Synthesis and properties of molybdenum disulphide: from bulk to atomic layers

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Molybdenum disulphide (MoS2) has been one of the most interesting materials for scientists and engineers for a long time. While its bulk form has been in use in conventional industries as an intercalation agent and a dry lubricant for many years, its two-dimensional forms have attracted growing attention in recent years for applications in nano-electronic applications. Specifically, the single layer form of MoS2 shows significant potential as a semiconductor analogue of graphene. These exciting applications are spread over many fields, from flexible and transparent transistor devices, to low-power, high efficiency biological and chemical sensing applications. This Review Article, for the first time, provides a comprehensive overview of the synthesis, structural polytypes, properties, and applications of bulk, few layer, and single layer MoS2.

1. Introduction

Layered crystalline materials have attracted researchers for several decades. Their unique crystallographic structure, as the term “layered” implies, is composed of separate two-dimensional (2D) layers, between which the van der Waals (vdW) interaction exists in place of ionic or covalent bonding.1,2 Therefore, most of their physical properties, such as charge carrier transport or mechanical friction, are anisotropic. Properties along the in-plane direction significantly differ from the out-of-plane counterparts.2–4 Historical applications of such structural uniqueness were confined to host lattices in intercalation chemistry5–7 or dry lubricants in mechanics.8 However, recent experimental advances have found these materials are capable of realising 2D nanomaterials, when the individual layers are isolated.8–11 These isolated single or few layers have been good topics for the fundamental research, because some of their properties are quite distinct from bulk counterparts. Researchers also expect that they have great utility in various fields, such as flexible and transparent components in nanoelectronics, active components for chemical sensors, catalysts for various electrochemical reactions, and so forth.12–14

Among a variety of 2D nanomaterials, a growing number of researchers have recently focused on two-dimensional molybdenum disulphide (MoS2), as witnessed in the exponentially rising number of publications on this subject (Fig. 1). Bulk MoS2, like graphite, is a layered material, where each layer of MoS2 is composed of three-atom-thick S–Mo–S stacks (Fig. 2a). Each layer of MoS2 is often referred as a “single layer” or a “monolayer” by convention. This is contrary to other chalcogenides such as Bi2Se3, in which case it is rather called a “quintuple layer” (QL), reflecting the atomic structure of 1 QL, i.e. a stack of Se–Bi–Se–Bi–Se. Such convention, however, rarely applies to MoS2 and other transition...
metal dichalcogenides, such as a “triple layer,” although single-layer MoS₂ or monolayer MoS₂ is in fact three atoms thick. In addition, depending on the coordination of Mo atoms within a single layer and the stacking order of single layers, there are three known polytypes—namely 1T, 2H, and 3R—of MoS₂.

MoS₂, especially of naturally abundant 2H polytype, has a long history of study and applications, because of its abundance in the Earth’s crust.¹⁻¹⁷ It its major industrial applications include dry lubricants,⁴⁺⁻¹⁸ hydrodesulphurisation catalysts,¹⁹ and cathode materials for lithium ion batteries.²⁰ Also, MoS₂ nanotubes and fullerenes are one of the first inorganic analogues of carbon nanotubes and fullerenes to be synthesised, but their proposed applications are still restricted to traditional lubrication.²¹⁻²⁴ However, the discovery of direct bandgap of 1.9 eV from single-layer MoS₂ has opened up new possibilities of utilising MoS₂ in electronics.¹⁹,²¹⁻²⁴ This analogous form of graphene, a well-known robust semi-metal, completes the palette of 2D materials, spanning all of conductor (graphene), insulator (hexagonal boron nitride), and now semiconductor (single-layer MoS₂). Furthermore, the discovery of the valley polarisation in single layers offers a novel, prospective carrier of information.²⁴⁻²⁶ Despite its indirect bandgap, two to several layers of MoS₂, or “few-layer MoS₂”, still have attractive properties for various electronic devices because of its semiconductivity. Various studies on single- to few-layer MoS₂ have ensured its suitability for flexible, transparent, low-power devices in electronics.²⁶ Finally, it can be utilised in important chemical applications such as hydrogen evolution reaction²³,²⁴ and chemical sensing.²⁵

Attracted by these immense potentials, an increasing number of researchers turn their attention to explore this material. Despite such increasing popularity, there is no comprehensive review, to the best of our knowledge, concentrating on atomic layers of MoS₂. Moreover most of the previous review papers on MoS₂ mainly focuses on the most abundant 2H polytype only, although the 3R and 1T types have their own interesting properties. Herein, we review, for the first time, synthesis, properties and applications of 2D atomic layers of MoS₂, including a concise overview of its bulk form and of its various polytypes. This review aims to provide a brief introduction of this attractive material to readers from various backgrounds in order to help them to understand and utilise this nanomaterial for their own demands. To this end, this review article is composed of following contents. The first part (Section 2) is a prelude to 2D layers, where we briefly summarise the fundamental nature and the historical application of various polytypes of bulk MoS₂. The second part (Section 3) provides an up-to-date review on the studies regarding the
preparation of 2D MoS$_2$ layers by means of mechanical exfoliation, chemical exfoliation and vapour-phase growth. The third part (Section 4 and 5) describes the physical properties of 2D atomic layers, focusing on their electronic (Section 4) and optoelectronic properties (Section 5). The final part (Section 6) describes the chemical reactivity of atomic layers of MoS$_2$, specifically in terms of their reactivity with various chemical and biological species, as well as related applications. For convenience, the term “2D MoS$_2$” in this review stands for single- to few-layer forms of MoS$_2$, where they have significantly different properties than the bulk form.

2. Overview on bulk MoS$_2$

2.1 Polytypes and crystallography

As we have briefly discussed in Section 1, each layer of MoS$_2$ is composed of S–Mo–S stacks, where a single molybdenum atom is surrounded by six sulphur atoms, as shown in Fig. 2a. MoS$_2$ has three natural or synthetic polytypes of MoS$_2$, which...
are 1T, 2H, and 3R, depending on (1) the coordination of sulphur atoms with respect to the central molybdenum atom and (2) the stacking order of each layer (Fig. 2a and Table 1). Here the former number denotes the number of layers within a single trigonal prismatic crystal unit cell, and the latter letter describes the trigonal prismatic structure, where T stands for trigonal, H for hexagonal, and R for rhombohedral structure. For example, a unit cell of the 2H polytype contains two layers that are centrosymmetric to each other (2), creating hexagonal structure (H). Note that it is a convention to denote the polytype as the prefix to MoS2, if specified, as following: 2H-MoS2 stands for the 2H polytype of MoS2.

Of these three polytypes, only 2H-MoS2 and 3R-MoS2 are stable and found in nature (see Table 1 for a list of their properties). Both the 2H and 3R polytypes commonly have trigonal prismatic coordination (D3h) of molybdenum atoms, but they have different stacking order; 2H has stacking order of AbA Bb AbA…, while that of 3R is AbA BbCb CaCc AbA… Note that the upper and lower cases represent relative position of sulphur and molybdenum atoms, respectively. Nonetheless, both polytypes share crystallographic parameters. The distance between a Mo atom and its nearest S atom is 2.41 Å. The thickness of each layer is 3.15 Å, while the distance between adjacent layers is 3.49 Å, suggesting that the interlayer vdW interaction is weaker than intralayer covalent bonding.

In contrast, 1T-MoS2 is metastable, which is distinct from the aforementioned polytypes. It has octahedral coordination (O6) of molybdenum atoms, and its stacking order is AbC AbC… There are three reported types of distortions in 1T-MoS2, namely 2a x 2a, 3a x a and 3a x 3a superstructures. The phase transformation between these superstructures is related to the intercalation and oxidation level of alkali metal during synthesis, as we described later on Section 2.3 (Fig. 2b).

### 2.2 The 2H and 3R polytypes with trigonal prismatic coordination

Pristine 2H-MoS2 is a diamagnetic semiconductor with indirect bandgap of 1.29 eV. Mo 4d orbitals are split by trigonal prismatic ligand field, and two d electrons of Mo5+ species occupy the lowest 4d_{x^2-y^2} orbital, leading to diamagnetism and semiconductivity (Fig. 2c). Since the gap between the d_{x^2-y^2} orbital (which mainly contributes to the valence band in the lattice) and d_{x^2} orbitals (which contributes to the conduction band in the lattice) is wide, a bandgap is formed even after the mixing with sulphur atoms occurs. Detailed band structure studies reveal that the momentum of the valence band maximum (VBM) is different from that of the conduction band minimum (CBM), and thus it has an indirect bandgap (the calculated band diagram is shown in Fig. 5a, and detailed discussion is given in Section 5). Therefore, the indirect bandgap leads to a negligible quantum yield for the photoluminescence (PL). UV-Vis absorption spectrum has two prominent peaks at 1.9 eV (λ ~ 640 nm) and 2.1 eV (λ ~ 580 nm), which are often referred to as the A1 and B1 exciton absorption, respectively (Fig. 2d). A detailed explanation on the origin and characteristics of these peaks are given in Section 5.1. Raman scattering has four characteristic vibration modes: the E_g mode (33 cm⁻¹, weak), E_1g mode (287 cm⁻¹, weak), E_{2g} mode (383 cm⁻¹, strong) and the A_{1g} mode (409 cm⁻¹, strong), which is shown in Fig. 2e.

In terms of charge carrier transport, Hall measurements show that 2H-MoS2 is an n-type semiconductor, with charge carrier mobility of 100 cm² V⁻¹ s⁻¹ at room temperature. However, application of high pressure (ca. 60 GPa) on 2H-MoS2 can induce a metallic state, along with change in Raman shifts due to the decrease in the interlayer distance and the change in the stacking order. Another viable way for semiconductor-to-metal transition is alkali metal or alkali earth metal doping, in which case metal-to-superconductor phase transition further occurs at low temperature (refer to Section 2.3). For instance, Rb-doped MoS2 (Rb0.88MoS2) has a superconducting critical temperature of 6.9 K.

2H-MoS2 is quite chemically inert. In vacuum, it is stable up to 1203 °C, at which point it turns into Mo2S3. It does not dissolve in most solvents, but strong oxidizing reagents such as aqua regia may oxidize and dissolve it. It also reacts with oxygen to yield MoO3 around 400 to 600 °C.

The physical and chemical properties of the 3R polytype is almost identical to those of the polytype, such as the Raman spectrum or the electronic band structure, except for minute differences in its band structure and UV-Vis absorption spectrum. For example, the A1 and B1 exciton absorption peaks are red-shifted by 10 meV and 62 meV respectively for 3R-MoS2, since the different stacking order alters the ionic contribution within interlayer interaction (Fig. 2d). These two stable polytypes of MoS2 are found in nature, and they are mostly obtained through mining. The majority of the...
80%) of natural molybdenite has 2H stacking, and only 3% of the ore is purely 3R polytype, with the remnants exist as a mixture. Otherwise, they are artificially prepared through chemical synthesis, most importantly the chemical vapour transport (CVD) method, where a mixture of Mo, S, and halogen (iodine for 2H-MoS₂, and chlorine for 3R-MoS₂) is annealed at high temperature for several days to grow large single crystals. Selective chemical synthesis of 2H-MoS₂ is achieved by (1) the direct sulfidation of elemental Mo or its compounds at elevated temperature, or (2) the pyrolysis of (NH₄)₂MoO₂S₂, which forms metastable intermediate MoS₂ and MoOS₂ respectively, all of which are reduced and crystallised to 2H-MoS₂ upon annealing at 350 °C or higher. Selective synthesis of 3R-MoS₂ is achieved by (1) the reaction of MoO₂ and S in liquid K₂CO₃ at 900 °C, or (2) the direct sulfidation of Mo under 4.7 GPa at 1050 °C, or (2) the transformation of 2H-MoS₂ under 4 to 7.5 GPa at 1900–2000 °C. Note that reverse transformation takes place under vacuum at 1000 °C.

Due to its high stability and unique layered structures, MoS₂, including both the 2H and 3R polytypes, has been widely used as a dry lubricant for several decades. Similar to other layered materials, the in-plane friction coefficient for bulk MoS₂ is much smaller (0.1) than that along c-axis (0.26). However, recent studies have discovered that the friction mechanism of MoS₂ is distinct from other layered materials, where the lubrication of MoS₂ is an intrinsic result of its inordinately weak vdW interlayer interaction. That is, lubrication of most layered materials requires the adsorption of vapour molecules, which can weaken the interlayer interaction. In case of some layered materials such as tere or muscovite mica, the interlayer interaction is so strong that they cannot even perform as lubricant. Therefore, most layered materials may not effectively lubricate in vacuum, where vapour molecules do not adsorb well. In contrast, friction in MoS₂ decreases in vacuum, since adsorbents, especially oxidizing water, deter easy friction of weakly bound MoS₂ layers. Therefore, MoS₂ has been favoured as a lubricant under extreme conditions like vacuum systems or in spacecraft machinery.

Another important field of industrial applications of MoS₂ is the catalysis of sulphur reactions for the purpose of hydro-desulphurisation (HDS), i.e. substitution of the sulphur atom in organic molecules with a hydrogen atom. Usually supported on silica or alumina, MoS₂ removes sulphur from various organic molecules containing sulphur as thiophenes. Such activity specifically occurs at the rim edge of the MoS₂ crystal, where sulphur vacancies easily adsorbs sulphur from the target molecule. A detailed mechanism study is given in Section 6.2.

2.3 The 1T polytype with octahedral coordination

1T-MoS₂, in contrast to the 2H and 3R polytypes, is metastable, metallic and paramagnetic because of the Mo atom’s octahedral coordination. In order to synthesize 1T-MoS₂, alkali-intercalated MoS₂ is hydrated and then oxidized. This reaction exploits electron donation from alkali metal to the MoS₂. As shown in Fig. 2c, an excess electrons from doped alkali metal stabilises octahedral coordination as in ReS₂. The subsequent oxidation process removes the excess electron, but the coordination still retains as octahedral form with slight level of distortion.

Notable consequences of the octahedral ligand field are the metallic conductivity and the metastable structure. As shown in Fig. 2c, two d electrons occupy triply degenerate d orbitals of the octahedral ligand field. Therefore, crystal distortion, similar to Jahn–Teller distortion or Fermi-surface nesting, takes place to break degeneracy and stabilise this metallic structure to some degree Equivalently, presence of excess electrons may stabilise the 1T phase, as witnessed in Re-doped nanotubes and 2D atomic layers as well.

Since the crystal distortion takes periodically, superstructures are formed. Diffraction and STM studies have found three types of superstructures at the intermediate and the final stages of the preparation process (Fig. 2b). At higher level of intercalation (i.e. lower level of oxidation; K_MoS₂, x ~ 0.7 in case of KMoS₂), triclinic or monoclinic structures of the 2a x 2a superstructure are found. This 2a x 2a superstructure are often found in other 1T transition metal dichalcogenides with the d² electronic configuration, like ReS₂. Further oxidation to K₂(H₂O)₉MoS₂ (x ≤ 0.3) results in the metallic 3a x a (equivalently) superstructure, which is formed by zigzag chain-like clustering of Mo atoms. Note that this superstructure is also found in “restacked MoS₂”, which is the precipitation from the aqueous dispersion of lithiated MoS₂ (we described the details of the preparation method of “restacked MoS₂” in Section 3.2). Further treatment of this superstructure with strong oxidising reagents such as Br₂ forms the 3a x 3a (a ≈ 0.3) results in the metallic 3a x a superstructure by trimerisation of the Mo atoms. However, according to theoretical calculations, this superstructure has a small bandgap, and it is even more unstable than the 3a x a superstructure (refer to Section 4.1).

Therefore, metallic 1T-MoS₂ does not have a precisely d² electronic configuration. The 1T-MoS₂ with the exactly d² electronic configuration would instead favour the 3a x 3a superstructure by trimerisation of the Mo atoms. However, according to theoretical calculations, this superstructure has a small bandgap, and it is even more unstable than the 3a x a superstructure.

Despite these distortions, 1T-MoS₂ is still metastable and susceptible to the transformation to the 2H polytype. Differential scanning calorimetry (DSC) studies found that annealing up to 95 °C transforms the 1T polytype into 2H polytype. Even simple aging is enough to induce the phase transformation to 2H polytype as well.

A well-known application of the metastable 1T polytype is as an intermediate in intercalation chemistry. A MoS₂ lattice is an excellent intercalation host, because it accepts intercalates of different sizes, from small lithium ions up to macromolecules. Stable 2H-MoS₂, however, does not accept most guest species directly, while 1T-MoS₂ is active for the intercalation chemistry. Since lithium ion can directly intercalate into 2H-MoS₂ without pre-treatment as well as convert the inert 2H polytype into the active 1T polytype, the intercalation of lithium ions, or lithiation, is done as matrix activation prior to...
intercalation of various guests species into inert 2H-MoS$_2$. A notable way of lithiation is refluxing a 2H-MoS$_2$ suspension with $n$-butyllithium, details are given in Section 3.2. An alternative way is creating an electrochemical cell comprised of Li and 2H-MoS$_2$ as respective electrodes.

Intercalation of other species then takes advantage of lithiation process by (1) exfoliation, where the lithiated MoS$_2$, LiMoS$_2$, colloid is hydrolysed to produce Li$_2$(H$_2$O)$_x$MoS$_2$ having the interlayer distance is 11.5 Å, or (2) restacking, which is treatment of LiMoS$_2$ with an oxidising reagent or acid to obtain metallic $\sqrt{3}a \times a$ superstructures. These “activated” MoS$_2$ can host various intercalates such as metalloocene, metallic clusters, or polymers. Intercalation of these guests often changes the properties of MoS$_2$; for instance, intercalation of conducting polymers such as polypyrrole (PPy) changes n-type MoS$_2$ into a p-type semiconductor. Intercalation of an alkali metal makes MoS$_2$ superconducting as well (refer to Section 2.2).

One of the major applications of MoS$_2$ intercalation chemistry is as an electrode in a lithium ion battery (LIB). A MoS$_2$ based anode has higher specific capacity (907 mAh g$^{-1}$ of reversible capacity after 50 cycles) than graphite (theoretical limit up to 372 mAh g$^{-1}$), better rate capability (554 mA h g$^{-1}$ for 20 cycles at 50 C rate) than Si or Ge (in case of Si, the theoretical specific capacity is 4212 mAh g$^{-1}$ at the initial lithiation, but it degrades rapidly upon repetitive charge and discharge), and significantly less volumetric expansion during lithiation (3% expansion upon full lithiation). Its energy density is comparable or higher than conventional LiCoO$_2$. A typical problem of both MoS$_2$ cathode and anode is their voltage, which is 2.0 V versus Li/Li$^+$. Since this voltage value is neither high (a high value is suitable for the cathode) nor low (a low value is suitable for the anode), such intermediate value reduces the net energy density. To this end, recent efforts have focused on overcoming this obstacle by forming MoS$_2$ nanostructures or nanocomposites, which are well reviewed in the literatures.

3. Preparation of 2D MoS$_2$

3.1 Mechanical exfoliation and direct visualisation

Conventional applications of MoS$_2$, such as tribology or intercalation chemistry, are not much different from those of other layered materials. However, the isolation of single-layer MoS$_2$ and the study on the nature of this atomically thin film have clearly distinguished this mineral from other layered materials because of its unique properties, most notably semiconductivity and valley polarisation. Preparation of 2D MoS$_2$ is therefore the first and the most crucial step to reveal and explore its nature.

The first report on single-layer MoS$_2$ used mechanical exfoliation, i.e. repetitive cleavage of bulk crystals using adhesive tapes. Since molybdenite, especially 2H-MoS$_2$, is naturally occurring mineral (refer to Section 2.2), the preparation of single crystals does not require chemical vapour transport technique as required for other TMDs. Thin film interference enables 2D MoS$_2$ visualisation on thin silicon oxide layers, with the best contrast achieved on either 90 nm or 270 nm SiO$_2$/Si substrate, which is comparable to that of graphene (90 nm and 280 nm). In addition, the monochromatic red channel images enhances the contrast among different numbers of layers for a 300 nm oxide layer (Fig. 3a–c).

Despite the excellent quality of the exfoliated samples, their limited size of up to tens of micrometres and their poor thickness-control renders them apt only for fundamental research and for prototype device fabrication. While laser thinning technique can overcome the thickness variation locally, the development of chemical exfoliation and vapour-phase growths have been significant steps in the ultimate goal of uniform, large-scale production.

3.2 Chemical exfoliation for mass production of 2D MoS$_2$

Chemical exfoliation, similar to the aforementioned mechanical exfoliation, peels off the layers of 2H-MoS$_2$ into 2D layers dispersed in a solvent. This approach is useful for the purpose of massive production and preparation of nanocomposites.

Early studies used the restacking process to chemically exfoliate MoS$_2$ with lithium intercalation separates layers away from each other. When MoS$_2$ is treated with strong reducing reagents containing lithium such as $n$-butyllithium or LiBH$_4$, lithium ions intercalate into MoS$_2$ and forms Li$_x$MoS$_2$. While pristine MoS$_2$ shows negligible dispersibility in water, Li$_x$MoS$_2$ disperses quite well in water, forming dispersion of 2D MoS$_2$ flakes. The dispersed flakes can be recovered by filtration or precipitation, and the resulting product is often called “restacked MoS$_2$”, because the layers are first exfoliated in dispersion and later “restacked” by filtration of the dispersion. A notable consequence of restacking process is the transformation of the 2H phase into the 1T phase, as mentioned in Section 2.3. A scanning transmission electron microscopy (STEM) study has revealed that resulting sheets contain both the 1T and 2H phases, forming coherent 2H/1T interface (Fig. 3d).

In other words, the restacking process offers a facile way to synthesise two-dimensional 1T-MoS$_2$ in large quantity, although the complete formation of the 1T polytype is not achieved.

Note that this restacked MoS$_2$ is metallic due to the formation of the $\sqrt{3}a \times a$ superstructure. Additional annealing process is therefore required to convert all 1T phase into the 2H phase.

In order to prepare 2D 2H-MoS$_2$ without any 1T phase, the use of lithium should be avoided, and a number of reports used surfactants like sodium cholate instead. An aqueous dispersion of MoS$_2$, with the proper surfactant, can be used for bioapplications such as described in Section 6.5, but in other applications remaining surfactants are often regarded as impurities.

Surfactant-free sonication of bulk crystal had problems with the stability of the exfoliated flakes, but it was recently discovered that using either certain good solvents or mixtures of poor solvents can resolve the problem; N-methyl-pyrrrolidinone (NMP) and N-vinyl-pyrrrolidinone (NVP) are typical examples of good solvents (Fig. 3e), while a mixture of ethanol and water is an example of the latter. The fundamental role of these solvents is to stabilise the layers of 2D MoS$_2$ by
maximizing interaction between the solvent molecules and the layers of 2D MoS₂, such as London dispersion force, polar interaction or hydrogen bonding, because both types of solvents have high surface energy comparable to that of 2D MoS₂ (ca. 75 mJ m⁻²).¹⁰⁷,¹⁰⁸ High surface energy also prevents the exfoliated flakes from agglomeration. Absent of additional surfactants, the products of these methods provide high quality 2D flakes (Fig. 3f) and can be isolated as free-standing films (Fig. 3g).

Another viable approach for larger flakes is the adaptation of interlayer bubbling by electrochemical reaction (Fig. 3h).¹⁰⁹ The principle guiding this process is interlamellar gas bubbling, which is also used in the restacking process. Electrochemical intercalation features high selectivity toward single layers with high quality and large size. However, this method results in a slight level of oxidation damage during the exfoliation process, though it can be cured by post-exfoliation annealing.

Chemical exfoliation methods produce 2D MoS₂ flakes in large quantity with the quality comparable to mechanically exfoliated ones. Demonstrably, chemically exfoliated samples show decent PL and comparable charge carrier mobility to mechanically exfoliated samples as well.¹¹⁰,¹¹¹ This versatile approach, however, shares the same intrinsic limitations as most top-down methods; that is, it cannot produce a uniform, large-scale product on a solid substrate, since the lateral dimensions of each 2D MoS₂ flake are no larger than a few tens of micrometres, even under optimised conditions.¹¹⁰,¹¹²,¹¹³ Additionally, some of solvents may contaminate the final products, and the film obtained by evaporating solvent is essentially a collection of discrete flakes rather than continuously connected film. In order to overcome these issues, a different way of preparation, *i.e.* the bottom-up approach, is required.

### 3.3 Vapour-phase growth of large-scale 2D MoS₂

Vapour phase growth of 2D MoS₂ is one of the most well-known examples of a bottom-up approach. This method enables the growth of 2D MoS₂ in large scale directly on top of solid substrates by means of chemical synthesis or physical assembly from gaseous precursors. This approach ultimately aims at scalability, uniformity, and the patternability of these continuous film product. Unlike mechanically exfoliated flakes, the films grown by vapour-phase growth contain ripples and grain boundaries, thus providing an interesting environment to study their properties.¹¹² Note that all of the processes mentioned below produce the 2H (or trigonal prismatic configuration) polytypes.

Direct evaporation of MoS₂ powder, *i.e.* vapour–solid growth, yields small flakes of high-quality single-layer MoS₂ on solid substrates.³⁰ This type of physical vapour deposition, however, cannot be used to grow large sheets of 2D MoS₂, leading researchers to pursue the most promising chemical synthesis methods using molybdenum and sulphur precursors.

Early studies used evaporation of molybdenum and sulphur precursors for the preparation of 2D MoS₂ on metallic substrates in a scanning tunnelling microscope (STM) chamber.¹¹⁴–¹¹⁵ These products, however, are still discontinuous nanoflakes rather than continuous films. The first genuine example of a large-scale, continuous 2D MoS₂ film produced by vapour phase growth is the direct sulfidation of a pre-deposited thin molybdenum film (Fig. 4a and d).¹¹⁶ Although delicate control of reaction conditions yields uniform double-layer MoS₂ in wafer scale¹¹⁷ or even vertically aligned MoS₂ films,¹¹⁸...
Stranski–Krastanov mechanism, which governs the physical deposition of the molybdenum film, hinders uniform growth over a large area. The preparation of molybdenum precursor film with uniformity is therefore the key issue in the synthesis of 2D \( \text{MoS}_2 \) over large scale.

To this end, chemical reactions that have been used to synthesise bulk 2H-\( \text{MoS}_2 \) (refer to Section 2.2) have been adapted to prepare 2D films. One example is the pyrolysis of \((\text{NH}_4)_2\text{MoS}_4\). Vapour-phase injection of \((\text{NH}_4)_2\text{MoS}_4\) dissolved in \(N,N\)-dime-thylformamide (DMF) results in the van der Waals epitaxy of 2D \( \text{MoS}_2 \) atomic layers transferred to a SiO\(_2\) substrate. Upon prolonged reaction, these 2D \( \text{MoS}_2 \) atomic layers grow and produce a rugged film. This graphene/\( \text{MoS}_2 \) heterostructure, however, has limited applicability, since such semiconducting layers that are inseparable from its metallic substrate cannot be utilised for device fabrication. In contrast, dip-coating \((\text{NH}_4)_2\text{MoS}_4\) on an insulating substrate resolves this problem to grow transferrable, high-crystalline three-layer \( \text{MoS}_2 \). Although the quality is comparable to mechanically exfoliated samples, the necessity of high temperature annealing (1000 °C) and the poor controllability over the number of layers (mainly three layers, with partial two layers) are the main limitations of this two-step reaction.

Evaporation of volatile \( \text{MoO}_3 \) on an arbitrary substrate followed by sulfidation process is another example that utilises bulk synthesis reaction (Fig. 4b and e). This process effectively grows \( \text{MoS}_2 \) atomic layers by coalescence of triangularly shaped single crystals, which all together result in large-scale, few-layer \( \text{MoS}_2 \) displaying a high level of crystallinity (Fig. 4e). Note that a more precise control of the number of layers, including single layers, can be achieved by use of...
hygroscopic MoCl₅ instead of MoO₃.¹²⁴ or sulfidation of pre-deposited inert MoO₃ followed by exfoliation.¹²⁵ This catalyst-free growth can be applied on arbitrary substrates, but provision of nucleation seeds by surface treatment with perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS) enhances its versatility.¹²⁶ In addition, certain substrates are known to show unique properties due to the interaction between 2D MoS₂ and the substrate. Mica is such an example; since MoS₂ and mica has a lattice mismatch, the single-layer MoS₂ directly grown on mica has an intrinsic compressive strain.¹²⁷ Therefore, the PL from this single-layer MoS₂ on mica has enhanced PL intensity and suppressed PL helicity (refer to Section 5.1 and 5.2). Note that the original PL properties are recovered when the 2D MoS₂ grown on mica is transferred onto a SiO₂ substrate. Despite these attractive properties of the product, the process of evaporation of volatile molybdenum compound followed by sulfidation, however, lacks patternability due to random nucleation of precursor. Scalability is another limitation, since the lateral growth, which increases the size of the product, often competes with the vertical growth, which increases the number of layers, especially under prolonged reaction.

A recent paper has reported a novel route that uses surface alloy of Mo and Au as the molybdenum precursor (Fig. 4c), where the surface alloy provides uniform, atomically thin Mo layer that is confined to the surface of immiscible Au film.¹²⁸ This Mo layer selectively reacts with H₂S to form MoS₂. This method features specific growth of atomic layers on top of Au film only, which can be easily patterned prior to reaction (Fig. 4f). However, the resulting 2D MoS₂ film exhibits low carrier mobility and small grain sizes, which should be overcome.

Vapour-phase-grown 2D MoS₂ exhibits various kinds of defects such as adlayers or grain boundaries (GB) (Fig. 4g and h). Adlayers on single-layer MoS₂ are quite visible with optical or electron microscopy. They are found in the middle of the MoS₂ flake due to the excessive growth or near the crystal edge due to overlap of neighbouring layers.¹²⁴,¹³⁰ These adlayers resemble double layers in terms of the structure, but they have higher conductivity than MoS₂ itself owing to excess carrier density.¹³⁰ In contrast, GBs are not directly visualised by optical or electron microscopy; they can be visualised by dark-field transmission electron microscopy (DF-TEM) because of the different crystal orientation of each grain.¹³¹ While certain grains may overlap with adjacent grains to form double layers, most grains coalesce and fuse with their neighbours to form an atomic boundary. Since pristine 2H-MoS₂ has hexagonal rings of Mo–S–Mo–S–Mo–S (Fig. 2a), GBs exhibit chains of defective rings, such as five- and seven-membered rings or even four- and eight-membered rings along their GB (Fig. 4i and j).¹²⁹,¹³²–¹³⁴ The type of GB is determined by the abundance of either sulphur or molybdenum during growth reaction as well as the angle between the grains.¹³⁵,¹³³ These grain boundaries often show electrical band structures distinct from pristine 2D MoS₂, such as formation of mid-gap states, or n-doping in case of excess molybdenum atoms.¹³³ Electrical transport across mirror grain boundaries is almost indistinguishable from that of pristine plane, but the transport across the tilted grain boundaries shows a drop in electrical conductivity.¹²⁹,¹³²,¹³⁴ Theoretical calculations also predict that chains of four-membered rings from 60° grain boundary would show metallic states.¹³⁵

Studying the synthesis of large-scale 2D MoS₂ is important not only for the realisation of the vast potentials of 2D MoS₂ but also for the related synthesis of other TMDs or heterostructures made of various 2D nanomaterials. Nonetheless, a way to synthesise single-crystalline single layers in wafer scale (i.e. larger than four inches) on arbitrary substrates is still yet to be found. In addition, the selective growth of 2D 1T-MoS₂ film in large scale has still not been achieved yet; currently, lithium intercalation can only produce 1T phase in small flakes,¹⁴⁴,¹⁰ⁱ,¹⁰⁶ and electron dosing by irradiation of electron beams can locally induce the phase transition from 2H to 1T phases in Re-doped single-layer MoS₂.¹⁰⁰

### 4. Charge carrier transport of 2D MoS₂ and applications to transistor devices

#### 4.1 Electronic band structure

One of the first studies on 2D 2H-MoS₂ that have triggered such popularity, as shown in Fig. 1, is the discovery of semiconductivity with direct bandgap of 1.9 eV (Fig. 5a) and characterisation of prototype transistor devices.²⁵,²⁶,¹³⁵ This was a significant discovery because such behaviour is impossible for graphene, the first 2D nanomaterial to be isolated; graphene is a native semi-metal that demands complex processes to open up a bandgap.¹³⁶

Such direct bandgap transition, which is one of the key characteristics of 2D MoS₂, is attributed to the contributions of atomic orbitals to the electronic band states at different points in momentum space.²⁵,¹³³,¹³⁷,¹³⁸ As shown in Fig. 5a, the bulk form of 2H-MoS₂ exhibits the indirect-gap transition from the valence band maximum (VBM) at the Γ point to the conduction band minimum (CBM) between the K point and the Γ point. The orbitals contributing to the conduction band states at the K point state are localised within the S–Mo–S sandwich, but the states at the Γ point and the CBM point have strong characters of the d orbitals of Mo and the antibonding pₓ orbitals of S, leading to strong dependence on vertical interlayer coupling. As the number of layers decreases, the K point state remains nearly constant, but the energy of the other states is reduced. To this end, when the number of layers is minimised (i.e. a single layer), the Γ point state in the valence band has less energy than that of the K point, and thus the K point state become the VBM. Also, the state between the K point and the Γ point, where the bulk CBM is located, has higher energy than that of the K point state in the conduction band. Therefore, single-layer 2H-MoS₂ shows the direct gap transition at the K point.

Nonetheless, all of these states are still nearly degenerate in single layers, and thus a small degree of changes in the orbital overlap will alter the transition. Indeed, upon application of tensile stress the fundamental transition in single layers becomes indirect bandgap transition between Γ and K points.¹³⁹–¹⁴¹
Electronic properties of the 1T single layer are unique in that they are predicted to display a bandgap opening of 0.7 eV (Fig. 5c) due to distortion from centrosymmetric (ideal) structure to trimerisation of molybdenum atoms having the $\sqrt{3}a \times \sqrt{3}a$ superstructure (Fig. 5b).\textsuperscript{142} Such trimerisation has been predicted and observed in bulk layers as well (refer to Section 2.3). Berry phase calculation shows that the distorted structure results in spontaneous polarisation along the z axis, while the in-plane polarisation vanishes. The coercive electric field required for switching the sign of polarisation domain is estimated to be $10^7$ V cm\textsuperscript{-1}, which is easily achieved by a field-effect transistor (FET) device. That is, if this phase can be stabilised, single-layer 1T-MoS\textsubscript{2} is an excellent candidate for the thinnest ferroelectric device ever.

4.2 Charge carrier transport properties

In order to take full advantage of semiconducting properties of 2D 2H-MoS\textsubscript{2}, in-depth studies on its semiconducting nature and properties is the first step, and a number of charge transport studies have been carried out so far.

A typical back-gated FET with single-layers MoS\textsubscript{2} as channel shows charge carrier mobility of 0.5 to 3 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} at room temperature with n-type semiconductivity.\textsuperscript{10} Introduction of an additional top gate with high-$\kappa$ dielectric material such as HfO\textsubscript{2}, as shown in Fig. 6a, may enhance the charge carrier mobility and transport characteristics (Fig. 6b).\textsuperscript{26,141-146} Such an effect is also valid for few-layer MoS\textsubscript{2} FET, stating that in spite of its indirect bandgap, few-layer MoS\textsubscript{2} is still an attractive semiconductor material.\textsuperscript{147}

Chemical doping is often an effective way to modulate electric transport properties in semiconductors. In general, the charge carrier mobility in 2D MoS\textsubscript{2} is robust against ionic doping; to induce a significant effect, the required carrier density is at least $5 \times 10^{11}$ cm\textsuperscript{-2}.\textsuperscript{148} Higher doping of Nb, a well-known p-type dopant for MoS\textsubscript{2} bulk,\textsuperscript{41} fullerene-\textsuperscript{148} and nanotube-\textsuperscript{148}type of MoS\textsubscript{2}, turns 2D MoS\textsubscript{2} into p-type semiconductor with hole mobility of 8.5 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}.\textsuperscript{158} Au is another example of p-dopants,\textsuperscript{153} which results in p-type transport from surface-alloy assisted growth.\textsuperscript{128} Re is an n-type dopant for MoS\textsubscript{2} fullerene and nanotubes,\textsuperscript{152} but theoretical study predicts that it may not be effective for 2D layers.\textsuperscript{153} Alkali metal is a better option; exposure of FET device into K vapour results in electron concentration up to $1 \times 10^{13}$ cm\textsuperscript{-2}.\textsuperscript{153,155} It was also shown that the Na impurities or the O dangling bonds from a SiO\textsubscript{2} substrate can become n-type and p-type dopants, respectively.\textsuperscript{155}
Electrical doping provides a reversible way to modulate the charge carrier transport properties of 2D MoS₂. While a mild level of electrical doping induces the gate effect just as in typical semiconductors, a higher level of doping, with charge carrier density more than $1 \times 10^{13} \text{ cm}^{-2}$, induces semiconductor-to-metal transition due to electron–electron interactions.156

A more extreme case of electrical doping by the electric double-layer transistor (EDLT) device with an ionic liquid gate (Fig. 6c) induces switchable, native superconductivity, i.e. without chemical doping (refer to Section 2.2).157,158 Fabrication of prototype devices demonstrates that the critical temperature of superconductivity can reach up to 10.8 K upon optimal electric doping, which is the highest value among all TMD materials. A combined study of both chemical doping and electrical doping shows that the superconductive state appears within a specific “dome-like” range of the temperature and the charge carrier density, where the critical temperature is maximised at carrier density of $1.2 \times 10^{14} \text{ cm}^{-2}$ (Fig. 6d).157

4.3 Toward fabrication of high-performance atomically thin FET

In order to fully exploit the aforementioned properties, it is essential to optimise the FET fabrication conditions as crucial as well. Typical electrode materials for 2D MoS₂ FET are Au (work function = 5.0 eV) and Ti (work function = 4.3 eV); Ti is a better option for Ohmic-like contact, since its work function is comparable to MoS₂ (electron affinity = 4.0 eV), and Ti has a smaller lattice mismatch (by 1%) with MoS₂.26,159 A more comprehensive study shows that an even better option is rare Sc (work function = 3.5 eV).160 Mo is another option, where the contact region becomes metallic, resulting in a small Schottky barrier of 0.1 eV.161

In terms of gate dielectrics, the fabrication of an FET device with both the bottom and top gates can enhance the 2D MoS₂ FET performance, leading to a high mobility of almost 15 to 55 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, an on–off ratio more than $10^{10}$, and a sub-threshold swing reaching down to 60 mV per decade at an extremely short channel (Fig. 6b).26,144,145,162 Note that special cares should be taken for the calculation of the mobility value of such dual-gate devices, since the capacity of the gate dielectrics may be underestimated, which results in the overestimation of the charge carrier mobility value.41,144,145 Such performance enhancement by dual gate fabrication is attributed to suppressed charged-impurity scattering, in accordance with theoretical calculations.143,145,156 In addition, the use of HFO₂ is also favoured over Al₂O₃ in flexible devices, because it features slow crack propagation and robust charge carrier mobility against bending.163

Special modification of device components further demonstrates novel properties of 2D MoS₂. For instance, the introduction of the previously mentioned EDLT device with an ionic liquid gate, which enables extremely high doping ($\sim 1 \times 10^{14} \text{ cm}^{-2}$), can establish a p-type conducting state, leading to ambipolar behaviour of few-layer MoS₂.164 Using PMMA as gate dielectric and capping material can further enhance charge carrier mobility.165 Also, applying different bias between source- and drain-gate in the EDLT device with an ionic liquid gate allows for a stable p–n junction within a single crystal of MoS₂, when the temperature is changed from 220 K to 180 K while the gate voltage is applied.166 This phenomenon is based on cooling across the glass transition temperature of the ionic liquid with simultaneous gating, where the motion of the ions of the ionic liquid couples with the accumulation of charges. Incorporation with light illumination or adsorption of small molecules can further tune transistor operation, suggesting utilisation as a phototransistor or a gas sensor, as described in Section 5.4 and 6.1, respectively.

Although the relatively low charge carrier mobility of 2D MoS₂ discourages direct competition with III–V semiconductors, 2D MoS₂ transistor devices show high on–off ratios and low stand-by power, which suggests suitable application for low-power electronics.163 As a proof of concept, a group of single-layer MoS₂ transistors have successfully demonstrated logic gate operations, which are the key functionality required for the fabrication of complex processing units.167

5. Optical behaviours of 2D MoS₂ and applications to optoelectronic devices

5.1 Absorption and emission characteristics of 2D MoS₂

Direct bandgap makes the optoelectronics of single layer 2H-MoS₂ exceptional among all types of MoS₂. The reflectance difference spectrum has two prominent peaks at 670 nm (A1) and 627 nm (B1), similar to the bulk form, but it shows strong emission corresponding to these absorption peaks (Fig. 7a), with quantum yield of $4 \times 10^{-3}$, which is four orders of magnitude higher than that of the bulk.25,144 These emissions are in fact PL generated from direct bandgap transition. Double-layer MoS₂ shows one PL peaks at 1.59 eV (ca. 780 nm) and two peaks near 1.88 eV (ca. 660 nm), with quantum yield around $10^{-2}$ to $10^{-6}$.25 These peaks shift with the increasing number of layers, where the first peak at 1.59 eV continuously approaches to indirect bandgap of 1.2 eV in the bulk. Band structure studies show that the first peak is indirect-gap luminescence, while the others are direct gap hot luminescence, i.e. the reverse process of the A1 and B1 excitonic absorption.25

The splitting of the A1 and B1 peaks is mainly attributed to the splitting of the VBM at the K point, which has different origins in the single layer case and the multilayer case.169 On the one hand, splitting of the VBM in single layer is purely attributed to spin–orbit coupling because of the lack of inversion symmetry. On the other hand, splitting in multilayers, which do possess inversion symmetry, is due to a combination of both spin–orbit coupling and interlayer coupling.

Since absorption and emission profiles are closely related to the band structure, modification of the band structure may change the intensity and energy of the PL peaks. For instance, electrochemical intercalation of alkali metal ions can reversibly quench PL in 2D 2H-MoS₂, because it induces the phase transformation to the metallic 1T phase.169 Also, the application of strain reduces the intensity and energy of A1 exciton peak, since the strain will reduce the direct gap at K point, as
discussed in Section 4.1. Note that the strain required for direct-to-indirect gap transition in optical bandgap is much less than that of the electrical bandgap due to the large exciton binding energy.

5.2 Unique valley polarisation and trion formation

A notable feature of PL from single-layer MoS2 is valley polarisation, where the PL conserves the circular dichroism of the incident light. The unique phenomenon is the results of spin–orbit coupling together with the absence of inversion symmetry. Single-layer MoS2 has six CBMs and VBMs, which are referred as "valleys", at the K points (refer to Section 4.1). Spin–orbit coupling further splits each valley into different spins (refer to Section 5.1), and circularly polarised light excites opposite spins at the K and K' valleys located at the opposite positions in k-space (Fig. 7b). Here, because of time reversal symmetry, single layer MoS2, which lacks inversion symmetry, does not allow inter-valley transition. This spin-selective population at opposite valleys is preserved upon the polarised illumination, and thus PL maintains the same circular dichroism as the incident light (Fig. 7c). Since this phenomenon requires the broken inversion symmetry and the spin–orbit coupling at the same time, even double-layer 2H MoS2 does not show valley polarisation. However, the 3R polytype shows valley polarisation regardless of the number of layers, since the structure inherently lacks inversion centres.48 Note that illuminating a single-layer MoS2 transistor with circularly polarised light results in valley Hall effect, where Hall voltage occurs due to valley polarisation.170

Another unique feature of the optoelectronics of single-layer MoS2 is the formation of a negative trion, a quasiparticle comprised of two electrons and one hole, upon illumination.171 Such phenomenon is absent in other conventional direct-gap semiconductors, where illumination only creates an exciton, a pair of an electron and a hole. Gate-voltage-dependent absorption and PL studies reveal the existence of two components in both PL and A1 exciton absorption in single-layer MoS2. The intensity of the higher energy component diminishes upon electron doping, but the other component largely retains its intensity regardless of the applied gate voltage. Here the former is attributed to the formation of neutral excitons, while the latter is related to trions, which are created by binding of electrons to pre-existing electron–hole pairs. Its binding energy is large enough (20 meV) to manifest at room temperature as well. One of the direct results of trions is the effect of chemical doping on the intensity of PL; for instance, p-type dopants like tetracyanoquinodimethane (TCNQ) enhance the PL intensity,172 because it promotes recombination of excitons rather than trions.

5.3 Raman spectroscopy and phonon–photon interaction

Phonon–photon interaction of 2D MoS2 features the shift of vibration energy upon the decreasing number of layers. Of the four major Raman-active vibration modes, out-of-plane (or equally A_1 mode in single layers, concerning their different symmetry from the bulk) and in-plane (or equally E_g mode in single layers) exhibit notable shifts.173 The A_1g vibration mode experiences softening, since interlayer coupling is weakened upon the decreasing number of layers. In contrast, the E_2g vibration mode shows anomalous stiffening, which is attributed to the stronger dielectric screening of the long-range Coulombic interaction with the decreasing number of layers.174 To this end, in single-layer MoS2, the A_1g vibration appears near 404 cm⁻¹ (cf. 408 cm⁻¹ for bulk), and the E_2g mode is near 385 cm⁻¹ (cf. 383 cm⁻¹ for bulk), regardless of the wavelength of the incident laser (Fig. 7d).173,175 Therefore, the energy difference between them is often a facile indicator of the number of layers (Fig. 7e).

In addition, the position of each vibration mode with respect to the zero-strain reference reflects the amount of applied strain.139–141 While the out-of-plane A_1g mode is robust against tensile strain, the in-plane E_2g mode significantly changes. At low strain, the in-plane E_2g vibration mode is softened, and thus the corresponding peak in Raman spectrum is red-shift and slightly broadened. However, at higher strain, the crystal symmetry is apparently changed, and thus the double
degeneracy of the $E_{1g}^1$ vibration mode is lifted, leading the splitting into two peaks in the Raman spectrum.

The aforementioned peaks are first-order Raman peaks, which are commonly found regardless of the wavelength of incident laser. However, 325 nm laser reveals additional resonant Raman spectrum within the range of 750 to 840 cm$^{-1}$. These peaks are attributed to spin–orbit splitting at the valence band, specifically because of electron-two-photon triple resonance via Fröhlich-interaction and deformation potential. Note that the energies of these peaks do not depend on the number of layers. Also, 633 nm laser induces resonant Raman peaks such as 2LA (M) peaks near 440 cm$^{-1}$ in thicker MoS$_2$.\(^{175}\)

### 5.4 Application to optoelective device

The direct bandgap of single-layer MoS$_2$ results in unique photon–electron interaction. Therefore, characterisation of FET devices under external illumination offers a versatile way to assess the optoelectric nature of 2D MoS$_2$. When light with lower energy than the direct bandgap illuminates the interface between an electrode and 2D MoS$_2$, it shows photothermal-electric effect.\(^{177}\) This is unique among semiconductors in that other materials do not flow photocurrent upon sub-bandgap illumination. This is attributed to the large mismatch of Seebeck coefficients between the electrodes and the single-layer MoS$_2$, with values ranging from $-4 \times 10^5$ to $-1 \times 10^5$ $\mu$V K$^{-1}$ depending on the gate voltage.

Upon super-bandgap illumination, single-layer MoS$_2$ phototransistors show photoresponsivity of 7.5 mA W$^{-1}$ up to 880 A W$^{-1}$ for optimised device geometry, on–off ratio of $10^3$ and switching time of 50 ms.\(^{174,179}\) Ultrahigh photoresponsivity is six orders of magnitude higher than that of graphene, because the existence of a bandgap hinders the exciton recombination. Moreover, it is sensitive to most of the visible light because of its direct bandgap, and its noise-equivalent power is $1.8 \times 10^{-15}$ W Hz$^{-1/2}$, which is an order less (better) than commercial silicon avalanche photodiodes. Such application is also demonstrated for vapour-phase-grown MoS$_2$, in which the photoresponsivity is up to 2200 A W$^{-1}$ and the time constant is down to 55 ms.\(^{180}\) Bandgap modulation by thickness control results in tuning of the photoresponse wavelength; for example, single-layer and double-layer MoS$_2$ are sensitive to green light, and triple-layer MoS$_2$ is sensitive to red light.\(^{181}\)

Based on the photon–electron interaction discussed above, 2D MoS$_2$ can be also incorporated into photovoltaic cells as the active layer in a heterojunction solar cell\(^{182}\) or as a hole-extraction layer.\(^{183}\) The former (ref. 182) has a structure of Al/2D MoS$_2$/p-/p-type Si/Ag, where n-type MoS$_2$ and p-type Si form type-II heterojunction. Its photoconversion efficiency is 5.23%, which is the highest among all single-layer TMD-based solar cells. In case of the latter (ref. 183), its band structure, chemical stability and lack of dangling bonds make 2D MoS$_2$ suitable for photovoltaic cell operation, and it shows power conversion efficiency of 8.11%, which is superior to the previously reported MoO$_3$ counterpart.

Electroluminescence is another fundamental optoelectric operation of direct bandgap semiconductors, which is required for light emitting devices. Electroluminescence of 2D MoS$_2$ is demonstrated using hot carrier process at a Schottky barrier.\(^{184}\) This hot carrier process occurs when excited electrons are injected into the conduction band through the Schottky barrier, where significant band bending generates excitons. These excitons are recombined through a radiative process, which enables electroluminescence without the formation of a p–n junction. This electroluminescence has prominent A1 excitonic characteristics (at 685 nm) only, because B1 excitonic states are not populated upon electric bias. Pristine MoS$_2$, however, still requires higher quantum yield for practical application, and this is expected to be achieved by formation of heterostructures.

Based on these novel electronic and optoelectronic properties, 2D MoS$_2$ is now one of the most promising materials for flexible, transparent electronic device components. For instance, an AFM study has proved its substantially high mechanical stiffness (Young’s modulus of 270 ± 100 GPa, and breaking stress of 22 ± 4 GPa). That is, it is flexible enough to be used with polyimide (PI) or polydimethyldilsiloxane (PDMS) substrate, which is one of the most frequently used substrates for flexible electronics.\(^{185,186}\)

### 6. Molecular and biomolecular interactions of 2D MoS$_2$

#### 6.1 Application to molecular and biomolecular sensors

The study of the interaction between 2D MoS$_2$ and other molecules often utilise FET devices, especially in case of the semiconducting 2H polytype, because these devices offer an appropriate environment to control and assess electron transport upon chemical modification of 2D MoS$_2$. That is, reversible adsorption of various moieties on 2D MoS$_2$ often changes its properties as well as the properties of the target molecules. Detection of such changes open up the possibility of developing 2D MoS$_2$ based sensors. In addition, flexibility, transparency, economic massive production, and high sensitivity are major advantages of 2D MoS$_2$ over other bulk or other nanomaterials, even including graphene and other 2D nanomaterials.\(^{181,182,187}\)

One such example is as an active sensing component for chemical and biomolecular sensors. Adsorption of target molecules changes the charge transport properties of the 2D MoS$_2$ FET device, so the electric conductivity correspondingly changes upon exposure. One of the first demonstrations is a NO gas sensor.\(^{13}\) This device shows remarkable detection power, with a detection limit which reaches down to 0.8 ppm and a high signal-to-noise ratio (Fig. 8a). A more comprehensive study shows that other molecules like NO$_2$, NH$_3$, and H$_2$O are well detected, and its detection power can be further enhanced by the incorporation of gate effect or light illumination.\(^{188}\) For example, a moderate level of illumination of green light significantly enhances the detection sensitivity of NO$_2$. A larger number of layers is favoured for better gas detection, since thicker samples have higher charge carrier concentration and higher on/off ratio. A first-principle calculation study has shown that this change of current is caused by the charge transfer from the adsorbent gas to the 2D MoS$_2$ film.\(^{189,190}\) Upon adsorption of
the gas molecules, the Fermi level of 2D MoS₂ changes without significant changes in the band structure due to charge transfer. In addition, most of the gas molecules, including NO, are charge acceptors, which turns 2D MoS₂ into p-type semiconductors, and NH₃ is shown to be a charge donor.

Another proposed application of 2D MoS₂ FET is a label-free sensor for pH and protein. When a top-gated 2D MoS₂ FET is immersed in an electrolyte, which can behave as a top gate electrode, the surface of the gate oxide is naturally decorated with OH moieties. Therefore protonation (low pH) or deprotonation (high pH) changes surface potential of the gate oxide, resembling gate effect. For example, a lower level of pH results in electron doping. Further decoration by biotin can detect streptavidin, a protein that can combine with biotin quite well, with a detection limit reaching down to 100 fM (Fig. 8b).

Unlike the aforementioned applications, where 2D MoS₂ is an active channel of an FET device, 2D MoS₂ itself can be utilised as a sensor for single-stranded DNA (ssDNA). That is, the basal plane of single-layer MoS₂ is a good adsorbent for ssDNA via van der Waals interactions. When FAM (fluorescein amidite; a type of fluorescent dye)-labelled DNA was mixed with the single-layer MoS₂ in dispersion, ssDNAs adsorb on the MoS₂ flakes, leading to the quenching of fluorescence. However, upon injection of a complementary strand, the fluorescence was turned on again, since the ssDNA is detached from the surface of the 2D MoS₂ flakes. A similar experiment was successfully carried out for aptamers, where the detection limit was 5 μM.

### 6.2 Surface chemistry: HDS catalysis and mechanism

Direct utilisation of 2D MoS₂ for chemical studies takes advantage of its similarity to bulk in terms of chemical reactivity. Therefore, it is now possible to directly observe and establish models for atomic changes during conventional surface chemistry reaction, by means of standard microscopic tools. One such study is HDS catalysis as described in Section 2.2. A recent STM-based study revealed that catalysis activity is maximised for S-terminated small clusters, where some of the corner sulphur atoms are easily removed to leave vacant sites. These vacant sites show least steric effect toward the chemisorption of thiophenes (Fig. 8c and d). In accordance with this observation, several attempts have been made to improve catalytic activity, i.e. (1) the substitution of edge sulphur with Ni or Co “promoters”, where sulphur atoms will adsorb on the S–Mo–Ni or –Co terminal edges, and (2) the formation of nanoparticles or nanoclusters, where the high exposure of rim sites improves catalytic activity.

### 6.3 Electrochemistry: catalyst for hydrogen evolution reaction

While most chemical properties of 2D 2H-MoS₂ are quite similar to bulk, still it has certain distinct and unique properties. Hydrogen evolution reaction (HER), or production of hydrogen by electrolysis of water, is one of such examples, which holds promising applicability, where the pristine bulk MoS₂ behaves as a less efficient HER catalyst. The role of 2D 2H-MoS₂ here is as an electrode; protons (H⁺) are adsorbed on the metallic edges of 2D 2H-MoS₂, where electrons transferred to reduce the protons into hydrogen gas. A STM study has shown that S-bonded Mo edges are active for HER, and the total length of edge has linear correlation with the HER catalytic efficiency. To this end, 2D 2H-MoS₂ is located at the middle of the volcano plot, which states high exchange current density and reversible hydrogen adsorption (ΔG ~ 0) (Fig. 8e). Nonetheless, pristine MoS₂ has low adsorption ratio (ca. 25%) on the edge sites and poor electric conductivity that hinders kinetics, resulting in, for instance, a Tafel slope of 55 to 60 mV per decade. In order to improve this, vertically aligned MoS₂ layers are used to create intentionally large exposure of edge sites. Incorporation with conductor provides another viable strategy to improve electron transfer kinetics, and examples include reduced graphene oxide (rGO) and epitaxially grown metal nanostructures. For instance, Pt–MoS₂ hybrid has Tafel slope...
of 40 mV per decade, which is attributed to the combination of Volmer–Tafel and Volmer–Heyrovsky mechanism.

An alternative route is using metallic 2D 1T-MoS2 prepared by the restacking process, and its Tafel slope is 40 to 43 mV per decade.103,104,196 As shown in Fig. 8f, edge oxidation study shows that metallic 1T-MoS2 provides the whole basal surface as HER catalytic surface, while 2H-MoS2 shows significantly low catalytic efficiency after edge oxidation. Lithium intercalation of vertically aligned MoS2 film118 further enhances the catalytic effect, because it results in a decrease of the Mo oxidation state, a modification of the electronic structure by creating a larger interlayer distance, and an enhancement of conductivity by the formation of the 1T phase.197

6.4 Photochemistry: catalyst for water splitting and chemical reaction

In its application as HER catalyst, both types of 2D MoS2 act as an electrode, which accepts an external electric power source. In contrast, photochemical water splitting is the electrolysis of a water molecule into hydrogen and oxygen gas using (sun-)light, without any electrical power sources. While bulk MoS2 has negligible photochemical water splitting power,196 single-layer 2H-MoS2 has considerable power to split water molecules because single-layer MoS2 has a suitable band structure for water splitting.199 For example, the CBM lies 0.41 V more negative than the proton reduction potential (H2/H+, NHE), and the VBM is located 0.07 V more positive than the oxygen reduction potential (O2/H2O, 1.229 V vs. NHE). The direct bandgap of 1.90 eV is also suitable for accepting sunlight as a power source for water splitting. In an experiment, a photo-electrochemical cell was successfully comprised of an electrode coated with single-layer MoS2, and with Au nanoparticles further enhancing the efficiency with the aid of surface plasmon.200

Another example of 2D 2H-MoS2 as photocatalyst is the photochemical reaction, which accepts external light to excite electrons from the valence band to the conduction band, and then to the target molecules.201 As a proof of concept, a dispersion of chemically exfoliated 2D MoS2 flakes is mixed with methylene blue molecule. While pristine methylene blue retains its colour and absorbance for several hours, 20 ppm of 2D MoS2 results in the photodegradation of methylene blue by 90% within 2 hours.

6.5 Biochemistry: various bioapplications of 2D MoS2 dispersion

The aqueous dispersion of 2D MoS2 prepared by the restacking process enables the utilisation of this attractive nanomaterial in the field of biochemistry. In principle, an aqueous dispersion of 2D MoS2 shows low cytotoxicity and high biocompatibility.202–205 Therefore, its adaptation into the human body will enable its application as a multipurpose biomaterial that takes advantage of its remarkable physical and chemical properties. One of the direct bio-applications is antibacterial activity, as confirmed by an experiment on E. coli DH5α cells (Fig. 9a).206 The key idea here is using metallic 2D 1T-MoS2 dispersion, where its large surface area and high conductivity easily transfers electrons from the inside of the bacteria cell to its external environment. In addition, 2D MoS2 dispersion generates reactive oxygen species (ROS), which is not observed from graphene oxide (GO).

Another application is photothermal therapy, which takes advantage of its good dispersibility and superior absorbance of near infrared (NIR).207 A 2D MoS2 dispersion shows 7.8 times higher absorbance than GO, and its extinction coefficients at 800 nm is 29.2 L g−1 cm−1, which is higher than gold nanorods. 2D MoS2 is biocompatible, as confirmed by complexation with α-chymotrypsin, where denaturation does not occur. A NIR and 2D MoS2 treatment of HeLa cells shows its superior in vitro photothermal therapy efficiency (Fig. 9b).208 In addition, incorporation of chitosan during exfoliation further enhances MoS2.
biocompatibility and increases the photothermal conversion efficiency up to 24.37%.\textsuperscript{284} In vivo experiment on mice with pancreatic cancer (Panc-1 tumour) also confirms that chitosan-incorporated 2D MoS\textsubscript{2} dispersion shows photothermal therapy upon NIR irradiation (Fig. 9c and d). A synergetic effect is created by further incorporation of doxorubicin (DOX), showing remarkable cancer-killing ability, as a result of the combination of hyperthermia and chemotherapy.

Visualisation of certain organs or cells is one of the most important functions for diagnosis and treatment. Based on the large atomic number of Mo, 2D MoS\textsubscript{2} flakes can be used as CT image contrast agent.\textsuperscript{285} Its contrasting efficiency is comparable to commercially used Iopromide 300 contrast agent (Fig. 9e). It is also possible to directly visualise cells by PL from 2D MoS\textsubscript{2}, as confirmed by the uptake by HeLa cell.\textsuperscript{285} As shown in Fig. 9f, its fluorescence under UV light is observed within live HeLa cells, stating that 2D MoS\textsubscript{2} does not harm the cells while retaining its properties.

7. Conclusions and outlooks

Atomic layers of MoS\textsubscript{2} are one of the most attractive nanomaterials in recent years. Historically, this material has been a topic of research mainly for tribologists, intercalation chemists and petroleum chemists because of its aptness for such applications in the industry. Now, recent surging interests have expanded to scientists and engineers of all fields because of the attractive, useful properties of 2D MoS\textsubscript{2} as an emerging nanomaterial. To this end, substantial research has been carried out in many fields of science and technology, which encompass not only historical research fields but also novel areas. These include nanoelectronics, which mainly concentrates on 2D MoS\textsubscript{2} as a direct-gap semiconducting alternative of the metallic graphene. In other fields of research, numerous demonstrations such as FETs, molecular sensors, HER catalysts, or bio-applications have successfully demonstrated its bright potential for future applications. Reflecting upon these important aspects, it is clear that 2D MoS\textsubscript{2} is now much closer to real applications than any other 2D nanomaterials.

However, there are still many hurdles to overcome in order to bring its full potential into reality. For example, large-scale synthesis of single layers with single crystalline domain is still not achieved. Continuous films of 2D 1T-MoS\textsubscript{2} have not been prepared yet. These high-quality large-scale films are the necessary starting point for applications such as large-scale device fabrication. In addition, catalyst efficiency is still too low to be applied in real industries, and thus further understanding and improvement are required. Heterostructure with other nanomaterials is still an unexplored area of research, which hold the potential of unprecedented, unique nature and applications.

2D MoS\textsubscript{2} is one of the first 2D nanomaterials that have been studied other than graphene; several experimental techniques, strategic approaches, and demonstration of applications that are applied for graphene have been employed to 2D MoS\textsubscript{2} as well. Such comparative studies suggest that these approaches are not only applicable to graphene but also applicable to other two-dimensional nanomaterials, providing a generalised route to study other unexplored 2D nanomaterials. In this sense, study on 2D MoS\textsubscript{2} possesses great importance as a bridge that provides ways to expanding the scope of 2D nanomaterials.

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