

Transition Metal Dichalcogenides and Beyond: Synthesis, Properties, and Applications of Single- and Few-Layer Nanosheets

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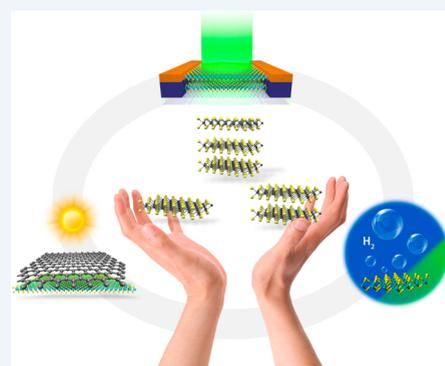
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CONSPECTUS: In the wake of the discovery of the remarkable electronic and physical properties of graphene, a vibrant research area on two-dimensional (2D) layered materials has emerged during the past decade. Transition metal dichalcogenides (TMDs) represent an alternative group of 2D layered materials that differ from the semimetallic character of graphene. They exhibit diverse properties that depend on their composition and can be *semiconductors* (e.g., MoS₂, WS₂), *semimetals* (e.g., WTe₂, TiSe₂), *true metals* (e.g., NbS₂, VSe₂), and *superconductors* (e.g., NbSe₂, TaS₂). The properties of TMDs can also be tailored according to the crystalline structure and the number and stacking sequence of layers in their crystals and thin films. For example, 2H-MoS₂ is *semiconducting*, whereas 1T-MoS₂ is *metallic*. Bulk 2H-MoS₂ possesses an *indirect* band gap, but when 2H-MoS₂ is exfoliated into monolayers, it exhibits *direct* electronic and optical band gaps, which leads to enhanced photoluminescence. Therefore, it is important to learn to control the growth of 2D TMD structures in order to exploit their properties in energy conversion and storage, catalysis, sensing, memory devices, and other applications.



In this Account, we first introduce the history and structural basics of TMDs. We then briefly introduce the Raman fingerprints of TMDs of different layer numbers. Then, we summarize our progress on the controlled synthesis of 2D layered materials using wet chemical approaches, chemical exfoliation, and chemical vapor deposition (CVD). It is now possible to control the number of layers when synthesizing these materials, and novel van der Waals heterostructures (e.g., MoS₂/graphene, WSe₂/graphene, hBN/graphene) have recently been successfully assembled. Finally, the unique optical, electrical, photovoltaic, and catalytic properties of few-layered TMDs are summarized and discussed. In particular, their enhanced photoluminescence (PL), photosensing, photovoltaic conversion, and hydrogen evolution reaction (HER) catalysis are discussed in detail. Finally, challenges along each direction are described. For instance, how to grow perfect single crystalline monolayer TMDs without the presence of grain boundaries and dislocations is still an open question. Moreover, the morphology and crystal structure control of few-layered TMDs still requires further research. For wet chemical approaches and chemical exfoliation methods, it is still a significant challenge to control the lateral growth of TMDs without expansion in the *c*-axis direction. In fact, there is plenty of room in the 2D world beyond graphene. We envisage that with increasing progress in the controlled synthesis of these systems the unusual properties of mono- and few-layered TMDs and TMD heterostructures will be unveiled.

1. INTRODUCTION

In December 1959, Richard P. Feynman in his famous lecture entitled "There's Plenty of Room at the Bottom", introduced the importance of layered materials and specifically proposed the isolation of individual layers. He stated "What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them..."¹ This prediction in 1959 was attempted a few years later by Robert Frindt when he tried to thin MoS₂ to a few layers using adhesive tape and synthesize monolayers of MoS₂ by Li intercalation.^{2,3} However, it wasn't until 2004 that

Novoselov et al. discovered the truly novel transport properties of individual graphene sheets through mechanical exfoliation of graphite.⁴ At present, researchers are realizing that by tuning the number of atomic layers of any layered material, it is possible to achieve unprecedented properties.⁵ In this context, two-dimensional (2D) materials, especially transition metal dichalcogenides

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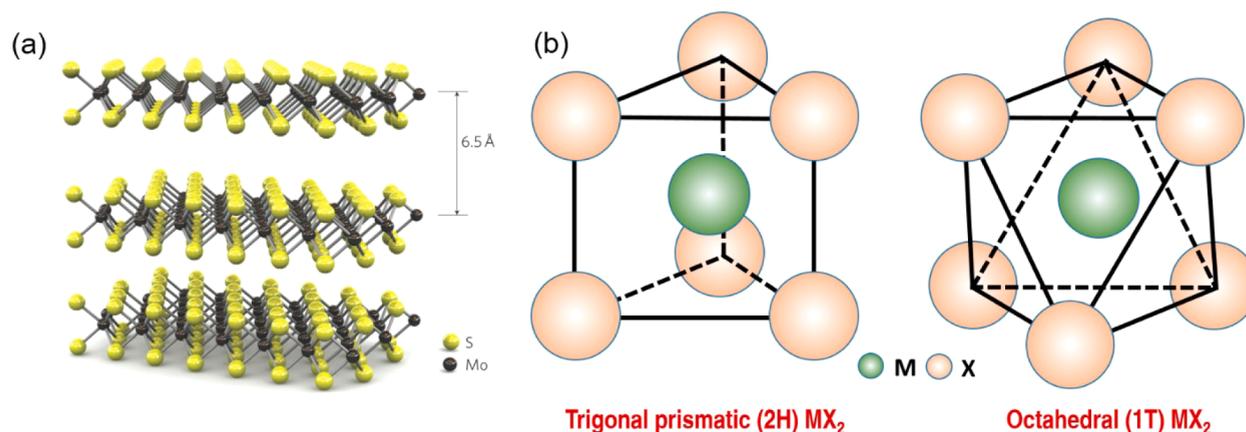


Figure 1. Crystal structures of TMDs with a typical formula of MX_2 . (a) Three-dimensional model of the MoS_2 crystal structure. Reprinted with permission from ref 59. Copyright 2011 Macmillan Publishers Ltd. (b) Unit cell structures of 2H- MX_2 and 1T- MX_2 .

(TMDs), have gained world-wide attention in recent years and are being heavily researched for use in photovoltaic devices, lithium ion batteries, hydrogen evolution catalysis, transistors, photodetectors, DNA detection, and memory devices.⁶ Unlike graphene's single carbon atomic-thick layer, TMDs (e.g. MoS_2 , WS_2 , WSe_2 , etc.) consist of a "sandwich" structure of a transition metal layer (e.g., Mo, W, Nb) between two chalcogen layers (e.g., S, Se, Te). Like graphene and other van der Waals solids, TMDs are characterized by weak, noncovalent bonding between layers and strong in-plane covalent bonding. Therefore, bulk TMDs can be exfoliated into single- or few-layered structures by physical or chemical means, such as adhesive tape exfoliation,² solvent-assisted exfoliation,⁷ and chemical exfoliation via lithium intercalation.^{3,8,9} Due to quantum confinement and surface effects, monolayer and few-layered TMDs exhibit a variety of exciting properties not seen in their bulk counterparts. For example, bulk semiconducting trigonal prismatic TMDs possess an *indirect* band gap, but when made as single layers, they exhibit *direct* electronic and optical band gaps,¹⁰ which leads to enhanced photoluminescence (PL).¹¹ More importantly, valley polarization has also been observed in *monolayers* of MoS_2 , an effect that is crucial for engineering valley-based electronic and optoelectronic devices.¹² Besides mono- and few-layered MoS_2 , many other 2D layered TMDs are ripe for exploration, including *semiconductors* (WS_2), *semimetals* (WTe_2 , TiSe_2), *true metals* (NbS_2 , VSe_2), and *superconductors* (NbSe_2 , TaS_2).¹³ Importantly, the *number of layers* in TMDs remarkably affects their properties. Heinz and co-workers isolated thin MoS_2 layers (from 1 to 6) by the adhesive tape method and found that monolayers exhibit PL around 1.84 eV, which is related to the smallest direct transition at the K point in the Brillouin zone; for bilayers and thicker MoS_2 structures the PL is quenched.¹⁰ In addition, the second-order nonlinear optical responses strongly depend on the number of layers. The centrosymmetry of bulk MoS_2 crystals prohibits second-order nonlinear optical processes. However, for a *monolayer* or few-layer MoS_2 film with an *odd number* of layers, the inversion center is removed, resulting in a strong second-order nonlinear optical response.¹⁴ Other semiconducting TMDs (e.g., WS_2 , WSe_2 , and MoSe_2) with the same trigonal prismatic structure as MoS_2 also exhibit direct band gaps as single molecular layers and indirect gaps as bi- or multilayers.¹⁵ Therefore, the controlled synthesis of TMD nanostructures is of great importance in order to carry out further studies of their electronic, optical, biological, chemical, and catalytic properties.

Synthetic routes to 2D TMDs can be classified as *top-down* (e.g., mechanical cleavage,² chemical exfoliation¹¹) and *bottom-up* (e.g., direct wet chemical synthesis¹⁶ and chemical vapor deposition^{11,17,18}) approaches. Controlling the type and number of layers, edge morphologies, and the degree of crystallinity are crucial for using these materials in high performance applications. In this Account, we summarize our recent progress on the controlled synthesis of different TMDs, show their unique properties, and discuss current challenges in the field.

2. CRYSTAL STRUCTURES AND PHASE IDENTIFICATION OF SINGLE- AND FEW-LAYERED TRANSITION METAL DICHALCOGENIDES

Every individual layer of bulk TMDs (MX_2) is composed of a transition metal (M) atomic layer between two chalcogen (X) atomic layers (Figure 1a). Depending on the atomic stacking configurations, MX_2 can form two crystal structures: a *trigonal prismatic* (2H) phase and an *octahedral* (1T) phase (Figure 1b). For example in 2H- MoS_2 , each Mo atom is prismatically coordinated to six surrounding S atoms, forming a thermodynamically stable phase, whereas for the metastable 1T- MoS_2 phase, six S atoms form a distorted octahedron around one Mo atom. Interestingly, each phase can be easily transformed to the other via intralayer atomic gliding. In this context, 2H- MoS_2 can be converted into 1T- MoS_2 by intercalating Li or K.^{19,20} Because 1T- MoS_2 is thermodynamically unstable it gradually converts back to the trigonal prismatic configuration (2H- MoS_2) at room temperature.²¹

These two phases show completely different electronic properties: 2H- MoS_2 is *semiconducting*, while 1T- MoS_2 is *metallic*,²² and 1T- MoS_2 appears to be a more active hydrogen evolution catalyst than 2H- MoS_2 .^{20,23} To understand these phenomena, it is important to develop simple methods, such as Raman spectroscopy, that can easily identify 1T and 2H phases. Actually, both 1T- MoS_2 and 2H- MoS_2 show A_{1g} and E_{2g} vibrational modes at ~ 380 and ~ 410 cm^{-1} , respectively. Due to their symmetry differences, 1T- MoS_2 shows several additional Raman vibrational modes, designated as J_1 (~ 160 cm^{-1}), J_2 (~ 230 cm^{-1}), and J_3 (~ 330 cm^{-1}), which are not active for 2H- MoS_2 .^{20,21,23} However, it is not easy to obtain an accurate quantitative analysis of the phase composition from the Raman spectra alone due to the weak Raman response of these modes. X-ray photoelectron spectroscopy (XPS) is an alternative technique for quantifying the 1T and 2H phases. An XPS fine

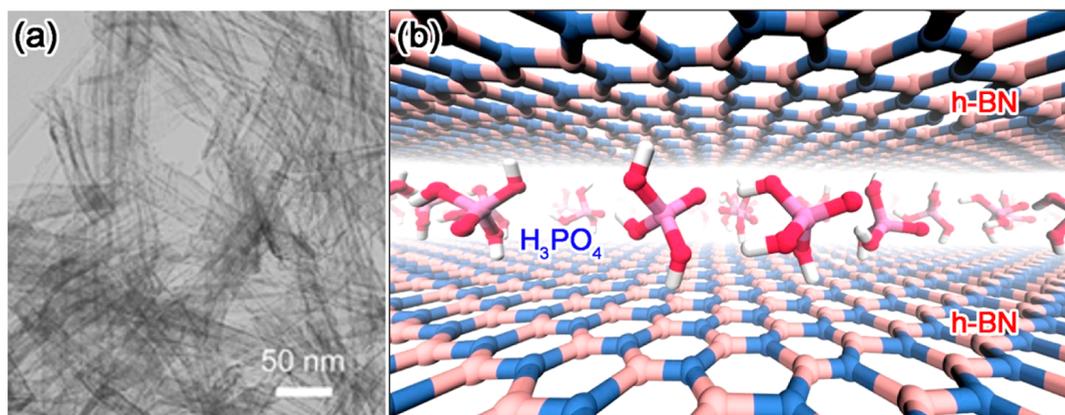


Figure 2. (a) The layered solid $\text{K}_4\text{Nb}_6\text{O}_{17}$ can be quantitatively converted to suspensions of nanoscrolls (rolled up single sheets) by acid-exchange of the layered solid and then reaction with tetra(*n*-butyl)ammonium hydroxide. (b) Model of the interlayer structure of the h-BN/ H_3PO_4 first-stage intercalation compound. Adapted from ref 33.

scan in the Mo 3d region usually resolves two peaks near binding energies of 220 and 232 eV, corresponding to photoelectrons from the $\text{Mo}^{4+} 3d_{5/2}$ and $\text{Mo}^{4+} 3d_{3/2}$ states, respectively. For pure 1T- MoS_2 , the Mo 3d region will show peaks at ~ 228.1 and ~ 231.1 eV, which have slightly lower binding energy than those reported for pure 2H- MoS_2 (~ 229.5 and ~ 232.0 eV).²³ Therefore, by deconvoluting the $\text{Mo}^{4+} 3d_{5/2}$ and $\text{Mo}^{4+} 3d_{3/2}$ peaks, we can obtain the relative concentrations of the 1T and 2H phases.

Raman spectroscopy can also be used to identify the number of layers in TMDs.²⁴ For monolayer MX_2 , a double resonant process involving the longitudinal acoustic mode (LA) may occur at a particular excitation wavelength (e.g., 514.5 nm laser excitation for WS_2).²⁴ For WS_2 , the Terrones group found that the A_{1g} mode softens while the 2LA and E_{2g}^1 modes show a very subtle hardening with the decrease in the number of layers.²⁴ Due to the similarities in crystal structures, double resonance Raman effects are expected to be present in other semiconducting MX_2 compounds and may be useful in determining the number of layers. However, more work is needed to uncover the characteristic Raman signatures corresponding to different semiconducting TMDs.²⁵

3. EXFOLIATION OF LAYERED SOLIDS

Mono- and few-layer sheets of TMDs, graphene, or hexagonal boron nitride (h-BN) can be accessed in small quantities by growing them directly on appropriate substrates, for example, by chemical vapor deposition (CVD; see below), or by mechanically peeling apart the layers of the parent solids.²⁶ While these methods have been indispensable for scientific studies of nanosheets, practical applications will ultimately require bulk quantities made by physical or chemical exfoliation of layered materials.

With respect to exfoliation, there are two classes of layered solids: (1) Those in which the sheets are *uncharged* and interact through van der Waals forces only include graphite, h-BN, TMDs, layered oxides such as MoO_3 , various layered halides, and silicates such as talc.⁷ (2) Those in which *charged* sheets are held together by charge-balancing counterions include clays, layer perovskites, layered double hydroxides (LDHs), layered phosphates, and numerous other ternary oxides that typically contain protons, alkali cations, or alkali earth cations between layers.²⁷ The sheets of layered oxides tend to be negatively charged because they are terminated with electronegative oxygen

atoms. The covalently bonded oxide sheets are typically charge compensated by alkali or alkaline earth cations in the solids that are precursors to oxide nanosheets and nanoscrolls. *Charged sheets* are generally easy to separate from each other if the cations or anions that hold them together have low charge density. It is straightforward to convert many of the layered solids with charged sheets quantitatively into suspensions of single sheets or scrolls (Figure 2a).^{28,29} However, the situation is quite different for *uncharged* sheets, which cannot be pried apart by chemical forces unless they are first intercalated by anions or cations.⁷ Recently, Coleman and co-workers introduced a new paradigm for the exfoliation of layered van der Waals solids without oxidation or reduction.^{30,31} Solvents of intermediate polarity minimize the energetic cost of separating the layers, so simple sonication can be used to make dispersions of few-layer and single-layer sheets. Although the yields of single sheets by this method are typically low (1% or less), they can be improved by performing the process at high shear rates.³² Recently, the Mallouk group discovered a nonoxidative route to intercalated h-BN³³ and graphite.³⁴ This reaction relies on the acid–base properties of the BN and carbon sheets and leads to fully intercalated (stage 1) materials by reaction of the parent solid with anhydrous Brønsted acids. Figure 2b shows a model of the structure of the H_3PO_4 intercalation compound of h-BN. Because the intercalation reaction does not involve redox reactions or formation of covalent bonds between the sheets, it is completely reversible. Small flakes of graphite intercalated by H_3PO_4 exfoliate readily by sonication in dimethylformamide (DMF) to yield suspensions of single and few-layer sheets.³⁴ We are currently exploring acid–base reactions as a “wedge” to open the galleries of h-BN, TMDs, and other layered materials in order to exfoliate them more fully via the Coleman method. Such reactions could be a valuable alternative to redox reactions for preparing bulk quantities of single- and few-layer sheets.

4. CHEMICAL VAPOR DEPOSITION GROWTH

CVD is an important and widely used technique for growing inorganic nanomaterials. By combining CVD with physical vapor deposition (PVD, e.g., electron-beam deposition), the Terrones group successfully grew triangular islands and large area monolayers of TMDs.^{11,17,18,24} Typically, a substrate (usually SiO_2/Si) is coated with a thin layer of transition metal (e.g., Mo^{35}) or oxide (MoO_3 ,¹⁸ WO_3 ^{11,18}), which has a lower melting point than the corresponding metal, through PVD, and then

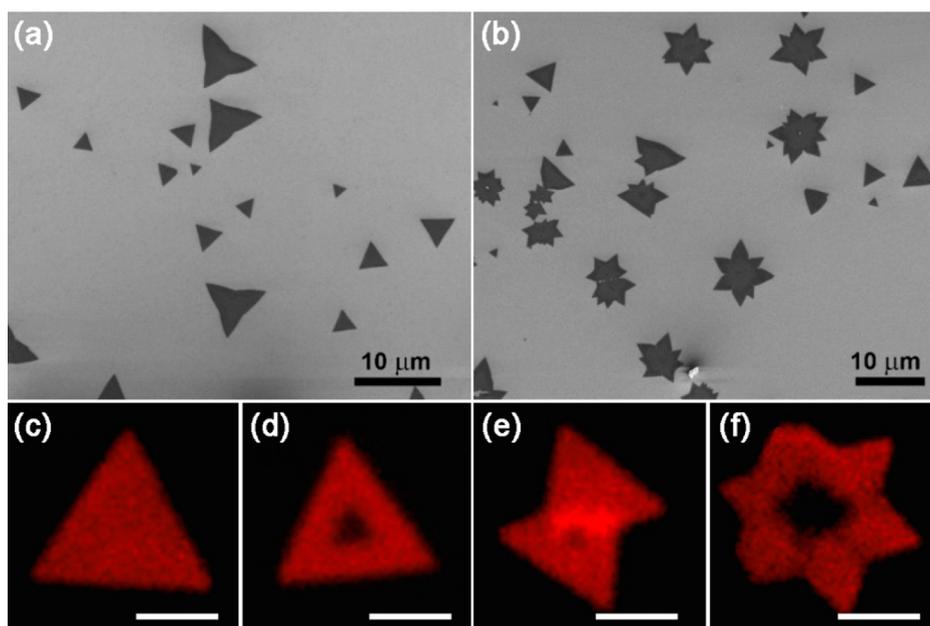


Figure 3. TMD monolayer islands with different morphologies. (a, b) Scanning electron microscopy (SEM) images of MoS₂ monolayered islands synthesized by heating powders of MoS₂ in the presence of S vapor at atmospheric pressure at 700 °C; (c–f) fluorescence images taken from MoS₂ monolayers with various morphologies: (c) uniform triangle, (d) triangle with a nucleation center, (e) polycrystalline “butterfly” with a tilt boundary, (f) polycrystalline “David star” with mirror boundaries. The scale bar in panels c–f is 5 μm.³⁸

exposed to a chalcogen atmosphere (e.g., S or Se powder).^{18,36} For example, controlling the thickness of the WO₃ coating allows for the large-area growth of *single-layer*, *bilayer*, and *few-layer* WS₂ sheets.¹⁸ Precursors such as (NH₄)₂MoS₄³⁷ and other sulfides³⁸ can also be used, although it can be difficult to control layer thicknesses. In some cases, to initiate the growth of atomically thick TMDs, seeds are used. For example, perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS) is an effective seed material for growing MoS₂ and WS₂ monolayers.³⁹ Depending on the growth kinetics and the chalcogen content during CVD, in addition to *triangular* islands¹¹ and continuous films,¹⁸ it is also possible to grow *butterfly-like* monolayers, *David stars*, and other polygonal monolayers (see Figure 3a,b).³⁸ Fluorescence microscopy has been used to study the optical properties of TMD monolayer islands grown into different morphologies, as shown in Figure 3c–f. It should be noted that the number of layers will remarkably affect the fluorescence intensity. The indirect bandgap of few-layered MoS₂ (e.g., the nucleation center of the triangle shown in Figure 3d) will quench the fluorescence. However, the fluorescence signal can be enhanced near the tilt boundary (Figure 3e) and reduced near the mirror boundary (Figure 3f).³⁸

5. WET CHEMICAL APPROACHES

Bottom-up wet chemical methods offer a potentially powerful alternative to exfoliation routes for synthesizing TMD nanosheets. Here, nanosheets form in high yield directly in solution. Parameters that are well-known to modulate nanoparticle size, shape, and uniformity, including judicious choice of surface stabilizing ligands and reaction conditions, may also be applicable to TMDs, which intrinsically form nanosheets because of their layered crystal structures. For example, Cheon and co-workers produced uniform, disc-shaped ZrS₂ nanosheets with thicknesses of <2 nm and lateral dimensions tunable from 20 to 60 nm by reacting ZrCl₄ and CS₂ in oleylamine at 300 °C.⁴⁰ This approach was later extended to a wider range of group IV and V transition

metal sulfide and selenide nanosheets.⁴¹ MoS₂ nanosheets have been produced solvothermally using (NH₄)₆Mo₇O₂₄·4H₂O and thiourea.⁴² Despite these successes, however, the wet chemical synthesis of TMD nanosheets is still in its infancy. The most significant synthetic challenges include (a) availability and selection of appropriate metal and chalcogen reagents, (b) careful control over metal oxidation states, (c) achieving high purity and yield, and (d) understanding how to truncate vertical growth while permitting lateral growth.^{40,41}

Given these challenges, we sought to study and understand how colloidal metal chalcogenide nanosheets grow in solution using SnSe and GeSe as model systems. SnSe and GeSe are members of a family of IV–VI layered metal monochalcogenides that also produce nanosheets when synthesized using wet chemical methods. Single-crystal SnSe nanosheets, which are exceptionally uniform and exhibit a regularly faceted square morphology, form in solution through a nanoparticle coalescence pathway. SnSe seed nanoparticles, which form first, attach to one another laterally to produce thin and uniform 2D nanosheets, with the morphology presumably driven by the crystal structure and the ligand–surface interactions.⁴³ Next, additional particle attachment occurs on the surfaces of these sheets to permit vertical growth.⁴³ Figure 4 shows TEM images of the SnSe nanosheets, as well as TEM snapshots characterizing their formation process.⁴³ For the related GeSe system, lateral growth could be further truncated by modifying the amount of trioctylphosphine-Se, which serves as a stabilizing ligand and Se source. Here, flat pseudo-1D nanobelts were formed.⁴⁴ While SnSe and GeSe are structurally and chemically distinct from the TMDs, both families have layered crystal structures that intrinsically produce nanosheets in solution. Therefore, our insights from the synthesis of SnSe and GeSe, including how lateral and vertical growth can be independently controlled, may be portable to TMDs in the future.

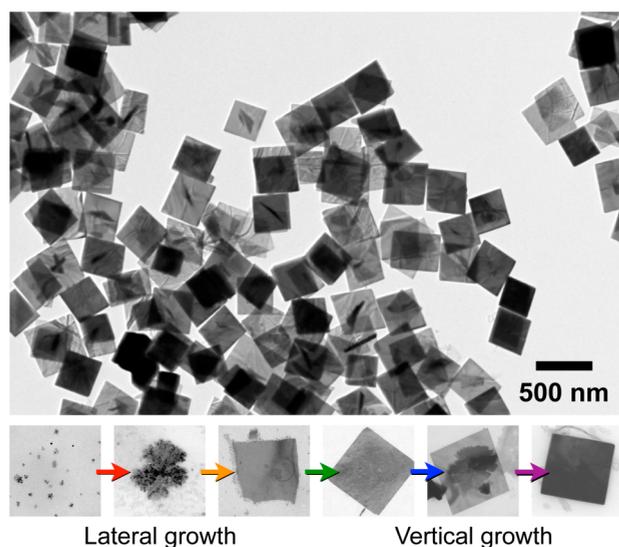


Figure 4. (Top) TEM image of laterally uniform SnSe nanosheets and (bottom) snapshots of their formation pathway, involving lateral nanoparticle coalescence followed by vertical growth. Reprinted with permission from ref 43. Copyright 2011 American Chemical Society.

6. VAN DER WAALS SOLIDS

Synthesizing and heterogeneously combining different TMD monolayers to form van der Waals (vdW) solids is the ultimate route to designing new and otherwise inaccessible TMDs with completely new electronic and photonic properties.⁴⁵ Recently, Terrones et al. predicted that MoS₂–WSe₂ heterostructures will exhibit electronic properties that are entirely different from their constituent layers (Figure 5a–c);⁴⁶ such heterogeneous stacking significantly reduces the bandgap energy. These exciting predictions are just now beginning to be realized experimentally through manual stacking of different layers.⁴⁷ For example, Robinson and co-workers demonstrated a variety of directly grown heterostructures based on MoS₂, WSe₂, hBN, and graphene with precise interfaces and atomic arrangements (Figure 5d).⁴⁸ The MoS₂/graphene heterostructures exhibit a

responsivity (R) of 40 mA/W when the optical power is $P_{\text{light}} = 40 \mu\text{W}$ (Figure 5e,f). Previously, the best reported R of a similarly biased monolayer MoS₂ photosensor with $P_{\text{light}} = 80 \mu\text{W}$ was 0.42 mA/W,⁴⁹ which was 2 times that of a WS₂ photosensor device (0.22 mA/W).¹⁷ Additionally, using a 514 nm laser, the photoresponsivity is further increased to 79 mA/W when $P_{\text{light}} = 40 \mu\text{W}$ and $V_{\text{ds}} = 1 \text{ V}$. Thus, the MoS₂/graphene photosensor represents a >100× improvement in photoresponsivity and up to 1000× improvement in absolute photoconductivity compared with exfoliated single-layer MoS₂. The advancement in performance is likely due to the ultraflat surface of graphene on SiC substrates, as well as very little layer coupling between the graphene and MoS₂. These processes being developed for TMD synthesis are the foundation for atomic control of the heterostructure interface and stacking, and eliminate the need for mechanical transfer processes that degrade performance.⁴⁵

7. OPTICAL, ELECTRICAL, PHOTOVOLTAIC, AND CATALYTIC PROPERTIES OF FEW-LAYERED TRANSITION METAL DICHALCOGENIDES

Interesting optical, electrical, photovoltaic, and catalytic properties emerge from the unique characteristics of the single- and few-layered TMDs. As mentioned above, the transition from indirect to direct band gap as the TMD thickness decreases from bulk to monolayer can be witnessed by PL, which exhibits a remarkable enhancement for monolayers.¹¹ Figure 6a,b shows an SEM image and corresponding PL map, respectively, for a WS₂ triangular island. Interestingly, the PL of monolayered WS₂ (Figure 6b, edge regions) is very intense and exhibits a single peak (Figure 6c, the black line marked with “1L”), corresponding to the direct excitonic transition at the K point.¹¹ When the WS₂ film thickness increases to two (2L) or three (3L) layers, the competition between the direct and indirect electronic transitions dramatically reduces the PL quantum efficiency and gives rise to a new feature at longer wavelength (Figure 6c, label I in the red line marked with “2L” and blue line marked with “3L”). The PL of bulk WS₂ is very weak and only shows the feature (I) associated with the indirect transition (Figure 6c, the green line marked with “Bulk”). Importantly, edges created mechanically

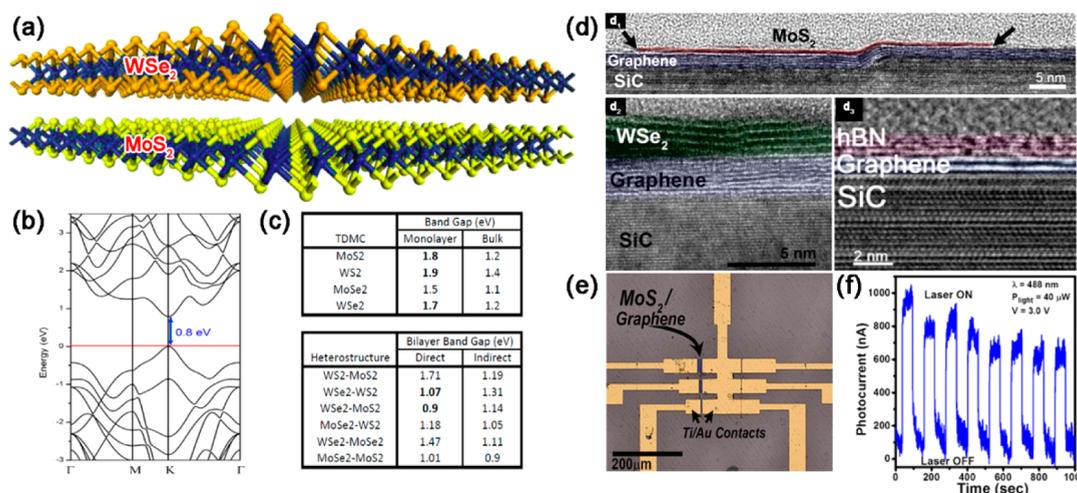


Figure 5. van der Waals Solids. (a) Simulated MoS₂–WSe₂ heterostructure that yields (b) a new direct band gap >0.6 eV. (c) Band gaps of TMDs and their heterostructures. Reprinted with permission from ref 46. Copyright 2013 Macmillan Publishers Ltd. (d) Cross-sectional HRTEM images of (d₁) MoS₂/graphene, (d₂) WSe₂/graphene, and (d₃) hBN/graphene. (e) Optical image of the fabricated MoS₂/graphene photosensor. (f) Transient measurement of the photosensor demonstrating a fast and stable response. Reprinted with permission from ref 48. Copyright 2014 American Chemical Society.

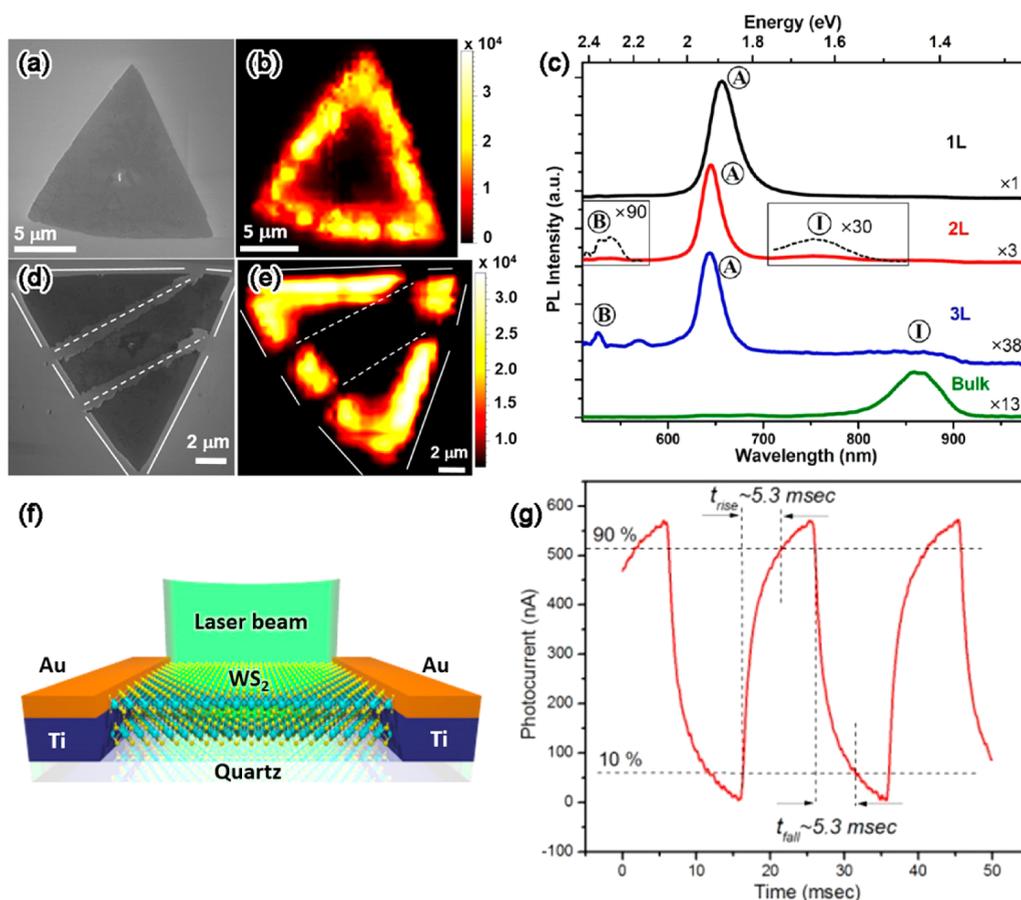


Figure 6. Optical and electrical response of single- and few-layer TMDs. (a) SEM image and (b) corresponding PL mapping of WS₂ triangular islands. (c) Room-temperature PL intensities for single-layer (1L), bilayer (2L), trilayer (3L), and bulk WS₂. (d) SEM image of a mechanically scratched island and (e) its corresponding PL mapping, demonstrate that the “new” edges (along dashed lines) created mechanically do not exhibit PL enhancement. Reprinted with permission from ref 11. Copyright 2013 American Chemical Society. (f) Schematic representation and (g) time response of a photosensor with few-layered WS₂ film. Reprinted with permission from ref 17. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

with an ultrasharp tungsten needle do not lead to significant PL enhancement (Figure 6d,e).¹¹ The Terrones group also demonstrated that *few-layer* WS₂ films (~10 layers) synthesized from low-pressure CVD can be used as a sensitive photodetector at room temperature.^{17,50} The FET device configuration (Figure 6f) shows very fast and stable response upon illumination (Figure 6g). However, FET devices containing *monolayer* WS₂ are usually highly resistive (GΩ range), possibly due to Schottky barrier effects between the electrodes and the WS₂ monolayers.

Monolayer TMDs could also be used for next-generation ultrathin and flexible optoelectronic devices.⁵¹ For example, Castro Neto et al. demonstrated a flexible photovoltaic device comprised of a graphene/WS₂/graphene sandwich-like heterostructure.⁵² In this design, the Van Hove singularities in the electronic density of states (DOS) of TMDs guarantees enhanced light–matter interactions, which will result in improved photon absorption and electron–hole creation.⁵² TMDs can show good response not only under *laser* excitation⁵² but also under *visible light* illumination, where they exhibit a photovoltaic response.⁵³ Liang et al. used plasma-assisted doping to construct a stable p–n junction in multilayer MoS₂.⁵³ Under AM1.5 illumination, the as-obtained MoS₂-based photovoltaic device showed a reasonably good power-conversion efficiency (PCE) up to 2.8% and a high short-circuit photocurrent density of 20.9 mA/cm².⁵³

TMDs also function as catalysts for the hydrogen evolution reaction (HER), in which molecular hydrogen is produced through electrocatalytic or photocatalytic water reduction.⁵⁴ The HER, which underpins several clean-energy technologies, is usually catalyzed by Pt, but its expense and scarcity limit global scalability opportunities.⁵⁵ Density functional theory (DFT) calculations showed that the hydrogen binding energy on MoS₂ is close to that on Pt, Rh, Re, and Ir.⁵⁶ MoS₂ therefore emerged as a potential low-cost alternative to the traditional noble metal HER catalysts.^{56,57} Both theoretical and experimental studies have indicated that the sulfide-terminated Mo-edge sites of 2H-MoS₂ are catalytically active while the basal plane remains inert.¹³ Many subsequent reports have demonstrated impressive HER activity for a variety of MoS₂ nanostructures, including high surface area MoS₂ mesoporous networks⁵⁷ and MoO₃–MoS₂ core–shell nanowires.⁵⁸ Moreover, converting 2H-MoS₂ (semiconducting) to 1T-MoS₂ (metallic) can also significantly improve the HER activity.²⁰ The promise of tuning the HER activity of MoS₂ through phase selection and nanostructuring, along with the possibility of identifying HER catalysts in other TMD systems, leaves room for significant future advances in this area.

8. CONCLUSIONS AND OUTLOOK

In this Account, we have summarized our progress in the controlled synthesis and physicochemical property studies of

monolayer and few-layer TMD nanostructures. CVD appears to be an adequate method able to grow TMD films with *specific number of layers* by controlling the thickness of the precursor (e.g., WO_3) coatings on insulating substrates (e.g., SiO_2/Si). However, this technique still requires the growth of perfect monocrystalline monolayers without the presence of grain boundaries and dislocations. In this context, the growth of centimeter-size triangular monolayers could be one solution, but this requires intense research. The van de Waals heterostructures assembled by combining TMDs and graphene have shown very competitive photosensing performance. It is also important that the controlled synthesis of other TMDs besides MoS_2 and WS_2 be tested by selecting suitable precursors for both transition metals and chalcogens. The morphology and crystalline structure control of these TMD few-layered systems still requires further research. For example, metallic phases (e.g., 1T- MoS_2) should demonstrate better HER catalytic performance than semiconducting ones (e.g., 2H- MoS_2). Wet chemical approaches and chemical exfoliation methods have a scalability advantage over CVD. However, the challenge of controlling the lateral growth of TMDs without expansion in the *c*-axis direction is still unsolved. Regarding exfoliation of layered systems, the intercalation of bulk layered materials including TMDs has not yet been carefully explored, and the challenge is to achieve intercalation followed by efficient exfoliation without damaging the sheets. Such methods have the potential to yield “buckets” of mono- and few-layer TMDs. It is clear that experimental research in conjunction with theoretical calculations is needed in order to more rapidly develop the field of 2D TMDs.

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Notes

The authors declare no competing financial interest.

Biographies

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