Two-dimensional layered MoS$_2$: rational design, properties and electrochemical applications†

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The layered molybdenum chalcogenide MoS$_2$ has attracted wide attention due to its potential electrochemical applications. Based on its unique physical and chemical properties, numerous advances have shown that nanostructured MoS$_2$, with the advantages of low cost and outstanding properties, is a promising candidate for environmentally benign energy conversion and storage (ECS) devices. Nowadays, in order to lessen the reliance on fossil fuels, the production of hydrogen from water splitting has become an important issue. Hence, developing catalysts composed of earth-abundant elements that possess activities comparable to those of noble metals is of great urgency. According to DFT calculations in terms of HER free-energy diagrams, MoS$_2$ could be used as an effective substitute for noble metals. Meanwhile, MoS$_2$ with various structures has also been applied in the field of energy storage, including batteries and supercapacitors. Additionally, due to their layer-dependent electrical properties, MoS$_2$-based electrochemical devices have been applied as sensors for a variety of chemicals. In this review, we summarize recent advances in the development of MoS$_2$ with high-performance in various electrochemical domains, and recent progress in discovering the mechanisms underlying the enhanced activity. Moreover, we summarize the critical obstacles facing MoS$_2$, and discuss strategies for further improving its activity. Lastly, we offer some suggestions on the pathways toward achieving high performance competitive with noble metal counterparts, and perspectives on practical applications of MoS$_2$ in the future.

Broader context

The development of inexhaustible and clean energy technologies has far-reaching benefits for our society. Owing to its high anisotropy and unique crystal structure, the attractive properties of 2D molybdenum disulfide (MoS$_2$) can be utilized in a variety of energy conversion and storage (ECS) applications. Therefore, understanding how these properties can be tuned and the tunable properties can be utilized becomes increasingly important. In this review, we first summarize recent synthetic strategies toward preparation of MoS$_2$ with different structures, and its role in several important renewable energy technologies. We then discuss the relationship between the tuned properties and the performance of MoS$_2$ in different applications, emerging trends during their development, and challenges facing them, offering our perspectives on how to effectively advance the development of MoS$_2$-based devices.

1. Introduction

The production of energy is currently the most important issue for society. Development of inexhaustible and clean energy technologies will have far-reaching long-term benefits. It will increase countries’ energy security via reliance on an indigenous and inexhaustible resource, and thereby enhance sustainability and reduce pollution. Thus, it is of great significance to develop highly efficient and environmentally benign energy conversion and storage (ECS) devices, including fuel cells, solar cells, water-splitting cells, batteries, and supercapacitors. The performance of these devices depends on the properties of the materials used. Therefore, breakthroughs in the field of nanomaterial chemistry are believed to be pivotal to the development of highly efficient ECS devices.

Molybdenum disulfide (MoS$_2$), a type of layered transition-metal dichalcogenide, has been widely applied in the field of catalysis and as a material in ECS devices, such as batteries, photovoltaics, and electronic transistors. The transition metals have different numbers of d-electrons, filling up d bands...
to different levels, resulting in varying electronic properties.\textsuperscript{13,14} This range of properties make possible the development of MoS\textsubscript{2} electronic and optoelectronic devices, and the applications of MoS\textsubscript{2} in catalysis.\textsuperscript{15} In MoS\textsubscript{2} crystals, layers of Mo in a hexagonal array are sandwiched between S layers. Strong covalent bonding characterizes the Mo–S interactions, while the interactions between S layers are van der Waals interactions along the \textit{z} axis to form the bulk material. Due to its high anisotropy and unique crystal structure, the properties of 2D MoS\textsubscript{2} can be tuned \textit{via} reducing dimensions, intercalation, and formation of heterostructures.\textsuperscript{16}

As a well-known hydro-desulfurization catalyst,\textsuperscript{17} MoS\textsubscript{2} has been considered as an ideal catalyst for the electrocatalytic hydrogen evolution reaction (HER) according to computational and experimental studies.\textsuperscript{18} Hydrogen, an ideal energy carrier, plays a significant role in future technologies.\textsuperscript{19,20} The DFT calculations in terms of the HER free-energy diagram predict that only the S–Mo–S edges in MoS\textsubscript{2} sheets are active for hydrogen atom adsorption, and the [10\textit{t}0] Mo edges are mainly responsible for bringing about a favorable free energy change for hydrogen atom adsorption, which is very close to that observed on state-of-the-art Pt surfaces.\textsuperscript{21} Therefore, increasing the number of active edge sites in MoS\textsubscript{2} by modifying the atomic structure, or by changing the electronic structure of the system to increase the enthalpy of hydrogen adsorption, or by incorporating the sheets into conducting nano- or micro-sized templates has remained an important issue for efficient hydrogen production.\textsuperscript{22–28} In addition, energy storage is another important technological and scientific problem that has global implications for humanity. MoS\textsubscript{3}, with a capacity three and half times higher than that of commercial graphite anodes (372 mAh g\textsuperscript{-1}),\textsuperscript{29} is becoming the subject of significant attention as a battery anode material. Generally, compared to other materials, MoS\textsubscript{2} displays much better capability and its lower rates of cycling induced degradation,\textsuperscript{30} and the less volumetric expansion upon lithiation is an attractive advantage. Moreover, 2D MoS\textsubscript{2}-based structures have also been widely applied in many other domains (Scheme 1), such as photocatalysis,\textsuperscript{31,32} sensing,\textsuperscript{33–36} and dielectric applications.\textsuperscript{37}

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{Scheme1.png}
\caption{Illustration of the nanostructured MoS\textsubscript{2} materials and their potential applications in various domains.}
\end{scheme}
Although there are already a number of excellent reviews on the attractive properties of MoS$_2$, understanding how these properties can be tuned and the tunable properties can be utilized becomes increasingly important. In this review, we first summarize the recent synthetic strategies towards preparation of MoS$_2$ with different nanostructures. Then, the tuning of MoS$_2$ structures through physical and chemical methods and optimization of properties are focused on. Following that, the relationships between the tuned properties and the performance of MoS$_2$ in different applications are elucidated. Finally, a perspective on major challenges and opportunities facing MoS$_2$ materials will be proposed.

2. Preparation methods for MoS$_2$

In order to enhance desired properties, the selection of an effective fabrication method should be the first and pivotal step. Numerous methods have been employed to prepare MoS$_2$, in order to optimize its properties and achieve the superior performance. Examples of materials prepared from a top-down approach have been based on the exfoliation of bulk MoS$_2$, such as mechanical cleavage, chemical intercalation followed by exfoliation, liquid phase exfoliation by direct sonication, and laser thinning techniques. Meanwhile, examples of bottom-up approaches are CVD growth and chemical synthesis.

2.1 Top-down methods

MoS$_2$ nanosheets containing tens to hundreds of crystal 2D layers can be achieved via mechanical cleavage from the bulk MoS$_2$. Novoselov et al. successfully applied this method to prepare single-layer MoS$_2$ from the bulk. After a fresh surface of a layered bulk crystal was rubbed against a Si/SiO$_2$ surface, flakes with various thicknesses of MoS$_2$ were detached and adsorbed onto the target surface. Single-layer MoS$_2$ sheets could be further obtained from the thicker flakes, which was confirmed by scanning electron microscopy (SEM). The mechanical cleavage for the preparation of nanosheets has been applied to obtain pristine 2D MoS$_2$ with high quality (Fig. 1A). Meanwhile, the as-obtained nanosheets can be utilized for the study of the properties and fabrication of electronic devices.

Although mechanical cleavage can produce 2D MoS$_2$ with high quality, low throughput limits this method in practical applications. To obtain the large quantities of single-layer MoS$_2$ sheets, the solution-based exfoliation methods are often used. Recently, some research groups have developed chemical or electrochemical Li-intercalation and exfoliation intercalation methods to produce MoS$_2$ nanosheets. In order to ameliorate the experimental conditions necessary for the chemical Li-intercalation (high temperature or long reaction time), an electrochemical Li-intercalation method was developed (Fig. 1B). The process was utilized in a Li-ion battery configuration comprised by using bulk MoS$_2$ as the cathode and lithium foil as the anode. In this system, the amount of inserted lithium can be adjusted by the discharge curve, leading to effective Li-insertion, thereby achieving the sufficient Li-intercalation. After discharge, Li$_x$MoS$_2$ was sonicated in water or ethanol. The reaction between lithium and solution generated H$_2$ gas, which exfoliated MoS$_2$ layers effectively. Under agitation, well-dispersed MoS$_2$ nanosheets were finally obtained (Fig. 1C).

For reliable and scaled-up production of atomically thin MoS$_2$ nanosheets, some studies demonstrated that the exfoliation process can be achieved by sonication of the bulk in various liquid phases, such as N-methylpyrrolidone, dimethyl-formamide, or a mixture of ethanol and water. These liquid phases can not only exfoliate MoS$_2$ but also stabilize the nanosheets to some given extent due to their effect on the surface energy. In addition, liquid-phase exfoliation has been extended to the application of surfactant-containing solutions. Accordingly, these methods hold great promise for scaled-up production of layered MoS$_2$ in environmentally benign solutions. Recently, by using bovine serum albumin (BSA) as an exfoliating agent, Guan and his coworkers demonstrated a layer-by-layer exfoliation route to produce layered MoS$_2$ nanosheets with high yield in aqueous...
solution (Fig. 1D).\textsuperscript{57} In contrast to earlier liquid-phase exfoliation methods, single-layer nanosheets with high dispersion were achieved due to the strong binding of BSA (Fig. 1E). Due to the strong binding of the chemical ligands in solutions, the chemical exfoliations produced highly dispersed single-layer MoS\textsubscript{2} nanosheets, which provide the significance platform to study some deep-seated properties and thereby exploiting the novel applications.

2.2 Bottom-up approach

Because of the violent nature of the chemical exfoliation, the crystal structure becomes deformed. However, large-area MoS\textsubscript{2} with mono- or several-layer structures can be prepared by using the chemical vapor deposition (CVD) method. Compared with chemical exfoliation, the CVD method is more efficient in growing MoS\textsubscript{2} monolayer films on substrates (SiO\textsubscript{2}/Si\textsuperscript{58} or Au\textsuperscript{59}), with high quality and controllable thickness.\textsuperscript{4,40} Moreover, the formation of the continuous MoS\textsubscript{2} films by CVD is compatible with the current electronic fabrication processes, making this a promising candidate for building atomically thin layered electrical,\textsuperscript{61} photovoltaic,\textsuperscript{62} optical\textsuperscript{63} or HER\textsuperscript{64} devices.

A two-step thermolysis process was recently reported for deposition of ultrathin MoS\textsubscript{2} nanosheets by dip-coating of ammonium thiomolybdates on Si/SiO\textsubscript{2} foils and converting the films to MoS\textsubscript{2} by annealing at 500 °C followed by sulfurization at 1000 °C under sulfur vapor (Fig. 2A). The chemical reaction resulted in the formation of MoS\textsubscript{2} layers. The second step at 1000 °C was required to enhance the crystallinity. Typically, MoO\textsubscript{3} and sulfur powders are used as precursors for deposition of MoS\textsubscript{2} films on acetone and isopropanol-cleaned Si/SiO\textsubscript{2} foils. Upon heating, the reaction of volatile suboxides (MoO\textsubscript{3-x}) with the sulfur vapor gave MoS\textsubscript{2} layers on the substrate. Using refined CVD, crystalline islands of monolayer molybdenum disulphide with high carrier mobility were grown up to 120 μm lateral size, which had the potential to provide superior optical or electrical properties to those of exfoliated samples.\textsuperscript{61} Moreover, some deep insights into the relationship between the lattice orientation, edge morphology and crystallinity and island shape were also provided by transmission electron microscopy. To obtain MoS\textsubscript{2} with high conductivity, Shi et al. also selected MoO\textsubscript{3} and sulfur powders as precursors for deposition of MoS\textsubscript{2} films on Au foils by the low pressure chemical vapor deposition (LPCVD) method (Fig. 2B).\textsuperscript{64}

Continuous films of MoS\textsubscript{2} samples, containing single- to few-layers, with tunable lateral sizes can be obtained. The sample can be transferred onto substrates like SiO\textsubscript{2}/Si and quartz for a variety of applications. In consideration of its characteristics of atomic flatness and hexagonally arranged in-plane lattice, mica would be a suitable substrate for the growth of materials with the same symmetry. The lattice symmetry of mica well-matched with MoS\textsubscript{2}, so that epitaxial growth monolayer MoS\textsubscript{2} could be predicted. Accordingly, Ji et al. have applied the LPCVD process to controllably synthesize centimeter-scale uniform monolayer MoS\textsubscript{2} on one type of mica (KMg\textsubscript{3}AlSi\textsubscript{3}O\textsubscript{10}F\textsubscript{2}).\textsuperscript{58} In addition to the use of various substrates, other researchers have explored different Mo and S precursors as an effective pathway for the fabrication of MoS\textsubscript{2} with better properties, such as direct deposition of sulfur vapor onto the Mo film.\textsuperscript{65} The size and thickness of the Mo film determined the size and thickness of the resulting MoS\textsubscript{2} film, making this synthesis process highly scalable.

Meanwhile, wet chemical synthesis is another common bottom-up method for preparing MoS\textsubscript{2}, e.g., hydrothermal and solvothermal reactions.\textsuperscript{24,64-70} Typically, (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}·4H\textsubscript{2}O and thiourea have been utilized as the precursors for the Mo and S elements in hydrothermal reactions. After reaction in a Teflon-lined stainless steel autoclave, the low-quality MoS\textsubscript{2} flakes with abundant active sites are obtained (Fig. 2C). These visible internal edges (tears, pinholes and defects) benefit its electrocatalysis performance.

3. Properties of MoS\textsubscript{2}

3.1 Crystal properties

 Naturally, MoS\textsubscript{2} can form a phase with trigonal prismatic or an octahedral Mo coordination. 2H and 3R MoS\textsubscript{2} both correspond to trigonal prismatic coordination.\textsuperscript{72,74} The 2H type, which is dominant and more stable in nature, has two layers per unit cell stacked in the hexagonal symmetry. The 3R-type has three layers per cell in rhombohedral symmetry, and is unstable and easily transforms to 2H upon heating. In most studies, MoS\textsubscript{2}
with 2H crystal structure has been used as a precursor to prepare mono- or few-layer MoS2 nanosheets. Meanwhile, the shift of one of the sulfur layers leads to an AbC stacking sequence, resulting in the generation of the 1T crystal phase, which has trigonal symmetry and corresponds to octahedral coordination of the metal atoms (Fig. 3A).

Generally, the filling of Mo d orbitals is directly influenced by the structure of MoS2. For the trigonal prismatic phase (2H), the d orbital splits into three degenerate states with an energy gap of 1 eV, while the d orbitals degenerate into other forms of orbitals in the tetragonal symmetry of the 1T phase, and up to six electrons can fill the e2g orbital.74 As shown in Fig. 3B, because the p orbitals of sulfur are at much lower energy than the Fermi level, the filling of d orbitals determines the nature of the different phases in MoS2 compounds. Complete filling of orbitals gives rise to semiconducting behavior (2H) while partial filling results in metallic behavior (1T).75 Thus, as orbital occupation varies, the electronic properties of MoS2 change, thereby the properties can be further extended. In contrast to the 2D MoS2 nanosheets obtained from mechanical exfoliation, the coexistence of the metallic and semiconducting phases has been reported in chemically exfoliated MoS2 by Eda and colleagues.76 By combining the results of X-ray photoelectron spectroscopy (XPS) and scanning TEM (STEM), mixtures of 2H and 1T phases in single-layer MoS2 were identified (Fig. 4A). Furthermore, the dynamic process of the transformation between 2H and 1T phases involving intralayer atomic plane gliding has been experimentally proven by...
using an aberration-corrected STEM. The dynamic process of the atomic motions was visualized in the single-layered MoS2. In addition to the glide of the sulfur plane, the phase transformation in the MoS2 sheet involves atomic displacements (Fig. 4B). The atomic process of phase transitions involves 2H–1T, 1T–2H, 2H–2H' and 1T–1T' phase transitions, and the transitions are composed of three elemental steps: (i) formation of the γ-phase as a precursor or an intermediate state, and (ii and iii) migration of the β and γ boundaries.

MoS2 samples with mixture 2H/1T phases can also be achieved via a facile chemical reaction, and the synergistic effect of the metallic and semiconducting properties can be utilized. The 1T phase was reported to be formed by transformation of 2H-MoS2 by Li and K intercalation. In addition, a strategy for the incorporation of the 1T phase into the 2H phase was recently reported involving a two-step wet chemical synthesis (Fig. 4C). After introduction of sulfur vacancies in the 2H-MoS2 nanosheet host during the solvothermal reaction, the transformation of the surrounding 2H-MoS2 local lattice into a trigonal (1T) phase was prompted. The result not only induces robust room-temperature ferromagnetism in a nonmagnetic form of MoS2, but also enhances the electron carrier concentration by an order of magnitude.

3.2 Electronic and optical structures

The band structures of MoS2 materials can be calculated based on density functional theory (DFT). When the bulk is reduced to a single layer, it had been predicted that an indirect to direct bandgap transition would occur in the d-electron system. Bulk MoS2 is an indirect-gap semiconductor having a bandgap of about 1 eV, with a valence band maximum (VBM) at the Γ point and a conduction band minimum (CBM) at the Γ-point along Γ–K symmetry lines (Fig. 5A), while the monolayer form is a direct-gap semiconductor with VBM and CBM coinciding at the K-point. Splendiani et al. reported on the thickness-dependent physical properties of MoS2. Combined with optical absorption, photoluminescence (PL), and photoconductivity, the evolution of electronic structure and the resulting optical properties of ultrathin MoS2 crystals were observed as a function of the number of layer numbers. The crossover from an indirect gap material to a direct gap material accounted for the enhancement of luminescence in the MoS2 monolayer. The observed dependence of the bandgap on the layer number was in agreement with band calculations. Furthermore, the bandgap transition was derived from quantum confinement effects, resulting in pronounced differences in the emissions from photo-excitation in the bulk and monolayer material. As depicted in Fig. 5C, the bulk showed negligible photoluminescence, while thinner exhibited much stronger PL signals.

Raman scattering is ultrasensitive to the number of layers in these materials. Thus, Raman spectroscopy serves as an essential tool for studying the structure and electronic properties of 2D MoS2. Theoretical calculations predicted four first-order Raman active modes for crystalline MoS2. The E2g mode, an interlayer mode, with a Raman shift at 32 cm⁻¹ is derived from the vibration of two rigid layers. The other three Raman active modes were mainly induced by the intralayer atomic vibrations. In contrast to the in-plane vibration modes (E1g or E2g), the A1g mode is an out-of-plane vibration mode. Lee et al. applied Raman scattering for the MoS2 nanosheets with various thicknesses. The frequency, intensity, and width of the peaks of in-plane E1g and out-of-plane A1g vibrations were found to be strongly dependent on the number of layers. With decreasing numbers of MoS2 layers, the E1g mode shows a red-shift of 2 cm⁻¹, while the A1g mode is blue-shifted by 4 cm⁻¹ (Fig. 5D), which is attributed to Columbic interactions and possible stacking-induced changes in the intra-layer bonding. The line width of the A1g mode achieved a peak value for the two-layered MoS2 nanosheets, whereas that of the E2g mode does not depend on the thickness. Meanwhile, a large frequency shift of the shear mode to higher wave numbers was found in MoS2 flakes with high numbers of layers.

4. Applications

4.1 Energy conversion from electrocatalysis

The progress achieved in MoS2 electrocatalysts for HER provides a great opportunity for ameliorating the energy crisis. In this work, fundamental mechanistic studies on the molecular systems, supported by theory and DFT calculations, led to the identification of MoS2 as a potential substitute for noble metal catalysts (Pt/C). Theoretical studies have identified the edges of MoS2 as active sites for HER electro-catalysis, and these results were further confirmed by combination of the layered structure.
vertically aligned layers. The structure predominantly exposes catalytic points, which are especially prevalent in 2D MoS$_2$ activity, it is important to expose large numbers of these centers for HER, in sharp contrast to HER-inert terrace sites. Additionally, these edge sites of MoS$_2$ have been demonstrated to possess metallic electronic states. Importantly, the edge sites of MoS$_2$ have been demonstrated to be active catalytic centers for HER, in sharp contrast to HER-inert terrace sites. Therefore, in order to design MoS$_2$ with the superior HER activity, it is important to expose large numbers of these catalytic points, which are especially prevalent in 2D MoS$_2$ nanosheets, indicating the potential for favorable HER performance with these 2D structures. However, due to its highly anisotropic character, the original 2D structure naturally converts to 3D along specific directions of the structure with formation of various morphologies, such as nanoplates, nanoribbons, or nanoparticles.

### 4.1.1 Tuning the active sites

To preserve these active sites as much as possible, Cui’s group synthesized MoS$_2$ films with vertically aligned layers. The structure predominantly exposes the edges of the layers, exposing the edges on the film surface maximally (Fig. 6E). TEM images show the presence of densely packed, stripe-like grains, which indicates that the layers are all vertically aligned on the substrate. The edge-terminated surface is considered to be thermodynamically unstable due to the large surface energy of the edges, while a metastable morphology is likely to be obtained by kinetically overcoming the free energy barrier through rapid sulfuration. Furthermore, reducing the size of the bulk MoS$_2$ material into nanostructured particles is another effective pathway toward maximizing exposure of active edge sites. Nanostructured MoS$_2$ with large surface curvature induces a high surface energy to enhance the number of exposed edges. Dai’s group developed a selective solvothermal synthesis of MoS$_2$ nanoparticles on reduced graphene oxide (RGO) sheets (Fig. 6F). According to the X-ray diffraction (XRD) pattern, the broad diffraction peaks indicated that nanosized MoS$_2$ crystal domains with hexagonal structure were anchored on the RGO nanosheets. Furthermore, with RGO severing as a frame, the nanostructured MoS$_2$ was maintained with an abundance of exposed edges. Similarly, MoS$_2$ nanoparticles anchored on a 3D carbon fiber paper (CFP) substrate were successfully synthesized through pyrolysis and sulfuration methods. As shown in Fig. 6G, smaller nanoparticles bonded to the surface of the CFP, and the large surface curvature helps to expose more active sites and enhances the activity of the catalytic centers.

Additionally, some effective synthetic strategies have been utilized to extend the active edge sites in order to increase catalytic activity. As observed in Fig. 7A, a facile method was applied for the synthesis of large-area contiguous thin films of an ordered mesoporous architecture of MoS$_2$ with a tunable film thickness exhibiting excellent catalytic activity for HER. By controlling the morphology, the surface structure of the catalyst was engineered at the atomic scale, enabling the active sites MoS$_2$ to be extensively exposed. Moreover, chemical exfoliation was an alternative effective pathway for MoS$_2$, with a large number of active sites. Interestingly, simultaneous conversion of the 2H to 1T polymorph was achieved during the process, which increased the electric conductivity of the layered MoS$_2$. Chhowalla’s group applied chemical exfoliation of intercalated MoS$_2$ prepared using butyllithium, for the preparation of MoS$_2$ with different crystal phases, and some deep insights into the mechanisms responsible for HER were provided (Fig. 7B). MoS$_2$ nanosheets with high concentration of metallic 1T phases exhibited superior HER electrocatalytic performance, whose formation was catalyzed by Li$^+$ during the synthesis process. To identify active sites in 2D mixed-phase MoS$_2$ sheets, the active edges in 2H or 1T MoS$_2$ nanosheets were chemically oxidized. The electrochemical oxidation led to a reduction in the HER for the 2H nanosheets, while unaffected catalytic performance was observed in chemical oxidation of the 1T phase, implying that the basal plane was catalytically active for HER performance. Furthermore, the catalytic activity of the 2H phase could be improved by increasing its conductivity through doping with metallic SWNTs, suggesting that charge transfer kinetics in metallic MoS$_2$ was another key parameter for achieving superior HER performance.

**Fig. 6** (A–C) A series of STM images of MoS$_2$ nanoparticles on Au (111): (A) low coverage (0.06 nm$^2$ MoS$_2$ per nm$^2$ geom.), annealed at 400°C (470 Å by 470 Å, 1.2 nA, 4 mV). (B) High coverage (0.23 nm$^2$ MoS$_2$ per nm$^2$ geom.), annealed to 550°C (470 Å by 470 Å, 1.2 nA, 19 V). (C) Atomically resolved MoS$_2$ particle, from a sample annealed to 550°C, showing the predominance of the sulfided Mo-edge. (D) Exchange current density versus (left) MoS$_2$ area coverage and (right) MoS$_2$ edge length. Copyright 2007, the American Association for the Advancement of Science. (E) Layered crystal structure of molybdenum chalcogenide with individual S–Mo–S layers stacked along the c-axis by weak van der Waals interaction. Copyright 2013, American Chemical Society. (F) MoS$_2$ nanoparticles on graphene in the MoS$_2$/RGO hybrid. Copyright 2011, American Chemical Society. (G) SEM images of the as-grown materials on the carbon fiber paper (CFP). Copyright 2013, American Chemical Society.
In addition to chemical exfoliation, CVD methods have been applied to prepare the mixed-phase MoS$_2$. As shown in Fig. 7C, low overpotentials (187 mV) requiring an electrocatalytic current density of 10 mA cm$^{-2}$ and a reduced Tafel slope (43 mV decade$^{-1}$) were observed in the HER process. According to structural characterization along with electrochemical studies, it is reasonable to speculate that MoS$_2$ with the 1T phase exhibited some superior characteristics for boosting electrocatalytic HER performance, such as facile electrode kinetics, low-loss electrical transport, and an increased density of active sites for catalysis. Hence, the distinct features of the 1T phase endowed the MoS$_2$ with highly competitive properties compared to existing HER catalysts. Therefore, in order to increase HER performance, simultaneous optimization of both active sites and electronic conductivity for MoS$_2$ electrocatalysts should be the most effective path. However, due to the contradictory relationship between active sites and conductivity, this situation cannot be easily achieved. As mentioned above, abundant active sites are prone to appear in these small MoS$_2$ nanostructures with large numbers of active sites, but the conductivity in such structures is hindered due to the poor electron transport. Recently, Xie’s group reported a facile hydrothermal method to fabricate defect-rich MoS$_2$ nanosheets with exposure of active edges. According to theoretical simulation, the formation of the nanodomains with quasi-periodic arrangement along MoS$_2$ nanosheets greatly promotes the conductivity of MoS$_2$, providing an opportunity for the coordination of the high conductivity with a high number of active sites for MoS$_2$ catalysts. According to theoretical calculations, the degree of disorder in oxygen-incorporated MoS$_2$ ultrathin nanosheets can be regulated to obtain the balance between the active sites and conductivity, thereby providing synergistic structure and electronic modulations for high HER performance (Fig. 7D).
ratio of Mo:S in the samples was determined through compositional analysis and found to vary from 1:2.02 to 1:2.10; this confirmed that the degree of disorder was dependent on the unsaturated sulfur atoms. Moreover, according to the results of EIS, the high concentration of effective active sites and high conductivity in the nano-sheet determined the HER activity. In the oxygen incorporated MoS2 nanosheets, a large cathodic current density of 126.5 mA cm⁻² at 300 mV with the Tafel slope of 53 mV decade⁻¹ was achieved.

4.1.2 Composite materials. As is well known, conductivity plays the key role in the performance of high-activity electrocatalysts. The poor conductivity of MoS2 can be ameliorated by the preparation of composites containing conductive additives.⁹⁸–¹⁰¹ Tsai and his coworkers have applied DFT to predict the support effects for MoS2 with different catalyst supports on the hydrogen adsorption free energy at the MoS2 Mo-edge and S-edge sites. They concluded that a general trend for the Mo-edge sites could be seen, and that stronger adhesion of the MoS2 catalyst onto the support led to weaker hydrogen binding. The results suggested that the support was crucial for determining the HER activity of supported MoS2 and the catalytic activity at the Mo-edge could be optimally tuned (Fig. 8A). Furthermore, the direct anchoring of MoS2 to a support with robust conductivity ensured a low resistance electrical transport pathway as well as reduced physical delamination, which enhanced its stability. Au foil was applied as the conductive support for preparation of MoS2 nanosheets through a LPCVD route.⁶⁴ The MoS2 composite, synthesized at low growth temperature with high crystal quality, monolayer thickness, tunable size, and transferability to other substrates, has the potential for applications in high HER performance electrocatalysis. A rather low Tafel slope (61 mV decade⁻¹) and a relatively high exchange current density of 38.1 μA cm⁻² were achieved (Fig. 8B). The superior HER performance was derived from electron coupling between MoS2 and Au foils. Similar support effects have been clearly demonstrated for MoS2 nanoparticles synthesized on RGO, as observed in Fig. 8C, the obtained catalyst exhibited enhanced intrinsic electrocatalytic performance toward HER compared to unsupported MoS2 particles.

The MoS2 nanoparticles on RGO sheets were obtained via a facile solvothermal approach. With its high density of exposed edges and excellent electrical coupling to the underlying conductive graphene, the MoS2/RGO hybrid material exhibited excellent HER activity with a small overpotential of ~100 mV, large cathodic currents, and a Tafel slope as small as 41 mV decade⁻¹. Thus, the approach of carrying out materials synthesis on RGO has led to an advanced MoS2 electrocatalyst with highly HER performance. Similarly, carbon nanotubes (CNTs) were also utilized as the conductive support, and a MoS2/NCNT forest catalyst was fabricated via a low-temperature precursor decomposition method.¹⁰² As depicted in Fig. 8D, the hybrid catalytic had a morphology consisting of an electro-conductive N-doped CNT forest densely coated with ~2 nm scale amorphous MoS2 catalysts. In the hybrid structure, the protonated N showed greatly improved surface energy and can not only provide favorable reaction affinity toward MoS2 precursors, avoiding the need for an adhesive layer, but also provide additional electrons to the graphitic carbon to maintain high conductivity.¹⁰³ The catalyst exhibited outstanding HER catalytic activity with an overpotential of 75 mV. In addition, only a minor deterioration of the current was observed after 1000 cycles. As for practical applications, the fabrication of MoS2 on CFP was also reported via a pyrolytic synthesis using MoO3 NPs.¹⁰⁴ MoS2 NPs with a diameter of 30 nm were obtained by a rapid sulfurization process, the scheme of which is depicted in Fig. 8E. To further enhance the HER performance of as-grown 2H MoS2, the catalyst was treated electrochemically with Li for layer exfoliation and 1T phase formation. Therefore, this system combined a high concentration of exposed edges, protected by the CFP, and the 1T phase, generated by Li electrochemical treatment. The achievement of 200 mA cm⁻² current at 200 mV overpotential and long-term stability promise high potential for practical applications.

Besides the application of supports with high conductivity, the utilization of materials with electrocatalytic HER activity as substrates is an effective alternative method. Yu’s group anchored MoS2 onto the CoSe2 nanobelts by using a solvothermal process (Fig. 9A).⁷⁶ As observed in the HRTEM images in Fig. 9B, layered MoS2 nanosheets, with an interlayer separation of 0.63 nm, were grown on CoSe2. The anchoring of MoS2 on CoSe2 generated more active edge sites. Meanwhile, CoSe2 chemically interacts with MoS2 by the formation of S-Co bonds, which can further improve the HER activity of MoS2. This is because Co, as a first-row transition metal ion, can promote the HER activity of MoS2 by coupling with the S-edges to lower ΔG_H from 0.18 to 0.10 eV to afford faster proton adsorption kinetics.¹⁰⁵,¹⁰⁶ Therefore, in this hybrid catalyst, the CoSe2 nanobelts can not only couple with MoS2 to promote the HER activity, but also serve as an effective substrate for mediating the growth of MoS2 to form more active HER sites. The MoS2/CoSe2 catalyst showed exceptional HER catalytic properties in an acidic electrolyte with an onset potential of a mere ~11 mV, a small Tafel slope of 36 mV decade⁻¹ and high exchange current density (Fig. 9C).

In addition, Jaramillo’s group reported the introduction of sulfur atoms into the surface of molybdenum phosphide (MoP) by a post-sulfidization treatment of MoP in a H2S atmosphere, to produce a molybdenum phosphosulfide (MoP/S).¹⁰⁷ The composite catalyst exhibited high HER performance and remained stable in accelerated durability testing. The superior performance might be derived from synergistic effects between sulfur and phosphorus atoms, and this process produced a high-surface-area electrode that was more active than those based on the pure sulfide or the pure phosphide. Moreover, the fabrication of amorphous MoS2Cl2 was reported via a LPCVD method, and found to be a high-performance electrocatalyst for electrocatalytic hydrogen generation.¹⁰⁸ MoS2Cl2 exhibited stable and high catalytic activity toward HER, which was evidenced by the large current densities at low overpotentials and the low Tafel slopes. It was clearly found that the addition of a Cl atom in MoS2 modified the electronic structure of the catalyst, which was due to the substitution of Cl into the ternary
MoS\textsubscript{x}Cl\textsubscript{y} and the introduction of defect states within the band gap. Therefore, the changed structure decreased the Gibbs free energy for hydrogen adsorption on the catalyst.

4.1.3 Perspective. In summary, various approaches have been applied to achieve high-performance in HER, e.g., increasing the number of active sites, modification of the phase structure, and doping or substitution in MoS\textsubscript{2}. Still, there is much considerable room for improvement in the development of MoS\textsubscript{2} with higher HER performance. For example, band structure and Fermi level tuning may become powerful tools; in this case, we should balance a combination of theoretical, fundamental, and performance-based studies to address our growing energy

**Fig. 8** (A) Change in hydrogen adsorption free energy on the Mo-edge at each coverage with MoS\textsubscript{2} adsorption onto the support. The activity maps for HER showed the exchange current density as a function of the calculated free energy of hydrogen adsorption. Copyright 2014, American Chemical Society. (B) SEM and TEM images of MoS\textsubscript{2} flakes with different coverages on Au foil. The polarization curves and the corresponding Tafel plots indicated the coverage-dependent HER activity of as-grown monolayer MoS\textsubscript{2} on Au foils. Copyright 2014, American Chemical Society. (C) Schematic solvothermal synthesis with GO sheets to afford the MoS\textsubscript{2}/RGO hybrid, and the SEM and TEM images of the MoS\textsubscript{2}/RGO hybrid. The polarization curves of the as-indicated catalysts and Tafel plots recorded on glassy carbon electrodes with a catalyst loading of 0.28 mg cm\textsuperscript{-2}. Copyright 2011, American Chemical Society. (D) Scheme for the MoS\textsubscript{x}/NCNT forest hybrid catalyst, and the polarization curves and Tafel plots of different catalysts. EIS for the MoS\textsubscript{x}/NCNT and bare MoS\textsubscript{x} at 0.2 V versus RHE from 5 MHz to 10 mHz. Copyright 2014, American Chemical Society. (E) (a) Schematic of the synthesis of large and small MoO\textsubscript{3} NPs on CFP. (b) The CFP was first dipped into the ammonium molybdate solution with or without the PVP additive. (c) During the pyrolysis at 600 \degree C, the surface of the nucleated NPs may be coated by PVP molecules, which prevents those particles from further aggregation. Without the addition of PVP, the small particles tend to aggregate during the process and form large particles in the end. (d) Schematic of the rapid sulfurization setup in a horizontal tube furnace. (e–h) Electrochemical characterization of as-grown catalysts on CFP. Copyright 2014, American Chemical Society.
Accordingly, the application of the low-cost noble-metal free co-catalysts with high efficiency is of great value for practical development of hydrogen technology.

Recently, Kanda et al. coupled MoS2 with TiO2, and the as-prepared photocatalyst exhibited good activity toward hydrogen generation under UV light irradiation. In contrast to pure TiO2, the loading of 0.043% of MoS2 onto the surface of TiO2 increased the rate of H2 generation by two orders of magnitude. Importantly, the matched electronic structure guaranteed the photostability of MoS2. The improved performance might be attributed to the high electrocatalytic activity of MoS2 for the reduction of water. In addition, Li and his co-workers reported the enhancement of photocatalytic H2 evolution on CdS/MoS2 by using a lactic acid solution as a sacrificial agent under visible-light irradiation. As co-catalysts, the loading of MoS2 on CdS led to a higher photoactivity than the noble metals, which was attributed to the formation of a phase junction between CdS and MoS2 that could greatly enhance photocatalytic activity for H2 production. However, the poor electrical conductivity of MoS2 restricts its cocatalytic activity, which can be ameliorated by tuning the phase structure or forming a composite with other conducting materials. Kun et al. reported the fabrication of a nanosized layer-structured MoS2/graphene nanosheet loaded with CdS nanoparticles by a wet chemistry synthetic method (Fig. 10A and B) and investigated the H2 production activity under visible light. The catalyst not only could reduce the recombination probability of photo-excited charge carriers but also could provide abundant reactive sites for hydrogen evolution. After loading graphene with MoS2, the composite exhibited an enhanced photocatalytic activity for HER with about 9 mmol evolved in 5 h from a 0.5 wt% mixture, almost 1.5 times higher than that obtained with MoS2/CdS (Fig. 10c). Furthermore, after several cycles, the hydrogen generation rate of MoS2/G–CdS almost remained constant at 1.8 mmol h$^{-1}$, indicating its stability. Serving as the 2D layered conductor in the composite, graphene matched well with layered MoS2 and enhanced its conductivity, facilitating fast charge transfer. The photogenerated electrons derived from CdS transferred to the edges of MoS2 through the conducting sheets and then reacted with the H+ to form H2.

Notably, the relationship between the light absorber that generates electron–hole pairs and the electrocatalyst that facilitates charge transfer determines the overpotential for H2 production. Ding et al. integrated a heterostructure of exfoliated 1T-MoS2 and planar p-Si as a photocathode for the PEC hydrogen generation (Fig. 10D). Under simulated 1 sun irradiation illumination, a current density of 17.6 mA cm$^{-2}$ at 0 V vs. the reversible hydrogen electrode (RHE) and an excellent onset of photocurrent are achieved with good stability (Fig. 10G). In comparison with the semiconducting 2H-MoS2 phase, electrochemical impedance spectroscopy (EIS) confirmed the smaller charge transfer resistance from Si to MoS2, enhancing the electrode kinetics of 1T-MoS2/Si for HER. Additionally, the results of surface photoresponse (SPR) measurements showed that fast and irreversible electron transfer took place from Si to 1T-MoS2, inhibiting the recombination of the photogenerated charge carriers. This also contributed to the superior performance of

4.2 Applications in photoelectrochemical systems

Solar light, as a clean and cost-free resource, can be utilized in the pursuit of renewable energy. Solar-driven water splitting, one of the most promising approaches for preparation of H2, can be achieved by photoelectrochemical (PEC) systems. Due to the fast recombination of the electron–hole pairs, the majority of photocatalysts cannot provide a high efficiency in the hydrogen evolution even in the presence of sacrificial agents. In order to retard recombination of the photogenerated charge carriers, the noble metals as co-catalysts have been commonly applied to achieve high performance in previous studies. The use of co-catalysts not only effectively separated the electron–hole pairs but also provided active sites for the reactions. Accordingly, the application of the low-cost noble-metal free
these 1T-MoS₂/Si photocathodes. However, the oxidation of Si to form SiO₂ caused problems with this approach; in order to resolve this issue, Chorkendorff and his co-workers deposited a thin layer of Ti on Si. The Ti layer not only acted as a conductive protection layer, but also enhanced the stability by the formation of TiO₂. In addition, the enhanced conductivity from this thin tunnel barrier contributed to its high HER performance, which was noticeably better than that of a pure Si electrode. The MoS₂-Ti-Si electrode exhibited comparable activity to that of the Pt electrode. Because of the protection afforded by the Ti layer, the electrode maintained an unprecedented anodic onset for the HER for a non-Pt catalyst in acidic medium even after 1 h.

Heterostructures of MoS₂ on p-type semiconductors exhibit high activity and stability, and are the promising alternatives to noble metal catalyst-based photocathodes. Accordingly, the development and practical application of MoS₂-based PEC solar energy conversion are of great urgency for the utilization of clean solar energy.

4.3 Energy conversion from mechanical stress

Piezoelectricity can arise in crystal structures with the broken inversion symmetry, allowing robust conversion between electrical and mechanical force. With their ability to withstand enormous strain, two-dimensional materials are of great interest as high-performance piezoelectric materials. Due to the lattice distortion induced by strain and the associated charge polarization, monolayer MoS₂ is theoretically predicted to be strongly piezoelectric, an effect that disappears in the bulk counterparts because of the opposite orientations between adjacent layers. Stretching and releasing of odd-layer MoS₂ causes an oscillating electrical charge, providing an ideal platform for converting mechanical energy into electricity.

On this basis, Wang and his coworkers developed a MoS₂-based nanogenerator. The layers of MoS₂ were exfoliated onto a polymer stack consisting of water-soluble polyvinyl alcohol on a Si substrate. The few-layered MoS₂ flakes were identified first using an optical microscope and the thickness was then measured by atomic force microscopy and confirmed by Raman spectroscopy. In addition, the second-harmonic generation (SHG) was used to determine the crystallographic orientation of the layered MoS₂. A typical device with single-layer MoS₂ outlined by a dashed border is depicted in Fig. 11A. After mechanically bending the substrate, strain (limited to 0.8%) was applied to the MoS₂ flakes proportional to the bending radius. The piezoelectric response was studied by applying strain to a device coupled with an external resistor. The induced charges at the MoS₂ edges can drive the flow of electrons in the circuit. With the release of strain, the electrons flowed back. Current outputs were observed after variation of external strain in the x direction, demonstrating the conversion of mechanical energy into electricity. A positive output was observed with increasing strain, while a negative output was shown after releasing the strain (Fig. 11B). The responses were proportional to the magnitude of the applied strain: for 1% change in strain, the peak open-circuit voltage and current of 18 mV and 27 pA increased to 32.8 mV and 55.1 pA. Furthermore, the evolution of the signal was investigated with increasing numbers of layers (n). MoS₂ with even layers is expected to be centro-symmetric and thus lose both its piezoresponse and SHG signal. In contrast, in samples with the odd number of layers, the piezoresponse and SHG are retained. As shown in Fig. 11C, the SHG intensity was increased to 32.8 mV and 55.1 pA. Almost no detectable current output can be seen for even-layer samples. For odd-layer samples the piezoelectric output is large, although it decreases as the layer number increases. In order to boost the piezoelectric output, four pieces of single-layer MoS₂ flakes were carefully integrated. By connecting these 2D MoS₂ flakes in series, enhancements in output voltages or currents were observed. This suggests the possibility of practically achieving energy conversion from the piezoelectric output by using large-scale 2D piezoelectric nanomaterials. Additionally, the robust
piezoelectricity of two dimensional MoS$_2$ materials makes them excellent material choices for the fabrication of nanoscale electromechanical systems, ultrasensitive sensors and generation of electricity for low-power electronics.

4.4 Applications in energy storage devices

Efficient energy storage is a long-standing technological and scientific problem that has global implications for humanity.$^{116,117}$ Due to the low atomic weight and the high absolute potential value of Li, the Li-ion battery (LIB) has been considered as a highly efficient energy storage system, with theoretical energy density values up to 400 W h kg$^{-1}$. As for the development of advanced lithium ion batteries with smaller scale and larger capacity, the selection of suitable materials is still a promising field of research. Due to their typical layered structure, Li$^+$ ions can easily intercalate between the layers of MoS$_2$. The highest reported specific capacity for MoS$_2$ was 1131 mA h g$^{-1}$ with a current of 50 mA g$^{-1}$. It was found that the charge capacity of bulk MoS$_2$ tended to sharply decrease after cycling, whereas the nanosheets prepared from chemical lithiation and exfoliation exhibited stability and retained a high capacity of 750 mA h g$^{-1}$ even after 50 cycles.$^{119}$ However, the capacity fading and inferior high rate properties of the MoS$_2$ anode are the main obstacles for the final applications. A large number of research groups have focused their attention in promoting the electrochemical performance of the MoS$_2$-based anodes by fabricating MoS$_2$-carbon composites or broadening the interlayer distance. According to the results of the increased

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**Fig. 11**  (A) (a) Polar plot of the SH intensity from single-layer MoS$_2$ as a function of the crystal’s azimuthal angle $\theta$. The symbols are experimental data and the solid lines are fits to the symmetry analysis described in the text. (b) A typical flexible device with single-layer MoS$_2$ flakes and electrodes at its zigzag edges. Inset: Optical image of the flexible device. (B) Voltage response with 1 GV external load and short-circuit current response of a single-layer MoS$_2$ device under periodic strain in two different principal directions. Top: Applied strain as a function of time. Middle: Piezoelectric outputs from single-atomic-layer MoS$_2$ when strain is applied in the x direction (armchair direction). Bottom: Corresponding piezoelectric outputs from the same device when strain is applied in the y direction (zigzag direction). The phase difference highlighted by black dashed lines is obtained by theoretical derivation and has been intentionally exaggerated for clarity, not experimental measurement. Red, blue and black arrows represent the directions of polarization, the polar axis of MoS$_2$ and principal strains, respectively. (b) Dependence of piezoelectric outputs from a single-layer MoS$_2$ device on the magnitude of the applied strain. Mean values from 20 technical replicates are indicated. Error bars represent s.d. (c) Dependence of voltage and current outputs from a single-layer MoS$_2$ device under 0.53% strain as a function of load resistance. Mean values from 20 technical replicates are indicated. Error bars represent s.d. (d) Cyclic test showing the stability of the single-layer MoS$_2$ device for a prolonged period. (e) Evolution of the piezoelectric outputs with increasing number of atomic layers (n) in MoS$_2$ flakes. For each device, mean values from 20 technical replicates are indicated. Error bars represent s.d. (C) Array integration of CVD single-layer MoS$_2$ flakes. (a) Optical image of an array consisting of four CVD single-layer MoS$_2$ flakes. (b) Constructive voltage outputs by serial connection of the individual flakes in the circuit. (c) Constructive current outputs by parallel connection of the individual flakes in the circuit. Copyright 2014, Macmillan Publishers.
charge capacity value (up to 1290 mA h g\(^{-1}\)) in MoS\(_2\)-graphene composites,\(^{29}\) the higher capacity, excellent rate capability, and long cycle life were further realized in the MoS\(_2\)NS-RGO composite.\(^{120}\) Moreover, Chen and his coworkers fabricated the MoS\(_2\)/graphene composite by using the l-cysteine assisted solution-phase method. The composite with a Mo/C molar ratio of 1:2 exhibited the capacity of \(\sim 1100\) mA h g\(^{-1}\) at a current of 100 mA g\(^{-1}\), as well as excellent cycling retention and high rate performance.\(^{121}\) Besides, the MoS\(_2@\)CMK-3 composite consisting of confined nanosized MoS\(_2\) in the CMK-3 carbon matrix was recently reported.\(^{120,122}\) The MoS\(_2@\)CMK-3 electrode was able to deliver a high discharge capacity of 934 mA h g\(^{-1}\) after 150 cycles at a current density of 400 mA g\(^{-1}\). Also, the interplanar space (d-spacing) played a decisive role in lithium ion diffusion in the solid state phase of the MoS\(_2\) anode. The MoS\(_2@\)TiO\(_2\) hybrid structures showed the improved cyclic capacity retention and rate capability.\(^{123}\) Liu et al. have developed a vacuum assisted impregnation route to prepare a highly ordered mesoporous MoS\(_2\) with expanded d-spacing of the (002) plane (0.66 nm), providing sufficient space for ultra-fast lithium ion intercalation.\(^{124}\) Similarly, the spacing of the (002) crystal plane was significantly expanded in the hierarchical MoS\(_2\) nanoflake array/carbon cloth, thereby the high specific capacity, good cycling stability, and the predominant rate performance were achieved.\(^{125}\)

Supercapacitors are also one of the most widely studied energy storage devices due to their high power density, high rate capability and long cycle life.\(^{126}\) Based on their storage mechanism, supercapacitors are classified into two types: electrochemical double layer capacitors (EDLCs) and pseudocapacitors. The capacitance of EDLCs arises from electrostatic adsorption of ions at the interface between the electrode and electrolyte (non-Faradaic charge storage). Pseudocapacitors operate by a different mechanism, where reversible Faradaic processes take place and chemical reactions occur within active materials and electrolytes. Thorough investigations of the origin of pseudocapacitance have revealed that the ion intercalation plays a crucial role in energy storage, for example the intercalation of Li\(^+\) into NbO\(_2\).\(^{127}\) The weak van der Waals interaction between S–Mo–S layers allows easy intercalation of foreign ions (H\(^+\), Li\(^+\)) in MoS\(_2\). Furthermore, Mo atoms are able to adopt a range of oxidation states from 2+ to 6+, enabling potential for pseudo-capacitance behavior with high specific capacitance for MoS\(_2\) nanosheets.\(^{128}\)

A typical example of ion intercalation is the use of 1T phase MoS\(_2\) nanosheets as electrode materials (Fig. 12A–G).\(^{129}\) The metallic 1T phase MoS\(_2\) was demonstrated to be an attractive electrode material for supercapacitors due to its intrinsic hydrophilicity and high conductivity combined with excellent pseudocapacitance via ion intercalation. In this study, 100% monolayered MoS\(_2\) nanosheets were obtained through chemical exfoliation of bulk MoS\(_2\). A 1T MoS\(_2\) film could be fabricated by restacking the suspended nanosheets using a simple filtration technique without any additives. The restacked MoS\(_2\) was able to electrochemically intercalate various ions (H\(^+\), Li\(^+\)/Na\(^+\) and K\(^+\)) with extraordinary efficiency and showed high volumetric capacitance ranging from 400 to 700 F cm\(^{-3}\). In non-aqueous electrolytes, the 1T MoS\(_2\) shows an energy density and power density as high as 0.11 W h cm\(^{-3}\) and 1.1 W cm\(^{-3}\), respectively. Cyclic stability testing of 1T phase MoS\(_2\) showed that the electrode retained a capacitance in excess of 90% over multiple cycles. The coulombic efficiency in various electrolytes at a current rate of 2 A g\(^{-1}\) was as high as 90–98%. Tour et al.\(^{130}\) reported the fabrication of an edge-oriented MoS\(_2\) thin-film by electrochemical anodization of molybdenum metal followed by sulfur vapor treatment (Fig. 12H–J). The cyclic voltammograms of the edge-oriented MoS\(_2\) thin-film electrode indicated that the pseudocapacitance could be attributed to cation intercalation and reversible redox reactions between different valence states of Mo (4+ to 3+). The voltammograms retained quasi-rectangular shapes even at scan rates as high as 100 V s\(^{-1}\) in 1 M LiOH solution. Furthermore, the quasi-triangular shape of galvanostatic charge/discharge curves indicated combined EDLC and pseudocapacitance behavior. The areal capacitance (\(C_A\)) of this flexible all-solid-state supercapacitor device increased from 2.2 to 10.5 mF cm\(^{-2}\) after 10 000 testing cycles at a current density of 10 mA cm\(^{-2}\). The increase in the \(C_A\) is probably due to the presence of more activated edges. This finding indicated that cation intercalation plays a major role rather than Mo redox reactions. Therefore, optimization of architectures would enable MoS\(_2\) with enhanced surface area and more activated edges for ion intercalation, thereby superior performance of supercapacitors can be obtained. Another example worth noting is the work by Yang et al.\(^{131}\) who reported a 2D MoS\(_2\)-based micro-supercapacitor. This MoS\(_2\) micro-supercapacitor was fabricated through laser patterning of a spray-coated MoS\(_2\) film and consisted of finger-like electrodes built from curly MoS\(_2\) nanosheets. The flexible micro-supercapacitor exhibited high \(C_A\) (8 mF cm\(^{-2}\)) and volumetric capacitance (178 F cm\(^{-3}\)) and good cyclic performance (8% loss of capacitance after 1000 cycles).

In addition, other factors such as morphology, structure and size have also been shown to be important parameters in the performance of supercapacitors. Wang et al.\(^{132}\) reported 3D flower-like MoS\(_2\) nanostructures obtained through a two-step hydrothermal treatment of MoO\(_3\) nanorods. This pure MoS\(_2\) showed a high specific capacitance of 168 F g\(^{-1}\) at 1 A g\(^{-1}\) in 1 M KCl solution. In addition, these MoS\(_2\) materials showed excellent long-term cycling stability. The capacitance still remained at 92.6% after 3000 cycles of charge–discharge at a current density of 1 A g\(^{-1}\). Other morphologies such as flower-like microspheres,\(^{133}\) spherically MoS\(_2\) clusters,\(^{134}\) and MoS\(_2\) spheres\(^{135}\) have also been reported. However, the main drawback of this approach is that the conductivity of MoS\(_2\) is too low for its effective implementation in electrodes. Although the synthesis of MoS\(_2\) can be well controlled, the structures of the active materials might become untailed after the electrode fabrication process.\(^{126}\) Hence, rational design of architectures based on forming hybrids with conducting materials is important to fully utilize MoS\(_2\) in high-performance supercapacitor electrodes. Graphene is also a 2D material and has good electrical conductivity with a large theoretical specific
Therefore, it can be a promising substrate to improve the charge-storage capacity of MoS$_2$-based devices. Leite et al.\textsuperscript{138} developed a simple chemical route to deposit MoS$_2$ on reduced graphene oxide (RGO) using microwave heating and obtained a MoS$_2$/RGO hybrid material with MoS$_2$ layers covalently bonded on the surface of the RGO. The specific capacitance measured at 10 mV s$^{-1}$ was 128 F g$^{-1}$ for MoS$_2$/RGO (with 5.6 wt% MoS$_2$) and the corresponding energy density was 63 W h kg$^{-1}$. The MoS$_2$/RGO electrode also exhibited good cyclic stability of up to 1000 cycles with 92% of the specific capacitance retained. Generally, graphene as a soft substrate for MoS$_2$ can facilitate electron transport through MoS$_2$ nanostructures, which can provide faster ion diffusion between MoS$_2$ layers/electrolytes. Bissett et al.\textsuperscript{139} reported the high performance of MoS$_2$–graphene composite membranes as supercapacitor electrodes in a symmetrical coin cell using an aqueous electrolyte. Graphene could reduce the resistivity of the electrode material and modify the morphology of the composite membrane, which significantly increased the specific capacitance of MoS$_2$. When the composite was synthesized with a weight ratio of 1:3 (MoS$_2$/graphene), the composite membrane achieved a high specific capacitance of $\sim$11 mF cm$^{-2}$ at 5 mV s$^{-1}$. Huang et al.\textsuperscript{140} reported fabrication of a MoS$_2$/MWCNT composite via a hydrothermal method. The composite showed a specific capacitance of 452.7 F g$^{-1}$ in 1 M Na$_2$SO$_4$ and exhibited an excellent cycle life (95.8% capacitance retention after 1000 cycles). Carbon aerogel-incorporated MoS$_2$ was also reported as a highly efficient supercapacitor electrode.\textsuperscript{141} The MoS$_2$/carbon aerogel hybrid film electrode showed a specific capacitance of 260 F g$^{-1}$ in Na$_2$SO$_4$ aqueous solution and exhibited good cycling stability (92.4% capacitance retention after 1500 cycles). The high surface area of these carbon materials could provide EDL capacitance in the hybrid electrode.
Besides those carbon materials, conducting polymers were also investigated for the incorporation of MoS$_2$. As another kind of pseudocapacitive material, conducting polymers can improve electrode conductivity and interfacial properties as well as capacitance.$^{142}$ Huang et al.$^{143}$ reported an in situ polymerization method to synthesize a polyaniline/MoS$_2$ nanocomposite for application in supercapacitor electrodes. The MoS$_2$ nanocomposite was supported by polyaniline with a high surface area, which provided a direct pathway for electron transfer. The layered nanostructure of polyaniline/MoS$_2$ composites provided a large surface area for ion intercalation/deintercalation, leading to a specific capacitance of $575 \mathrm{F} \cdot \mathrm{g}^{-1}$ at $1 \mathrm{~A} \cdot \mathrm{g}^{-1}$. The polyaniline/MoS$_2$ composite also shows an energy density of $265 \mathrm{Wh} \cdot \mathrm{kg}^{-1}$ at a power density of $18.0 \mathrm{kw} \cdot \mathrm{kg}^{-1}$. Ma et al.$^{144}$ reported fabrication of a polypyrrole/MoS$_2$ nanocomposite as a supercapacitor electrode. The polypyrrole/MoS$_2$ composite was synthesized through in situ intercalative polymerization of pyrrole in MoS$_2$. Electrochemical tests showed that the polypyrrole/MoS$_2$ electrode exhibited a high specific capacitance of $553.7 \mathrm{F} \cdot \mathrm{g}^{-1}$ in 1 M KCl aqueous solution and good cyclic performance (90% capacitance retention after 500 cycles).

4.5 Applications in sensors

In addition to applications in ESCs, MoS$_2$-based platforms have been also applied as sensors in different fields. According to the direct bandgap character of monolayer MoS$_2$, Zhang’s group prepared a phototransistor based on single-layer MoS$_2$, which exhibited an on/off ratio of $10^3$ within $0.8$ ppm. Furthermore, a planar sensor structure consisting of a high sensitivity toward NO, with a detection limit down to $0.8$ ppm. The polyaniline/MoS$_2$ composite also shows an energy density of $265 \mathrm{Wh} \cdot \mathrm{kg}^{-1}$ within $1 \mathrm{M} \mathrm{KCl}$ aqueous solution and good cyclic performance (90% capacitance retention after 500 cycles).

Fig. 13  (A) Schematic and image of the MoS$_2$ monolayer sensor: a single monolayer of MoS$_2$ is supported on the SiO$_2$/Si substrate and contacted with Au contact pads. Transient physisorption of molecules induces temporary changes in the conductivity of the monolayer channel. (B) Change in conductivity of the monolayer MoS$_2$ sensor channel upon exposure to a sequence of 0.002% $P_0$ TEA pulses (black line). The dashed blue lines show the pulse timing (15 s on/30 s off) and concentration. The solid red line shows the response to exposure of nitrogen only and serves as a control experiment. The solid green and purple lines show the response of the MoS$_2$ and graphene sensors to water vapor pulses (0.025% $P_0$), respectively. (C) Change in conductivity of the monolayer MoS$_2$ sensor channel upon exposure to a sequence of pulses in which the acetone concentration increases from 0.02% $P_0$ to 2% $P_0$ (black line). 2013, American Chemical Society.
Moreover, electrochemical sensors having the attributes of simplicity, low cost, ultrahigh sensitivity and selectivity have been applied for the detection of various chemicals in aqueous environments. Generally, the working mechanism of the sensors is based on electron transfer between the surface of a working electrode and a target in the electrolyte solution. Meanwhile, voltammetry, amperometry and potentiometry are the three main techniques used for the detection of aqueous chemical species. Recently, MoS\(_2\) has been used as a sensing material for electrochemical sensors because of the superior electrochemical properties derived from its amplified edge effects and enhanced surface to volume ratios in contrast to metal oxides and conducting polymers. Additionally, some noble metals have also been anchored on the surface of these 2D TMDs to enhance the sensor signals. Huang et al. designed an electrochemical sensor for detection of Bisphenol A using a MoS\(_2\) nanoflower–chitosan–Au nanoparticle modified glassy carbon electrode (GCE).\(^{156}\) In the presence of bisphenol, the MoS\(_2\)-modified GCE had an anodic peak with remarkably enhanced current at a low oxidation overpotential of 0.9 V. More importantly, the stability and quantitatively reproducible analytical performance of the electrode promise to make this an excellent sensor for practical applications. Thus, it is reasonable to speculate that the formation of MoS\(_2\) hybrids with other nanostructures may provide ideal platforms for electrochemical sensors.

Therefore, research should be carried out to improve the understanding of MoS\(_2\) and large-scale fabrication of single-layer MoS\(_2\) with controllable properties, thereby resulting in the fabrication of inexpensive, high-sensitivity and flexible MoS\(_2\)-based devices for practical applications in the field of sensing.

5. Conclusion and outlook

In this review, we summarized the recent progress in the development of MoS\(_2\) nanostructures in a broad range of applications, such as energy conversion, energy storage and sensors. The discussion has focused on the optimization of structure for superior performance. We identified the key challenges facing MoS\(_2\)-based applications, and enumerated some current and emerging strategies for improving their performance.

In the pursuit of solutions for the energy crisis, theoretical studies predicted that MoS\(_2\) could be used as an effective and lower cost substitute for the noble metals in the ESCs. In HER, the maximization of active edges and the conductivity are identified as the core issues in MoS\(_2\)-based electrocatalysts. A large number of synthetic strategies have been focused on maximizing the exposure of edge sites; phase structure tuning has also been as a potential tool for enhancing the electrical transport properties of MoS\(_2\) which is another key factor in HER performance. To combine high carrier transport and maximum exposure of active sites, MoS\(_2\)-based composites have been prepared, and exhibited much higher activity in contrast to MoS\(_2\) alone. Moreover, the composites have been found to be the efficient materials in the fields of MoS\(_2\)-based sensors, LIBs and supercapacitors as well.

Overall, the rich chemistry of the layered TMDs constructs an extensive platform for the study of fundamental scientific phenomena, and their versatile properties make them attractive for a wide range of practical applications. Still, there is much room for improvement in the development of TMDs with higher performance. In particular, the band structure and Fermi level tuning may be powerful tools. Thus, we should first explore the balance point in the combination of theoretical, fundamental, and performance-based studies. In addition, to enable final applications, the rate of the synthesis of large-scale and high quality MoS\(_2\) should be accelerated. To provide solutions for the energy crisis, a number of important and exciting studies based on the tunable properties of MoS\(_2\) and its family numbers (MoSe\(_2\), WS\(_2\), WSe\(_2\)…) will certainly emerge in the near future.

Acknowledgements

Financial support from the National Science Fund for Distinguished Young Scholars of China (Grant No. 51225805), the Funds for Creative Research Groups of China (No. 51221892), National Natural Science Foundation of China (No. 51225805, No. 51221892, and No. 21235004), National Basic Research Program of China (No. 2013CB934004), and Tsinghua University Initiative Scientific Research Program is acknowledged.

Notes and references

1  Y.-J. Wang, D. P. Wilkinson and J. Zhang, Chem. Rev., 2011, 111, 7625–7651.
2  N. G. Sahoo, Y. Pan, L. Li and S. H. Chan, Adv. Mater., 2012, 24, 4203–4210.
3  S. E. Habas, H. A. S. Platt, M. F. A. M. van Hest and D. S. Ginley, Chem. Rev., 2010, 110, 6571–6594.
4  A. Kubacka, M. Fernández-García and G. Colón, Chem. Rev., 2012, 112, 1555–1614.
5  M. Grätzel, Nature, 2001, 414, 338–344.
6  H. Li, Z. Wang, L. Chen and X. Huang, Adv. Mater., 2009, 21, 4593–4607.
7  P. G. Bruce, B. Scrosati and J.-M. Tarascon, Angew. Chem., Int. Ed., 2008, 47, 2930–2946.
8  K. Naoi, W. Naoi, S. Aoyagi, J.-i. Miyamoto and T. Kamino, Acc. Chem. Res., 2013, 46, 1075–1083.
9  H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long and C. J. Chang, Science, 2012, 335, 698–702.
10  C. Zhu, X. Mu, P. A. van Aken, Y. Yu and J. Maier, Angew. Chem., Int. Ed., 2014, 53, 2152–2156.
11  E. Gourmelon, O. Lignier, H. Hadouda, G. Couturier, J. C. Bernède, J. Tedd, J. Pouzet and J. Salardenne, Sol. Energy Mater. Sol. Cells, 1997, 46, 115–121.
12  B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti and A. Kis, Nat. Nanotechnol., 2011, 6, 147–150.
13  M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh and H. Zhang, Nat. Chem., 2013, 5, 263–275.
