ambient transfer environment or organics left when the polymer is dissolved in the solvent. To solve these problems, a programmed vacuum stacking process operated in vacuum conditions was developed by Kang et al., in which wafer-scale TMDCs were stacked with thermal release tape (Figure 4b). The whole transfer process avoids any contact of liquid with the 2D materials being transferred. Cross-sectional STEM measurements (Figure 4c) have verified that the interface of these large heterostructures is contamination-free. Up to now, vdW stacking has become a common method to construct graphene and semiconducting TMDCs into vertical MSHSs, and these hybrids provide more opportunities for electronics and optoelectronics. However, due to the difficulty of cleaving other 2D metallic materials into few layer or monolayer, the category of manually stacked MSHSs is still limited. Compared with other methods, precise control of

| Preparation methods | Materials                  | Notes                                                                 | Ref. |
|---------------------|----------------------------|----------------------------------------------------------------------|------|
| vdW stacking        | Graphene/WS₂/Graphene      | Dry transfer FET with \( I_{ON/OFF} \) ratio \( \gg 10^6 \)           | [17] |
|                     | Graphene/MoS₂/Graphene     | Dry transfer Photovoltaic devices with an external quantum efficiency of 55% | [134]|
| CVD                 | MoS₂/Graphene              | Two-step CVD Continuous polycrystalline MoS₂ film on graphene        | [142]|
| VSe₂/WSe₂           | Two-step CVD; Periodic 2D MSHSs arrays with wafer scale FET with \( I_{ON} \) of up to 900 \( \mu A \ \mu m ^{-1} \) | [153]|
| CNTs/MoS₂           | Two-step CVD; Random orientation of CNTs film Photodetector with higher photoresponsivity than Au-contacted ones | [44] |
| Other methods       | Graphene/WS₂/Graphene      | Solution-assembly; Small domain size of the exfoliated 2D flakes Large-size arrays of photodetectors on flexible substrates | [168]|
| 1T/2H MoTe₂         | Phase transition via laser irradiation; Limited by the laser beam size FET with \( \approx 50 \) times higher mobility than pure 2H-MoTe₂ | [175]|

Figure 4. Fabrication of vertical MSHSs by vdW stacking. a) Schematic of the layer-resolved splitting technique. (Right: OM image of the isolated mono-layer WS₂ with a diameter of 5 cm). Reproduced with permission.© 2018, American Association for the Advancement of Science (AAAS). b) OM image of the as-transferred MoS₂ films based on the programmed vacuum stacking process. c) Cross-sectional STEM-HAADF image showing the clean interface of the stacked MoSe₂/MoS₂/WS₂ heterostructure. b,c) Reproduced with permission.© 2017, Springer Nature. d) Schematic of folding graphene into a sandwich structure by an STM tip. e) 3D STM topography of the folded structure. d,e) Reproduced with permission.© 2019, AAAS.

Table 2. Summary of vertical MSHSs.
the rotation angle is one extra degree of freedom for the vdW stacking of 2D materials, and this will accelerate the use of vertical MSHSs in twistronics.[136]

It has recently been found that a scanning tunneling microscope (STM) tip can be used to fold graphene from the edge, forming folded bilayer graphene homostructures (Figure 4d,e).[137] This flake-folding operation suggests another way of constructing vertical MSHSs. By picking up the edge of an air-stable 2D semiconductor flake, 2D metallic material could be sandwiched inside the folded semiconductor. This novel method could not only protect the air-sensitive 2D metallic material from ambient conditions, but also control the stacking angle between the top and bottom semiconductor layers and the metal layer between them. Similarly, an atomic force microscope tip or a dome-shaped polymer probe also shows potential for this manipulation process.[138]

3.2.2. CVD Growth

Although manual stacking can produce a variety of vertical heterostructures, the process is highly dependent on the researcher’s experience and is difficult to scale up. As a bottom-up strategy, CVD method has the potential to prepare a number of vertical MSHSs with high quality and large quantity.

Graphene is an ideal substrate for the epitaxial growth of TMDCs due to their similar hexagonal structure.[139,140] However, the metal substrate (Cu, Ni, etc.) used for graphene growth is not suitable for growing TMDCs due to the reaction between S and these transition metals. Therefore, graphene is typically transferred onto a SiO2/Si substrate for the later growth of TMDCs to form vertical MSHSs.[141] To decrease contamination caused by transfer, an all-CVD process is necessary. Pioneering work by Shi et al. produced a two-step CVD method to obtain MoS2/graphene vertical MSHSs.[142] In this work, the liquid precursor (NH4)2MoS4 was deposited on pregrown graphene, followed by decomposing it into MoS2 at 400 °C (Figure 5a). The epitaxial relationship between MoS2 and graphene was revealed by fast Fourier transform analysis (Figure 5b) extracted from the heterostructure area. Due to the being no transfer in the growth process, it produces a clean overlapped area without much contamination (Figure 5c). There are other reports of integrating semiconducting TMDCs with graphene by similar CVD process.[143,144]

Because of their similarity to graphene, semiconducting TMDCs can also be used as templates for the growth of metallic TMDCs on their surface by vdW epitaxy. In such a growth method, a wide range of vertical TMDC MSHSs have been fabricated, including NbS2/MoS2,[145] WTe2/WSe2,[146] VSe2/WSe2 vertical MSHS array. (Figure 5d,e). Cross-sectional STEM-HAADF image showing the sharp interface of a VSe2/WSe2 vertical MSHS. d,e) Reproduced with permission.[153] Copyright 2020, Springer Nature. f) Schematic of a CNTs/MoS2 MSHS film. g) TEM image of a CNTs/MoS2 hybrid film. h) SEM image of a transistor array based on a CNTs/MoS2 MSHS film. f–h) Reproduced with permission.[148] Copyright 2018, Wiley-VCH.
NbTe$_2$/WSe$_2$,[147] VTe$_2$/WSe$_2$,[147] TaTe$_2$/WSe$_2$,[147] and VSe$_2$/WSe$_2$.[148] Precisely defining the location of the nucleation sites on the TMDC 2D flake is critical for the CVD growth of the heterostructures. Recently, defects like boundaries, exposed edges or dislocations in the TMDCs have been found to act as low energy nucleation sites,[149–152] and based on this, Li et al. recently proposed a universal method for synthesizing 2D vertical MSHSs arrays by creating periodic defect arrays on a large-scale semiconducting WSe$_2$ film, which serve as the nucleation sites for secondary-grown metallic TMDCs (Figure 5d).[153] The periodic arrangement and lateral size of the top 2D metal layer could be modulated by changing the defect pattern. A clean interface is shown by the STEM-HAADF image in Figure 5e.

2D material-based vdW heterostructures have been found to be scissored into 1D forms. For example, Xiang et al. synthesized a 1D vdW heterostructure by CVD, in which single-wall CNTs were wrapped by outer h-BN and MoS$_2$ nanotubes.[154] This 1D tubular structure provides a new structure design idea for vdW MSHSs.

Apart from these two 2D vertical MSHSs, mixed heterostructures including 1D/2D[44,155,156] and 3D/2D[157–160] can also be realized by CVD growth. For 1D/2D MSHSs, as demonstrated by Li et al., a CVD method to produce metallic CNTs/semiconducting TMDC hybrid films was developed.[146] First, CNTs were grown by a floating catalyst CVD method and transferred onto sapphire. MoS$_2$ was then nucleated under the CNTs and continued to grow, forming CNTs/MoS$_2$ vertical heterostructures (Figure 5f,g). By oxygen plasma etching, device arrays with MoS$_2$ as channels and CNTs/MoS$_2$ as electrodes were fabricated (Figure 5h), and used for photodetection. For 3D/2D heterostructures, Au/MoS$_2$ is a classical combination because Au is a good metal but is little studied, and this may be a novel approach to decorate noble metals (Au or Ag) on W- or Mo-based TMDCs.[152] In addition, post-treatment could change the electronic properties of the upper layers while leaving the lower ones in their original state.

**Solution Assembly:** Top down exfoliation is seen as an important strategy for the mass production of 2D materials for industrial applications.[161–163] Recently, some encouraging exfoliation methods have been reported which can produce 2D metallic and semiconducting materials with electronics-grade quality that have few layer or even monolayer thickness.[164–166] Such exfoliated 2D flakes can be dispersed in a variety of solvents, giving dispersions with needed concentrations. Compared with traditional spin coating or vacuum filtration, inkjet printing has shown great advantages in constructing heterostructures.[167] In addition to preparing suitable inks, how to avoid different 2D materials remixing is a key element for constructing vertical heterostructure with sharp interfaces. McManus et al. designed a modified water-based 2D material ink with suitable viscosity and surface tension for inkjet printing.[168] With the help of a suitable binder the 2D materials did not disperse during the subsequent printing process. Figure 6a shows an as-printed graphene/WS$_2$/graphene MSHS, which has a high photocurrent response and shows potential for use in flexible photosensors. Solution processing also provides a scalable method for building mixed dimensional heterostructures, such as the integration of 0D/2D[160] and 1D/2D configurations.[169] As shown in Figure 6b, after a droplet of graphene QDs was placed on a 2D MoS$_2$ monolayer, they became uniformly dispersed on the surface, which changed the valley polarization of the underlying MoS$_2$. Limited by the lateral size and thickness of present exfoliation technique, it is difficult for solution assembled MSHS-based devices to match the performance of samples produced using nanoscale methods. However, due to its high yield and low cost, solution assembly must be an important process for future industry-scale flexible electronics.

**Wet Chemistry Synthesis:** Hydrothermal and solvothermal processes are widely used to synthesize nanomaterials, including 2D TMDCs.[10] The reaction always happens in a sealed environment with high temperature and high pressure, and water or organic solvents act as reaction media. By adjusting the precursors, this simple and inexpensive method has been used to obtain a series of vertical MSHSs, including rGO/MoS$_2$,[170] MoS$_2$/CoSe$_2$,[171] Sn$_0.3$W$_0.7$S$_2$/SnS$_2$[172] etc. Another advantage of these processes is the various complex structures of the synthesized materials, which could contribute to their electrocatalysis and energy storage performance.

A hot-injection reaction, in which a precursor solution is rapidly injected into the reaction solvent, is another method to synthesize MSHSs.[173,174] Recently, Sun et al. proposed a universal approach to decorate noble metals (Au or Ag) on W- or Mo-based TMDC nanosheets to form 0D/2D and 2D/2D hybrid structures.[174] As shown in Figure 6c, Au tends to deposit as nanoparticles distributed on all MS$_2$, MSe$_2$ and MTe$_2$ compounds (M = Mo or W), whereas when Ag spreads over MTe$_2$, forming a Ag/MTe$_2$ 2D/2D heterostructures. These different deposited morphologies are explained by the different reducing ability of the TMDCs.

**Post-synthesis Treatment:** Shining an energy beam like a laser on 2D multilayers may cause the formation of vacancies or a phase transition, which may change the electronic states of the upper layers and form vertical homostructures. An interesting study by Cho et al. shows that laser irradiation converts the upper semiconducting 2H MoTe$_2$ layers into a metallic 1T’ phase with a reduction of thickness.[175] Similarly, for 2D PdSe$_2$, which is a novel semiconductor with a layer-dependent bandgap, external irradiation was found to induce a semiconducting-to-metallic phase change, leading to the formation of PdSe$_2$/Pd$_3$Se$_7$ vertical MSHSs (Figure 6d).[176] The generated Se vacancies play a key role in the structural change of PdSe$_2$.[177] These examples have shown the ability of post-treatment in preparing vertical MSHSs.
Such direct processing of 2D materials is scalable and appropriate for the potential batch fabrication of MSHSs.

4. Applications of 2D MSHSs

With continued research in MSHSs, this integrated metal/semiconductor structure has shown potential for use in electronic and optoelectronic devices, energy storage, and electrocatalysis, and as a platform to explore new physics like 2D magnetism and superconductivity. In this section, recent progress on the applications of MSHSs in these areas is discussed.

4.1. Electronic and Optoelectronic Devices

2D materials are seen as promising channel materials in transistors. On the one hand, their natural atomic thickness gives 2D semiconductors short conduction channels, leading to a rapid switching performance, and their thinness ensures that they have the good flexibility required for wearable devices. Although in recent years, great efforts have been made to obtain 2D-based transistors for electronic devices, there is still great difficulty in bringing this to fruition and there are gaps between theory and practice. Considering MoS\textsubscript{2} as example, which is a representative 2D semiconductor, it has a theoretical room-temperature electron mobility of over 400 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}[179] but experimentally it is usually below 200 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}[180,181].

Apart from defects in the 2D channel, the large resistance caused by the less-than-ideal contact between the channel and the electrode is mainly responsible for the reduced value.[27,182,183] Therefore, optimizing contact is of significance for high-performance devices.

The Schottky barrier height (SBH) is a measure of the quality of a metal-semiconductor junction, where a higher SBH means a higher energy barrier for carriers to overcome when crossing the junction. Ideally, the SBH could be described by the energy difference between the work function of the metal and the band edge of the semiconductor, namely the Schottky–Mott rule.[184,185] This means that the contact could be modified by selecting a different metal with a suitable work function depending on the channel material. Unfortunately, for a typical top contact, the inevitable Fermi-level pinning effect (FLPE) means that the selection of a different metal may have a limited role. It may be attributed to the poor interface states between the metal electrode and the semiconductor produced by conventional device fabrication processes, such as metal deposition and lithography.[186–188] As shown in Figure 7a, obvious defects, fractures, and an amorphous area appear at the interface during “high energy” deposition,[189] which causes a nonnegligible FLPE and leads to the poor transport performance of the FETs.

One major advantage of MSHSs is the low contact resistance between the electrode and the channel. For vertical MSHSs, a 2D metallic material has face-to-face contact with a 2D semiconductor with only weak vdW forces between them. This novel contact geometry is efficient in eliminating the FLPE. Liu et al showed the origin of the weak FLPE of vdW contact by theoretical simulation.[190] Considering 1T-MoS\textsubscript{2}/1H-MoS\textsubscript{2} as an example, the distribution of the states within the bandgap of the interface is almost dominated by the metal, which means the combination does not give rise to metal-induced gap states (MIGS) so that the
FLPE does not occur. Experimentally, with the continuous discovery of 2D metallic materials, the types of vdW contact are expanding by either transfer methods or epitaxial growth. Graphene is the first choice for a 2D electrode. In an early study, Das et al. assembled all 2D thin-film transistor with graphene as the electrode, WSe₂ as the channel, and h-BN as the dielectric material. This low-resistance device exhibited a high \( I_{ON/OFF} \) ratio of 10⁷ as well as a high carrier mobility of 45 cm² V⁻¹ s⁻¹.¹⁹¹ Metallic TMDCs have also become promising electrode candidates. Ji et al. synthesized a few-layer metallic VS₂ nanosheet by CVD and stacked it on MoS₂ as the electrode. Compared with a Ni/Au contacted MoS₂ FET, the contact resistance of the VS₂ contacted MoS₂ FET was decreased more than 75%.³⁸⁶ Although recently reported transfer¹⁸⁹ or imprinting¹⁹² 3D electrode methods could also form defect-free 3D/2D vdW contacts (Figure 7b), they require either a precise transfer process or not too high a temperature of combination, which is difficult to match with current electronic fabrication requirements.

For lateral MSHSs, a 2D semiconductor and a 2D metal have been seamlessly stitched together with a sharp interface, generating an edge contact. Analogous to vdW contact, the FLPE should also be negligible for edge contact geometry, but the underlying mechanism is different.²⁵,¹⁹³,¹⁹⁴ As ab initio simulation based on a monolayer 1T-2H MoS₂ lateral MSHS shows that MIGS will penetrate the Schottky barrier, significantly reducing the energy gap for carriers to move from the metal to the semiconductor.¹⁹⁴ Kappera et al. observed superior transport performance in such lateral MSHSs. A 1T-2H MoS₂ lateral heterostructure was prepared by Li ion intercalation, and contact between the metallic 1T phase and the semiconducting 2H phase was ohmic with a low value of 200–300 Ωm at zero gate bias (Figure 7c), which is less than a fifth of typical Au top contact.¹⁰³ This Li-ion intercalation strategy also works for other 2D materials like WSe₂.¹⁰⁴

As discussed earlier, for both vertical MSHSs with vdW contact and lateral MSHSs with edge contact, the FLPE is negligible.
meaning the Schottky–Mott rule should be followed for the selection of the individual MSHS components. To lower the SBH, for n-type semiconductors 2D metals with low work functions will match better, whereas 2D metals with a high work function are preferred for p-type ones. Figure 7d shows a library of simulated work function values for different 2D metallic materials and the bandgap of 2D semiconductors.[139] It is obvious that 2D metallic materials have a wider range of work functions than traditional 3D bulk metals, from the low work function of highly N-doped graphene (as low as 5 eV) to the very high value of 2H-NbS2 (even much higher than Pt), which provides a really large range of ways to moderate the SBH of MSHSs. Recently, Zhang et al. prepared VSe2/MoSe2 and VSe2/WSe2 vertical heterostructures and used a Kelvin probe force microscope to investigate the Fermi-level difference between the metallic VSe2 and the semiconducting components.[140] For n-type MoSe2, there is ohmic contact at the interface of VSe2/MoSe2 heterostructure, whereas for p-type WSe2, VSe2 tends to combine with it to form a Schottky barrier diode. In conclusion, the Schottky–Mott rule will provide a guideline for future MSHS design.

For the commercial production and application of 2D electronics, 2D material-based MSHSs should be able to be used in the device manufacturing process. The CVD production method, in which a metallic electrode is bridged on a semiconductor during in situ growth without any destructive post-processing treatments, will be a possible choice. Ideally, because of its high controllability, CVD should be able to produce a patterned array of MSHSs, which is a precondition for integrated circuits. As mentioned earlier, Li et al. synthesized large-scale WSe2 transistors arrays (Figure 7e), with superimposed VSe2 working as source and drain electrodes.[153] Thanks to the high-quality interface of the MSHSs, the as-fabricated WSe2 transistors showed ohmic contact (Figure 7f) with a cumulative mobility of around 100 cm2 V−1 s−1, whereas the contact performance of the WSe2 with deposited Cr/Au electrodes was much poorer with a mobility of around 10 cm2 V−1 s−1 and a nearly 1000 times lower ION/OFF ratio.

In addition to electronics, optoelectronics is another important application for 2D MSHSs. One apparent advantage of 2D-based MSHSs is their nm-scale thickness, enabling tunable light absorption and transmittance, which is crucial for optoelectronic devices such as photodetectors and photovoltaic devices. For MSHSs, in addition to their superior contact performance, the metallic layer could help in the separation of photogenic carrier pairs, leading to a high photoreponse efficiency. For example, Yu et al. fabricated a graphene/MoS2/graphene vertical MSHS-based photovoltaic device with a maximum external quantum efficiency of 55% and an internal quantum efficiency up to 85% (λ = 488 nm).[134] This sandwich structure provides a new approach to moderate photocarrier generation, separation and transport with the help of an external back-gate voltage. In addition, a metallic layer could also be inserted in the p/n junction as an interlayer, forming a p-type metal/n-type vdW heterostructure. In one study, Li et al. produced a MoTe2/graphene/SnSe2 MSHS and investigated its photodetecting performance.[139] For this vertical heterostructure, MoTe2 is in the 2H-phase and is p-type, whereas SnSe2 is an n-type semiconductor. The sandwiched graphene not only accelerated electron transport but also delayed interface charge traps, leading to a much higher photoreponse. The photodetector achieved an ultrahigh response of over 2600 A W−1 and a specific detectivity up to 1.1 × 1013 Jones over a broad spectrum from ultraviolet to short-wave infrared. Until now, for MSHS-based optoelectronics, most reports have used graphene as a conductive layer rather than 2D metal because it has a low theoretical absorption value of 2.3% per layer.[136] The advantages of other metallic materials in optoelectronic applications still need to be explored.

4.2. Energy Storage and Conversion

Due to the increasing demand for energy and the resulting environmental problems, developing environmentally friendly and sustainable energy pathways with high efficiency is becoming important. Recently, many 2D materials have shown excellent performance as electrodes or electrocatalysts for water splitting, including graphene, TMDCs (like MoS2), MXenes (like TiC2), etc.[197–199] In addition to defect and phase engineering, which are common methods to improve the intrinsic performance of 2D materials,[200,201] integrating them with different components into heterostructures provides a novel way to change the performance by synergetic chemical coupling effects.

Ion batteries are important energy storage systems. Thanks to their layer structure and large specific surface area, 2D material-based electrodes have abundant ion intercalation sites, leading to a high charge storage ability. Stacking different 2D materials into heterostructures will also modify the battery performance.[31] Compared with pristine 2D building blocks, vdW heterostructures have a weaker interaction between the layers, which increases the interlayer spacing between them.[202] This allows the accommodation of more ions and increases the ion diffusion speed, so both energy and power densities are improved for vdW heterostructures. Especially for MSHSs, in which metallic materials increase the electric conductivity of the overall electrode, ensuring the superior performance during high-speed charge-discharge cycling. In addition to graphene-based MSHSs, which have become a common electrode material,[170,202,203] some combinations of 2D semiconductors and other metallic materials (metallic CNTs, TMDCs, and MXenes) may also be useful.[204–206] For example, Chen et al. synthesized MoS2/MXene MSHSs by the in situ annealing of hybrids of Mo2TiC2T and sulfur particles.[207] The prepared compound has a high reversible average capacity of 548 mA h g−1 at a current density of 50 mA g−1 for Li-ion batteries. It also has a much higher capacity and better cycling stability than individual Mo2TiC2T and MoS2.

For electrocatalysis, water electrolysis has become a crucial technology for energy conversion. Through the hydrogen evolution reaction (HER), H+ or water is reduced at the electrode/electrolyte interface, generating H2. MoS2 is an important HER catalyst because its edges and intrinsic defects function as active sites.[208] Combining MoS2 and graphene into MSHSs is an effective way of increasing the HER activity, which can be explained by both electronic coupling and an overall increased conductivity.[209,210] Also, for MSHSs catalysts, metallic TMDCs may replace the function of graphene because they have a much higher performance originating from their basal-plane active sites.[211,212] Some TMDC-based MSHSs, such as 1T-MoS2/2H-MoS2,[213] MoSe2/NiSe,[173] MoS2/VS2,[214] and MoS2/CoSe2[217]
have been synthesized and show a better HER performance than the single components. For these MSHS catalysts, the underlying mechanism needs more research. Some studies attribute the better performance to synergistic effect; however, more detailed understanding is very important to design suitable MSHS catalysts with superior performance.

4.3. Platform to Exploit New Physics

In addition to the aforementioned applications, 2D MSHSs are also a good platform to explore new physics. Metallic TMDCs have attracted a lot of attention because of their unique physical properties, including 2D superconductivity,[33] magnetism[215] and CDW states.[134] How to take advantage of and change the new physics is always an important research topic. Until now, many methods have been explored, including thinning, straininduced, and hole/electron doping the 2D materials.[216–218] Stacking a 2D semiconductor with a metallic TMDC provides an effective way of changing these properties. Unfortunately, due to the difficulty of mechanically exfoliating or synthesizing 2D metallic TMDCs, it is difficult to obtain their corresponding heterostructures. Although only a few pioneering studies have been reported, it is believed that metallic TMDC-based MSHSs are a suitable platform for the fundamental study of these 2D-related new physics.[219–221]

Wang et al. transformed the top layer of bulk 1T–TaS2 into the 2H phase by annealing, forming a monolayer 2H–TaS2/bulk 1T–TaS2 vertical homostructure.[219] The superconducting transition temperature (Tc) of the sample is around 2.1 K, which is about a threefold increase over that of bulk 2H–TaS2. The authors claimed that the suppressed 3 × 3 CDW and charge doping from the substrate contribute to the higher Tc. This work also provided a way to investigate the proximity effect between 2D CDW and superconductivity. Later, the same group changed the CDW order in 1T–TaS2 by forming a 1T–TaS2/black phosphorus vdW heterostructure.[221] A nearly commensurate CDW (NCCDW) exists until 4.5 K, much lower than the phase transition temperature from NCCDW to CDW. Interestingly, due to the anisotropic property of black phosphorus substrate, the transport properties of 1T–TaS2/black phosphorus are also anisotropic.

Stacked vdW MSHSs are an important platform for studying and understanding the 2D physics, and the twist angle is an additional important factor.[222,223] For stacked MSHSs, twisted structures are still unreported and there are many opportunities to explore the relationship between the interlayer interaction and the twist angle.

5. Conclusion and Outlook

We have reviewed recent progress in 2D material-based MSHSs. From the structural viewpoint, MSHSs are classified into all 2D MSHSs (lateral and vertical) as well as xD/2D hybrid MSHSs (0D/2D, 1D/2D, and 3D/2D). Several preparation methods for MSHSs have been introduced and comparisons between these methods are discussed. Finally, the uses of MSHSs in electronics, optoelectronics, energy storage and conversion, and fundamental studies have been considered. MSHSs are still in their infancy and there are many issues waiting to be investigated, such as finding new 2D metallic materials, improving control of their preparation, understanding the interfaces, and exploring further applications, as shown in Figure 8.

First, new preparation methods for 2D metallic materials need to be developed. Compared with 2D semiconductors, the number of 2D metals is very limited. In addition to graphene, metallic TMDCs and MXenes, some newly emerging 2D metals, such as metallene,[224–226] borophene,[227,228] Fe3Te2,[229] have become potential components to expand the MSHS family. However, they are not easy to prepare and may be unstable. For metallene and borophene, there are no natural parent layer materials for exfoliation, and only bottom-up strategies with rigorous conditions can synthesize these 2D materials. For materials like Fe3Te2, bulk layer materials can be synthesized by the flux method, but the strong interaction between the layers makes it difficult to cleave them into the 2D form. Therefore, using a special substrate with which they have a strong interaction or intercalating specific ions/molecules into bulk layer materials may provide a new way to prepare the 2D form. Some recently developed new methods, for example, the dissolution–precipitation growth method, may be helpful to grow such 2D materials and need further development.[230] In addition, many metallic materials easily degrade in ambient conditions and how to protect them during the preparation process is an important topic. To this end, Briggs et al. synthesized 2D Ga, In, and Sn in the confined space between a silicon carbide substrate and graphene, which significantly improved their stability.[231] Such in situ encapsulation may be a way to grow unstable 2D materials, especially metallic ones. The use of stable 2D materials like graphene oxide or TMDCs as substrates to grow and stabilize unstable or metastable 2D metals is another interesting direction and needs investigations, such substrates can protect the oxidation of 2D metals from the bottom surface.[232] Also, decreasing the defects level of the as-prepared 2D metals can enhance the stability. The
vacancies of 2D materials tend to absorb oxygen molecules and promote the oxidation process, therefore preparing 2D metals with high quality is essential to address this challenge.\textsuperscript{[213]} Second, the controllability of preparing MSHSs needs to be improved. CVD is most likely to achieve scalable of electronic-grade 2D MSHSs for the semiconductor industry,\textsuperscript{[234]} however, compared with growing individual 2D materials, controlling the growth of heterostructures is far more difficult. In a conventional CVD process for preparing MSHSs, it is difficult to control the nucleation sites for the second component located at the edges or on the surface of the first one, which leads to a low yield. In addition to creating defects on TMDCs to serve as nucleation sites,\textsuperscript{[153]} coating the substrate with seeding promoters\textsuperscript{[92]} or depositing Au seeds\textsuperscript{[235]} at selected positions during the time between the two growth steps may also guide the nucleation process. These methods will also contribute to the aligned or patterned growth of MSHSs. For MSHSs obtained by post-treatment methods, although patterning techniques like e-beam lithography have been used to enhance the controllability, the patterning process is complicated and may leave residues on the surface. Techniques with high spatial resolution, such as electron beam irradiation, may help achieve the lithography-free preparation of MSHSs. Among all these methods, obtaining a sharp (for lateral MSHSs) or clean (for vertical MSHSs) interface is always a key challenge. During the preparation process, it is difficult to prevent the contaminations absorbed on the edges or surfaces of 2D materials in ambient environment. Therefore, finishing all the preparation process in inert atmosphere or high vacuum condition would be helpful. Furthermore, the preparation process must be controlled precisely to avoid the unexpected defects caused by harsh reaction conditions. Computing or simulation techniques may be helpful to reduce the workload for finding the optimum experimental parameters. Recently, substitutional doping has also become a strategy to increase the electrical conductivity of semiconducting TMDCs,\textsuperscript{[28,29]} even to producing metal-like conduction.\textsuperscript{[236]} To realize this goal, a universal doping strategy with tunable dopant concentrations is needed,\textsuperscript{[137,238]} and the influence of different dopant atoms remains to be determined. Beyond simple MSHSs with two components, the design and fabrication of complicated MSHSs or superlattices with multiple alternatively stitched or stacked components is an interesting topic to pursuit.

Third, more effort is needed to study the new physics in MSHSs which is quite different from that of their single components. Researchers have paid much attention to the electronic transport properties in MSHSs due to their potential use in 2D electronics. The state of the interface plays a key role in determining the carrier transport behavior across the interface, and defects or contaminations at the interface will significantly degrade the device performance. For lateral MSHSs, there is an accumulated strain at the 1D interface because of the different lattice constants. However, the relationship between strain and the change of transport behavior between a metal and a semiconductor is still not clear. Recently, Ugeda et al. observed topologically protected states at the interface of 1T'-2H WTe\textsubscript{2},\textsuperscript{[239]} which will broaden the study of the interface of lateral MSHSs. For vertical MSHSs, in addition to transport properties, some pioneering studies have investigated or predicted their optical and magnetic properties induced by the interlayer coupling.\textsuperscript{[26,220]} This will be an important topic for 2D physics.

Finally, in addition to the applications mentioned in Section 4, more applications need to be explored based on the intriguing coupling between metals and semiconductors in MSHSs. For example, some pioneering studies have shown the suitability of 2D material-based MSHSs in the sensing of gases,\textsuperscript{[240,241]} organics,\textsuperscript{[242]} and DNA.\textsuperscript{[243]} In addition, the ultrafast excitonic behavior in MSHSs could broaden the applications of 2D materials in optoelectronic devices,\textsuperscript{[220]} and the unique spintronic states in Fe\textsubscript{2}GeTe\textsubscript{2}-based MSHSs will be used in future magnetic storage applications. Meanwhile, some 2D materials are anisotropic in electronic and optical properties, and considering the large intrinsic anisotropic of 1D system, the 1D/2D MSHSs may be particularly interesting in polarized optics. Along with the development of advanced fabrication techniques and a deep understanding of the physics involved, it is believed that 2D material-based MSHSs will offer many uses in materials science, electronics, energy, physics, and nanotechnology.

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Conflict of Interest
The authors declare no conflict of interest.

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