Synthesis, properties and applications of 2D non-graphene materials

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Topical Review

Synthesis, properties and applications of 2D non-graphene materials

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Abstract
As an emerging class of new materials, two-dimensional (2D) non-graphene materials, including layered and non-layered, and their heterostructures are currently attracting increasing interest due to their promising applications in electronics, optoelectronics and clean energy. In contrast to traditional semiconductors, such as Si, Ge and III–V group materials, 2D materials show significant merits of ultrathin thickness, very high surface-to-volume ratio, and high compatibility with flexible devices. Owing to these unique properties, while scaling down to ultrathin thickness, devices based on these materials as well as artificially synthetic heterostructures exhibit novel and surprising functions and performances. In this review, we aim to provide a summary on the state-of-the-art research activities on 2D non-graphene materials. The scope of the review will cover the preparation of layered and non-layered 2D materials, construction of 2D vertical van der Waals and lateral ultrathin heterostructures, and especially focus on the applications in electronics, optoelectronics and clean energy. Moreover, the review is concluded with some perspectives on the future developments in this field.

Keywords: 2D non-graphene materials, electronics, optoelectronics, HER

(Some figures may appear in colour only in the online journal)

1. Introduction
It was right after Novoselov and Geim discovered graphene in 2004 that the research on this mono- or few-layer counterpart of graphite attracted great attention [1]. This was stimulated by the fact that confined electrons in graphene behave like massless Dirac fermions, which gives rise to an ultimate high charge carrier mobility of up to \(10^5\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) at room temperature [2]. Combined with excellent mechanical properties, large specific areas and low charge scattering as a result of no dangling bonds, graphene has been studied in a wide range of areas, such as high-speed electronics, optoelectronics, sensors and energy storage [3–7]. However, in spite of this progress, one of the most important applications of graphene has been hindered. Due to zero band-gap, transistors based on intrinsic graphene have low on/off current ratio resulting in high stand-by power dissipation, which limits its real circuit applications [1]. Even though many ways, like chemical doping and preparing graphene nanoribbon, have been proposed to modulate its band-gaps, poor transport properties and/or increased fabricating complexity will be induced as a result [8].

In the modern microelectronic industry, silicon-based complementary metal-oxide semiconductors (CMOS) have been extensively used in microprocessors, static RAM and other digital logical circuits. For a long time, researchers have been trying to find new materials compatible or complementary to silicon in the field of electronics. Inspired by...
graphene, interest in materials having a similar two-dimensional (2D) structure but with intrinsic band-gaps reappeared in the past few years [9–13]. These materials, including transition metal dichalcogenides (TMDs), transition metal chalcogenides (TMCs) and BP etc, have a layered structure: atoms are saturated and bonded with each other forming 2D layers (with a few angstroms in vertical dimension) without dangling bonds, which are connected together by weak van der Waals forces. As a consequence, similar to graphene, these layered materials are easily peeled off in 2D nanomaterials with mono- or few-layer in thickness. Table 1 summarizes some of the most studied 2D non-graphene materials. Due to their intrinsic high performance of bulk materials and novel properties while scaling down to ultrathin thickness, field effect transistors based on 2D layered materials have exhibited surprising electronic properties such as high electron mobility and high on/off ratio [11]. For example, a mono-layer MoS2 field effect transistor (FET) with ultrahigh current on/off ratio of 108 has been achieved [14]. What is more, unique 2D geometry also makes them the ideal building blocks for manufacturing flexible and wearable electronic devices due to its high compatibility with traditional microfabrication techniques and flexible substrates.

In addition, unlike the indirect band-gap of silicon, many 2D layered materials either have intrinsic direct band-gap in bulk state or exhibit an indirect-to-direct band-gap transition while scaling down to single-layer thickness [11, 15]. This makes them show strong light–matter interaction. Further, having a large active area coming from a special 2D configuration, along with the ease of synthesis and abundant resources, 2D layered materials are seen as ideal candidates for optoelectronic devices. Besides, while scaling down to single- or few-layer thickness, TMDs, such as MoS2 and WS2, were utilized as electrocatalysts for H2 evolution in an acid electrolyte owing to the explosion of the edges and increased surface area. Thus, these TMD nanostructures are promising as replacements for the rare and expensive noble metal catalysts, such as Pt etc, for hydrogen evolution reaction (HER) to produce H2 [10, 16]. To achieve the practical applications mentioned above, developing controllable and scalable methods to prepare 2D layered materials is an important step. Until now, both top-down exfoliation and bottom-up synthesis methods are developed to prepare mono- or few-layer 2D layered materials. The former, which includes mechanical exfoliation, liquid-phase exfoliation and laser thinning, is based on peeling off layers from bulk crystals using adhesive tape, liquid molecules (or Li ions) intercalation or laser burning. Bottom-up methods, including wet chemical synthesis and chemical vapor deposition (CVD), rely on synthesizing 2D layered materials directly on substrates using respective precursors. Up to now, many 2D layered materials, like MoS2, MoSe2, WSe2, and InSe etc, have been synthesized successfully by both bottom-up and top-down methods [12, 13].

Heterostructures are the core of the modern semiconductor industry. With the advent of individual 2D layered materials, 2D van der Waals heterostructures (vdWH) have received growing attention in the past few years. Different from conventional bulk heterostructures, 2D layered heterostructures may exhibit many novel properties due to their ultrathin junction thickness. It is still unclear whether traditional bulk junction theory is suitable for this emerging class of junctions. To take a deep insight into the physical mechanism, various vertical or lateral 2D heterostructures have been investigated. For example, MoS2/WS2 junctions with both vertical and lateral configurations have been fabricated and rectifying characteristics have been found [17]. Further, due to direct band-gap and type II band-gap alignment, optoelectronic devices based on 2D heterostructures have been proven to have a high performance [18, 19]. However, compared with individual 2D layered materials, research on 2D heterostructures is just beginning.

Besides the 2D layered materials mentioned above, recently, 2D non-layered materials have attracted increasing attention. Unlike their three-dimensional (3D) counterparts, in 2D configuration, carriers are strongly confined to a plane giving rise to novel phenomena, such as the quantum Hall effect and quantum anomalous Hall effect [20]. Owing to the fact that many materials with significant functions are non-layered crystal structures, exploration of 2D non-layered materials will unambiguously bring us novel physical and chemical properties as well as high-performance electronic and optoelectronic devices.

Here, we present a brief review on the state-of-the-art 2D non-graphene materials. First, crystal and electronic structures will be introduced briefly. Then, we will discuss the methods to prepare these materials. Finally, their applications, especially on electronic and optoelectronic devices, are highlighted.

2. Crystal structures

According to the materials paradigm, the properties of the materials are strongly affected by the microstructure. Two-dimensional non-graphene materials are no exception. For a better understanding, a brief introduction about crystalline structures of some typical 2D layered non-graphene materials will be given in this part.

There are more than 40 types of 2D non-graphene materials [12, 18, 21]. On the basis of chemical compositions, they can be divided into the following categories: TMDs in the form of MX2 (M stands for transition metal, like Mo, W, Nb, Re, Ni and V, X stands for chalcogens, including S, Se and Te); TMCs with an MX stoichiometry (III–VI group, and IV–VI group compounds); layered insulator h-BN; single element materials like black phosphorus (BP), silicene and gemanene; VI–VI group topological insulators (TIs) of Bi2Se3, Sb2Se3 and Bi2Te3; transition metal oxides/hydroxides, such as MoO3, V2O5, Ni(OH)2 etc; as well as others (including metal-organic frames and mica etc). Within this part, we will emphasize some of the most studied ones including TMDs, TMCs, TIs and BP.

TMDs can be seen as strongly covalent bonded 2D X-M-X layers loosely buckled to another by a weak Van der Waals force [10–12, 18, 21, 22]. Variation in the stacking sequence
Table 1. Summary of selected 2D non-graphene materials and their properties.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMDs and TMCs</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>MoS₂ (1.8±a, c, d)₁, f-i</td>
</tr>
<tr>
<td></td>
<td>MoSe₂ (1.38±a, c, d)₁, f-i</td>
</tr>
<tr>
<td>2D layered materials</td>
<td>Se</td>
</tr>
<tr>
<td></td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>WSe₂ (2.1±a, c, d)₁, f-i</td>
</tr>
<tr>
<td></td>
<td>GeS (1.56)₁, g</td>
</tr>
<tr>
<td></td>
<td>GeSe (1.14)₁, c, f, g</td>
</tr>
<tr>
<td></td>
<td>SnS (0.9)₁, g</td>
</tr>
<tr>
<td></td>
<td>Ga₄S (2.6)₁, f, and g</td>
</tr>
<tr>
<td></td>
<td>InS (1.4)₁, c, d, f</td>
</tr>
<tr>
<td>2D non-layered materials</td>
<td>Te</td>
</tr>
<tr>
<td></td>
<td>MoTe₂ (1.07±a, c, d)₁, f</td>
</tr>
<tr>
<td></td>
<td>WTe₂ (1.03±a, c)₁</td>
</tr>
<tr>
<td></td>
<td>Bi₄Te₃ (0.15)</td>
</tr>
<tr>
<td></td>
<td>Bi₄Se₃ (0.2-0.3)</td>
</tr>
<tr>
<td></td>
<td>SnTe</td>
</tr>
<tr>
<td></td>
<td>GaTe (1.7±c)₁, e, f, g</td>
</tr>
<tr>
<td></td>
<td>InTe</td>
</tr>
<tr>
<td></td>
<td>Pb¹₋ₓSnₓSeₓ f, g, j and k</td>
</tr>
<tr>
<td></td>
<td>Silicene (Si₂)₁, f</td>
</tr>
<tr>
<td></td>
<td>Germanene (Ge₂)</td>
</tr>
<tr>
<td></td>
<td>GeSn²</td>
</tr>
<tr>
<td></td>
<td>PbS²</td>
</tr>
<tr>
<td></td>
<td>Rh</td>
</tr>
</tbody>
</table>

Band-gap values are given in the respective brackets:
- ± direct band-gap.
- in-direct band-gap.
- value of monolayer thickness.
- n-type semiconductor, and.
- p-type semiconductor. The most important applications are given as superscripts.
- FET.
- photodetector.
- HER.
- spintronics.
- pressure sensor, and.
- topological transistor. Data are collected from [12–15], [20–24], [28], [35–40], [43–45], [47], [68], [72–74], [82], [158], [193].
along the $c$-axis leads to six different polytypes in 3D [21]. Among them, 1T (refers to trigonal) and 2H (refers to hexagonal) are usually the most stable states. In the 1T phase, metal atoms are octahedrally coordinated with six neighboring chalcogens, whereas the coordination in 2H is trigonal prismatic [21]. Figure 1(a) shows the crystal structures of 1T and 2H type MoS$_2$, respectively. In the upper diagram, the trigonal prismatic and octahedral coordination are shown. The lower panel shows the $c$-axis view of single-layer MoS$_2$. Atom colour: purple, Mo; yellow, S. (b) Two layers of GaSe, where the selenium and gallium atoms are represented by orange and green spheres, respectively. The lattice constant along the $a$-axis is 0.374 nm and in the vertical direction is about 0.8 nm. (c) Scheme of GaTe crystal structure. Blue balls, Te; yellow balls, Ga. (d) GeS shows a rhombohedra structure with lattice constants $a=10.48$ Å, $b=3.65$ Å, and $c=4.30$ Å. The black arrow indicates the direction of [100]. (e) Layered crystal structure of Bi$_2$Se$_3$ and Bi$_2$Te$_3$, with each quintuple layer formed by five Bi and Se (or Te) atomic sheets. (f) Atomic structure of black phosphorus. Figures reproduced with permission from: (a) in [42], © 2014 Nature Publishing Group; (b) in [43], © 2013 American Chemical Society; (c) in [44], © 2014 American Chemical Society; (d) in [45], © 2013 American Chemical Society; (e) in [39], © 2010 American Chemical Society; (f) in [40], © 2014 Nature Publishing Group.

TIs are materials with an insulating bulk state and a metallic state at the surface/edge [30, 31]. Holding this special property, TIs are seen to provide great help in designing novel spintronic, electronic and optoelectronic devices [32–34]. Layered TIs, including Bi$_2$Te$_3$, Bi$_2$Se$_3$ and Sb$_2$Se$_3$, are of great interest for their large surface-to-volume ratio, which favors the manipulations of surface states [35–38]. All these layered TIs share the same structure, as shown in figure 1(e). Each layer consists of covalently bonded X-Se-Te-M (Bi and Sb)-X-M-X sheets, and these quintuple layers (with a thickness of about 1 nm) are stacked together by weak van der Waals forces [39].

BP (phosphorene) is another single element layered material besides graphite (graphene) [40, 41]. Its crystal structure is given in figure 1(f). In a layer, each phosphorous atom is covalently bonded with three neighbors forming a zigzag configuration. Weak van der Waals strength stacks each layer together to form a puckered honeycomb structure.
3. Synthesis

Because the individual sheets in 2D layered materials (2DLMs) are bonded together by relatively weak van der Waals forces, the monolayer 2DLM can be easily fabricated by a mechanical exfoliation method, first used to generate monolayer graphene [1]. Since then, various other 2DLM have been fabricated by this method [10, 11, 22, 44, 46]. As is well known, few-layer, even monolayer 2DLM produced by the mechanical exfoliation method exhibit high purity and cleanliness, suitable for fabrication of an individual device and fundamental research. However, this method is not scalable and feasible for large mass production with large size, uniform thickness, and low time cost. Until now, many other methods have been employed to prepare monolayer or few-layered 2DLM for large scale production, such as the CVD method, liquid-phase exfoliation and the hydrothermal method. In the following context, we will focus on these methods. Besides, preparation methods for 2D non-layered materials are also briefly reviewed in the following part.

3.1. CVD method

CVD, by precisely adjusting the growth parameter and precursor stoichiometry, is considered as the most promising route to realize growth of 2DLM with large-scale, uniform thickness, regular shape and high yield. For 2DLM growth, one strategy is to use the 2DLM powders as the precursors directly. For example, Xu et al [47] demonstrate a straightforward vapor–solid growth method using WSe2 power as the evaporation source to synthesize ultrathin, even monolayer WSe2 nanosheets. Figure 2(a) illustrates the scheme of the WSe2 precursor transported to the sapphire substrates and figure 2(b) presents the optical image of obtained ultrathin triangular WSe2 sheets. The synthesized WSe2 nanosheets display comparable photoluminescence (PL) properties to those fabricated by the ‘Scotch-tape’ method. Compared to binary 2DLM, ternary semiconductors with different bandgaps have been widely used in band-gap engineering, which also can be synthesized by this strategy. For instance, Feng et al [48] employed a tree-zone furnace to synthesize large-area 2D MoS2(1−x)Se2x semiconductor alloys, as shown in figures 2(c) and (d). Another strategy is utilizing reaction precursors, such as MoO3, Mo and (NH4)2MoS4 to grow 2DLM through chemical reaction processes, such as sulfurization and selenization [49–51]. Especially, Choudhary et al [52] demonstrate a layer controllable and wafer-scale growth method of MoS2 on Si/SiO2 substrates by combining a magnetron sputtering, followed by a CVD process, as shown in figures 2(e) and (f). For ternary semiconductor growth, Li et al [53] simultaneously synthesized atomically thin uniform 2D MoS2/Se2(1−x) with complete composition (0≤x≤1) tenability, by a one-step temperature gradient assisted CVD method, as shown in figure 2(g). The PL spectra show that the as-synthesized 2DLM have continuously spectral tunability from 668 nm to 795 nm, as shown in figure 2(h).

3.2. Liquid-phase exfoliation

Liquid-phase exfoliation is another common method to obtain individual sheets from 2DLMs through breaking the weak van der Waals bonds between the layers. Typically, this method creates dispersions of 2DLMs in diverse solvents or aqueous solutions with the assistance of sonication. The mixtures of single-layer and multilayered 2DLMs are usually produced. Organic solvents [54, 55], such as N-methyl-pyrrolidinone (NMP), isopropanol, low-boiling-point solvent mixture [56], and lithium intercalation are involved in this process. The feasible solvents have dispersive, polar, and H-bonding components of the cohesive energy density within certain well-defined ranges, which can minimize the enthalpy of exfoliation [10, 55]. For instance, MoS2 and WS2 with a thickness from single to few layers were achieved using NMP with a surface energy of ~70 mJ/m² (figure 3(a)). Unfortunately, due to the slow evaporation, it is difficult to remove the solvent and aggregation away after exfoliation. As a consequence, it is difficult to directly utilize the nanosheets obtained from this method into electronic and optoelectronic devices. To surmount this barrier, Zhou et al developed a versatile and scalable strategy by exfoliating 2DLMs in mixed volatile solvents [56]. Based on the theory of Hansen solubility parameters (HSP), the HSP distance of Ra in equation (1) is used to evaluate the level of adaptation between the HSP parameters of solvents and solutes.

\[
R_a = \sqrt{\left(\sigma_D - \sigma_{D,solu}\right)^2 + \left(\sigma_P - \sigma_{P,solu}\right)^2 + \left(\sigma_H - \sigma_{H,solu}\right)^2}
\]

where \(\sigma_D\), \(\sigma_P\) and \(\sigma_H\) are the dispersive, polar, and hydrogen-bonding solubility parameters, respectively. For a pair of solvent and solutes, the smaller \(R_a\) value means a higher solubility. In their work, for obtaining the few-layer nanosheets, mixed water and ethanol with different ratios were used to give high solubility to various 2DLMs.

Lithium intercalation is another effective method for producing mono- or few-layer nanosheets. In this case, a chemical (using n-butyl lithium) [16, 57] method was used to accomplish lithium intercalation. Usually, the exfoliation is based upon the reaction between intercalated lithium and the excess water or ethanol, which generates H2 gas and produces the individual nanosheets. During this process, a high temperature (~100 °C) and long reaction time (3 d) are requisite. Meanwhile, this method has a lack of controllability over the degree of lithium insertion. Recently, Zeng et al developed an electrochemical Li intercalation and exfoliation to prepare high-yield single-layer 2DLMs, including MoS2, WS2, TiS2, TaS2, ZrS2, NbSe2, WSe2, Sb2Se3 and Bi2Te3. [58, 59]. As shown in figure 3(d), the 2D layered bulk materials and Li foil are the cathode and anode in this electrochemical set-up, respectively. After discharging for a fixed time, the bulk crystals would be exfoliated into thin nanosheets (as shown in figure 3(e)). To be noted, the as-exfoliated nanosheets were predominantly the 1T metallic phase instead of the semiconducting 2H phase, which will affect the electronic and optical properties [60].
3.3. Hydrothermal method

Another important method to synthesize few-layer 2DLMs is the hydrothermal method [61]. In a typical procedure, the homogeneous solution was transferred into a Teflon-lined stainless steel autoclave and maintained at different temperatures for a given time. Usually, ammonium molybdate/tungsten hexachloride [62, 63] and thiourea/selenoureacan act as the Mo or W precursors and sulfur/selenium sources when synthesizing the MoS2 or WS2 nanostructures, respectively. Abundant ultrathin nanosheets can be realized through this method. In addition, the defects and structures of the MoS2 or WS2 nanosheets can be controlled by choosing different precursors. The dispersions of 2D nanomaterials synthesized via this method were usually utilized as catalysts for H2 generation.

3.4. 2D non-layered materials

Different from layered semiconductors such as MoS2 and WSe2 which have lamellar structures, non-layered materials (NLMs) normally have 3D close-packed crystal structures such as a cubic and hexagonal crystal system. Therefore, NLMs lack the intrinsic driving force for the 2D anisotropic growth, which makes it particularly challenging to prepare their 2D nanostructures [20]. For example, topological crystalline insulators SnTe have an isotropic cubic structure which determines the 3D isotropic growth of SnTe in the crystallization process. As demonstrated by Wang et al [64] and Zhang et al [65], 3D micro- or nano-structures of SnTe were always obtained in the CVD process without the induction of a metal catalyst such as a gold nanoparticle. In addition, hexagonal ZnO inclines to form 1D nanoarchitectures in both hydrothermal and CVD methods due to the strong polarity of the ZnO [0001] direction [66], and hexagonal Te tends to form nanowires with [0001] growth direction due to its chain-like structure. Consequently, exciting the 2D growth trend is essential to synthesize the 2D nanostructures of a non-layered semiconductor.

Thanks to the developments of chemical synthetic techniques such as the self-assembly strategy [67], oriented...
attachment strategy [68] and template-directed strategy, [69] 2D crystals with ultrathin thickness of non-layered materials have been successfully prepared. For example, Zhang et al grew atomic-thick Co₈Ce₈ nanosheets by a 2D oriented attachment method [70]. In this work, Co(Ac)₂·4H₂O (1.2 mmol) and SeO₂ (1.0 mmol) were used as the precursors with solvent of benzyl alcohol. In the reaction process, quadruple layers assemble layer-by-layer and form the planar nanostructures. Here each quadruple layer is composed by four covalently bonded atomic sheets. Morin et al reported the screw dislocation-driven growth of 2D nanoplates [71]. The differences of step velocities between the dislocation core and the outer edges of the growth spiral explained various dislocation-driven morphologies. They discovered, when the velocity of steps at the core is equal to those at the outer edges of the dislocation hillocks, that a step pile up cannot be generated and the steps grow up in the 2D mode. Recently, Duan et al synthesized ultrathin rhodium nanosheets by a facile solvothermal method [72]. The thickness of poly (vinylpyrrolidone) (PVP)-supported single-layered rhodium nanosheets is controlled within 4 Å. Results of density functional theory suggests that the δ-bonding framework in rhodium nanosheets stabilizes the single-layered rhodium structure with PVP ligands. Although great progress has been made in the synthesis of ultrathin nanosheets by chemical synthesis strategy, the domain size of the products is so small that it is particularly difficult to fabricate their electronic devices. Lateral dimensions of previous reported 2DNLMS are always less than 1 μm. Moreover, the ultrathin nanosheets are free-standing without planar orientation, which makes them incompatible with microfabrication techniques. Recently, Wang et al proposed van der Waals epitaxy (vdWE) growth of ultrathin 2D nanoplates of 2DNLMs by using CVD method [73]. As shown in figures 4, 2D hexagonal Te nanoplates were synthesized on flexible mica sheets although Te strongly tends to form 1D nanowires due to its chain-like structure (figure 4(a)). The thickness ranges from 30 to 80 nm and the lateral dimension reaches ~10 μm. The nanoplates array shows planar architecture with uniform orientation, enabling the fabrication of the integrated device system. vdWE of 2D non-layered semiconductor requires that (1) the materials are of 2D anisotropic growth and (2) the growth is performed on a van der Waals substrate such as layered mica. For the former condition, the trend of 2D anisotropic growth of some NMs can be excited by modulating experiment parameters, such as temperature and pressure. For the latter condition, the chemically inert surface of layered mica is crucial for the formation of 2DNLMS: (1) the
overlayer is perfectly relaxed without excessive strain in the heterointerface, and (2) the strict requirement of lattice matching is circumvented, enabling the growth of the defect-free overlayer with different crystalline symmetry to that of the substrate, and (3) the chemically inert mica surface facilitates the migration of adatoms. This work paves the way towards leveraging vdWE as a useful channel to prepare 2DNLMs. Although conceptually simple, the growth of 2D nanostructures is difficult.

Ultrathin 2D nanostructures of non-layered materials not only improve the intrinsic properties of their bulk counterpart, but also bring us novel electronics. Our group \[74\] in situ fabricated two-terminal photodetectors based on planar Pb\(_{1-x}\)Sn\(_x\)Se nanoplates on flexible mica sheets. As shown in figures 4(j)–(l), the device exhibits a fast response, high stability and broad spectra detection ranging from UV to infrared light. Even after bending the device 100 times, it still exhibits high sensitivity, which is due to: (1) high compatibility of the planar Pb\(_{1-x}\)Sn\(_x\)Se nanoplates with flexible mica substrate; and (2) intrinsic high responsivity of Pb\(_{1-x}\)Sn\(_x\)Se nanoplates. This work suggests that 2D Pb\(_{1-x}\)Sn\(_x\)Se nanoplates grown on a flexible mica sheet have great potential in the application of highly efficient wearable optoelectronic devices.

4. Properties and applications

4.1. Electronics

In contrast to traditional semiconductors, such as Si and III–V group materials, 2D layered semiconducting materials

Figure 4. CVD synthesis and photodetectors of 2D non-layered materials. (a) The chain-like crystal structure of Te. (b) Schematic illustration of van der Waals epitaxial 2D Te hexagonal nanoplates on a flexible mica sheet. (c) OM image of Te hexagonal nanoplates array, scale bar = 30 μm. The inset is the SEM image of a 2D Te hexagonal nanoplate, scale bar = 4 μm. (d) AFM image of single Te hexagonal nanoplate, scale bar = 2 μm. (e)–(i) Schematic illuminations of van der Waals epitaxial 2D Te hexagonal nanoplate. (e) AFM images of Te nanoislands formed at the initial growth process. (f) AFM images of one complete 2D Te hexagonal nanoplate, scale bar = 2 μm. (g) and (h) The schematic illuminations for the growth process, scale bar in (d) is 2 μm. (i) Interface crystal structure model, (001) surface of Te nanoplate is parallel to (001) surface of mica. (j) Photograph of flexible photodetector based on planar Pb\(_{1-x}\)Sn\(_x\)Se nanoplates, inset shows the OM image of electrodes array. (k) I–V curves with light on and off, the inset exhibits the SEM image of a single device. (l) Time trace of photoresponse with various light intensity. (a)–(i) Reproduced with permission from [73] © 2014, American Chemical Society. (j)–(l) Reproduced with permission from [74] © 2015, American Chemical Society.
(2DLSM) have ultrathin thickness, a smooth surface, and high flexibility, which make them promising to solve the new challenges the current semiconductor industry is facing, including short-channel effects, higher vertical integration degree, lower power dissipation and flexible applications etc. Recently, one of the hottest points in the field of 2DLSM is focusing on understanding the fundamental electronics properties, such as FET performance. Figure 5 is a basic configuration of a 2DLSM-based FET device, which is composed of three parts: source-drain metal contacts, a 2DLSM channel, and dielectric layer (gate electrode). The FET performances are strongly affected by the metal contacts of the source and drain, the channel material properties (doping and defects), and electrostatic tuning efficiency (dielectric layer materials). We have to agree that various other factors besides those mentioned above also have significant influences on the device performance, such as the channel length [75, 76], the channel thickness (layer numbers) [77, 78], surface adsorbates [79–81] and so on. However, due to the limits of the length of this review paper, we will just discuss the effects arising from metal contacts, doping and defects, and dielectric layers in this section.

4.1.1. Contacts. The metals used for the electrical contacts play a very important role in the FET properties. The FET functionality and efficiency remarkably depend on the charge injection into the materials through metal contacts. To realize the practical applications of 2DLSM-based FET in the future, it is mandatory to investigate well the detailed properties of the contacts between 2DLSM and metal electrodes. Recently, both theoretical and experimental researches on metal contacts have been widely reported. Figure 6 shows the relative relationship between band edge positions of several representative 2DLSMs and work functions of common metals. The band structure data of MoS2, MoSe2, WS2 and WSe2 come from a previous literature [82]. In general, metals with high work functions favor hole conduction by pinning the chemical potential closer to the valence bands. Conversely, those with low work functions prefer electron conduction.

MoS2 is one of most important 2DLSMs with a relatively large band gap and small electron affinity, thus a considerable Schottky barrier forms between MoS2 and the contact metal, which suppress the MoS2 FET performance [14]. To circumvent this phenomenon, construction of the contacts with a small Schottky barrier or ohmic characteristics is an efficiency strategy. Walia et al [83] explored the characteristics of aluminum, tungsten, gold, and platinum contacts on 2D MoS2 flakes. It is observed that lower work functions of the contact metals lead to a smaller Schottky barrier size and thus higher charge carrier injection through the contacts. This study indicates that choosing a suitable metal contact is crucial to tune the barrier height at the interface of the metal-semiconductor. Similarly, Wang et al [84] developed an ohmic contact on a multilayer MoS2 using a permalloy as the metal electrodes, which yields a high field-effect mobility exceeding 55 cm2 V−1 s−1. Kang et al [85] presented high-performance MoS2 transistors with low-resistance Mo contacts. Density functional theory (DFT) simulations indicate Mo can form a high quality contact interface with monolayer MoS2 with zero tunnel barrier and zero Schottky barrier. Kappera et al [42] demonstrated a novel contact method using 1T MoS2 as the contact electrode, which generates a record low-resistance value of 200 Ωμm. Based on the deep understanding and proper design of source/drain contacts, Das et al [86] demonstrated a high-performance MoS2 transistor with extremely high mobility of ∼700 cm2 V−1 s−1, high saturation current density of 240 μA μm−1 and high transconductance values of 4.7 μS μm−1, as shown in figure 7. These results are attributed to the lower work function of Sc strongly pinning the Fermi level close to the conduction band of MoS2.

So far, most of the MoS2 FETs reported previously monotonically demonstrate n-type behaviors. To meet the requirements in designing complementary logic circuits, the search for a complementary p-type MoS2 has been one of the current hottest research topics and still remains a challenge. Kaushik et al [87] employed high work function metals, such as Au and Pd to investigate the operation type of a MoS2 monolayer FET. Unexpectedly, both of them display n-type behaviors. By qualitatively and quantitatively analyzing, it reinforced that the Fermi-level of the MoS2—metal interface is

Figure 5. Scheme of a typical FET device based on 2D layered semiconducting materials.

Figure 6. Band edge position of several 2D layered semiconducting materials and work function of some representative metals.
strongly pinned in the upper half of the MoS$_2$ band gap, which leads to a large p-type Schottky barrier and results in the failure of hole injection from the contacts. Recently, using the first-principles calculation, Musso et al [88] demonstrated that graphene oxide can form a p-type contact with monolayer MoS$_2$ as an efficient hole injection layer. Additionally, MoX also shows promising potential as an efficient hole injection layer for p-FETs [89]. However, the p-type MoS$_2$ prototype device still leaves the theory simulation far behind.

Contrary to MoS$_2$, WSe$_2$ has been discovered to be a 2DLSM combining the p-type and n-type conducting behaviors in the same materials [90–92]. Due to its relatively weak Fermi level pinning phenomenon, a p-n-junction on one WSe$_2$ monolayer can be obtained just by dual electrostatically gating [93]. Different metal contacts can extract different carriers from WSe$_2$. For instance, as shown in figure 8, higher work function Pd-contacted WSe$_2$ FETs indicate clear p-type conduction, however, lower work function Ti contacts lead to an ambipolar behavior [91]. This is because Ti forms near midgap Schottky barriers to WSe$_2$, reflecting larger Schottky barrier height and lower current levels than Pd. Das et al [94] demonstrated an interesting WSe$_2$ FET with enhanced ambipolar characteristics using Ni as the source and Pd as the drain contact electrodes. This study reveals that Ni facilitates electron injection while Pd favors hole injection. In contrast, WSe$_2$ demonstrates high-performance n-type transistors using Ag and In contacts [95].

Coincidentally, mechanically exfoliated ultrathin MoSe$_2$ FET manifests n-type conduction behavior with a high on/off ratio larger than 10$^6$ by depositing Ni as the electrical contacts [96]. Pradhan et al report MoSe$_2$ FETs electrically contacted with Ti display ambipolar behavior with an on/off ratio up to 10$^6$ for both electron and hole channels [97]. In addition, WS$_2$ transistors also can be tuned to display ambipolar behavior by the choices of suitable metal contacts [98]. BP is another rising star in 2DLSM because of its extremely high carrier mobility $\sim$1000 cm$^2$ V$^{-1}$ s$^{-1}$ [40]. By applying different metal

Figure 7. MoS$_2$ FET with different metals contacts. (a) Transfer characteristics of 10 nm thin MoS$_2$ back-gated transistors with Sc, Ti, Ni, and Pt metal contacts at 300 K for $V_{DS} = 0.2$ V. (b) Output characteristics of a high-performance MoS$_2$ transistor exhibiting extremely high mobility, saturation current density, and transconductance for different gate overdrive voltages with 15 nm of high-k dielectric (Al$_2$O$_3$). Figures reproduced with permission from [86], © 2013, American Chemical Society.

Figure 8. Back-gated WSe$_2$ FETs with different metal contacts. (a) $I_{DS}$–$V_{GS}$ characteristics of Pd (red curve) and Ti (black curve) contacted WSe$_2$ FETs on a Si substrate with 50 nm SiO$_2$ as the back-gated dielectric. Here WSe$_2$ is few layered ($\sim$5 nm). (b) Qualitative energy band diagrams for Pd (top) and Ti (bottom) contacted WSe$_2$ FETs in the on-state, depicting the height of the SBs for hole injection at the metal–WSe$_2$ interfaces. Figures reproduced with permission from [91], © 2012, American Chemical Society.
contacts, n-type, p-type and ambipolar BP based FETs can be effectively achieved [99, 100].

4.1.2. Defects and doping. Defects are usually seen as imperfections in materials that could deteriorate their properties. For most 2DLSMs, the defects have been demonstrated as playing a key role in their electronic properties. For example, as shown in figure 9, combining electrical transport measurements at variable temperatures and first-principles calculations, Wang et al [44] found that the Ga ion vacancy is the critical factor that leads to degraded GaTe FET performance at room temperature, such as the high off-state current, low on/off ratio and large hysteresis. By suppressing thermally activated Ga vacancy defects at liquid nitrogen temperature, the FET properties can be significantly enhanced. These findings are important to understand the physical nature of GaTe FET performance degradation and are also beneficial to unlock the hurdle for practical applications of GaTe transistors in the future. Recently, various theoretical calculations and experimental research have systematically investigated the defect effects on MoS2, including point defects, dislocations, grain boundaries and so on [101–105]. Specifically, Liu et al [106] calculated the band structure and defect states in monolayer and bulk MoS2 using the screened exchange hybrid functional. They found the S vacancies lead to Fermi level pinning near the conduction band edge and account for the n-type behavior of MoS2 FETs. Further, by combining variable-temperature transport measurements and aberration-corrected transmission electron microscopy, Qiu et al [107] directly confirm that sulfur vacancies exist in MoS2, introducing localized electron donor states inside the band-gap. To repair the sulfur vacancies and improve the device performance, Yu et al [108] demonstrate a facile low-temperature thiol chemistry doping method as shown in figure 10. Monolayer MoS2 treated by (3-mercaptopropyl) trimethoxysilane (MPS) shows significant reduction of charge impurity and short-range scattering and achieves a record-high room temperature mobility 81 cm²V⁻¹s⁻¹. Now for 2DLSMs, the defects, such as vacancies, charge impurities, and trap states severely degrade their device performance. How to repair the defects and restore the intrinsic properties is still a challenging issue. Wang [44] and Yu [108] et al provide two kinds of possible routes by lowering the temperature and chemical doping. However, for practical applications of 2DLSM devices in the
future, a new synthesis method to grow high crystalline quality material is highly desired.

In modern electronics, doping is largely used to adjust the carrier density and tailor the electronic characteristics of the devices. In the case of 2DLSMs, dopants can govern the properties such as the major carrier density and types. MoS2 is a native n-type material due to the presence of electron–donor S vacancies. Suh et al [109] realize a stable p-type MoS2 by substitutional Nb doping, which has a degenerate hole density of $\sim 3 \times 10^{19} \text{ cm}^{-3}$. Further vertical van der Waals p–n junctions based on doped and undoped MoS2 are fabricated, which display excellent gate-tunable current rectification, as shown in figure 11. Liang et al employed the selected-area F or O-contained plasma to treat MoS2 flakes, thus successfully obtaining p-doping MoS2 with a superior long-term stability at ambient conditions [110]. The fabricated photovoltaic devices based on this technique exhibit greatly enhanced properties [111]. Air-stable n-type WSe2 FETs can be obtained by degenerately doping the p-type WSe2 FETs using potassium [112]. A lateral homogeneous 2D MoS2 p–n junction is demonstrated by partially stacking 2D h-BN as a mask using AuCl3 to p-dope MoS2 [113]. In addition, NO2, N2O, O2, benzyl viologen and chloride molecules also have been used to adjust the properties of 2DLSMs. [114–117]

4.1.3. Dielectrics. With scaling of the gate length downward, the gate dielectric thickness must be reduced. Conventional SiO2 will generate a large leakage current with its thickness decreasing. However, high-κ dielectrics, such as HfO2, ZrO2, Al2O3 and h-BN, allow scaling with a much larger thickness due to their higher dielectric constants. The so-called dielectric engineering means selecting suitable high-κ dielectrics to replace conventional SiO2 in order to achieve high FET performance including high mobility, a high on/off ratio, high saturated current and low off-state current. The mobility of carriers in 2DLSMs is strongly affected by the various scattering mechanism such as acoustic and optical phonon scattering, Coulomb scattering by charged impurities, surface interface phonon scattering and roughness scattering [11]. High-κ dielectrics can effectively screen Coulomb scattering at the charged impurities, thus significantly improving the carrier mobility [118]. For instance, HfO2 is widely used as top-gated dielectrics in 2DLSM-based FET [14, 119]. Because of absence of an efficient dangling bond or nucleation site on the 2DLSMs, conformal deposition of HfO2 on MoS2 still is a great challenge. Zou et al [120] constructed a conformal HfO2/MoS2 interface with the minimal interface defect density by utilizing an ultrathin metal oxide (MgO, Al2O3 and Y2O3) buffer layer inserted between HfO2 and MoS2. The fabricated device exhibits a high electron mobility of 63.7 cm2 V$^{-1}$ s$^{-1}$ and large on/off ratio exceeding $10^8$. In addition, a near-ideal sub-threshold wing and highest saturation current are attained, as show in figure 12. Chang et al [121] apply conventional solid-state high-κ dielectrics on flexible MoS2 FET, exhibiting an on/off ratio greater than $10^7$, sub-threshold slope of $\sim 82 \text{ mV/decade}$, and a reasonable field mobility of $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This work suggests that the solid high-κ dielectrics can be applied in flexible devices. It is worth noting that besides those

![Figure 10. Kinetics and transient states of the reaction between single sulfur vacancies and (3-mercaptopropyl)trimethoxysilane (MPS). Figures reproduced with permission from [108], © 2014, Nature Publishing Group.](image)

![Figure 11. Gate-tunable rectification across a van der Waals MoS2 p–n junction. (a) Gate voltage ($V_g$) dependence of channel current of multilayer MoS2: Nb and undoped MoS2 devices at a bias voltage ($V_{ds}$) of 1 V. Ti/Au was used for the source (s) and drain (d) contacts. (b) I–V characteristic at variable back-gate voltages measured across the van der Waals p–n junction assembled with MoS2:Nb (60 nm) and undoped MoS2 (4 nm). The inset is a false-color SEM image along with a scale bar of 10 μm. Figures reproduced with permission from [109], © 2014, American Chemical Society.](image)
mentioned above, h-BN and liquid electric double-layer dielectrics are also current active research areas [122–126].

The above achievements show that 2DLSMs could be interesting not only for digital applications but also for analogue applications. After the demonstration of high performance 2DLSM-based FETs, many attempts to construct building blocks with logical functions have been performed [127, 128]. Radisavljevic et al realized the first integrated circuit based on a monolayer MoS$_2$ nanosheet, which is capable of acting as an inverter and performing ‘NOR’ logic operation [129]. Wang et al demonstrated the integrated circuits based on bilayer MoS$_2$, including an inverter, a static random access memory, and a five-stage ring oscillator [130]. Besides MoS$_2$, Tosun et al realized a complementary logic inverter on the same WSe$_2$ flake for the first time, which demonstrated the on/off current ratio >10$^4$ and a direct current voltage gain >12 [131]. In addition, recently, a flexible amplitude-modulated demodulator has been realized based on ambipolar BP FETs [132]. These results suggest 2DLSMs own the capability for complex digital logic and high-frequency device applications. However, it should be noted that most 2DLSMs have a relatively low carrier mobility, which is just comparable to that of silicon (few hundreds of cm$^2$V$^{-1}$s$^{-1}$) and much smaller than that of III–V materials (a few thousands of cm$^2$V$^{-1}$s$^{-1}$). Further exploration of new 2DLSMs with high mobility is highly desired.

4.2. Optoelectronics

Optoelectronic devices, including photodetectors, solar cells and LEDs etc are electric devices that can generate, detect, interact with or control light [11]. The performances of an optoelectronic device depend directly on the electrical properties of the materials used. Due to a large active area, strong light–matter interaction and novel electrical properties, optoelectronic devices based on 2D materials have attracted much interest since they appeared. In this part, we will give a brief review about optoelectronics based on 2D non-graphene materials, emphasizing the research situation of photodetectors.

Generally, there are basically two types of mechanism for photodetection: photodiodes (photovoltaic effect, PV) and photoconductors [9, 133–135]. In a photodiode, photo-generated carriers are separated and pull away in opposite directions under the effect of a build-in field of p-n or Schottky junctions. Due to the fast drift process, photodiodes usually show a fast response time (at the magnitude of ms or lower) but low external quantum efficiency (EQE) (<100%). On the other hand, photoconductors depend on the diffusion process of photogenerated carriers, which give rise to a slow response time (at the magnitude of seconds). However, owing to large numbers of trap states, only the carriers with a relatively long life time contribute to the addition of the current. As a consequence, a high EQE (>100%) will be induced. In practice, for a typical photodetector, the photodiode and photoconductor often appear at the same time due to the usual Schottky contact between the semiconductor and metal electrodes (i.e. photodiode near the interfaces of the contact, and photoconductor at the neutral zone far away from the contact) [135]. Several figures of merit are used to evaluate the performance of a photodetector. Response (rise
and decay) time is the time used for the photocurrent rising to a steady state (recovering to the original state). Responsivity ($R$):

$$R = \frac{I_{ph}}{p}$$

(2)

where $I_{ph}$ is the photocurrent, $p$ is the power of incident light. It has the unit of A W$^{-1}$. Another is EQE:

$$EQE = \frac{I_{ph}}{q\Phi}$$

(3)

where $q$ is the unit electron charge, $\Phi$ is the photon flux, and detectivity:

$$D = \frac{I_{ph}}{I_{dark}^{1/2}}$$

(4)

where $I_{dark}$ is the dark current.

The first trial was on MoS$_2$ [136]. This was inspired by the findings that, unlike semimetallic graphene, MoS$_2$ has a layer-dependent electronic property: an indirect band-gap of 1.29 eV in bulk increases to the direct band-gap of about 1.8 eV in the monolayer (see figure 13(a)) [15]. As a result,
strong light–matter interaction will show while scaling down to atomic thickness. On the basis of this theoretical study, Yin et al. fabricated the first phototransistor based on a single-layer MoS$_2$, shown in figure 13(b) [136]. They found that the device exhibits a responsivity of 0.42–7.5 mA W$^{-1}$ and a response time of 50 ms. Just after this initial try, multilayer MoS$_2$ phototransistors on top of an Al$_2$O$_3$ dielectric layer were fabricated (see figure 13(c)) [137]. Thanks to the strong screening effect of the dielectric layer with high-k [14, 118], the phototransistor with a high carrier mobility (>70 cm$^2$ V$^{-1}$ s$^{-1}$) and then higher responsivity of >100 mA W$^{-1}$, which is comparable with commercial Si photodetectors, were achieved. In addition, as a result of the impressive high responsivity of 880 A W$^{-1}$, the transistors show a detectivity of more than 5 s. In contrast, by taking a high Schottky barrier (Ti contact), a faster response time of <23 ms was obtained, but along with decreased photogain and detectivity (figure 14(c)). To achieve high responsivity while keeping a fast response time, more work is needed. Combining different 2D materials together to form heterostructures may be a possible solution [9, 11, 134, 146]. This will be further discussed in the 2D heterostructures part.

The III–VI group of layered compounds, GaS, GaSe, GaTe and InSe etc are another object studied for photodetectors. Figures 15(a)–(d) show photodetectors based on GaS, GaSe and GaTe respectively. GaS has an indirect band-gap of 2.59 eV and a direct band-gap of 3.05 eV, which is considered as a promising material for detecting near-blue light [147]. Further, splitting into double peaks of VBM as well as decreasing effective electron mass along with scaling down to less than a five-layer thickness were demonstrated [140]. Based on these findings, the responsivity of 4.2 A W$^{-1}$, EQE of 2050% and response time less than 30 ms were achieved for few-layer GaS on a SiO$_2$/Si substrate [147]. In addition, phototransistors on flexible substrates (PET) show higher and stable performances. Compared with GaS, photodetectors based on GaSe, which has an indirect band-gap of 2.11 eV and is only 25 meV higher than a direct one [43], have received more attention. For example, Zhou et al. presented a size- and position-controllable synthesis method of mono- and few-layer GaSe on flexible substrates of mica. Flexible patterned photodetector devices based on GaSe nanosheets demonstrated durable high performances [148]. Monoclinic GaTe is another intriguing III–VI group layered material. Theoretical studies have shown that it has direct band-gaps for both bulk (1.7 eV in value) and monolayer stations [44]. Taking this advantage, Liu et al described high-sensitivity photodetectors based on an exfoliated multilayer GaTe. The devices show a high responsivity of 10$^4$ A W$^{-1}$ and response time of 6 ms [149]. InSe, having light electron effective mass (m$^*$ = 0.143 m$_0$), a high carrier mobility of about 10$^3$ cm$^2$ V$^{-1}$ s$^{-1}$ as well as a narrow band-gap of 1.2 eV (1.4 eV) for bulk (few layer), is seen as one of the most promising materials for visible light detection [150, 151]. Based on these merits, few-layer InSe photodetectors with a responsivity of up to 157 A W$^{-1}$, EQE of 1367%, detectivity of 1.07$\times10^{11}$ Jones were demonstrated. Moreover, flexible devices after bending still show acceptable performance of 1.7 A W$^{-1}$ and 1010 Jones [152].
Even though TMDs and III–VI metal chalcogenides show good performances, the detection coverage is mainly limited in visible light. For wider range detection, i.e. a longer wavelength (like NIR), they become helpless. Semimetallic graphene, with ultrahigh mobility and excellent mechanical properties, is a candidate and much research has been done [4, 153, 154]. However, an absence of a band-gap gives rise to a high dark current (low on-off ratio), which reduces its applicability in photodetecting [9, 11, 134]. Even though much work has been done, it is still not an easy job to split graphene’s VBM and CBM without damaging its electrical properties [155–157]. BP, with a direct band-gap of 0.35 eV in bulk and 1.5 eV in monolayer, provides another option [41]. Further, exfoliated BP (10 nm in thickness) with a mobility as high as 1000 cm$^2$ V$^{-1}$ s$^{-1}$ has been demonstrated [40]. Recently, phototransistors based on few-layer BP were studied. The devices (figure 16(a)) show fast response (1 ms) through the broad spectrum (wavelength from visible to 940 nm) [158]. Engel et al took a step further. Photodetectors based on a multilayer BP were fabricated and used to image real objects (see figure 16(b)). Their results strongly demonstrated BP’s potential applications in multi-spectral photodetection and imaging [159].

4.3. Electronics and optoelectronics based on 2D heterostructures

On the basis of pristine 2D layered materials, a new structure—vdWH has attracted growing attention in the past few years. This heterostructure was first introduced by Dean et al in 2010, when they demonstrated that the electrical performances of graphene devices stacked on the top of a multilayer h-BN were almost an order of magnitude better than the devices on bare SiO$_2$ [160]. After that, many works have been done on a similar construction. Its initial concept was proposed by Geim and Grigorieva in 2013 [18]. In principle, vdWHs refer to artificial structures made by stacking different 2D layered materials, which can be seen as individual building blocks on top of each other in a chosen sequence [18]. Just as its name shows, adjacent building blocks are assembled together by weak van der Waals forces. This structure does not pose critical requirements on lattice-matching between contacting layers, which is significantly different from the traditional heterostructures. Combined with building blocks of different properties, this structure may show controllable and/or brand-new properties [18]. Besides the vertical configuration mentioned above, individual 2D
layered building blocks can also be interconnected in a seamless in-plane, forming so-called 2D lateral heterostructures [17, 161–163]. The same as its traditional 3D analogues, 2D lateral heterostructures form junctions through covalent bonds. However, due to their very thin thickness and horizontal layout, new performances, for example, better gate tunable characteristics, can be achieved. Now, with the advent of 2D layered materials, electronic and optoelectronic properties and devices based on 2D heterostructures have been attracting more and more attention [18, 164]. In this part, we will discuss its fabrication methods, properties and applications.

Two ways are usually used to fabricate layered heterostructures: the mechanical transfer and in situ growth method. A typical transfer procedure was first developed by Dean et al [160], as shown in figure 17. The key point is: one of the wanted 2D layered building blocks is transferred onto a transparent thin polymer film, so that it can be seen under an optical microscope, manipulated precisely by a micro-manipulator and dropped off on the top of another building block. Figure 17(a) shows the scheme they used to fabricate graphene/h-BN heterostructures. This method is simple and requires only basic facilities. However, to achieve tight and clean contact between surfaces, operations must be done very carefully, and thermal annealing in a vacuum condition is helpful in squeezing contaminations out [164–166]. To eliminate this problem, new transfer methods without using liquid are needed. In 2013, Wang et al developed a van der Waals pick-up method to assemble layered materials [167]. As its name suggests, van der Waals interaction between layered materials was used to pick up and drop off the building blocks. Figure 17(b) shows the schematic and the assembly. Both the AFM and cross section STEM image of the heterostructure part demonstrate the clean contact between the adjacent layers. This method is also simple and can fabricate devices with better performance. However, it only suits layered materials obtained from the mechanical exfoliation method. In the situation of ones directly grown on substrates (like SiO₂ and sapphire), wet transfer will be unavoidable.

The methods mentioned above can only be applied to fabricate heterostructures with vertical construction. As to the lateral ones, up to now, in situ synthesis is the only choice. Further, considering its limited yield, the transfer method is merely suitable for lab research. Hence, a controllable and scalable synthesis method is highly desired. At the time of writing, four independent groups have published their works on in situ growth of 2D non-graphene heterostructures by the CVD method [17, 161–163]. The first work was done by Huang et al in which they successfully synthesized mono-layer MoSe₂/WS₂ lateral heterostructures by CVD [161]. This attempt is really a breakthrough. However, the interfaces of their heterostructures appeared to be a binary alloy, WₓMo1−ₓSe₂. This could seriously affect the performances, even though the composition gradient is very steep (in several nanometers) [161]. Almost at the same time, Guo et al reported synthesizing vertical and lateral WS₂/MoSe₂ heterostructures by CVD, as shown in figure 17(c) [17]. The key parameter that determines the type of synthesized product is the temperature used: 850 °C for vertical and 650 °C for lateral ones. It is to be noted that STEM images demonstrate heterostructures with atomically sharp interfaces [17]. Recently, Duan et al and Zhang et al reported growth of
MoS$_2$/MoSe$_2$, WS$_2$/WSe$_2$ [162] and WS$_2$/MoS$_2$, MoSe$_2$/WSe$_2$ lateral heterostructures respectively [163]. All these works pave the way for practical application of devices based on heterostructures. However, up to now, CVD growth is limited in TMDs, and in situ synthesis of other 2D layered materials is desired.

P-n junctions are the foundation of the modern semiconductor industry. In 3D p-n junctions, when p- and n-type semiconductors contact together, free charge carriers will deplete while leaving fixed charge behind, and then form so-called space charge regions and built-in potentials at the interfaces. While connecting to an electric circuit, under the effect of built-in potential, a rectification characteristic will appear. A similar phenomenon has been found in 2D heterostructures. For example, 2D heterostructures based on BP/MoS$_2$ [168] and MoS$_2$/WS$_2$ heterostructures [17] were fabricated, both of which show rectification characteristics. Despite a similar appearance, the mechanism behind it may be different. For example, as for vdWHs, no space charge region or built-in potentials may exit due to the ultrathin thickness in the vertical direction. To find out the answer, Lee et al fabricated an atomically WSe$_2$/MoS$_2$ p-n junction by mechanical cleavage and transfer method [164]. A gate tunable rectification characteristic was found in their device, which is apparently similar to those of a traditional p-n junction. By comparing simulation and experimental results, they found that interlayer carriers recombination played a decisive role in the rectifying properties displayed. When applied with different bias and/or gate voltages, carrier densities, the potential drop between individual and overlapped regions,
and the recombination rate would be tuned, giving rise to the gate tunable $I-V$ characteristic appearing, as shown in figure 18(a). Note that the discussion above is only applicable for vertical van der Waals structures. For 2D heterostructures with lateral configuration, due to a space large enough for carriers deletion, the phenomenon can be understood by traditional built-in potential theory. With this fundamental property in hand, functions that traditional heterostructures provide now can be done in two dimensions. For example, as shown in figure 18(b), Duan et al constructed a CMOS inverter based on a WSe$_2$/WS$_2$ 2D p-n heterostructure, which shows a voltage gain of about 24 [162].

Due to their direct band-gaps, strong light–matter interaction and type II band-gap alignments of many 2D layered materials, optical properties of 2D heterostructures are at the core of interest as soon as they appear [146, 168–171]. While forming type II heterostructures, electrons will transfer spontaneously from the conduct bands with relatively high energy to ones with relatively low energy, while holes will transfer on the opposite direction. As a result, electrons and holes will prefer to separate and stay in individual materials, forming intra-layer excitons. In practical applications, both the separation time and life-time of formed intra-layer excitons make a big difference on the properties of the devices. To study this basic issue, Hong et al built an atomically MoS$_2$/WS$_2$ heterostructure, and observed a fast carriers separation process, as shown in figure 19(a) [146]. In their work, pump–probe spectroscopy, i.e. pumping one material with a laser while probing the optical response on the other, was used to detect the transfer time. They found it only takes about 50 fs for holes transfer from the MoS$_2$ layer to the WS$_2$ layer. This holes transfer time is almost two magnitudes shorter than that in individual materials. The physical mechanism behind this fast transfer is still unclear even though some probable reasons were proposed by the authors. A similar fast transfer process (sub-picosecond) was also observed in the MoS$_2$/MoSe$_2$ system. After separation, electron–hole pairs bonded in different materials (intra-layer excitons) will form, as shown in figure 19(b) [171]. Recently, Rivera et al found that the life-time of intra-layer excitons in the MoSe$_2$/WSe$_2$ system is about 1.8 ns, nearly one magnitude longer than the excitons in individual ones. Figure 19(b) gives the results. Similar to the separation process, the reasons for the long-lived life-time are still unclear and further studies are needed.
As a result of its special electric and superior optical properties mentioned above, optoelectronic devices based on 2D heterostructures attract increasing attention. Prototype devices, like photodetectors and solar cells, have been demonstrated [17, 161–164, 168, 169, 172]. For example, Huo et al demonstrated a photodetector with photo-switching ratio exceeding 1000 based on MoS2/WS2 heterostructures [169]. Deng et al fabricated a p-n junction based on a multilayer BP and monolayer MoS2 and found it showed a maximum photodetection responsivity of 418 mA W−1 under 633 nm laser [168]. PV effects and solar cells are one of the most important optoelectronic applications of heterostructures. As for 2D heterostructures, a similar effect has been found. For example, Gong et al synthesized a lateral WS2/MoS2 heterostructure showing an open-loop voltage and close-loop current of 0.12 V and 5.7 pA respectively [17]. Deng et al fabricated a p-n junction based on a multilayer BP and monolayer MoS2 and found it showed a maximum photodetection responsivity of 418 mA W−1 under 633 nm laser [168]. PV effects and solar cells are one of the most important optoelectronic applications of heterostructures. As for 2D heterostructures, a similar effect has been found. For example, Gong et al synthesized a lateral WS2/MoS2 heterostructure showing an open-loop voltage and close-loop current of 0.12 V and 5.7 pA respectively [17]. Similarly, Duan et al demonstrated a lateral WS2/WSe2 photodiode with an external and internal quantum efficiency of 9.9% and 43% respectively [162]. Note that PV effects in both of these two works were based on 2D heterostructures with lateral layout, which can be understood by the traditional built-in potential mechanism: while under illumination, photo-generated carriers separated under the effect of built-in potential and gave rise to an external electrical potential and photo-generated current, producing so-called PV effects. However, for vdWHs, owing to no built-in potential as we mentioned above, the situation is still unclear. Recently, Furchi et al fabricated MoS2/WSe2 vdWHs and demonstrated a similar PV effect [172]. To achieve a better understanding, Lee et al studied the optoelectronic properties of an atomically WSe2/MoS2 p-n junction in the same work to study the underlying mechanism behind the rectification characteristic of vdWH [164]. Based on their findings of the carriers transport mechanism, they found that tunable interlayer recombination of photo-generated carriers play a critical role in the optoelectronic properties of vdWHs (see figure 20).

Although relatively extensive studies have been done on individual 2D non-graphene materials, research on heterostructures based on them is just beginning. The mechanical exfoliation and transfer method is time consuming and only suitable for lab research. Reports on direct synthesis by the vapor deposition method are still limited. More work on in situ growth is urgently needed. Besides, many fundamental issues are still unclear and need to be addressed. In addition, more unique properties and devices, such as valleytronic devices and tunneling FETs, are expected.

4.4. Hydrogen evolution

Energy storage, such as Li-batteries [173–175], supercapacitors [176–178], catalysts for hydrodesulfurization (HDS) [179] and H2 evolution, is another important
application of layered TMD materials due to the suitable interlayer spacing and catalytic active sites. In particular, the need to replace rare and expensive noble metal catalysts (such as Pt) with earth-abundant TMD materials for producing hydrogen fuel in HER continues to be a strong driving force behind research in sustainable energy technologies. To date, numerous researches have demonstrated the effective utility of the layered TMDs for HER [180]. The following are typical steps by which cathodic H2 evolution occurs at various catalysts in acidic media [181, 182]:

\[ \text{H}_2\text{O}^+ + e^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O} \quad \text{Volmer reaction} \]  
\[ (b \approx 120 \text{ mV}) \quad \text{Step I} \]

\[ \text{H}_{\text{ads}} + \text{H}_2\text{O}^+ + e^- \rightarrow \text{H}_2 + \text{H}_2\text{O} \quad \text{Heyrovsky reaction} \]  
\[ (b \approx 40 \text{ mV}) \quad \text{Step II} \]

\[ \text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2 \quad \text{Tafel reaction} \]  
\[ (b \approx 30 \text{ mV}) \quad \text{Step III} \]

Where the \( \text{H}_{\text{ads}} \) is the absorbed H intermediate, and \( b \) is the Tafel slope. Generally, steps II and III are alternative desorption steps for H2 formation but each is continuous with respect to step I. The distinction between step I, II and III, as a possible rate-controlling step in HER, is in connection with the differences of Tafel slopes, which are determined by the potential versus the log-logarithm of the current density. TMDs, such as MoS2, WS2, WSe2 and WS\(_{2n-1-x}\)Se\(_{2x}\), open up interesting paths in cathodic H2 production to replace the precious metals. Theoretical studies have indicated that MoS2 with nanoparticulate configuration is active for HER. The ‘volcano plot’ in figure 21(a) summarizes the HER activity of various catalysts, predicting reasonable high active sites on the MoS2 nanoparticles [183]. Importantly, the sites located along the edges of the trigonal prismatic (2H) MoS2 layers are crucial for electrocatalytic activity, while the basal surfaces are catalytically inert [183–185]. The active edge, which is a catalytic H2 evolution from H\(_2\)O, consists of the sulfide Mo terminated edge (10-10) owing to the low Gibbs free energy of absorbed atomic hydrogen (\( \Delta G_{11} = 0.18 \text{ eV} \)) (figure 21(b)) [186]. Besides edge sites, the vacancy defects of the few-layered MoS2 also are favorable to the dissociation of H\(_2\)O for H2 production, which has been predicted through first-principles density functional theory and a finite temperature molecular dynamic [187]. Thus, in order to improve the performance of MoS2 in HER, Xie et al designed a controllable disorder engineering method to prepare the defect-rich MoS2 nanosheets, demonstrating a small onset overpotential of 120 mV for HER [62, 63]. Conductivity of the catalyst is another crucial factor affecting the
electrocatalytic activity. As we mentioned before, the lithium intercalated reaction usually destabilized the semiconducting trigonal prismatic 2H structure, causing a transition to the octahedral 1T polymorph with better conductivity [188]. The Jin group reported that the HER catalytic activity can be significantly enhanced when the semiconducting TMDs are chemically exfoliated into 1T polymorph metallic nanosheets [189, 190]. The much lower overpotential and smaller Tafel slope shown in figures 21(c) and (d) demonstrate the enhanced catalytic activity of the 1T phase MoS2 [189]. Additionally, incorporating the MoS2 nanosheets into the conductive templates, such as Ni foam and r-GO, is also an important strategy to enhance efficient HER performance. The r-GO and MoS2 composite show much higher HER activity with a Tafel slope of 41 mV per decade at a low onset potential [182]. Here, the r-GO not only acts as a template for the growth of MoS2 nanosheets but also improves the electron-transfer from MoS2 nanosheets to the electrode. The edge sites along with good electrical coupling to graphene are of excellent activity. For popular members of TMDs family, tungsten disulfide (WS2) [16, 190], tungsten selenide (WSe2) [191] and ternary compound W5S21−xSe2x [192] also exhibit promising activity. Moreover, several recent reports have confirmed that the Tafel slopes for TMDC-based HER are in a similar magnitude, ranging from 40 to 120 mV per decade. As mentioned above, the Tafel slope with this scope suggests that the Volmer–Heyrovsky HER mechanism (step I and II) is operative in the HER catalyzed by Mo or W dischalcogenides based electrocatalysts [181, 182].

5. Conclusion and perspectives

Two-dimensional semiconductors, with both layered and non-layered structures, have been a rising new star in material science. In this review, we discussed recent achievements, including preparation methods, and applications in electronics, optoelectronics and HER. Mechanical exfoliation is the most used method for lab research, while CVD is seen as the most promising method for controllable and scalable synthesis of high quality 2D semiconductors. With intrinsic large band-gaps, these materials exhibit great potential applications in FETs as channel materials when scaling down to single- or few-layer thickness. Strong light–matter interaction and direct band-gaps make them promising candidates for high-performance optoelectronic devices. For example, an MoS2 phototransistor demonstrates a very high current on/off ratio of $10^5$ and remarkable responsivity of 880 A W$^{-1}$. Containing more active sites, 2D semiconductors with ultrathin thickness have been explored as substitutes of expensive metal in HER. Two-dimensional heterostructures with rectifying characteristics and PV effects have been constructed, showing great potential in applications of logic circuits, photodetectors as well as solar cells. Inspired by layer-structured semiconductors, 2D non-layered materials have been synthesized successfully by the CVD method. In contrast with their 3D counterpart, they have shown unusual properties and promising applications on flexible electronics and optoelectronic devices.

It is worth noting that although great achievements have been obtained, research on semiconductors with 2D geometry still faces some critical challenges for practical applications. New synthesis methods for high quality 2D semiconductors with a large-area, mass-amount, thickness controllability, high crystallinity and considerable uniformity, are still highly desired. With access to high quality 2D materials, a further hurdle is how to obtain considerable carrier mobility for high-performance FET devices. Of crucial importance is to suppress the possible effects arising from Schottky contacts, material defects and dielectric layer roughness as well. In addition, to achieve building blocks with a complementary conducting type, doping is an effective method. Two-dimensional vertical vdWH own ultrathin junction thickness,

**Figure 20.** PV effect of 2D heterostructures. Photoresponse characteristics at various gate voltages under white-light illumination. Inset: color plot of photocurrent as a function of voltages $V_{ds}$ (x-axis) and $V_g$ (y-axis). The dashed line represents the profile of short-circuit current density $J_{sc}$ at $V_{ds} = 0$ V. The second panel: schematic illustrations of exciton dissociation and interlayer recombination processes. The third panel: simulations of the gate-voltage-dependent majority (red curve for holes in WSe2; blue curve for electrons in MoS2) and minority (red dashed curve for holes in MoS2; blue dashed curve for electrons in WSe2) carrier densities in each layer (top), spatially averaged (from [164], © 2014 Nature Publishing Group.)
strikingly different with conventional bulk heterojunctions. Traditional bulk junction theory is not suitable for this emerging class of junctions. To investigate these heterojunctions and explore the fundamental theory will be the next urgent topic. Two-dimensional materials are a relatively new but exciting research area and it is really worth anticipating what they will bring to us in the future.

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References


Figure 21. Hydrogen evolution reaction catalysis with TMDs. (a) Volcano plot of the exchange current density as a function of the DFT-calculated Gibbs free energy of adsorbed atomic hydrogen for nanoparticulate MoS2 and the pure metals. MoS2 follows the same trend as the pure metals. (b) Model system of the single-layer MoS2 stripe with rows of Mo atoms in the x-, y-direction. The yellow spheres represent S atoms, whereas the magenta spheres correspond to Mo atoms. (c) Simple lithium intercalation chemistry is used to drive the phase transformation from the 2H- to the 1T-MoS2 polymorph (left), SEM image (top-right) of the grown 2H MoS2 nanostructures and HRTEM image (bottom right) of lithium intercalated and exfoliated 1T MoS2 nanosheets. (d) Electrocatalytic properties of the 2H-MoS2 nanostructure and 1T MoS2 nanosheets: polarization curves at higher potentials and corresponding Tafel plots (the inset). Figures reproduced with permission from: (a) in [183], © 2007 The American Association for the Advancement of Science; (b) in [184], © 2001 American Physical Society; (c), (d) in [189], © 2013 American Chemical Society.