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Emerging Energy Applications of Two-Dimensional Layered Transition Metal Dichalcogenides

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Abstract:

Transition metal dichalcogenides (TMDCs) have attracted significant attention for their great potential in nano energy. TMDC layered materials represent a diverse and largely untapped source of 2D systems. High-quality TMDC layers with an appropriate size, variable thickness, superior electronic and optical properties can be produced by the exfoliation or vapour phase deposition method. Semiconducting TMDC monolayers have been demonstrated feasible for various energy related applications, where their electronic properties and uniquely high surface areas offer opportunities for various applications such as nano generators, green electronics, electrocatalytic hydrogen generation and energy storage. In this review, we start from the structure, properties and preparation, followed by detailed discussions on the development of TMDC-based nano energy applications.

Keywords: 2D Materials; Transition Metal Dichalcogenides; Energy Applications

1. Introduction

Owing to the limited natural fossil energy sources, green energy resources are widely recognized as the only feasible option to ensure a sustainable development of the world economy and society. However, renewable energy sources (e.g., solar, wind, and hydraulic power) generate electricity intermittently, posing a grand challenge to use them in an efficient and reliable way. Huge efforts have been contributed to develop novel energy generation and storage devices. Meanwhile, “low power consumption and high performance” electronics are required for smart and efficient energy utilization.

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have attracted significant interest due to their promising energy applications and exotic fundamental properties.[1-7] As shown in Figure 1 (a), 2D TMDCs are a family of layered materials with generalized formula of MX_2 , where one layer TMDC is composed of one layer transition metal M sandwiched by two atomic layers of chalcogens X. Similar to graphene, there exists only weak van Der Waals interaction between each layer of TMDC. Interestingly, the weak interlayer coupling also changes their electronic structures, where TMDCs have shown dramatic property changes when they are approaching to one monolayer thick.

Monolayer 2D TMDCs possess unique fundamental properties that never seen in their bulk counterparts, which enables them to serve for wide range of promising green energy applications such as energy generator,[8] energy storage,[9-12] catalysis [13-17] and electronic devices.[2] Monolayer semiconducting TMDCs with a direct band gap exhibit many distinct properties including strong interaction with light, [18, 19]

valley-dependent physics,[20] strong piezoelectric coupling [8, 21, 22] and high current on-off ratio for field effect transistors.[23] These unique properties of 2D TMDCs pave a broad way for their applications in the field of nano energy. The strong piezoelectric coupling of TMDCs are comparable to the traditional bulk wurtzite structures, making them promising active materials in piezoelectric nano energy generator. TMDC-based optoelectronics are expected to enjoy the advantages of ultrafast in responses, compact, light-weighted and energy-efficient. The TMDC-based transistor is of great potential for low power consumption devices and might completely revolutionize the current electronics industry. [2] Furthermore, modification of the properties of these materials are achievable through doping, surface adsorption, straining and interfacing with other materials with the aim at exploring the possibility to achieve material band structure engineering for emerging energy applications such as solar energy harvesting,[24, 25] electrochemical energy storage [9] and catalytic energy conversion.[13, 14] Therefore, nowadays 2D TMDCs have become one of the most active research areas especially in the field of nano energy. In this review, we provide insights for the synthesis and property of 2D TMDCs, and herein reveal their promising potentials in various nano energy systems.

2. Structure and preparation of transition metal dichalcogenides:

2.1 Atomic structure of monolayer transition metal dichalcogenides:

The atomic structure of TMDCs determines their electrical, optical and catalytic properties. The absence of interlayer interaction in monolayer TMDCs gives rise to the charge carrier redistribution and appearance of their direct band gap.[19] While the low coordinated atoms in TMDCs, such as atoms from TMDCs edges or grain boundaries can serve as the active sites [26] to promote the electrochemical and

catalytic reaction. As shown in Figure 1 (a), only weak van der Waals force exists in between each TMDC layer, which allows the bulk crystal to be isolated down to monolayers along the 2D surface. Each individual TMDC monolayer is formed by sandwiching the hexagonally packed transition metal atoms by two layers of chalcogen atoms. The transition metals are typically from group IV and VI (such as Mo and W), while the chalcogen group is commonly seen as S, Se and Te. In the individual TMDC layer the transition metal and chalcogen atoms are covalently bonded, giving rise to different stacking polytypes and polymorphs. As displayed in Figure 1 (b), three main structural polytypes, 1T, 2H and 3R, have been identified. All the three polytypes have regular layered structures with six fold trigonal prismatic coordination of transition metal atoms by the chalcogen atoms within the TMDC layers. The term 1T, 2H and 3R represents the presence of one (1), two (2) and three (3) layers in the tetragonal (T), hexagonal (H) and rhombohedral (R) unit cell respectively. The 2H and 3R polytypes are thermodynamically stable phases that can be found in nature. Incorporation of impurity elements in the 2H-TMDC will transform it to the 3R phase; for example, the presence of Re or Nb in MoS₂ structures leads to the partial substitution of Mo atoms and forms a more stable 3R packing.[27, 28] The 3R phase of TMDCs is a less studied polytype. However, semiconducting transport behaviors have been observed in NbS₂ layers that are mechanically exfoliated from their bulk crystal in the 3R form. [29] Compared to 2H and 3R, 1T phase is a metastable metallic phase. Experimental results show that the lithium ion intercalation can result in the transformation of 2H to 1T phase, where a transversal displacement of one of its chalcogen planes occurs.[30]

2.2 Preparation of 2D transition metal dichalcogenides:

One major research field of TMDCs is the controllable production of atomically thin 2D layers. Since the first demonstration of a thermodynamically stable monolayer graphene in 2004, [31, 32] several types of TMDC monolayers have been successfully fabricated. To date, two major strategies have been developed to produce monolayer TMDCs: one is the exfoliation method from TMDC bulk crystals; the other is through the synthesis using vapour phase deposition techniques. More recently, epitaxial growth of 2D systems bridges different materials such as TMDCs, boron nitride [33] and phosphorene [34] together to form promising and functionalized heterostructures. These 2D materials and their heterostructures also offer great potential for energy applications.

2.2.1 Exfoliation of monolayer TMDCs from bulk crystals:

Mechanical cleavage [23] is not suitable for large scale production due to the absence of layer number and lateral size control capability. Chemical exfoliation enables the high yield and scalable preparation of micrometer-sized monolayers and low-dimensional composites [35]. TMDC layers can be exfoliated by ultrasonication in liquids. Theoretical calculation and experimental results show that the surface energy match between TMDC layer and solvent are critical for effective exfoliation, where the solvents with the surface tensions close to 40 mJ/m^2 [36-38] are most suitable for effective exfoliation. Coleman and coworkers demonstrates the direct sonication of TMDC bulk crystals in common solvents such as N-methyl-pyrrolidone (NMP) and dimethylformamide (DMF) to produce TMDC monolayers.[37] Exfoliation of TMDCs in water is an environmental friendly and economical approach. However, water has a surface tension of 72 mJ/m^2 , which is too high for exfoliation of TMDC sheets. The same group further discovers that water soluble polymer can promote the

TMDCs exfoliation in water.[39] The change in solubility parameters greatly facilitates the exfoliation and makes the sonication method more scalable and energy efficient. However, the use of polymer may contaminate the TMDCs, which is not desirable for certain applications. To address this issue, Zhang and coworkers use a mixture of water and ethanol to exfoliate TMDC nanosheets via sonication.[40] A series of TMDCs nanodots including MoS₂, WS₂, ReS₂, TaS₂, MoSe₂, WSe₂ and NbSe₂ can also be prepared by combination of grinding and sonication techniques.[41]

In addition to the direct exfoliation, a two-step process, ion intercalation followed by exfoliation is able to produce TMDCs with a higher yield. As shown in Figure 1 (c), lithium, sodium or potassium ions are intercalated into the interlayer space and form ion-intercalated compounds, which can be further sonicated in water or organic solvents to form TMDC dispersions. Exfoliation of the bulk TMDC crystals can also be achieved using organolithium compounds; for example, the n-BuLi chemically reacts with TMDCs, forming Li-intercalated compounds.[42] The compounds are further exfoliated by the reaction of Li with water. Alternatively, Loh and co-worker reported the use of sodium naphthalenide as the intercalation agent to expand the TMDC crystals.[43] A variety of TMDC sheets, including MoS₂, TiS₂, TaS₂ and WS₂ can be produced with the lateral size up to few microns. Zhang and coworkers have further developed a controllable process for ion intercalation, where the Li-ion insertion to the TMDC crystals is controlled electrochemically.[44]

Large quantities of micron-sized monolayer TMDCs can be produced using various liquid exfoliation methods as mentioned and the produced TMDC nanosheets can be

adopted for solution-based or printable electronics. Yet, the wet chemical method may unavoidably alter the lattice structure of thin TMDCs and introduce extrinsic defects during exfoliation process. These defects may be helpful in electrocatalytic reactions. Nevertheless, a post treatment may be required to reconstruct the structure of monolayer TMDCs for electronic or optical applications.

2.2.2 Synthetic routes for atomically thin TMDCs:

The synthesis of atomically thin TMDCs with layer controllability and large-area uniformity is an essential requirement for their application in electronic and optical devices. Tremendous efforts have been devoted to the controlled growth of 2D TMDCs. The chemical vapour deposition (CVD) method provides the way for controlled synthesis of wafer-scale TMDCs. [1, 45] The CVD technique shows great promise to produce high-quality TMDC layers with controllable thickness, scalable size and excellent electronic properties. The vapour phase reaction also allows the growth of single-crystalline TMDC flakes directly on arbitrary substrates and there is no need of additional transfer process for electronic device fabrication. Hence, it soon becomes a widely adopted approach. Practically, it is more challenging to obtain crystalline monolayer TMDC thin film by CVD method compared to other 2D materials synthesis such as graphene and boron nitride, since the growth of TMDCs does not normally involve any catalytic substrates. Meanwhile, it is also common to obtain transition metal oxide microcrystals by-products due to insufficient reduction of the transition metal oxide precursors.[46] Thus far, a better understanding of the growth mechanism and further developing a method which is capable of producing large monolayer TMDC crystals in a controlled manner is demanding.

The synthesis of TMDC layers have been studied, such as sulfurization of a transition metal [47] or metal oxide thin film [48], thermal decomposition of thiosalts [49] and vapour phase transport method [50-52]. However, it remains a challenge to control the thickness and crystallinity of TMDCs until Li and coworkers developed the growth method of TMDCs via vapour phase chemical reaction of transition metal oxide and chalcogen. [53, 54] The synthesis of MoS₂ monolayer is illustrated in Figure 1(d), where the metal oxide MoO₃ is used as transition metal source and it undergoes a two-step reaction. The suboxide MoO_{3-x} is firstly produced during the reaction. It further serves as an intermediate to react with chalcogen vapour (sulfur) and form the monolayer TMDCs with a triangular shape.

Further studies show that the surface energy of substrate controls the formation of TMDCs. The aromatic molecules can significantly enhance the wetting between precursors and the substrate surfaces and thus promote the nucleation and lateral growth of TMDCs.[55] The vapour phase reaction has been further refined by several research groups,[1] TMDCs single crystal domain with lateral size up to several hundred μm can be produced.[56] The direct vapour phase reaction of transition metal oxide and sulfur/ selenium has been widely adopted to produce TMDC layers including MoS₂,[57] WS₂,[58] MoSe₂,[59] and WSe₂. [60]

Eichfeld et al. has developed a scalable approach of synthesizing WSe₂ using metal-organic CVD (MOCVD) with tungsten hexacarbonyl (W(CO)₆) and dimethylselenium (CH₃)₂Se as growth precursors.[61] Recently, Kang and coworkers realized the large scale TMDCs film growth on a 4-inch wafer via the MOCVD technique.[62] The growth applies Mo(CO)₆ and (C₂H₅)₂S as precursors and the TMDCs film can directly grow on SiO₂ substrates by this MOCVD approach. In

additional, Kang and coworkers also demonstrated the potential of MOCVD TMDCs synthesis by producing multi-stacked monolayer MoS_2 films which enable the electronic device fabrication at different vertical stacking levels. In addition, the combination of different 2D layered materials, including graphene, h-BN and TMDCs, into a hybrid heterostructures offers the chance to create novel 3D clusters with new functionalities.[63] For example, graphene/ MoS_2 heterostructures have also shown their great potential in the devices for logic and memory applications,[64] ultrasensitive detection of DNA hybridization,[65] photodetectors [66], hydrogen evolution reaction [67] and energy storage.[68] More recently, considerable efforts have also been put in constructing heterostructures formed by various 2D semiconductors. The most straightforward method is through the “peel-and-paste” processes,[69] i.e., mechanical transfer of one monolayer onto another to build TMDC heterostructures. Direct CVD growth is more promising towards large-scale production of high-quality TMDC heterostructures with a controllable thickness, clean interface and reproducible electronic and optical properties [70, 71]. Lateral heterostructures of WS_2 - MoS_2 , [72, 73] MoSe_2 - WSe_2 , [73] MoS_2 - MoSe_2 , [74] and WS_2 - WSe_2 , [74] have been realized using one-pot CVD synthesis processes. Remarkably, Li’s group developed a synthetic approach for 2D p-n heterostructures.[75] As shown in Figure 1(e), using a two-step CVD synthesis method, they have realized thin van der Waals p-n junction which combines n-type MoS_2 and p-type WSe_2 monolayers with an atomically sharp interface.[75]

3. Green energy generator:

3.1 TMDC-based piezoelectronics

Self-powered devices requiring no external power supply are highly desirable for developing wireless nanodevices and nanosystems, such as implantable medical sensors, environmental monitor, and personal electronics. Nanogenerators are devices aiming at supplying self-sustainable power sources for micro/nanosystems.[76] The nanogenerators based on the piezoelectric effect of 2D materials have been developed recently.[77, 78] Piezoelectric materials exhibit an electrical polarization in response to an applied mechanical stress, and the piezoelectricity is originated from the structural non-centrosymmetry. Among the 32 crystal classes, 21 of them are non-centrosymmetric for the lack of a center of symmetry, and 20 of these show direct piezoelectricity. The bulk TMDC crystals consisting of a stacked-layer structure are not expected to be piezoelectric because of the presence of an interlayer inversion center. While this is not true for the two-dimensional monolayer TMDC, as the thickness reduces to a single layer, there will be a loss of the inversion center. Due to this distinct crystal symmetric property from the bulk crystals, single to few-layer TMDC are potentially piezoelectric as a result of strain-induced lattice distortion and the associated ion charge polarization. Reed et al. have derived the piezoelectric coefficients for a series of monolayer TMDCs based on density-functional theory calculations.[79] According to their prediction, these materials exhibit strong piezoelectric coupling that are comparable to the traditional bulk wurtzite structures.

Recently the pioneer experiments for piezoelectric properties of the atomically thin 2D TMDC crystal have been reported by Z. L. Wang's group.[8] Figure 2(a) shows that with a typical flexible device consisting of a monolayer MoS₂ membrane and metal electrodes at its zigzag edges, a strong piezoelectric response can be observed

by mechanically bending the substrate. As demonstrated in Figure 2(b), applying strain to the device will induce piezoelectric polarization charges of opposite polarity at the zigzag edges of the single-layer MoS₂ flake. Therefore, piezoelectric outputs of alternating polarity can be generated by periodic stretching and releasing of the substrate. Furthermore, for the most common 2H form of TMDCs, the alternating stacking layers possess opposite orientations and thus a centrosymmetry is expected for even number of layers. Experimental results have proved the loss of piezo responses for even-layer TMDC flakes. The piezoelectric output decreases with increasing layer numbers for odd-layer flakes, which follows the decaying trend towards zero for the bulk as shown in Figure 2(c).

Xiang Zhang et al. has also reported the experimental evidence of piezoelectricity in a free-standing single layer of MoS₂. [22] Through a method combining a laterally applied electric field and nano-indentation in an atomic force microscope (AFM), quantitative determination of piezoelectric coefficient can be achieved. As shown in Figure 2(d), besides the layer-number dependence of the piezoelectricity, the angular dependence of piezoelectric response was observed with varied rotation (θ) of the monolayer on a series of devices. In consistence with predictions from the crystalline three-fold symmetry, the measured piezoelectric coupling strength followed the $\cos 3\theta$ dependence and this distinguished feature allows the determination of 2D crystal orientations uniquely without the need to use atomic imaging techniques.

K. L. Wang et al. reported the experimental study of the theoretically predicted piezoelectric effect in triangle monolayer MoS₂ under isotropic mechanical deformation. [21] As shown in Figure 2(e) and (f) respectively, the I-V characteristic curves of the MoS₂ device are measured at two fixed source-drain electrodes, while the AFM tip contact at the centre and the edge of the triangular MoS₂ layer. The

current decreases under compressive strain and increases under tensile strain, respectively. The asymmetry relation between compressive and tensile strain was explained by the difference in local strain induced charge polarization, enabling a novel strain/force sensor using the MoS₂ devices.

In summary, owing to their robust piezoelectricity, stretchability and flexibility, the 2D piezoelectric materials possess great potential for applications in atomically thin piezoelectric devices. As a newly developed low-dimensional piezoelectric material, the TMDC layered crystals would make profound impacts in a wide range of applications such as electromechanical sensors, piezoelectric-gated diodes and mechanical resonator for low-power logic circuits, etc. With the concept of nanogenerators that convert nanoscale mechanical energy into electricity, the 2D piezoelectric materials can also be adopted in a number of self-powered wireless nanodevices and nanosystems for energy harvesting from the ambient environment. To meet the practical requirements from the rapid emerging field of nanopiezoelectronics, large-area TMDC with precisely controlled layer numbers is crucial and the piezoelectric performance of various heterojunctions could be an interesting field to be explored.

3.2 Solar energy harvest and conversion

Layered semiconductors are considered as attractive candidates for photovoltaic applications owing to their large surface area, free of dangling chemical bonds on surfaces and potential as sunlight absorbers. 2D TMDCs are applied in solar cells by forming a Schottky or p-n junction that works as an interface for the separation of charge carriers. For the Schottky junction type, the TMDC semiconductor adjoins a metal or graphene contact to form junctions. The MoS₂ nanomembrane/metal (Au)

based Schottky-barrier solar cell was demonstrated with a power conversion efficiency (PCE) of 1.8% for ~220 nm thick of MoS₂ stacks.[80] The WS₂/graphene based solar cell was able to yield a higher PCE of 3.3% with the WS₂ nanosheet of thickness ~37 nm and a multilayer graphene contact.[81] Furthermore, TMDC monolayers were predicted to absorb up to 5-10% incident sunlight, which is about one order of magnitude higher than GaAs and Si of the same thickness (< 1 nm). An ultrathin solar cell comprising MoS₂/graphene stacked monolayers can attain a PCE of ~1% in just 1 nm thickness.[25] Besides the Schottky junction, monolayer lateral p-n junctions and type II van der Waals heterojunctions have also been demonstrated. For a monolayer WSe₂ p-n diode, the PCE was estimated to be around 0.5%.[82] The solar cell consisting of stacked MoS₂ and WSe₂ monolayers exhibit a PCE of 0.2%.[83] The n-type monolayer MoS₂ and p-type silicon heterostructure exhibits the external quantum efficiency (EQE) exceeding 4%,[84] and a high PCE over 5% could be reached by the MoS₂/Si-based photovoltaic device.[24] Extraordinarily, the application of TMDCs in the photovoltaic field is not limited to a photoactive semiconductor layer, they can also work as catalytic counter electrode (CE) materials or hole extraction buffer layers. As MoS₂ exhibits good catalytic activity for the reduction of electrolyte from triiodide (I₃⁻) to iodide (I⁻) in a dye-sensitized solar cell (DSSC), the MoS₂ based CEs have been demonstrated in DSSCs and good photovoltaic performance was observed with PCE ranging from 5.7-7.23%.[85-87] Moreover, ultrathin 2D MoS₂ nanosheets can be integrated into organic solar cells as an effective hole-extraction layer and a relatively high PCE of 8.11% can be reached.[88] Different types of solar cells and their corresponding performance are summarized in Table 1. The open-circuit voltage V_{OC} , short-circuit current density J_{SC} , fill factor (FF) and the corresponding PCE are listed in Table 1 for comparison.

Table 1. Performance of various solar cells fabricated with TMDCs.

Type	Solar Cell structure	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
p-n junction	MoS ₂ /WS ₂ bilayer [25]	0.5-1.0	3.5	0.3-0.6	0.4-1.5
	MoS ₂ /WSe ₂ bilayer [83]	~0.43-0.56	~0.13-4.56	~0.5	~0.2
	Monolayer WSe ₂ p-n diode [82]	~0.75-0.88	~0.47-3.88	~0.5	~0.5
	Monolayer MoS ₂ /p-Si [24]	0.41	22.36	0.57	5.23
Schottky Junction	MoS ₂ /Graphene bilayer [25]	0.1-0.5	4.5	0.3-0.6	0.1-1.0
	MoS ₂ /Au based solar cell[80]	0.597	5.37	0.55	1.8
	WS ₂ /Graphene based solar cell[81]	0.70	16	-	3.3
DSSC	CNTs [†] /MoS ₂ /carbon CEs based DSSC[85]	0.79	16.44	0.57	7.23
	MoS ₂ /PEDOT-PSS* CEs based DSSC[86]	0.68	14.55	0.58	5.7
	MoS ₂ porous sheets CEs based DSSC[87]	0.763	15.40	0.53	6.35
Hole-extraction Layer	PTB7-PC ₇₁ BM [‡] /MoS ₂ organic solar [88]	0.72	15.90	0.71	8.11

[†]CNTs: carbon nanotubes

*PEDOT-PSS: Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)

[‡]PTB7-PC₇₁BM: poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno [3,4-b]thiophenediyl]] (PTB7)-[6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM)

4. Low-power and high-performance integrated circuits:

Green electronics represent an emerging research area aiming at establishing electronic devices which can operate at a low power but with high performance. For integrated circuits, scaling improves the transistor density and functionality on a chip; however, with the decreasing geometry the leakage current increases exponentially and the leakage power is catching up with the dynamic power in circuits. Especially for deep submicron process technology nodes (<50 nm), more than 40% of the total energy is consumed due to the leakage of switching component.[89] Depending on the composition of TMDCs, their bandgap ranges from metallic to wide bandgap semiconductors such as MoS₂ (1.8 -2.4 eV). 2D TMDCs with a relatively large bandgap possess high on/off current ratios and high mobility values. Their ultra-thin body minimizes the short channel effect caused by the down scaling of electrical

circuits. Furthermore, the pristine surface of TMDCs is free of dangling bonds and their smooth surfaces greatly limit the charge carrier scattering effect, leading to a high mobility and lower energy loss.

Kis and co-workers reported the first implementation of a top-gated field effect transistor (FET) based on exfoliated MoS₂ monolayer,[23] as shown in Figure 3(a). The top-gated MoS₂ n-type FET shows fairly high electron mobility ($\sim 200 \text{ cm}^2/\text{Vs}$), high on/off current ratio ($\sim 10^8$) and low subthreshold swing. As proof of concept, Wang and coworkers demonstrated MoS₂ based integrated circuits such as inverters, NAND gates, and static random access memory (shown in Figure 3(b)).[90] To fabricate complementary metal–oxide–semiconductor based logic devices, a p-type TMDC FET is required. Monolayer WSe₂ has been shown as one of the option for p-channel materials. Banerjee and co-workers have fabricated WSe₂ based field effect transistor with a record breaking on-current of $210 \text{ } \mu\text{A}/\mu\text{m}$, while maintaining a high electron mobility of $142 \text{ cm}^2/\text{V}$ and the on/off current ratio exceeding 10^6 . [91]

The formation of low resistivity ohmic contact between 2D TMDCs and metal is critical for high performance green electronics. The realization of ohmic contacts strongly depends on the Fermi energy of TMDCs. However, for the 2D TMDCs which are only few atomic layer thick, their Fermi level is extremely sensitive to the environment. Theoretical works have shown that the d-orbitals of contact metals determine the contact resistance between TMDCs and metal contact. By carefully selection of the contact metal materials, Banerjee and co-workers demonstrated the role of metal contacts in designing high-performance monolayer n-type WSe₂ FETs, as shown in Figure 3(c). [91] Their ab initio density functional theory (DFT) calculations suggest that the d-orbitals of the contact metal play a key role in

determining the contact resistance with monolayer WSe₂. Based on this understanding, indium-WSe₂ contact is found as ohmic. The performance of WSe₂ based FET can be further improved by high-k dielectric top coating, which significantly suppresses the Coulomb scattering.

TMDCs can exist in a variety of different phases, such as 1T, 2H and 3R. [30] Recently, a new strategy based on phase engineering has been used to realize low contact resistances for improving FET performance.[92] Chhowalla and co-workers reported the metallic 1T phase can be selectively transformed from the semiconducting MoS₂ 2H phase by organolithium chemical method.[93, 94] The atomically sharp interface and similar work function of the 1T phase to the conduction band energy of 2H MoS₂ phase lead to low contact resistances of 200 to 300 Ω . Yang and co-workers use laser-induced phase to pattern metallic distorted octahedral structures (1T') on semiconducting MoTe₂ flakes and this technique is used to fabricate MoTe₂ based 2D transistors with an ohmic contact.[95] The 2H to 1T' phase transition is clarified by in-situ STEM, which suggests the phase change originates from the formation of Te vacancy [96] by laser irradiation. [95]

Briefly, although the mobility of TMDC based FET is not higher than that of silicon, the atomically thin channel materials could typically improve the scale length of FETs which leads to a better gate length scalability. Typically, monolayer TMDCs show much higher mobility compared to atomically thin silicon.[23, 97] Meanwhile, TMDCs show higher mobility than other competing materials such as organic semiconductors and amorphous silicon, which pave the way for their applications in back-plane electronics of displays, chemical and optical sensors.[2]

5. Electrical energy conversion and Storage:

5.1 High efficiency catalysis for hydrogen energy generation

Hydrogen is a clean and high-density energy carrier which could replace petroleum fuels to relieve issues associated with global warming. Hydrogen production by water electrolysis using renewable energy has become one of the most promising options for a sustainable society. The hydrogen production by water splitting relies on the electrochemical reactions where catalysis can speed up chemical reactions and achieve low over potential and high power conversion efficiency. Atomically thin 2D materials are commonly accepted as an ideal model for catalysis study and practical applications due to their high fraction of active sites that compared to the overall atoms.

Recent work has also suggested that MoS_2 is a promising H_2 evolution catalyst with excellent kinetics for driving the hydrogen evolution reaction (HER). The catalytic effects were suggested to stem from the sulphur edges of MoS_2 plates while the basal planes were catalytically inert.[98] Therefore the surface area and the crystallinity of the catalysts play an important role in the H_2 activation property. Promising results have been reported using MoS_2 nanoparticles with a high concentration of edges. As shown in Figure 4 (a), Dai's group has demonstrated a high HER efficiency using MoS_2 -graphene oxide composites as the catalysts.[13] MoS_2 -graphene hybrid nanomaterials can be obtained by a one-step solvothermal reaction of $(\text{NH}_4)\text{MoS}_4$ and hydrazine in an N,N-dimethylformamide (DMF) solution of mildly oxidized graphene oxide at 200 °C. The MoS_2 synthesized on graphene surface has abundant open edges, which facilitate the electrochemical reaction for H_2 generation.

The polytypes of TMDCs can also significantly affect its catalytic activity. In order to

further enhance the catalytic activity, Chhowalla's group has successfully activated the WS₂ basal planes by converting its crystalline phase from 2H to 1T.[99] Figures 4(b) and 4(c) show the structure of WS₂ nanosheets reacted with the n-butyl lithium in hexane. The as-exfoliated WS₂ nanosheets contain a high concentration of strained 1T phase regions (number of active sites is $\sim 4.5 \times 10^{14}$ sites cm⁻² or higher). It is known that a catalyst is active in hydrogen evolution when the free energy of adsorbed atomic hydrogen is close to thermoneutral. Using DFT calculations, Chhowalla's group further demonstrated that the strain on TMDCs can significantly influence the free energy of atomic hydrogen adsorption on the surface of distorted 1T WS₂. The free energy is close to thermoneutral when the strain on 1T WS₂ is varied between 2.0 and 3.0%. Their results clearly suggest that the 1T WS₂ phase is catalytically active.

The crystallinity and chemical composition of MoS₂ could also tailor the catalytic reactivity for H₂ generation. Li and other groups have formulated amorphous MoS_x ($x \geq 2$) catalytic materials on glassy carbon or graphene foam.[14, 67, 100] The catalytic sites are likely related to the bridging S₂²⁻ or apical S²⁻ that exist in MoS_x. The as-prepared MoS_x shows reasonably good catalytic performance and lifetime in HER. The high current density is attributed to the large electrochemical surface area and the S-rich structure. These cheap and active HER materials are of great potential for future hydrogen evolution applications.

In order to further improve the catalytic efficiency and stability of TMDC-based electrocatalysts, enormous research efforts have been devoted to the incorporation of TMDCs with other materials, such as noble metals [101] and carbon materials.[102] Zhang and co-workers demonstrated the wet-chemical synthesis of noble metal

nanostructures epitaxially grown on TMDC nanosheets. The noble metal-TMDCs composites exhibit good electrocatalytic activity in hydrogen evolution reaction. [103, 104]

5.2 Electrode materials with high specific energy capacitance

The utilization of renewable energy resources such as solar, wind, and thermal energies enables the sustainable development of the society. The intermittent nature of renewable energy sources has stimulated the development of efficient energy storage devices with high energy capacity and long cycle operation. Meanwhile, efficient energy storage devices are also highly desirable in the portable electronic devices and hybrid electrical vehicles.

TMDCs based energy storage devices such as supercapacitors and batteries have been investigated recently. MoS₂ of a 1T phase is intrinsically hydrophilic and possesses high electrical conductivity. Chhowalla and co-workers demonstrate that chemically exfoliated nanosheets of MoS₂ can be efficiently intercalated with ions and achieve high capacitance.[105] The high capacitance has been attributed to the high concentration of metallic 1T phases generated by chemical exfoliation. Further study shows the chemically exfoliated MoS₂ operating in non-aqueous organic electrolytes exhibits prime volumetric energy and power density values with excellent cycling performance. This work provokes the study of metallic phase TMDCs, which could exhibit superior electrochemical properties for energy generation and storage.

Lithium ion batteries (LIBs) are the most promising candidate for high energy storage devices. However, the energy capacity of current LIBs is still far below the requirements of many applications. To provide higher lithiation capability and

enhanced performance, new designs with the introduction of nanomaterials as electrodes in the cells, in place of conventional electrodes, are imperative.

MoS₂ is also attracting attention as a battery anode material.[9] MoS₂ has a high reversible capacity value which is three and a half fold larger than the commercial graphite anode (372 mAhg⁻¹). MoS₂ has a layered structure which facilitates the lithium insertion and extraction process during battery charge and discharge, and it generally shows much better rate capability with long cycling life time. Meanwhile, MoS₂ electrode are quite attractive due to its small volumetric expansion upon lithiation. [9]

There has been various reports for MoS₂ electrode preparations [9] and the MoS₂-carbon hybrid is one promising candidate for high performance lithium ion battery. Benefited from their nanoscale structure, MoS₂-carbon hybrids display high energy density, good cycling stability and high rate capability.[46, 68] Generally for MoS₂-carbon hybrid, graphene or carbon nanotubes are also introduced into the hydrothermal synthesis process for MoS₂, producing various nanocomposites. The introduction of carbon based materials into MoS₂ basically improve the overall electrical conductivity of the electrode. Meanwhile, the carbon layers could allow MoS₂ expansion at the MoS₂-carbon interface, which improves the cycling performance.[9] Cho and coworkers have reported the successful MoS₂ full cell battery using LiCoO₂ as cathode,[106] where the graphene-like MoS₂ nanoplates were synthesized by solvothermal reaction of Mo(CO)₆ and sulphur in xylene. The graphene-like MoS₂ electrode shows a high rate performance which is around 800 mAhg⁻¹ at 30 °C and 700 mAhg⁻¹ at 50 °C. This high rate performance has been attributed to the large charge transfer surface area with short diffusion distances.

6. Summary

Energy issue is one of the most urgent and critical topic in our modern society. Recently, there is increasing demand for cost-effective, efficient and environmental friendly energy conversion and storage devices to reduce the excessive reliance on non-renewable fossil fuels. TMDCs have shown great potential in this scenario. Although layered materials have been known and studied for decades, recent advances in monolayer 2D TMDCs materials, including characterization, synthesis and device fabrication have cast light and stimulated the research on related 2D materials. Many of the distinctive properties in 2D TMDCs could pave the way for nano energy applications such as photovoltaic devices, H_2 generation, piezoelectronics and lithium ion battery. More and more efforts have been allocated on other 2D TMDCs and it is anticipated that new and exciting applications may be developed in the near future.

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Reference

- [1] Y. Shi, H. Li, L.-J. Li, *Chemical Society Reviews*, 44 (2015) 2744-2756.
- [2] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, *Nat Nano*, 7 (2012) 699-712.
- [3] M. Chhowalla, H.S. Shin, G. Eda, L.-J. Li, K.P. Loh, H. Zhang, *Nat Chem*, 5 (2013) 263-275.
- [4] H. Zhang, *ACS Nano*, (2015). DOI: 10.1021/acsnano.5b05040
- [5] C. Tan, H. Zhang, *Chemical Society Reviews*, 44 (2015) 2713-2731.
- [6] X. Huang, C. Tan, Z. Yin, H. Zhang, *Advanced Materials*, 26 (2014) 2185-2204.
- [7] X. Huang, Z. Zeng, H. Zhang, *Chemical Society Reviews*, 42 (2013) 1934-1946.
- [8] W. Wu, L. Wang, Y. Li, F. Zhang, L. Lin, S. Niu, D. Chenet, X. Zhang, Y. Hao, T.F. Heinz, J. Hone, Z.L. Wang, *Nature*, 514 (2014) 470-474.
- [9] T. Stephenson, Z. Li, B. Olsen, D. Mitlin, *Energy & Environmental Science*, 7 (2014) 209-231.
- [10] G. Sun, J. Liu, X. Zhang, X. Wang, H. Li, Y. Yu, W. Huang, H. Zhang, P. Chen, *Angewandte Chemie International Edition*, 53 (2014) 12576-12580.
- [11] G. Sun, X. Zhang, R. Lin, J. Yang, H. Zhang, P. Chen, *Angewandte Chemie International Edition*, 54 (2015) 4651-4656.
- [12] X. Cao, Y. Shi, W. Shi, X. Rui, Q. Yan, J. Kong, H. Zhang, *Small*, 9 (2013) 3433-3438.
- [13] Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, *Journal of the American Chemical Society*, 133 (2011) 7296-7299.
- [14] Y.-H. Chang, C.-T. Lin, T.-Y. Chen, C.-L. Hsu, Y.-H. Lee, W. Zhang, K.-H. Wei, L.-J. Li, *Advanced Materials*, 25 (2013) 756-760.
- [15] Z. Yin, B. Chen, M. Bosman, X. Cao, J. Chen, B. Zheng, H. Zhang, *Small*, 10 (2014) 3537-3543.
- [16] C.-B. Ma, X. Qi, B. Chen, S. Bao, Z. Yin, X.-J. Wu, Z. Luo, J. Wei, H.-L. Zhang, H. Zhang, *Nanoscale*, 6 (2014) 5624-5629.
- [17] J. Chen, X.-J. Wu, L. Yin, B. Li, X. Hong, Z. Fan, B. Chen, C. Xue, H. Zhang, *Angewandte Chemie International Edition*, 54 (2015) 1210-1214.
- [18] H. Li, Q. Zhang, C.C.R. Yap, B.K. Tay, T.H.T. Edwin, A. Olivier, D. Baillargeat, *Advanced Functional Materials*, 22 (2012) 1385-1390.
- [19] K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, *Physical Review Letters*, 105 (2010) 136805.
- [20] K.F. Mak, K. He, J. Shan, T.F. Heinz, *Nat Nano*, 7 (2012) 494-498.
- [21] J. Qi, Y.-W. Lan, A.Z. Stieg, J.-H. Chen, Y.-L. Zhong, L.-J. Li, C.-D. Chen, Y. Zhang, K.L. Wang, *Nat Commun*, 6 (2015) 7430.
- [22] H. Zhu, Y. Wang, J. Xiao, M. Liu, S. Xiong, Z.J. Wong, Z. Ye, Y. Ye, X. Yin, X. Zhang, *Nat Nano*, 10 (2015) 151-155.
- [23] RadisavljevicB, RadenovicA, BrivioJ, GiacomettiV, KisA, *Nat Nano*, 6 (2011) 147-150.
- [24] M.-L. Tsai, S.-H. Su, J.-K. Chang, D.-S. Tsai, C.-H. Chen, C.-I. Wu, L.-J. Li, L.-J. Chen, J.-H. He, *ACS Nano*, 8 (2014) 8317-8322.
- [25] M. Bernardi, M. Palummo, J.C. Grossman, *Nano Letters*, 13 (2013) 3664-3670.
- [26] C. Tsai, F. Abild-Pedersen, J.K. Nørskov, *Nano Letters*, 14 (2014) 1381-1387.
- [27] K.K. Tiong, T.S. Shou, *Journal of Physics: Condensed Matter*, 12 (2000) 5043.
- [28] J. Suh, T.-E. Park, D.-Y. Lin, D. Fu, J. Park, H.J. Jung, Y. Chen, C. Ko, C. Jang, Y. Sun, R. Sinclair, J. Chang, S. Tongay, J. Wu, *Nano Letters*, 14 (2014) 6976-6982.

- [29] Y.H. Huang, C.C. Peng, R.S. Chen, Y.S. Huang, C.H. Ho, *Applied Physics Letters*, 105 (2014) 093106.
- [30] D. Voiry, A. Mohite, M. Chhowalla, *Chemical Society Reviews*, 44 (2015) 2702-2712.
- [31] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science*, 306 (2004) 666-669.
- [32] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov, A.K. Geim, *Proceedings of the National Academy of Sciences of the United States of America*, 102 (2005) 10451-10453.
- [33] Y. Shi, C. Hamsen, X. Jia, K.K. Kim, A. Reina, M. Hofmann, A.L. Hsu, K. Zhang, H. Li, Z.-Y. Juang, M.S. Dresselhaus, L.-J. Li, J. Kong, *Nano Letters*, 10 (2010) 4134-4139.
- [34] H. Liu, Y. Du, Y. Deng, P.D. Ye, *Chemical Society Reviews*, 44 (2015) 2732-2743.
- [35] C. Tan, X. Qi, Z. Liu, F. Zhao, H. Li, X. Huang, L. Shi, B. Zheng, X. Zhang, L. Xie, Z. Tang, W. Huang, H. Zhang, *Journal of the American Chemical Society*, 137 (2015) 1565-1571.
- [36] G. Cunningham, M. Lotya, C.S. Cucinotta, S. Sanvito, S.D. Bergin, R. Menzel, M.S.P. Shaffer, J.N. Coleman, *ACS Nano*, 6 (2012) 3468-3480.
- [37] J.N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, U. Khan, K. Young, A. Gaucher, S. De, R.J. Smith, I.V. Shvets, S.K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G.T. Kim, G.S. Duesberg, T. Hallam, J.J. Boland, J.J. Wang, J.F. Donegan, J.C. Grunlan, G. Moriarty, A. Shmeliov, R.J. Nicholls, J.M. Perkins, E.M. Grieveson, K. Theuvsen, D.W. McComb, P.D. Nellist, V. Nicolosi, *Science*, 331 (2011) 568-571.
- [38] V. Nicolosi, M. Chhowalla, M.G. Kanatzidis, M.S. Strano, J.N. Coleman, *Science*, 340 (2013) 6139.
- [39] R.J. Smith, P.J. King, M. Lotya, C. Wirtz, U. Khan, S. De, A. O'Neill, G.S. Duesberg, J.C. Grunlan, G. Moriarty, J. Chen, J. Wang, A.I. Minett, V. Nicolosi, J.N. Coleman, *Advanced Materials*, 23 (2011) 3944-3948.
- [40] K.-G. Zhou, N.-N. Mao, H.-X. Wang, Y. Peng, H.-L. Zhang, *Angewandte Chemie International Edition*, 50 (2011) 10839-10842.
- [41] X. Zhang, Z. Lai, Z. Liu, C. Tan, Y. Huang, B. Li, M. Zhao, L. Xie, W. Huang, H. Zhang, *Angewandte Chemie International Edition*, 54 (2015) 5425-5428.
- [42] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, M. Chhowalla, *Nano Letters*, 11 (2011) 5111-5116.
- [43] J. Zheng, H. Zhang, S. Dong, Y. Liu, C. Tai Nai, H. Suk Shin, H. Young Jeong, B. Liu, K. Ping Loh, *Nat Commun*, 5 (2014) 2995.
- [44] Z. Zeng, T. Sun, J. Zhu, X. Huang, Z. Yin, G. Lu, Z. Fan, Q. Yan, H.H. Hng, H. Zhang, *Angewandte Chemie International Edition*, 51 (2012) 9052-9056.
- [45] Q. Ji, Y. Zhang, Y. Zhang, Z. Liu, *Chemical Society Reviews*, 44 (2015) 2587-2602.
- [46] Y. Shi, H. Li, J.I. Wong, X. Zhang, Y. Wang, H. Song, H.Y. Yang, *Sci. Rep.*, 5 (2015) 10378.
- [47] Y. Zhan, Z. Liu, S. Najmaei, P.M. Ajayan, J. Lou, *Small*, 8 (2012) 966-971.
- [48] Y.-C. Lin, W. Zhang, J.-K. Huang, K.-K. Liu, Y.-H. Lee, C.-T. Liang, C.-W. Chu, L.-J. Li, *Nanoscale*, 4 (2012) 6637-6641.
- [49] K.-K. Liu, W. Zhang, Y.-H. Lee, Y.-C. Lin, M.-T. Chang, C.-Y. Su, C.-S. Chang, H. Li, Y. Shi, H. Zhang, C.-S. Lai, L.-J. Li, *Nano Letters*, 12 (2012) 1538-1544.
- [50] S. Wu, C. Huang, G. Aivazian, J.S. Ross, D.H. Cobden, X. Xu, *ACS Nano*, 7 (2013) 2768-2772.

- [51] A. Ubaldini, J. Jacimovic, N. Ubrig, E. Giannini, *Crystal Growth & Design*, 13 (2013) 4453-4459.
- [52] A. Ubaldini, E. Giannini, *Journal of Crystal Growth*, 401 (2014) 878-882.
- [53] Y.-H. Lee, X.-Q. Zhang, W. Zhang, M.-T. Chang, C.-T. Lin, K.-D. Chang, Y.-C. Yu, J.T.-W. Wang, C.-S. Chang, L.-J. Li, T.-W. Lin, *Advanced Materials*, 24 (2012) 2320-2325.
- [54] Y.-H. Lee, L. Yu, H. Wang, W. Fang, X. Ling, Y. Shi, C.-T. Lin, J.-K. Huang, M.-T. Chang, C.-S. Chang, M. Dresselhaus, T. Palacios, L.-J. Li, J. Kong, *Nano Letters*, 13 (2013) 1852-1857.
- [55] X. Ling, Y.-H. Lee, Y. Lin, W. Fang, L. Yu, M.S. Dresselhaus, J. Kong, *Nano Letters*, 14 (2014) 464-472.
- [56] A.M. van der Zande, P.Y. Huang, D.A. Chenet, T.C. Berkelbach, Y. You, G.-H. Lee, T.F. Heinz, D.R. Reichman, D.A. Muller, J.C. Hone, *Nat Mater*, 12 (2013) 554-561.
- [57] S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B.I. Yakobson, J.-C. Idrobo, P.M. Ajayan, J. Lou, *Nat Mater*, 12 (2013) 754-759.
- [58] Y. Zhang, Y. Zhang, Q. Ji, J. Ju, H. Yuan, J. Shi, T. Gao, D. Ma, M. Liu, Y. Chen, X. Song, H.Y. Hwang, Y. Cui, Z. Liu, *ACS Nano*, 7 (2013) 8963-8971.
- [59] Y.-H. Chang, W. Zhang, Y. Zhu, Y. Han, J. Pu, J.-K. Chang, W.-T. Hsu, J.-K. Huang, C.-L. Hsu, M.-H. Chiu, T. Takenobu, H. Li, C.-I. Wu, W.-H. Chang, A.T.S. Wee, L.-J. Li, *ACS Nano*, 8 (2014) 8582-8590.
- [60] J.-K. Huang, J. Pu, C.-L. Hsu, M.-H. Chiu, Z.-Y. Juang, Y.-H. Chang, W.-H. Chang, Y. Iwasa, T. Takenobu, L.-J. Li, *ACS Nano*, 8 (2014) 923-930.
- [61] S.M. Eichfeld, L. Hossain, Y.-C. Lin, A.F. Piasecki, B. Kupp, A.G. Birdwell, R.A. Burke, N. Lu, X. Peng, J. Li, A. Azcatl, S. McDonnell, R.M. Wallace, M.J. Kim, T.S. Mayer, J.M. Redwing, J.A. Robinson, *ACS Nano*, 9 (2015) 2080-2087.
- [62] K. Kang, S. Xie, L. Huang, Y. Han, P.Y. Huang, K.F. Mak, C.-J. Kim, D. Muller, J. Park, *Nature*, 520 (2015) 656-660.
- [63] X. Wang, F. Xia, *Nat Mater*, 14 (2015) 264-265.
- [64] K. Roy, M. Padmanabhan, S. Goswami, T.P. Sai, G. Ramalingam, S. Raghavan, A. Ghosh, *Nat Nano*, 8 (2013) 826-830.
- [65] P.T.K. Loan, W. Zhang, C.-T. Lin, K.-H. Wei, L.-J. Li, C.-H. Chen, *Advanced Materials*, 26 (2014) 4838-4844.
- [66] W. Zhang, C.-P. Chuu, J.-K. Huang, C.-H. Chen, M.-L. Tsai, Y.-H. Chang, C.-T. Liang, Y.-Z. Chen, Y.-L. Chueh, J.-H. He, M.-Y. Chou, L.-J. Li, *Scientific Reports*, 4 (2014) 3826.
- [67] Y.-H. Chang, F.-Y. Wu, T.-Y. Chen, C.-L. Hsu, C.-H. Chen, F. Wiryo, K.-H. Wei, C.-Y. Chiang, L.-J. Li, *Small*, 10 (2014) 895-900.
- [68] Y. Shi, Y. Wang, J.I. Wong, A.Y.S. Tan, C.-L. Hsu, L.-J. Li, Y.-C. Lu, H.Y. Yang, *Sci. Rep.*, 3 (2013) 2169.
- [69] M.-H. Chiu, M.-Y. Li, W. Zhang, W.-T. Hsu, W.-H. Chang, M. Terrones, H. Terrones, L.-J. Li, *ACS Nano*, 8 (2014) 9649-9656.
- [70] Y.-C. Lin, C.-Y.S. Chang, R.K. Ghosh, J. Li, H. Zhu, R. Addou, B. Diaconescu, T. Ohta, X. Peng, N. Lu, M.J. Kim, J.T. Robinson, R.M. Wallace, T.S. Mayer, S. Datta, L.-J. Li, J.A. Robinson, *Nano Letters*, 14 (2014) 6936-6941.
- [71] Y.-C. Lin, R.K. Ghosh, R. Addou, N. Lu, S.M. Eichfeld, H. Zhu, M.-Y. Li, X. Peng, M.J. Kim, L.-J. Li, R.M. Wallace, S. Datta, J.A. Robinson, *Nat Commun*, 6 (2015).

- [72] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B.I. Yakobson, H. Terrones, M. Terrones, Beng K. Tay, J. Lou, S.T. Pantelides, Z. Liu, W. Zhou, P.M. Ajayan, *Nat Mater*, 13 (2014) 1135-1142.
- [73] X.-Q. Zhang, C.-H. Lin, Y.-W. Tseng, K.-H. Huang, Y.-H. Lee, *Nano Letters*, 15 (2015) 410-415.
- [74] X. Duan, C. Wang, J.C. Shaw, R. Cheng, Y. Chen, H. Li, X. Wu, Y. Tang, Q. Zhang, A. Pan, J. Jiang, R. Yu, Y. Huang, X. Duan, *Nat Nano*, 9 (2014) 1024-1030.
- [75] M.-Y. Li, Y. Shi, C.-C. Cheng, L.-S. Lu, Y.-C. Lin, H.-L. Tang, M.-L. Tsai, C.-W. Chu, K.-H. Wei, J.-H. He, W.-H. Chang, K. Suenaga, L.-J. Li, *Science*, 349 (2015) 524-528.
- [76] Z.L. Wang, G. Zhu, Y. Yang, S. Wang, C. Pan, *Materials Today*, 15 (2012) 532-543.
- [77] M.K. Gupta, J.-H. Lee, K.Y. Lee, S.-W. Kim, *ACS Nano*, 7 (2013) 8932-8939.
- [78] K.-H. Kim, B. Kumar, K.Y. Lee, H.-K. Park, J.-H. Lee, H.H. Lee, H. Jun, D. Lee, S.-W. Kim, *Sci. Rep.*, 3 (2013) 2017.
- [79] K.-A.N. Duerloo, M.T. Ong, E.J. Reed, *The Journal of Physical Chemistry Letters*, 3 (2012) 2871-2876.
- [80] M. Shanmugam, C.A. Durcan, B. Yu, *Nanoscale*, 4 (2012) 7399-7405.
- [81] M. Shanmugam, R. Jacobs-Gedrim, E.S. Song, B. Yu, *Nanoscale*, 6 (2014) 12682-12689.
- [82] A. Pospischil, M.M. Furchi, T. Mueller, *Nat Nano*, 9 (2014) 257-261.
- [83] M.M. Furchi, A. Pospischil, F. Libisch, J. Burgdörfer, T. Mueller, *Nano Letters*, 14 (2014) 4785-4791.
- [84] O. Lopez-Sanchez, E. Alarcon Llado, V. Koman, A. Fontcuberta i Morral, A. Radenovic, A. Kis, *ACS Nano*, 8 (2014) 3042-3048.
- [85] W. Liu, S. He, Y. Wang, Y. Dou, D. Pan, Y. Feng, G. Qian, J. Xu, S. Miao, *Electrochimica Acta*, 144 (2014) 119-126.
- [86] D. Song, M. Li, Y. Jiang, Z. Chen, F. Bai, Y. Li, B. Jiang, *Journal of Photochemistry and Photobiology A: Chemistry*, 279 (2014) 47-51.
- [87] W. Liu, S. He, T. Yang, Y. Feng, G. Qian, J. Xu, S. Miao, *Applied Surface Science*, 313 (2014) 498-503.
- [88] X. Gu, W. Cui, H. Li, Z. Wu, Z. Zeng, S.-T. Lee, H. Zhang, B. Sun, *Advanced Energy Materials*, 3 (2013) 1262-1268.
- [89] N.S. Kim, T. Austin, D. Baauw, T. Mudge, K. Flautner, J.S. Hu, M.J. Irwin, M. Kandemir, V. Narayanan, *Computer*, 36 (2003) 68-75.
- [90] H. Wang, L. Yu, Y.-H. Lee, Y. Shi, A. Hsu, M.L. Chin, L.-J. Li, M. Dubey, J. Kong, T. Palacios, *Nano Letters*, 12 (2012) 4674-4680.
- [91] W. Liu, J. Kang, D. Sarkar, Y. Khatami, D. Jena, K. Banerjee, *Nano Letters*, 13 (2013) 1983-1990.
- [92] M. Chhowalla, D. Voiry, J. Yang, H.S. Shin, K.P. Loh, *MRS Bulletin*, 40 (2015) 585-591.
- [93] R. Kappera, D. Voiry, S.E. Yalcin, W. Jen, M. Acerce, S. Torrel, B. Branch, S. Lei, W. Chen, S. Najmaei, J. Lou, P.M. Ajayan, G. Gupta, A.D. Mohite, M. Chhowalla, *APL Materials*, 2 (2014) 092516.
- [94] R. Kappera, D. Voiry, S.E. Yalcin, B. Branch, G. Gupta, A.D. Mohite, M. Chhowalla, *Nat Mater*, 13 (2014) 1128-1134.
- [95] S. Cho, S. Kim, J.H. Kim, J. Zhao, J. Seok, D.H. Keum, J. Baik, D.-H. Choe, K.J. Chang, K. Suenaga, S.W. Kim, Y.H. Lee, H. Yang, *Science*, 349 (2015) 625-628.
- [96] J.C. Park, S.J. Yun, H. Kim, J.-H. Park, S.H. Chae, S.-J. An, J.-G. Kim, S.M. Kim, K.K. Kim, Y.H. Lee, *ACS Nano*, 9 (2015) 6548-6554.

- [97] L. Tao, E. Cinquanta, D. Chiappe, C. Grazianetti, M. Fanciulli, M. Dubey, A. Molle, D. Akinwande, *Nat Nano*, 10 (2015) 227-231.
- [98] J. Kibsgaard, Z. Chen, B.N. Reinecke, T.F. Jaramillo, *Nat Mater*, 11 (2012) 963-969.
- [99] D. Voiry, H. Yamaguchi, J. Li, R. Silva, D.C.B. Alves, T. Fujita, M. Chen, T. Asefa, V.B. Shenoy, G. Eda, M. Chhowalla, *Nat Mater*, 12 (2013) 850-855.
- [100] D. Merki, S. Fierro, H. Vrubel, X. Hu, *Chemical Science*, 2 (2011) 1262-1267.
- [101] X. Hong, J. Liu, B. Zheng, X. Huang, X. Zhang, C. Tan, J. Chen, Z. Fan, H. Zhang, *Advanced Materials*, 26 (2014) 6250-6254.
- [102] X. Zheng, J. Xu, K. Yan, H. Wang, Z. Wang, S. Yang, *Chemistry of Materials*, 26 (2014) 2344-2353.
- [103] X. Huang, Z. Zeng, S. Bao, M. Wang, X. Qi, Z. Fan, H. Zhang, *Nat Commun*, 4 (2013) 1444.
- [104] Z. Zeng, C. Tan, X. Huang, S. Bao, H. Zhang, *Energy & Environmental Science*, 7 (2014) 797-803.
- [105] M. Acerce, D. Voiry, M. Chhowalla, *Nat Nano*, 10 (2015) 313-318.
- [106] H. Hwang, H. Kim, J. Cho, *Nano Letters*, 11 (2011) 4826-4830.

Figure. 1 Structure and preparative methods of transition metal dichalcogenides (TMDCs). (a) Structure of TMDCs. Reproduced with permission from Ref. [23] Copyright 2011 Nature Publishing Group. (b) Three main structural polytypes identified as one tetragonal (1T), two hexagonal (2H), and three rhombohedral (3R). Reproduced with permission from Ref. [2] Copyright 2012 Nature Publishing Group. (c) Chemical exfoliation process of TMDCs. Reproduced with permission from Ref. [43] Copyright Nature Publishing Group. (d) Chemical vapour deposition of TMDCs. Reproduced with permission from Ref. [1] Copyright 2014 Royal Society of Chemistry (e) Schematic illustration of two step synthesis of WSe_2 - MoS_2 heterostructure (left); optical and transmission electron microscopic images(right). Reproduced with permission from Ref. [75] Copyright 2015 American Association for the Advancement of Science.

Figure. 2 Piezoelectric behaviours of TMDCs. (a) Operation scheme of the single-layer MoS₂ piezoelectric device. Reproduced with permission from Ref. [8]. Copyright 2014 Nature Publishing Group. (b) Voltage and short-circuit current responses of a single-layer MoS₂ device under periodic strain in two different principal directions. Reproduced with permission from Ref. [8]. Copyright 2014 Nature Publishing Group. (c) Evolution of the piezoelectric outputs with increasing number of atomic layers. Reproduced with permission from Ref. [8]. Copyright 2014 Nature Publishing Group. (d) Optical image of multiple electrode pairs integrated on a long stripe of MoS₂, rotated by 10 ° at each section (left). Measured piezoelectric coupling strength as a function of rotation of the crystal with respect to the electric field and mechanical boundary, where inset shows the definition of θ achieved by patterning the electrodes at different angles. Reproduced with permission from Ref. [22]. Copyright 2014 Nature Publishing Group. (e) and (f) show the I-V characteristics of the MoS₂ device at different applied forces under compressive and tensile strain respectively. Reproduced with permission from Ref. [21]. Copyright 2015 Nature Publishing Group.

Figure. 3 Electrical device structures and electrical performances. (a) Three dimensional schematic view of MoS₂ transistor with the high- κ material as dielectrics. Reproduced with permission from Ref. [23]. Copyright 2011 Nature Publishing Group. (b) Top figure shows the optical image of the ring oscillator fabricated on a bilayer MoS₂ thin film, and the schematic of the electronic circuit of the five-stage ring oscillator. Bottom figure shows optical micrograph of the NAND gate and the SRAM fabricated on bilayer MoS₂ thin film. The corresponding schematics of the electronic circuits for the NAND gate and SRAM are also shown. Reprinted with permission from Ref. [90]. Copyright 2012 American Chemical Society. (c) Transfer characteristics of back-gated monolayer WSe₂ transistors with Ti, In, and Ag electrodes respectively. Reprinted with permission from Ref. [91]. Copyright 2013 American Chemical Society.

Figure 4. TMDC application in the field of hydrogen generation via electrochemical water splitting. (a) Schematic illustration of solvothermal synthesis of MoS₂/graphene hybrids for hydrogen evolution reaction. Reprinted with permission from Ref. [13]. Copyright 2011 American Chemical Society. (b) Atomic force microscope image of individual exfoliated WS₂, scale bar 500 nm (top left) and high-resolution scanning transmission electron microscope image of the as-exfoliated WS₂ monolayer with 1T superlattice. Inset shows the strain tensor map (bottom left). Reproduced with permission from Ref. [99]. Copyright 2013 Nature Publishing Group. (c) Polarization curves of bulk and as-exfoliated WS₂ (1T phase), and WS₂ after annealing at 300 °C (2H phase) along with Pt nanoparticles for comparison. Reproduced with permission from Ref. [99]. Copyright 2013 Nature Publishing Group.

Graphical Abstract:

The structure characterizations and preparative methods of 2D TMDCs have obtained significant progresses. Their recent advances for nano energy generation, solar harvesting, conversion and storage, and green electronics are reviewed.

- The unique structure and properties of two-dimensional transition metal dichalcogenides (TMDC) are discussed for energy applications.
- Energy applications such as piezoelectric-based energy generators, solar energy harvesting, conversion and storage, green electronics and catalysis for hydrogen generation are reviewed in details.
- Perspectives on future development of TMDCs in energy applications are presented.

Accepted manuscript