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Synthesis and Optoelectronic Applications of Graphene/Transition Metal Dichalcogenides Flat-Pack Assembly

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Abstract:

Being a representative candidate from the two-dimensional (2D) materials family, graphene has been one of the most intensively researched candidates because of its ultrahigh carrier mobility, quantum Hall effects, excellent mechanical property and high optical transmittance. Unfortunately, the lack of a band gap makes graphene a poor fit for digital electronics, where the current on/off ratio is critical. Huge efforts have been advocated to discover new 2D layered materials with wonderful properties, which complements the needs of 2D electronics. Appropriately designed graphene based hybrid structure could perform better than its counterpart alone. The graphene hybrid structure soon become one of the most exciting frontiers in advanced 2D materials, and many efforts have been made to create artificial heterostructures by

assembling of graphene with various layered materials. In this review, we present the recent development in synthesis and applications of graphene based 2D heterostructures. Although 2D transition metal dichalcogenide semiconductors have been demonstrated as strong candidates for next-generation electronics and optoelectronics, by combining advantages of various properties of 2D materials together with graphene, it is highly possible to build entire digital circuits using atomically thin components, and create many novel devices that can be utilized in different areas.

1. Introduction

The emerging atomically thin two-dimensional (2D) materials, ranging from semimetallic graphene [1-3], semiconducting transition-metal dichalcogenides [4-7] and black phosphorus [8, 9], to insulating hexagonal boron nitride [10-12], have attracted great interests owing to their unique structures and remarkable properties. These 2D materials with atomically thin layered structures offer a convenient platform for studying the origin of diverse properties at the atomic level. Monolayer graphene is the very first and intensively studied carbon based 2D nanomaterials. It has been demonstrated to have extraordinary properties including ultra-high electron mobility [1], excellent optical transmittance [13], good thermal conductivity [14], and exceptionally large Young's modulus [15]. Because of the unique electrical properties and high charge sensitivity of graphene [16-18], it has been considered and demonstrated as a potential material for a variety of applications including field-effect transistors (FETs) [16, 19], memory devices [20], photovoltaic devices [21], strain sensors [22], and chemical/biological sensors [23]. However, the lack of an

intrinsic bandgap in graphene has impeded its applications in digital electronics. On the other hand, research on semiconducting 2D materials ignited the interest of many fields especially in the electronics community. Remarkably, 2D semiconducting transition metal dichalcogenide (TMDC) monolayers, such as MoS₂ [4], MoSe₂ [24], MoTe₂ [25], WS₂ [26] and WSe₂ [27], have received tremendous attention, due to their unique and striking properties [28-30]. With a significantly improved charge mobility and good mechanical property, 2D TMDCs are also considered as promising candidates for wearable and flexible systems [31]. Not alone, the heterostructures formed by alien semiconducting 2D layers together with graphene play an important role in 2D electronics, where the graphene layers perform as an excellent conductor with a high carrier mobility, while semiconducting TMDCs can serve as high on/off ratio semiconductors and for high quantum efficiency optical/optoelectronic applications [32]. Therefore, the complementary properties between graphene and TMDCs enable their heterostructures widely used as an essential building block for various electronic devices. Because of their distinct properties and high specific surface area, the 2D materials and hybrids exhibit promising applications in optoelectronics [33], catalysts [34, 35], biological sensors [36], supercapacitors [37], solar cells [21, 38], and lithium ion batteries [39]. This review provides insights into the recent advances of layered 2D graphene based heterostructures, with a concise introduction to the synthetic approaches and potential applications in electronics and optoelectronics.

2. Synthetic Routes of Graphene-Transition Metal Dichalcogenides Heterostructures:

Graphene is formed by a single layer of carbon atoms arranged in a 2D honeycomb lattice. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or layer-by-layer stacked into 3D graphite [18] as illustrated in Fig. 1(a). Being an inorganic graphite analogue, all the 2D TMDCs members share the similar material structure. For example, Fig. 1(b) shows the lattice structure of MoS_2 , where each TMDC layer is formed by sandwiching a layer of transition metal atoms with two layers of chalcogen atoms in a hexagonal packing geometry. The weak van der Waals force holding each TMDC layer together allows the bulk crystal to be exfoliated along the interlayer space. The isolated atomically thin TMDCs monolayers could possess dramatically different electrical, optical and thermal properties, and thus provide a wide range of building blocks for electrical and optical applications [33, 40]. Furthermore, it is possible to stack various 2D crystals one on top of another in a chosen sequence to create multilayer van der Waals heterostructures [41]. Fig. 1 (c) presents the resulting artificial 2D materials by vertically stacking different layered materials like assembling atomic scale Lego.

Fig. 1. (a) Schematic illustration of graphene and its evolution to three different graphitic forms. Adapted with permission from Ref. [18]. (b) The layered structure of MoS₂. Adapted with permission from Ref. [4]. (c) Building van der Waals heterostructures by vertical layer-by-layer stacking of various 2D materials, which can be analogous to Lego blocks (right panel). Adapted with permission from Ref. [41]. (A colour version of this figure can be viewed online.)

The controlled synthesis of large-area atomically thin 2D nanomaterials and their hybrids is an essential requirement for their practical applications in electronic devices [24, 29]. In recent years, various methods have been developed for the production of monolayer and few-layer 2D nanosheets. For example, atomically thin 2D layered materials can be obtained by mechanical or chemical exfoliation from their bulk crystals. However, the exfoliation method may destroy the lattice structure

of the 2D thin layers and introduce extrinsic defects or surface contaminations during the chemical or physical exfoliation process. Nevertheless, the layer number and crystallinity control of the grown materials are crucial for their various applications. Among all the synthetic strategies, chemical vapor deposition (CVD) has emerged as a scalable method for producing large-area graphene and TMDCs films with good layer number tunability [42, 43]. Meanwhile, due to its compatibility to semiconducting industry, CVD-grown 2D layered materials are more practical for large scale device applications.

2.1 Vapor Phase Synthesis of Graphene and TMDCs for Artificially Stacked Heterostructure

2.1.1 Graphene Vapor Phase Synthesis

The CVD growth of single- to few-layer graphene and h-BN has been demonstrated using transition metal foil or thin film as growth substrates [12, 44, 45]. To date, copper substrates are more commonly used for graphene synthesis compared to other transition metals such as nickel when monolayer thickness is required. Figs. 2 (a-d) display that the lower carbon solubility in copper at the growth temperature leads to the surface-limited growth which preferably delivers single-layer graphene. The transparency of the films promises their potential as alternative candidates for optoelectronic applications. The large area films of single- to few-layer graphene have also been synthesized via ambient pressure CVD on polycrystalline Ni films [44], where the layer number of the graphene films typically ranges from 1 to ~12. The lateral size of the single or bilayer regions is normally up to 20 μm . Figs. 2(e) and (f) show that the films can be either continuous over the whole substrate area or be patterned by the underlying pre-patterned Ni film [44]. Furthermore, Cu-Ni alloy can

be utilized for the synthesis to control the carbon solubility and produce bilayer to few-layer graphene [46, 47]. In addition, the direct growth of large domains of graphene can be achieved by the epitaxial growth on 6H-SiC substrates [48, 49]. The advantages of epitaxial growth method are mainly originated from the insulating property of SiC, which does not require transfer processes after synthesis. However, the surface uniformity over large area of graphene on SiC could be challenging due to the presence of the surface steps in SiC.

Fig. 2 (a), (b) Scanning electron microscope (SEM) images of CVD grown monolayer graphene on Cu foil surface. (c), (d) Optical microscope images of large-area graphene grown by CVD method and transferred to SiO₂/Si and glass substrates. (a-d) were adapted with permission from Ref. [45]. Few-layer graphene synthesized on

polycrystalline Ni thin film, before (e) and after (f) transferred to SiO₂/Si wafer. (e & f) were adapted with permission from Ref. [44]. (g), (h) Ultra large MoS₂ single crystal directly synthesized on SiO₂/Si substrate. (g & h) were adapted with permission from Ref. [57]. (A colour version of this figure can be viewed online.)

2.1.2 Synthesis of Transition Metal Dichalcogenides

Various TMDCs and even heterostructures can be synthesized in research labs for fundamental research purposes [29]. According to different applications, several synthetic approaches for TMDC layers have been developed [43], such as sulfurization of transition metal or metal oxide films [50, 51], thermal decomposition of thiosalts [52, 53], solvent thermal method [39], metal organic vapor deposition [54] and vapor phase transport method [55]. Among all the various methods, the CVD approach for TMDCs synthesis has shown great promise to produce high-quality TMDC layers with scalable sizes, controllable thicknesses, and excellent electronic/optical properties. Therefore, the CVD method has become a widely-adopted approach for growing TMDC monolayers. In the pioneer experimental reports for monolayer TMDC CVD synthesis, sulfur (or selenium) and transition metal oxides were typically chosen as growth precursors [56]. Where the transition metal sub-oxides are likely formed during the reaction and these reaction intermediates diffuse to the substrate surface and further react with chalcogen vapors to grow TMDC layers. Figs. 2(e) and (f) demonstrate that highly crystalline islands of monolayer MoS₂ with lateral size up to 100 μm can be obtained directly on SiO₂/Si substrates [57].

To date, various monolayer and few-layer TMDC nanosheets like MoS₂ [56], WS₂ [58], WSe₂ [59, 60] and MoSe₂ [61] have been synthesized by the sulfurization/selenization process [43].

2.2 Epitaxial Growth of Graphene and TMDCs Heterostructure

Although the 2D layered materials can be vertically stacked with mechanical stacking, considered as a convenient way to form heterostructures. However, due to the controllability and scalability limitations of mechanical stacking method, a direct synthetic approach to obtain 2D heterostructure is demanding, especially for the large scale electronic applications.

The recent development of vapor phase growth for graphene and other 2D materials, paves the way to directly synthesize heterojunctions. Taking advantages of surface reaction, CVD method becomes the mainstream to construct 2D heterojunction in recent years. The obtained heterojunction has a clean interface which could demonstrate better device performance. The advances in growth methods for TMDC layers also lead to the diversity of Graphene/TMDCs heterostructure synthesis. As afore mentioned, the CVD process not only provides large-size 2D materials as building blocks but also produces desired stacking structures directly. With edge-epitaxial growth, it is even possible to synthesize lateral 2D heterojunction [62, 63], which cannot be achieved by the mechanical stacking method. As an incommensurate epitaxy, van der Waals epitaxy has been proposed as an important platform for the growth of graphene based heterostructures. The van der Waals epitaxy allows the direct synthesis of defect-free crystals on growth substrates, which is irrespective of the nature of the grown materials and the method of crystallization, since the lattice mismatch between different layered materials can be effectively relaxed through the weak van der Waals force [64, 65]. An essence of the van der Waals epitaxy is to obtain a substrate surface that is free of dangling bonds. The graphene surface, formed by sp^2 bonded carbon atoms, is atomically flat and free of dangling bonds, which

makes it an ideal starting template for a variety of 2D materials to grow via van der Waals epitaxy [66, 67]. Among the current synthetic routes for graphene production, graphene grown on metal substrates is a more attractive approach for the fabrication of 2D heterostructures, due to its simplicity and the ease of graphene transfer to target substrates. As shown in Fig. 3 (a), Shi et al. utilized CVD graphene on Cu foil as the growth template to grow MoS₂ with the (NH₄)₂MoS₄ precursor followed by a thermal annealing process [53]. Post-synthesis and patterning method of graphene layers have been proven to be an effective approach for lateral 2D heterostructure synthesis, where the graphene layer with desired patterns is firstly fabricated by lithography methods, then followed by CVD synthesis of the TMDC layer forming lateral junctions. It has been shown that such one dimensional (1D) “edge contact” is very advantageous for electrical contacting of graphene with other 2D materials to achieve high performance devices. Recently, Ling et al. have reported CVD synthesis of graphene-MoS₂ lateral heterojunctions with nanometer overlapped region [68]. As displayed in Fig. 3 (b) and (c), the graphene-TMDC overlapped junction releases the requirement to match the lattices at the interface. However, the lithography method unavoidably produces graphene with disordered edges and unwanted defects due to the etching process, which hinder the formation of atomically sharp graphene-TMDC interfaces. The poor graphene-TMDC interfaces are typically associated with defects, dislocations and charges at the interfaces which degrade the carrier transport properties. More seriously, the residues from transfer and lithography processes for the CVD-grown graphene may also significantly change the affinity of nucleation for TMDC growth [69], hindering the formation of well-defined heterojunction.

Therefore, it demands more efforts for the synthesis of heterostructured graphene and TMDC layers. Alternative approaches have been developed recently, Lin et al.

demonstrated that epitaxial graphene on 6H-SiC can form heterostructures with MoS₂ and WSe₂ via the vapor phase reaction [70], where graphene layers are formed without the metal layer underneath and no transfer process is necessary. To minimize chemical impurities introduced during the patterning process, Li et al. have shown a lithographically patterning strategy for 2D materials by photoresist-free focused ion beam method [63], which offers better controllability for the fabrication of 2D heterojunctions.

Besides the defects and impurities introduced by processing of graphene layers, the conditions for TMDC synthesis such as temperature, pressure, gas flow rate, substrate interface property, and precursor delivery can significantly affect the synthetic pathway and thus produce TMDC layers with different surface structures and chemical compositions at TMDC-graphene junctions. It has been demonstrated that the nucleation of TMDC monolayers can be significantly affected by seeding the growth substrates with graphene-like species [56, 71, 72]. Meanwhile, carbon-based materials play a role in the reduction process of transition metal oxides, which have been widely used for TMDC synthesis [73]. The presence of carbon or graphene species during the TMDC synthesis may affect the TMDC growth, which could result in different levels of vacancies, point defects and multiple layer formation at the heterojunction interfaces. Therefore, deep understanding of the reaction between carbon materials and TMDC precursors is desired. The crystallization of TMDC monolayers on graphene should be carefully tuned in a controlled manner, when using graphene based materials as the growth template for TMDC monolayers.

Fig.3 (a) Vertical stacking of MoS₂/graphene heterostructure directly grown by CVD method. Adapted with permission from Ref. [53]. (b), (c) STEM images of graphene-MoS₂ lateral heterojunction. Adapted with permission from Ref. [68]. (A colour version of this figure can be viewed online.)

3. Applications

Assembling distinct 2D layers together can offer the possibility to fine-tune material properties, but it is usually challenging for traditional materials owing to the large strain caused by lattice mismatches between different crystals. While, for 2D materials, the atoms in each layer are connected strongly by the in-plane chemical bonding and only weak van der Waals force exists between layers allowing the release of strain. Therefore, distinct layers including insulators, conductors, and semiconductors can be stacked to form complex 2D van der Waals heterostructures. And with these various artificial 2D building blocks, most critical components in

electronic devices can be redesigned. The devices with functionalities can be constructed by combining the electronic properties of graphene and different 2D layered materials. Various new devices based on the heterostructures of graphene and TMDCs have been successfully fabricated. For example, logic and memory devices [74] have already been demonstrated with graphene–MoS₂ hybrids. The graphene/MoS₂ heterostructures also show extremely high photogain [75, 76] and ultrasensitive detection of DNA hybridization [36].

3.1 Vertical and Planar Field Effect Transistors

2D nanomaterials, such as graphene and TMDCs, hold great promises for various applications owing their unique properties including their transparency, mechanical flexibility and strong confinement of electron and holes. Vertically stacked TMDC and graphene heterostructures have been adopted for field-effect transistors (FETs) and flexible electronics. As shown in Figs. 4 (a-c), Yu et al. have constructed electronic systems based on CVD grown heterostructure graphene/MoS₂ in a large scale [77]. MoS₂ was used as the active channel material in transistors while graphene works as contact electrodes and/or interconnects. The work function of graphene can be tunable by electrostatic doping, which would significantly improve the ohmic contact to MoS₂ [21, 77].

Besides the planar FETs, layer-by-layer stacked 2D heterojunctions can be used to build vertical FETs [78]. Relying on tunneling mechanism, the charge carrier transit time in vertical FETs could be faster than that in planar FETs, and thus promising for high-speed operation. The facial stacking feature with a large contact area between 2D materials also leads to a large current density, potentially useful for integrated circuits. As shown in Fig. 4(d) and (e), Yu and co-workers have reported a vertical

FET based on the metal/few-layer MoS₂/graphene three-layer heterostructure, which demonstrates an on/off ratio $>10^3$ and a current density at around 5,000 A/cm² [78]. Moriya et al. have further enhanced the current on/off ratio to a value larger than 10^5 and current density up to 10^4 A/cm² based on a heterostructure with clean interfaces [79].

Fig. 4 (a) Schematic illustration of important fabrication steps and the layout of vertically assembled graphene/MoS₂ FETs. (b) The optical (left) and atomic force microscopy (AFM) images (right) of the corresponding dual gate graphene/MoS₂ field-effect transistor with graphene as the electrodes. The scale bar in the AFM image is 10 μ m. (c) Optical micrograph of Graphene and MoS₂ integrated circuits, with the scale bar of 500 μ m. (a-c) were adapted with permission from Ref. [77]. (d), (e) Layout of the vertical heterostructured graphene/MoS₂ transistor device: top view and side view. Adapted with permission from Ref. [78]. (A colour version of this figure can be viewed online.)

On the other hand, recent works have shown that the use of lateral stitched graphene-TMDCs heterostructures, as the contacts to TMDCs channels, can result in a much lower contact resistance than conventional metal contacts. Lin et al. have reported a recent development of graphene-MoS₂ lateral heterojunctions obtained by CVD

methods [68]. High-resolution transmission microscope imaging (TEM) reveals that instead of a sharp in-plane junction, the two materials form an overlapped junction with a few nanometers up to 20 nm in width. A large photocurrent has been observed from this heterojunction.

3.2 Photodetectors and Photovoltaic Devices

The optoelectronic applications of graphene have been widely explored. The response speed, quantum efficiency and photo sensitivity are the critical aspects for high performance optoelectronics [80]. The gapless and high mobility graphene layers are known to exhibit broad absorption bands and rapid response time in optoelectronics. Because of the large mean-free path and high Fermi velocity in the graphene layer, excellent quantum efficiency approaching 100% can be achieved [81]. However, monolayer graphene can only absorb 2.3% of incident photon in the visible spectra range and thus limits its photoresponsivity. The graphene-based photodetectors still have much room to improve. Alternatively, semiconducting TMDC monolayers with a direct band gap in visible ranges possess a high absorption coefficient. Nevertheless, compared to graphene, the relatively low mobility reduces the response time. The 2D heterostructures with strong light-matter interactions typically present strong photon absorption and generate a large photocurrent. For example, due to the superb optical and electrical properties in graphene, transparent graphene electrode can work efficiently to collect the photo generated current. Meanwhile, exotic photoelectrical response may be largely modulated in the devices based on the graphene/TMDC heterostructures.

Recently, significant improvements in the photoconductivity of graphene have been achieved by combining graphene layers with other light-absorbing 2D layers such as

TMDCs. Typically, TMDCs layers are adopted as a photon absorber and the interface with graphene enables fast carrier separation; meanwhile, the Fermi energy of graphene is tunable by doping. Roy and co-workers have shown that a high photoresponsivity near 5×10^8 A/W can be achieved using graphene/multi-layer MoS₂ heterojunction [76]. The graphene and TMDCs hybrids exhibit persistent photoconductivity under the modulation of an electric field, serving as fast optical switches and gate-controllable photodetectors. As shown in Fig. 5 (a), Britnell and co-workers have shown an efficient photodetector with the graphene/TMDCs/graphene trilayer heterostructure [82]. Specifically, the graphene/WS₂/graphene-based optoelectronic device exhibits the photoresponsivity above 0.1 A/W, corresponding to an external quantum efficiency (EQE) up to 30%. The extrinsic quantum efficiency does not depend on the photon wavelength, as anticipated due to the approximately constant optical absorption at different wavelengths. The quantum efficiency decreases with the increasing power, which is likely owing to the built-in electric field screening by the excited electrons in the conduction band of WS₂. The EQE can be further increased by optimizing the light absorption of the active layer. As shown in Fig. 5 (b), by adding plasmonic nanostructures such as gold nanospheres on top of the graphene/TMDCs/graphene heterostructure, a 10-fold increase in the photocurrent can be further achieved.

Fig. 5 Heterostructure for photodetector. (a) External quantum efficiency (EQE) of the graphene/WS₂/graphene heterostructure at different wavelengths and powers. The inset shows the sublinear dependence of the measured photocurrent with laser power. Open symbols are for a device on Si/SiO₂ substrate, and crossed symbols are for a device on a flexible substrate. (b) The photocurrent maps of an h-BN/Gr/MoS₂/Gr device without (up) and with (down) spattering of gold nanoparticles for plasmonic enhancement. (a & b) adapted with permission from Ref. [82]. (c) Schematic illustration of the side view of the graphene/MoS₂/graphene stacking heterostructure device. Adapted with permission from Ref. [83]. (d) Optical image of large-area stacked graphene/MoS₂ bilayer and schematic illustration of the photodetector based on this heterostructure with the top view of the comb-shaped source and drain metals. Adapted with permission from Ref. [75]. (A colour version of this figure can be viewed online.)

Similarly, as shown in Fig. 5(c), Yu and co-workers provide an extra gate voltage control in graphene/MoS₂/graphene heterostructure to adjust the Schottky barrier between graphene and MoS₂, where the external electrical field can enhance the photo-carrier generation, separation and transport processes in this vertical stacking device [83]. It has been demonstrated that an EQE of 55% and internal quantum efficiency (IQE) of 85% can be achieved by proper photocurrent modulation. As shown in Fig. 5 (d), Zhang and co-workers have built a large-scale graphene/MoS₂ heterojunction consisting of monolayer graphene and CVD grown MoS₂ [75]. The high mobility in graphene facilitates the fast electron extraction, while the holes trapped in MoS₂ result in a multiple recirculation of electrons in graphene, which leads to a high photogain $> 10^8$ and a photoresponsivity $> 10^7$ A/W.

Besides photodetectors, layered semiconducting TMDCs have also been considered as attractive candidates for solar applications because of their large surface area, and potential as sunlight absorbers [38, 84]. The graphene/TMDCs heterostructure based photovoltaic devices can be fabricated with the simple Schottky junction between semi-metal (graphene) and semiconductor (TMDCs). The Schottky junction formed by graphene/TMDCs establishes the built-in electric field, and works as an interface for the charge separation. Shanmugam and co-workers have demonstrated a graphene/WS₂ Schottky barrier photovoltaic cell, where WS₂ is a photoactive layer. The photovoltaic device shows excellent photon absorption capability in the visible range and a photoelectric conversion efficiency (PCE) around 3.3% can be achieved [85].

3.3 Memory Devices

In addition to the electronic logic devices, nonvolatile memory cells have been demonstrated using the graphene/MoS₂ hybrids [74]. As shown in Fig. 6, Bertolazzi *et al.* have successfully fabricated a field-effect transistor with MoS₂ acting as a channel material, which in an intimate contact with graphene source/drain electrodes. A multilayer graphene charge trapping layer was introduced into the MoS₂ device. Due to the semiconducting nature of MoS₂ monolayer, it is highly sensitive to the presence of charges in the trapping layer of charges, which leads to a factor of 10⁴ difference in the program/erase states.

Fig. 6 MoS₂/graphene heterostructure memory layout. (a) Three-dimensional schematic view of the memory device based on monolayer MoS₂ and graphene. (b) Schematics of a heterostructure memory cell with a single-layer MoS₂ semiconducting channel, graphene contacts and few-layer graphene floating gate. (c) Optical micrographs of two graphene/MoS₂ heterostructure transistors fabricated on the MoS₂ monolayer flake at various stages of fabrication. Adapted with permission from Ref. [74]. (A colour version of this figure can be viewed online.)

3.4 Biosensors

The large aspect ratio of graphene and its ultra-sensitivity to environmental charge perturbation makes it suitable for applications in bio-sensing [86, 87]. Previous works

have demonstrated semiconducting TMDCs also show great promises for the DNA sequence differentiating via simple optical and electro-chemical characterizations [88]. However, compared to the chemically inert graphene, TMDCs monolayers are sensitive to the presence of oxygen and water molecules, which could limit their applications in biosensing performed in an aqueous solution. In order to increase the stability and sensitivity, Loan and co-workers have shown a graphene/MoS₂ heterostructure, where the photoluminescence (PL) intensity of MoS₂ is sensitive to the DNA hybridization on graphene (Fig. 7) [36]. The monolayer MoS₂ was covered by a top graphene layer. The capping graphene layer protects MoS₂ to avoid direct contacts with moisture and oxygen, meanwhile hosts the DNA owing to its biocompatibility. The detection lower limit as low as 1 atto mole (10^{-18} M) within a few minutes promises the ultrasensitive DNA detection of graphene/TMDC heterostructures.

Fig. 7 2D vertical heterostructures for a biosensor. Schematic illustration of the graphene/MoS₂ heterostructure sensor and measurement setup. Bottom images show the MoS₂ photoluminescence peak area mappings when hybridized with the complementary target DNA (up) and the mismatched DNA (down) at different concentrations. Adapted with permission from Ref. [36]. (A colour version of this figure can be viewed online.)

Although the recent advances in 2D materials engineering have provided practical ways to produce “materials on demand”, offering opportunities to many promising applications, graphene-based 2D heterostructures still face many challenges. Combining the unique properties of semi-metallic graphene and semiconducting TMDC monolayers have shown superior performance at the individual device levels. However, currently the synthesis and device assembly processes of 2D heterostructures are still not fully scalable. In 2D electronics, the electrical properties between 2D junctions greatly dominate the device behaviors. Considering the nature

of atomic layer thickness, even a subtle growth condition shift may result in different detailed atomic geometries. The variation of materials crystallinity and uncertainties in layer-to-layer contact conditions often result in scattered device performance, which hinders it from achieving good device reproducibility in large scales. Therefore, building graphene-based heterostructures with well-defined, clean interface via controlled synthesis and growth is critical for their various applications. To form high quality graphene-TMDC junctions, the graphene edge should be formed with precise incision and graphene layer should stay highly crystalline during the whole processes for reproducible formation of graphene-TMDC heterojunctions. Recently, joule-heating was used to create graphene with well-arranged atomically sharp edges [89, 90]. These pioneer works may shine light on the precise atomic structure engineering for graphene-TMDCs edge epitaxy.

4. Summary

Two-dimensional materials hold a great promise for next-generation nanoelectronic devices. Graphene is one of the most widely explored 2D materials, due to its rich physics and high mobility. Graphene exhibits exciting potential in wideband and high-speed photodetection due to its broad spectral absorption, superior carrier mobility and short carrier lifetime. Nevertheless, the semi-metallic graphene does not have a bandgap, resulting a low on/off ratio in transistor devices. The lack of switch off property hinders its application where a semiconducting property needed. Yet, the layered lattice structure of graphene makes it relatively easy to fabricate complex structures such as vertical and lateral heterostructures from a number of 2D materials. We have reviewed various heterostructures based on 2D materials in the paper, where the band structure engineering with the heterostructural formation greatly expands the

property of graphene. It is believed that further progresses in the growth of 2D heterostructures and the new approaches to construct 2D devices will lead to fully integrated 2D nanoelectronics with superb performance in the future.

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