A Review on MoS₂ Energy Applications: Recent Developments and Challenges

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Abstract: Molybdenum disulfide (MoS₂) is a promising transition metal dichalcogenide (TMD) that has exceptional electronic, magnetic, optical, and mechanical properties. It can be semiconducting, superconducting, or an insulator according to its polymorph. Its bandgap structure changes from indirect to direct when moving towards its nanostructures, which opens a door to bandgap engineering for MoS₂. Its supercapacitive and catalytic activity was recently noticed and studied, in order to include this material in a wide range of energy applications. In this work, we present MoS₂ as a future material for energy storage and generation applications, especially solar cells, which are a cornerstone for a clean and abundant source of energy. Its role in water splitting reactions can be utilized for energy generation (hydrogen evolution) and water treatment at the same time. Although MoS₂ seems to be a breakthrough in the energy field, it still faces some challenges regarding its structure stability, production scalability, and manufacturing costs.

Keywords: molybdenum disulfide; MoS₂ energy applications; lithium-ion batteries; sodium-ion batteries; MoS₂ energy applications; solar cells; hydrogen evolution reactions (HER); CO₂ reduction; metallic MoS₂; 1T MoS₂

1. Introduction

MoS₂ is one of the transition metal dichalcogenides (TMDs) that has gained a high reputation in recent years due to its distinct chemical, electronic, mechanical, magnetic, and optical properties [1,2]. Its unique properties enabled its use in different applications such as sensing applications, high-efficiency field effect transistors, and energy and medical (curing) applications. MoS₂ exists in different crystalline structures, such as hexagonal (H), tetrahedral (T), or rhombohedral (R). It naturally exists as 2H MoS₂, and its most popular structures are the semiconducting 2H and 3R phases and the 1T metallic phase, where 2H is more stable but less conductive than 1T. Metallic MoS₂ has a higher conductivity (10⁵ times) than semiconducting 2H MoS₂ and high catalytic activity [3].

MoS₂ is expected to substitute silicon in the electronics industry in the next nano era [4–7] and has attracted attention to be used in energy applications [8–9]. MoS₂ energy applications can be summarized into two main categories: energy storage devices (batteries and supercapacitors, Etc) and energy generation, where MoS₂ acts as a catalyst in energy generation reactions, as shown in Figure 1. Hydrogen is known to be a promising clean source of energy, but, still, different studies have been conducted to obtain it at a low cost and with affordable methods. Two main reactions are needed for hydrogen generation: hydrogen evolution reactions (HERs) and oxygen evolution reactions (OERs). MoS₂ is used as a catalyst for both reactions during the water splitting process, which is a clean and cheap substitute when compared to hydrogen extraction from coal or natural gas [10]. It is to be noted that MoS₂ is also a catalyst in CO₂ reduction reactions, which is a cheap substitute for expensive metal catalysts [11]. Many previous reviews discussed the properties of MoS₂, its synthesis, its applications, and the future expectations about it [12–17], and some were dedicated to its energy applications [18,19]. In this work, we present a comprehensive
study of MoS$_2$ applications including one of the most important applications, solar cells, that was not deeply discussed in previous reviews. Since 1929, MoS$_2$ has been introduced as a dry lubricant in mechanics [20–24] and engines, with more than 1000 papers published on it [25]. The hexagonal packed structure and the weak van der Waal forces between its layers make the movement of layers easier. Recently, nano-MoS$_2$ quantum dots were used as a liquid lubricant [26] for a better engine efficiency, where they showed a friction coefficient of 0.061, which is much lower than that for pure paroline oil (0.169). Inorganic fullerene-like (IF) MoS$_2$ nanoparticles were examined in other works [27,28] and were found to have a very low friction coefficient of 0.04 under ultra-high vacuum (UHV). The effect of the crystal structure of IF-MoS$_2$ on its lubrication properties was also studied [29], and it was found that IF-MoS$_2$ nanoparticles with poor crystallization and a large number of defects reduce the friction between steel surfaces better than crystalline IF-MoS$_2$.

![Figure 1. A schematic diagram for MoS$_2$ energy applications.](image)

In this review, we first introduce the structure and properties of MoS$_2$, especially those which are promising for energy applications, and then we discuss some synthesizing techniques for energy applications. We divide the energy applications part into two main categories: energy storage and energy generation, and then we discuss the challenges facing MoS$_2$ in the energy industry.

2. Structure and Properties

MoS$_2$ layers are formed by covalent bonds between sulfur and molybdenum S-Mo-S, as a layer of Mo sandwiched between two layers of sulfur. The layers are connected together through weak van der Waal forces [30]. MoS$_2$ exists in many phases, where its characteristics and properties differ according to its phase. The 1T phase is an octahedral structure, while 2H and 3R are trigonal prismatic structures [31]. The 3R phase showed better catalytic activity in hydrogen evolution reactions than the 2H and 1T phases [32]; however, not much work has been conducted on the 3R MoS$_2$ phase. Monolayer 2H-MoS$_2$ is semiconducting, with a direct bandgap of ~1.8 eV [33,34]. 2H MoS$_2$ exists in nature and is stable under ambient temperature. Metallic MoS$_2$ is a metastable structure that does not exist in nature and is synthesized from the 2H phase or formed by controlled transitions, e.g., using an electron beam [35], ion intercalation [36], or laser irradiation [37,38]. It has superconductivity and high catalytic activity [39] that render it promising for energy applications. Although the metallic phase of MoS$_2$ has challenges with stability and synthesis, research is directed towards it because of its high conductivity, which renders it promising for energy storage applications, such as its use in supercapacitors [40,41] and batteries [42–44].
The 1T MoS$_2$ phase is metastable and coexists with other phases such as 1T', 1T'', and 1T''' (Figure 2). The phases are easily transformed to the 2H phase by annealing at nearly 70 °C [45]. The 1T' phase is a superconductor, while 1T''' can be either a superconductor or an insulator depending on the synthesizing technique [45]. Generally, the 1T metastable phases have superconductivity and catalytic activity in hydrogen evolution reactions, which directed energy studies to these metastable phases. However, their electronic and magnetic properties and their device applications have not been studied extensively due to their metastability. A quantum spin Hall effect is expected from the 1T' polytype [46]. The 1T metallic phase was proposed to decrease the contact resistance in ultrathin MoS$_2$ transistors [36,47]. The 1T phase is laid over the 2H semiconducting phase (which is known for its high resistance (0.7–10 kΩ µm)) to decrease the contact resistance to 200–300 Ω µm at zero gate bias.

**Figure 2.** MoS$_2$ different crystal structures. (a) The top and side views of monolayer MoS$_2$ for H and T phases. (b) Different lattice structures of MoS$_2$ metallic phases 1T', 1T'', and 1T'''. Adapted from [45]. American Physical Society 2018.

3. Synthesis

There are two main approaches to synthesizing transition metal dichalcogenides (TMDs); the top-down approach and the bottom-up approach [15,48]. Top-down techniques are mainly exfoliation techniques, while bottom-up methods grow MoS$_2$ over a substrate. Bottom-up techniques include different types of depositions such as chemical vapor deposition (CVD), physical layer deposition (PVD), and atomic layer deposition (ALD). Solution-based techniques in preparing MoS$_2$ layers are considered as a bottom-up approach, which are known to be scalable and of low cost in contrast to exfoliation techniques that lack scalability [17]. Different types of exfoliation techniques are used to synthesize MoS$_2$ such as mechanical exfoliation, liquid-phase exfoliation, and ion intercalation, which is categorized into lithium and non-lithium ion intercalation methods [49]. A study in [50] showed that the effect of intercalation cations such as Na$^+$, Ca$^{2+}$, Ni$^{2+}$, and Co$^{2+}$ on MoS$_2$ lowers the overpotential for hydrogen evolution reactions (HER). On the other hand, hydrothermal and solvothermal synthesis mechanisms are solution-based bottom-up techniques where the material is synthesized in closed vessels under high temperature and pressure [48]. When the process is carried out in water, it is called a hydrothermal technique, and when it is conducted with non-aqueous solvents, it is called a solvothermal technique. Different works discussed the above techniques in detail [51–56]; however, here, we are more concerned with techniques that have a low cost and are scalable to be used in energy applications on a large scale. We will focus on lithium ion intercalation as a top-down method and solution-based techniques as some of the bottom-up techniques. Additionally, we will focus on the synthesis of the 1T MoS$_2$ phase since this is the most used in energy applications due to its high conductivity.
3.1. Lithium Intercalation and Exfoliation

In order to obtain the 1T MoS\textsubscript{2} phase, MoS\textsubscript{2} is intercalated with alkali metals such as potassium (K) or Li, and the product is hydrated and then oxidized [25,57]. Through hydration reactions, electrons transfer from the alkali metal to MoS\textsubscript{2}, which maintains the octahedral coordination of Mo atoms. Excess electrons are then removed through oxidation, while the octahedral coordination is kept the same with little distortion. The ligand—the ion attached to Mo through a coordinate bond—is responsible for the metallic conductivity and the metastable structure of 1T MoS\textsubscript{2}, where three degenerate d orbitals are occupied by two electrons; thus, crystal distortion occurs. The distortion breaks the degeneracy and stabilizes the structure. The excess electrons can also stabilize the 1T phase. The different phases and crystalline structures of 2D MoS\textsubscript{2} and distorted 1T MoS\textsubscript{2} were investigated in detail [25]. It is to be noted that the 1T metallic phase does not have an exact d\textsuperscript{2} electronic configuration because this configuration yields a $\sqrt{3}a \ast \sqrt{3}a$ superstructure which is not metallic, but restacking MoS\textsubscript{2} with incomplete oxidation yields a $\sqrt{3}a \ast a$ superstructure which is metallic. Restacked MoS\textsubscript{2} and 1T metallic MoS\textsubscript{2} are considered the same due to the octahedral coordination of Mo atoms. When MoS\textsubscript{2} is treated with reducing agents such as n-butyllithium or LiBH\textsubscript{4}, lithium ions intercalate into MoS\textsubscript{2} and separate its layers, forming LiMoS\textsubscript{2}. LiMoS\textsubscript{2} disperses in water, forming 2D MoS\textsubscript{2} flakes, which are then filtered or precipitated to form restacked MoS\textsubscript{2} flakes [25]. It is then exfoliated using sonication. The restacking causes the transformation of 2D MoS\textsubscript{2} into 1T MoS\textsubscript{2}, which is the dominating phase. Additionally, the geometry of MoS\textsubscript{2} changes from prismatic to octahedral. As a result, the material shifts from semiconducting to metallic, with a $\sqrt{3}a \ast a$ orthorhombic superlattice [58]. The advantage of this method is that we can control the distance between MoS\textsubscript{2} layers by changing the amount of intercalating Li; however, the production scalability of this technique is limited. Additionally, some lithium residues may exist with the MoS\textsubscript{2} layers, which affects its performance. One solution to the residue problem is to use the electrochemical lithium intercalation and exfoliation technique. The work in [59] produced the MoS\textsubscript{2} metallic phase from the semiconducting phase, where MoS\textsubscript{2} was assembled as an anode in lithium-ion battery semicells and then charged to a certain voltage to obtain the MoS\textsubscript{2} metallic phase. Another work used bulk MoS\textsubscript{2} as a cathode and lithium foil as an anode [60]. The Li content and MoS\textsubscript{2} metallic phase can be controlled by the applied voltage.

3.2. Hydrothermal and Solvothermal Synthesis

The hydrothermal and solvothermal synthesis techniques are bottom-up synthesis techniques based on chemical reactions at high temperatures. They do not require catalysts or hazardous materials in their reactions as with other techniques, which renders them the preferred techniques. The synthesis is conducted through chemical solutions of precursors and surfactants with the solvent at a temperature above the boiling point of the solvent. The synthesis process is easy and can be produced on a large scale. Many trials to prepare metallic MoS\textsubscript{2} through these techniques were performed, and we summarize them in Table 1.

Table 1. Solvothermal and hydrothermal synthesis techniques and their applications.

| Synthesis Technique | Specifications | Application | References |
|---------------------|----------------|-------------|------------|
| Solvothermal        | Vertical 1T-MoS\textsubscript{2} nanosheets interlayer spacing = 9.8 Å | Capacity = 666 mA h g\textsuperscript{−1} at current density = 3500 mA g\textsuperscript{−1} | [61]         |
| Solvothermal        | 1D metallic MoS\textsubscript{2} nanotube | Capacity = 1100 mA h g\textsuperscript{−1} at current density = 5000 mA g\textsuperscript{−1} and capacity = 589 mA h g\textsuperscript{−1} at a high current density = 20,000 mA g\textsuperscript{−1} | [62]         |
Table 1. Cont.

| Synthesis Technique | Specifications | Application | References |
|---------------------|----------------|-------------|------------|
| Solvothermal        | 1T-MoS\(_2\) nanosheet arrays | Lithium-ion battery<br>Reversible specific capacity of 1789 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\) and a retained capacity of 853 mA h g\(^{-1}\) after 140 cycles at 1 A g\(^{-1}\) | [63] |
| Solvothermal        | 1T-MoS\(_2\) | HER<br>Low potential of 203 mV at 10 mA cm\(^{-2}\), Tafel slope = 60 mV dec\(^{-1}\) | [64] |
| Solvothermal        | STable 1T-MoS\(_2\) slabs<br>grown on CdS nanorods<br>1T-MoS\(_2\)@CdS | Photocatalytic HER<br>39 times better photocatalytic activity when compared to bare CdS | [65] |
| Hydrothermal        | Stabilized 1T-MoS\(_2\) layers<br>Mo–Mo bond length = 2.72 Å | Hydrogen evolution<br>21 times higher than pure CdS and 3 times higher than annealed CdS: 2H-MoS\(_2\) | [66] |
| Hydrothermal        | Metallic MoS\(_2\) nanopetals | (HER)<br>Overpotential = 210 mV at current density = 10 mA cm\(^{-2}\) and a Tafel slope of 44 mV dec\(^{-1}\) | [67] |
| Hydrothermal        | Pure and stable metallic MoS\(_2\) nanosheets | HER<br>Current density of 10 mA cm\(^{-2}\)<br>Overpotential = 175 mV<br>Tafel slope = 41 mV dec\(^{-1}\) | [68] |
| Hydrothermal followed by solvothermal method | Both 1T and 2H phases | HER<br>Overpotential = 180 mV<br>Tafel slope = 88 mV dec\(^{-1}\) | [69] |

3.3. Other Methods
Some other novel techniques to produce MoS\(_2\) for energy applications such as the one in [70] were based on the direct synthesis of MoS\(_2\) on p-Si through thermolysis, where a (NH\(_4\))\(_2\)MoS\(_4\) precursor is deposited onto a non-oxide substrate. The substrate has to be a super-hydrophilic surface, meaning an extra step is added when MoO\(_3\) is deposited over the p-Si substrate to convert it from a poor hydrophilic to a super-hydrophilic surface. The method was controllable, and the produced MoS\(_2\)/p-Si heterojunction was tested for solar hydrogen production and showed good results, as shown in Figure 3. It is worth mentioning that the synthesis of atomically thin MoS\(_2\) photoanodes, AT-MoS\(_2\), using CVD and ALD techniques can be used in water splitting and wastewater treatment [71]. This work proposes the idea of studying the combination of water treatment and hydrogen production in future studies for efficient and environmentally friendly approaches.
4. Energy Applications

In this section, we will discuss the energy storage and energy generation applications of MoS$_2$. Batteries and supercapacitors are the main energy storage devices, where MoS$_2$ serves as an anode in lithium-ion and sodium-ion batteries. Although the performance of sodium-ion batteries is low if compared to lithium batteries (due to its atomic structure), sodium is more abundant and less toxic [72]. Na has high stability and a low diffusion energy, but it has lower mobility, which decreases its favorability in batteries. Na-ion batteries have a larger weight but a lower cost than Li-ion batteries, which make them suitable for stationary applications. Not many studies have been conducted on Na-ion batteries until now, but they still represent a low-cost battery choice.

4.1. Energy Storage Applications

4.1.1. Lithium-Ion Batteries (LIB)

Lithium-ion batteries (LIB) have a high capacity and are recyclable. Most portable devices have LIB; however, their capacity is still too low to be used in some electrical vehicles. Metallic MoS$_2$ can serve as an anode in LIB due to its high conductivity, specific capacity, and large surface area which enable better intercalation of the incoming ions and enhance the battery’s stability and rate performance [73]. The chemical composition of metallic MoS$_2$ (1T MoS$_2$) was investigated using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and X-ray diffraction (XRD), and it was found to have binding energies of 228.8 and 231.9 eV corresponding to the 3d$_{5/2}$ and 3d$_{3/2}$ components, respectively, for Mo–S bonding. The S 2p components have binding energies of 161.5 eV and 162.5 eV.
corresponding to S 2P\textsubscript{3/2} and 2P\textsubscript{1/2}, respectively [43,62]. The bonding of both Mo and S is nearly 1 eV less than that of 2H MoS\textsubscript{2}.

The research work in this area is based on two directions, namely, whether to enhance the stability of metallic MoS\textsubscript{2}-based LIB or to enhance the conductivity of 2H MoS\textsubscript{2} to serve as an anode in LIB, since it has better stability. In a trial to suppress the high intrinsic electric conductivity of metallic MoS\textsubscript{2}, it was aligned over graphene with a relatively large separation distance of 0.98 nm between them. The first cycle showed a high capacity of \(\approx 1700\) mA h g\(^{-1}\) at a current density of 70 mA g\(^{-1}\) and an initial coulombic efficiency of 70%.

MoS\textsubscript{2} was mounted on carbon fiber cloth to obtain a high reversible specific capacity of \(\approx 1789\) mA h g\(^{-1}\) at 0.1 A g\(^{-1}\) and a retained capacity of 853 mA h g\(^{-1}\) after 140 cycles at 1 A g\(^{-1}\) [63]. A composite of 1T-MoS\textsubscript{2} and conductive molybdate (NiMoO\textsubscript{4}) was used to obtain a coulombic efficiency of 99.5%, and it had stability after 750 cycle [74]. A pure metallic MoS\textsubscript{2} structure was developed in [62] to avoid stability problems in material stacking. The battery had a specific capacity of \(\approx 935\) mA h g\(^{-1}\) for 200 cycles at 5 A g\(^{-1}\) that can be increased to 1150 mA h g\(^{-1}\). It had a high rate performance at the current density range from 0.2 to 20 A g\(^{-1}\) and a reversible capacity of 589 mA h g\(^{-1}\).

Table 2 summarizes some MoS\textsubscript{2}-based LIB showing the used structure and phase of MoS\textsubscript{2} and its specifications.

| Battery Type | MoS\textsubscript{2} Phase | Structure | Capacity | References |
|--------------|-----------------------------|-----------|----------|------------|
| Lithium-ion  | 1T (Metallic)               | Nanotube-like MoS\textsubscript{2} over graphene | Discharge capacity = 666 mA h g\(^{-1}\) at current density = 3500 mA g\(^{-1}\) | [61] |
| Lithium-ion  | 1T (Metallic)               | MoS\textsubscript{2} over carbon cloth | Reversible specific capacity = 1789 mA h g\(^{-1}\) at 0.1 Ag\(^{-1}\) Retained capacity = 853 mA h g\(^{-1}\) after 140 cycles at 1 Ag\(^{-1}\) | [63] |
| Lithium-ion  | 1T (Metallic)               | 1T MoS\textsubscript{2} + (NiMoO\textsubscript{4}) | Charged mass capacity = 940.1 mA h g\(^{-1}\) Discharged mass capacity = 941.6 mA h g\(^{-1}\) | [74] |
| Lithium-ion  | 1T (Metallic)               | Pure MoS\textsubscript{2} | Specific capacity \(\approx 935\) mA h g\(^{-1}\) for 200 cycles at 5 A g\(^{-1}\) can be increased to 1150 mA h g\(^{-1}\) | [62] |
| Sodium-ion   | 1T (Metallic)               | MoS\textsubscript{2}-graphene-MoS\textsubscript{2} | Capacity of 175 mA h g\(^{-1}\) at a high current density of 2 A g\(^{-1}\) Reverse capacity of \(\approx 313\) mA h g\(^{-1}\) at low current density of 50 mA g\(^{-1}\). Stabilizes at current density = 313 mA h g\(^{-1}\) after 200 cycles | [43] |
| Sodium-ion   | 2H and 1T MoS\textsubscript{2} | Dual phase of 2H and 1T MoS\textsubscript{2} | Capacity = 300 mA h g\(^{-1}\) after 200 cycles, and coulombic efficiency = 99% | [75] |
| Sodium-ion   | 2H phase transfers to 1T through chemical reactions | MoS\textsubscript{2} and amorphous carbon (C) | Capacity = 563.5 mA h g\(^{-1}\) at 0.2 A g\(^{-1}\) Coulombic efficiency = 86.6% Cyclic stability = 484.9 mA h g\(^{-1}\) at 2 A g\(^{-1}\) | [76] |
| Supercapacitor | 2D MoS\textsubscript{2} | Spraying MoS\textsubscript{2} nanosheets on Si/SiO\textsubscript{2} | Area capacitance = 8 mF cm\(^{-2}\), and volumetric capacitance = 178 F cm\(^{-3}\) | [77] |
| Supercapacitor | Nanoflower-like MoS\textsubscript{2} structure | 3D-graphene/MoS\textsubscript{2} nanohybrid | Dimensions 23.6 \times 22.4 \times 0.6 mm\(^3\) Specific capacitance \(C_{sp} = 58\) F g\(^{-1}\), energy density of 24.59 W h Kg\(^{-1}\), and power density of 8.8 W Kg\(^{-1}\) with operating window of 2.7 V (−1.5 to +1.2 V) | [78] |
Table 2. Cont.

| Battery Type | MoS₂ Phase | Structure | Capacity | References |
|--------------|------------|-----------|----------|------------|
| Supercapacitor | Brush-like arrangement MoS₂ | MoS₂ nanowires over Ni foam | The high mass loading of MoS₂ (30 mg cm⁻²) retains 92% of maximum capacitance after 9000 charge–discharge cycles at 5 A g⁻¹ | [79] |
| Supercapacitor | MoS₂ QSs | Exfoliated MoS₂ QSs lateral size (5–10 nm) | Capacitance = 162 F g⁻¹ Energy density = 14.4 W h kg⁻¹ | [80] |
| Hybrid Supercapacitor | N-3DG and 3D-IEMoS₂@G | Prepared using solvothermal process | Energy density = 140 W h kg⁻¹ at 630 W kg⁻¹, and 43 W h kg⁻¹ at power density of 103 kW kg⁻¹ Lifecycle over 10,000 | [81] |

4.1.2. Sodium-Ion Batteries (NIB)

Since NIB are less efficient than LIB, there is not much research work about the role of MoS₂ in Na-ion batteries; however, an early theoretical study in [82] showed that monolayer MoS₂ can have a higher Na adsorption when compared to bulk MoS₂. It is perfect as an anode electrode in Na-ion batteries, with a theoretical capacity of 335 mA h g⁻¹. The monolayer maintains a lower applicable voltage of 1.0 V when compared to the bulk (1.7–2.0 V). The low mobility of Na is overcome by the monolayer structure because when the dimensions decrease, the diffusion barrier decreases from 0.7 to 0.11 eV. A graphene sandwich of MoS₂, MoS₂-graphene-MoS₂, in [43] had a high capacity of 175 mA h g⁻¹ at a high current density of 2 A g⁻¹ and a reverse capacity of ≈313 mA h g⁻¹ at a low current density of 50 mA g⁻¹. It stabilized at a current density of 313 mA h g⁻¹ after 200 cycles. A dual phase of 2H and 1T MoS₂ was used to obtain a capacity of 300 mA h g⁻¹ after 200 cycles and 99% coulombic efficiency. The good interlayer spacing permitted a high reversibility of Na ion intercalation [75]. MoS₂ and amorphous carbon (C) microtubes (MTs) in [76] were used to improve the capacity to 563.5 mA h g⁻¹ at 0.2 A g⁻¹ and obtain 86.6% coulombic efficiency with cyclic stability of 484.9 mA h g⁻¹ at 2.0 A g⁻¹. Table 2 summarizes some MoS₂-based NIB showing the used structure and phase of MoS₂ and its specifications.

It is worth mentioning that, recently, multilayer intercalation of alkali metals (AM) (Li, K, Na) between bilayer graphene was possible and showed a higher storage capacity than the bulk structure [83]. A study in [84] compared the intercalation energetics of bilayer graphene and MoS₂ for a number of alkali metals (Li, Na, K, Rb, Cs). The weak van der Waal forces between MoS₂ layers enabled easy intercalation of Li ions without excess volume, and the Li storage capacity could reach 700 mA h g⁻¹. The study showed that the storage capacity of MoS₂ is significantly lower than graphene, but it can be increased through vertical van der Waals forces between graphene-MoS₂ heterostructures where it will benefit from the light weight of graphene and the low formation energy of MoS₂.

4.1.3. Supercapacitors

Supercapacitors are energy storage devices that have a lower energy density than batteries and a higher power density, meaning they can be used as a complementary device in electric vehicles beside batteries [73]. MoS₂ is a good capacitor since it is formed of layers (sheets) that provide a large area for charge storage, where ions are inserted between layers through intercalation. The layers are exfoliated and then restacked to form electrodes with improved electrochemical features [85]. Carbon-based supercapacitors are leading the market due to their fast charge–discharge, versatile synthesis, and stability [86], but MoS₂ can achieve extraordinary capacitances from 400 to 700 F cm⁻³ [85]. The charge storage mechanism of 1T MoS₂ was investigated in [87] for an interlayer spacing ranging from 0.615 to 1.615 nm in ionic liquids. It was found that the highest volumetric and gravimetric capacitances were 118 F cm⁻³ and 42 F g⁻¹, respectively, and occurred at a MoS₂ interlayer...
spacings of 1.115 nm. A micro-supercapacitor proposed in [77], developed through spraying MoS\(_2\) nanosheets on a Si/SiO\(_2\) chip followed by laser patterning, had excellent cyclic and electrochemical performance compared to graphene-based micro-supercapacitors. It had a high area capacitance of 8 mF cm\(^{-2}\) and a volumetric capacitance of 178 F cm\(^{-3}\). The idea opens the door for portable and flexible micro-electronic devices. Some studies were directed towards the nano-MoS\(_2\) structure, where it showed a better performance in energy storage. Metallic 1T phase MoS\(_2\) nanosheets were found to efficiently intercalate ions such as H\(^+\), Li\(^+\), Na\(^+\), and K\(^+\) with capacitance values ranging from \(\sim 400\) to \(\sim 700\) F cm\(^{-3}\) in different aqueous electrolytes [85]. Their coulombic efficiencies were more than 95% and were stable until 5000 cycles. The MoS\(_2\) flower-shaped nanostructure was paired with 3D graphene to develop a supercapacitor prototype with dimensions of 23.6 \(\times\) 22.4 \(\times\) 0.6 mm\(^3\) by stacking a MoS\(_2\) nanoflower structure over 3D graphene over a graphite electrode [78]. The prototype had a high specific capacitance \(C_{sp}\) of 58 F g\(^{-1}\), an energy density of 24.59 W h Kg\(^{-1}\), and a power density of 8.8 W Kg\(^{-1}\), with an operating window of nearly 2.7 V (−1.5 to +1.2 V). The study represents an inexpensive supercapacitor without the need for ionic liquid media. The nanostructures of MoS\(_2\) showed excellent supercapacitance when grown on Ni foam through the hydrothermal process [79]. It was able to maintain 92\% of its maximum capacitance after 9000 charge–discharge cycles at 5 A g\(^{-1}\). The study confirmed that the high mass loading of MoS\(_2\) nanostructures grown over conducting substrates corresponds to superior energy storage electrodes. A recent work studying the capacitance of MoS\(_2\) quantum sheets (QSs) in [80] demonstrated that MoS\(_2\) quantum sheets have a high capacitance of 162 F g\(^{-1}\), which is very high if compared to typical MoS\(_2\) supercapacitors. MoS\(_2\) QSs have an energy density of 14.4 W h kg\(^{-1}\) and a long cycle life. In [81], a 3D interlayer-expanded MoS\(_2/rGO\) nanocomposite (3D-IEMoS\(_2@G\)) was synthesized and experimented as an anode in lithium-ion and sodium-ion batteries. It was then modified by pairing it with nitrogen-doped hierarchically porous 3D graphene (N-3DG) to obtain sodium and lithium hybrid supercapacitors (HSCs). The Na-HSC showed an excellent performance of 140 W h kg\(^{-1}\) at 630 W kg\(^{-1}\), and 43 W h kg\(^{-1}\) at an ultra-high power density of 103 kW kg\(^{-1}\) (charge finished within 1.5 s). It can retain its capacitance even after 10,000 cycles. Table 2 summarizes some MoS\(_2\)-based supercapacitors showing the used structure and phase of MoS\(_2\) and its specifications.

4.2. Energy Generation Applications
4.2.1. Hydrogen Evolution Reactions (HER)

Hydrogen was recently studied to substitute fuel as a source of energy. It is not a source of energy by itself but rather a carrier of energy. It has to be manufactured as with electricity. It has to be manufactured from coal or natural gas; however, in both cases, carbon is released, and environmental pollution occurs. It is also generated from water, which represents a better environmental solution. It is not toxic, as opposed to fuel, has a high octane number, and does not cause ozone issues [88]. MoS\(_2\) is a cheap catalyst in electrochemical HER [89] and water splitting reactions [90]. The large number of electrostatic active edges and high structural defects makes MoS\(_2\) a good catalyst. 1T MoS\(_2\) is known to be a better catalyst in HER than 2H MoS\(_2\) because of its reactive basal planes, which gains its activity from the hydrogen binding affinity at the surface S sites [91]. Studies have been conducted to enhance the catalytic activity and stability of MoS\(_2\) so that it can replace noble metals. The catalytic activity of MoS\(_2\) mainly depends on the active edges or the cell vacancies. The work in [92], based on the first-principle density functional theory (DFT), studied different possible cell vacancies of MoS\(_2\) and found that the best catalytic activity for MoS\(_2\) occurs with Mo and MoS\(_2\) cell vacancies. The efficiency of HER is enhanced when compared to platinum catalyst reactions. A later study conducted by the same researchers [90] focused on Mo defects on the inert basal plane of MoS\(_2\) and showed its better performance in HER and water splitting reactions. The active sites of MoS\(_2\) basal planes are restricted to edges and missing primitive cell vacancies. The weak van der Waal interactions between MoS\(_2\) layers result in a hydrophobic characteristic which assigns more
importance to layer defects [93]. A detailed study of five types of defects in MoS\textsubscript{2} layers was conducted [92]. The study investigated the effect of disulfur vacancy (VS\textsubscript{2}), vacancy complex of Mo and nearby tri-sulfur (VMoS\textsubscript{3}), Mo vacancy (VMo), nearby S tri-vacancy (VS\textsubscript{3}), and VMoS\textsubscript{2}, and it was found that VMo and VMoS\textsubscript{2} can activate inert basal planes and have a role in dissociating water in HER. The Gibbs energy for hydrogen adsorption (\(\Delta G^0_H^*\)) for VMo is \(-0.198\) eV, and for VS\textsubscript{3}, it is \(0.06\) eV, which is comparable to platinum, which has a value of \(-0.09\) eV.

The effect of strain on Mo vacancies in single-layer MoS\textsubscript{2} was investigated in [94], where a biaxial compressive strain of 4.5%, carried out by modifying the Mo and S interaction around the vacancy, showed optimal catalytic properties, with Gibbs free energy between \(-0.03\) and \(-0.04\) eV at the active sites. A hybrid catalyst made by growing MoS\textsubscript{2} over cobalt diselenide (MoS\textsubscript{2}/CoSe\textsubscript{2}) approached the commercial platinum catalyst behavior [95]. The reaction in the acidic electrolyte had a Tafel slope of 36 mV dec\textsuperscript{−1}, onset potential of \(-11\) mV, and exchange current density of \(7.3 \times 10^{-2}\) mA cm\textsuperscript{−2}. A trial to increase the active sites of MoS\textsubscript{2} was introduced in [96] using cracked monolayers of 1T MoS\textsubscript{2}. The monolayers were obtained through hydrothermal synthesis. 2H MoS\textsubscript{2} was ultrasonicated with lithium which facilitated the intercalation of MoS\textsubscript{2} layers, which were then exfoliated to obtain 1T MoS\textsubscript{2}. The resulting MoS\textsubscript{2} had a favorable HER performance characteristic, with a low overpotential of 156 mV, at 10 mA cm\textsuperscript{−2} in an acidic medium, and a low Tafel slope of 42.7 mV dec\textsuperscript{−1}. Table 3 summarizes some MoS\textsubscript{2} applications in HER.

### Table 3. Energy generation applications of different MoS\textsubscript{2} structures and composites.

| Type of Reaction | Catalyst Used | Specification | References |
|------------------|---------------|---------------|------------|
| HER              | (MoS\textsubscript{2}/CoSe\textsubscript{2}) | Tafel slope = 36 mV dec\textsuperscript{−1}  
Onset potential = \(-11\) mV  
Exchange current density = \(7.3 \times 10^{-2}\) mA cm\textsuperscript{−2} | [95] |
| HER              | 1T MoS\textsubscript{2} | Overpotential = 156 mV, at 10 mA cm\textsuperscript{−2}  
Tafel slope = 42.7 mV dec\textsuperscript{−1} | [96] |
| HER/OER          | Amorphous Ni–Co complexes hybridized with 1T MoS\textsubscript{2} | Overpotentials = 70 mV HER  
and 235 mV for OER at 10 mA cm\textsuperscript{−2}  
Tafel slope = 38.1 to 45.7 mV dec\textsuperscript{−1} | [97] |
| OER              | Rhombohedral MoS\textsubscript{2} microspheres over conductive Ni | Overpotential \(\approx 310\) mV  
Tafel slope \(\approx 105\) mV dec\textsuperscript{−1} | [98] |
| OER              | MoS\textsubscript{2} quantum dots (MSQDs) | Overpotential = 280 mV  
Tafel slope = 39 mV dec\textsuperscript{−1} | [99] |
| CO\textsubscript{2} reduction | Vertically aligned MoS\textsubscript{2} nanoflakes (2H and 1T phases coexist) | Overpotential = 54 mV  
Reduction current density = 130 mA cm\textsuperscript{−2} at \(-0.764\) V | [100] |
| CO\textsubscript{2} reduction | p–n junction Bi\textsubscript{2}S\textsubscript{3}/MoS\textsubscript{2} composite | Photocatalytic CO\textsubscript{2} reduction  
20 times higher than single catalysts under visible light irradiation | [101] |
| CO\textsubscript{2} reduction | 3R MoS\textsubscript{2} nanoflower powder | Synthesized using CVD  
CO production < 0.01 \(\mu\)mol-g\textsubscript{cat}\textsuperscript{−1} hr\textsuperscript{−1} at 25 \(^\circ\)C which is negligible | [102] |

4.2.2. Oxygen Evolution Reactions (OER)

MoS\textsubscript{2} acts as a catalyst in OER which is a step in water splitting. Few studies have been conducted related to the role of MoS\textsubscript{2} in OER. 1T MoS\textsubscript{2} with amorphous nickel–cobalt complexes was used as a catalyst in water splitting to generate hydrogen and oxygen [97]. The method represents a low-cost, easy, and stable way to perform water splitting instead of using expensive noble metal catalysts. Another hybrid nanocomposite made of MoS\textsubscript{2} microspheres over Ni foam was proposed in [98]. The study made use of the efficient
catalytic activity of MoS$_2$ while increasing its conductivity by attaching it to the conductive Ni foam. The overpotential decreased rapidly (nearly by 290 mV) when compared with RuO$_2$ as a catalyst. MoS$_2$ quantum dots (MSQDs) in [99] were used as a catalyst for OER. The quantum dots were synthesized using (NH$_4$)$_2$MoS$_4$ as a precursor to produce MoS$_2$ quantum dots (MSQDs), and then activation of QDs was carried out using potential cycling under electrolyte conditions to produce the as-synthesized materials after cycling (MSQDs-AC). The catalytic current density increased as the number of potential cycles increased, and it reached its maximum after 50 potential cycles. The technique avoids using carbon that leaves carbon QDs behind which negatively interfere with the process. The resulting MSQDs-AC had the lowest Tafel slope (39 mV dec$^{-1}$) when compared to other state-of-the-art catalysts such as IrO$_2$/C, and they also had fast reaction kinetics. Table 3 summarizes some of the MoS$_2$ applications in OER.

4.2.3. CO$_2$ Reduction

CO$_2$ is one of the main reasons for climatic change, global warming, and ozone layer decrease. It also causes serious health problems that lead to human death [103]. The direction nowadays is towards reducing CO$_2$ into CO or producing fuel from it. This is called e-fuel (electrofuels), which means producing fuel from hydrogen and CO$_2$ through photocatalytic or electrocatalytic activity. There are a lot of studies regarding the photoreduction of CO$_2$ on semiconductors [104], such as solar-driven CO$_2$ conversion, where the semiconductor used in solar cells acts as a biocatalyst that converts CO$_2$ directly into fuel (methane or ethanol) [105]. Although there may be some extended costs and climatic mitigations in synthetic fuel production, it still represents a cheap and efficient energy source [106].

Metal chalcogenides are known for their catalytic activity in HER, OER, and CO$_2$ reduction [107,108] due to their atomic arrangement and structure. They have good electrical transport and large-scale production. MoS$_2$ is one of the metal chalcogenides that can be used in CO$_2$ reduction reactions due to its excellent light absorption; however, studies are still being conducted to increase its conductivity and catalytic activity to be compared with other noble metal-based catalysts. The catalytic activity of MoS$_2$ in CO$_2$ reduction reactions was investigated in [109]. The inclined (sharp) MoS$_2$ edges could adsorb CO$_2$ and reduce it to CO [100]. A p–n junction Bi$_2$S$_3$/MoS$_2$ composite in [101] showed better light absorption and CO$_2$ adsorption than single catalysts. The high light absorption of p-type MoS$_2$ and high catalytic activity of n-type Bi$_2$S$_3$ were utilized. Nanoflower MoS$_2$ powder prepared through CVD showed enhanced photocatalytic activity [102], as illustrated in Figure 4, but, still, the CO production rate was less than 0.01 µmol-g$^{-1}$hr$^{-1}$ at ambient temperature (25°C), which is very small and can be neglected. When treated with H$_2$, the CO production doubled after 30 min of treatment. The work presented an easy synthesis technique of MoS$_2$ for CO and H$_2$O production, but, still, there is a lot of work to carry out to enhance it. Table 3 summarizes a few works regarding CO$_2$ reduction.

4.2.4. Solar Cells

Amorphous silicon and organic semiconductors are mainly used to synthesize nanosolar cells. As the thickness of solar cells decreases, efficiency increases, and losses and costs decrease [110]. Thin MoS$_2$ monolayers were a good choice to be used in photovoltaics due to their optical characteristics and the easiness of synthesizing very thin structures with favorable properties. A very thin structure (1 nm thick) of MoS$_2$ and graphene was proposed in [111] with triple the efficiency of ordinary photovoltaics. However, the light absorbance of the extra-thin structure was only 10%, which is low when compared with that of silicon (40%). Different structures were proposed to enhance light absorbance or trap the incident light [110-114]. A graphene-MoS$_2$ wedge-shaped microcavity achieved a 90% increase in light absorbance [110]. A heterostructure of mercury cadmium telluride (Hg$_{0.33}$Cd$_{0.66}$Te) and monolayer MoS$_2$ was used to shift the absorbance of the whole structure to
MoS$_2$ flakes were used as a buffer with copper zinc tin sulfide (CZTS) solar cells, where they showed a high efficiency of 17.03% and enhanced thermal stability at high temperatures [115]. They can work as an electron transport layer (ETL) [116] or a hole transport layer (HTL) [117]. The flakes were used as an HTL in [118], where they acted as high-stability cells, with a long shelf time of 800 h and a relatively high efficiency of 3.9%. In [119], a MoS$_2$ film was used to decrease the defects and increase the depth of the depletion region of solar cells, and the performance of the cell was enhanced by decreasing the impurity concentration and increasing the built-in potential at the MoS$_2$-p-Si interface. MoS$_2$ has a role in the newest solar cell structures (organometallic-halide perovskite solar cells) [120], where MoS$_2$ nanoflakes work as a buffer to improve stability and obtain a high efficiency of 14.9%. The open-circuit voltage ($V_{oc}$) and the short-circuit current ($J_{sc}$) are higher than standard cells, as shown in Figure 5. Table 4 summarizes the role of MoS$_2$ in solar cells, whether it acts as a hole transport layer (HTL), as an electron transport layer (ETL), or as a buffer or used with other materials to enhance the efficiency of the solar cell.

Table 4. MoS$_2$ applications in solar cells.

| Structure | Role of MoS$_2$ | Enhanced Property | References |
|-----------|----------------|-------------------|------------|
| Graphene-MoS$_2$ | Enhance the cell performance | Enhance the light absorbance to above 90% | [110] |
| Wedge-shaped microcavity | | | |
| (Hg$_{0.33}$ Cd$_{0.66}$ Te) and monolayer MoS$_2$ | Enhance the cell performance | Shift the cell absorbance to visible light range | [112] |
| Microdome texture on MoS$_2$ thin film | Enhance the cell performance | Decreases reflections and traps light for incident angles (0–50) | [113] |
| MoS$_2$/GaAs over boron nitride | Enhance the cell performance | PCE increased to 9.03% | [114] |
| MoS$_2$ spray coating over perovskite cells | HTL | PCE = 3.9% | [118] |
| 5 monolayer MoS$_2$ nanosheets onto indium tin oxide ITO substrate | ETL | $J_{sc} = 16.24$ mA cm$^{-2}$, $V_{oc} = 0.56$ V, (fill-factor) $FF = 0.37$, PCE = 3.36% | [121] |
| Structure                          | Role of MoS<sub>2</sub> | Enhanced Property                                                                 | References |
|-----------------------------------|-------------------------|-----------------------------------------------------------------------------------|------------|
| ZnO-MoS<sub>2</sub>-CZTS Buffer   | Buffer                  | \( J_{sc} = 29.42 \text{ mA cm}^{-2} \) \( V_{oc} = 1.01 \text{ V} \) \( FF = 0.574 \) Efficiency = 17.03\% | [115]      |
| Organometallic-halide perovskite solar cell | Buffer                | \( J_{sc} \approx 22 \text{ mA cm}^{-2} \) \( V_{oc} \approx 0.96 \text{ V} \) \( FF \approx 0.6 \) PCE = 14.9\% | [120]      |

Figure 5. Structure and characteristics of organometallic-halide pervoskite solar cells: (a) schematic of pervoskite solar cell with 2D MoS<sub>2</sub> as a buffer layer; (b) power conversion efficiency of standard solar cell and modified cell with MoS<sub>2</sub> layer; (c) \( V_{oc} \) versus time for standard and modified cells; (d) \( J_{sc} \) versus time for standard and modified cells. Adapted from [120]. npj 2D Materials and Applications Nature 2020.

5. Challenges

The unique properties of MoS<sub>2</sub> enabled its use in various energy storage and generation applications; however, it faces some challenges and needs more improvements to be used on a commercial scale. The synthesis techniques are facing challenges to produce MoS<sub>2</sub> on a large scale and with a low cost. If we are moving towards using 2H MoS<sub>2</sub> in energy applications, we will have to increase its conductivity, and if we are going to include 1T MoS<sub>2</sub>, we will have to address its stability. Due to the astounding properties of 1T MoS<sub>2</sub> in energy applications, research has focused more on scaling up its production using...
different synthesis techniques and increasing its stability [122]. Although MoS\textsubscript{2}-based LIB are competitive in their specific capacities, their cycling stability and manufacturing cost have to be improved [73]. MoS\textsubscript{2} enhances LIB safety when used as an interlay or protective layer [123], but, still, there are some concerns about its oxidation in air and its conversion when it is in direct contact with Li, which will affect the battery storage and quality. Moreover, we do not have a full picture of MoS\textsubscript{2} layers’ immobilization of polysulfides, and their phase transformation during cycling.

The catalytic activity of MoS\textsubscript{2} for energy generation applications is good but it is still less than that of noble metals [124], even though it is a cheap choice if compared to noble metal catalysts. The catalytic activity of platinum has outperformed MoS\textsubscript{2} until now [125]. The computational and experimental calculations related to MoS\textsubscript{2} doping for its use as a catalyst for HER have still not been fully studied [126,127]. The study of pure MoS\textsubscript{2} is nearly mature, but the study of its composites for exceptional characteristics in energy applications needs more research [128]. Reduced graphene oxide with a MoS\textsubscript{2} hollow sphere (MoS\textsubscript{2}-HS) (rGO/MoS\textsubscript{2}-S) was studied to be used in energy conversion and storage, and it showed enhanced gravimetric capacitance of approximately 318 F g\textsuperscript{−1}, a high specific energy of ~44.1 W h kg\textsuperscript{−1}, a high power output of ~159.16 W kg\textsuperscript{−1}, and good cyclability for above 5000 cycles [129]. It also showed a unique performance in HER with a low overpotential of ~0.16 V, a low Tafel slope of ~75 mV dec\textsuperscript{−1}, and a high current density of ~0.072 mA cm\textsuperscript{−2}. This proves that we have to give MoS\textsubscript{2} composites more attention in energy applications. The composite materials of MoS\textsubscript{2} with carbon or noble metals or metal oxides need more attention to be used commercially. The purity, crystalline structure, and particle size of MoS\textsubscript{2} need more engineering as well.

6. Conclusions

In this review, we presented MoS\textsubscript{2} as a future material for energy applications. MoS\textsubscript{2} is cheap, abundant, and easily synthesized. Moreover, its photocatalytic and electrocatalytic properties and its structure have paved the way to its use in energy storage devices and energy generation reactions. The high conductivity and the weak van der Waal forces between the layers of the MoS\textsubscript{2} metallic phase (1T MoS\textsubscript{2}) have allowed its use in LIB as an anode where it is easy for Li ions to intercalate between its layers. Additionally, its large area together with its superconductivity and easy restacking renders it optimum for supercapacitors [130]. Its high electrocatalytic and photocatalytic activity has allowed its use as a catalyst in hydrogen evolution reactions and in solar cells where it can be used to reduce CO\textsubscript{2} and produce energy as well. The latter will be a comprehensive environmental solution to produce clean energy and decrease the CO\textsubscript{2} percentage in our environment. Thin MoS\textsubscript{2} layers are known to enhance solar cells’ efficiency, working as an electron transport layer (ETL), a hole transport layer (HTL), or a buffer, but their light absorbency is still low, and that is why different studies have worked on modifying solar cells through heterostructures [131] or modifying the cell shape to increase absorbency.

On the other hand, MoS\textsubscript{2} is facing some challenges in its large-scale production with the required properties (fewer impurities, and better conductivity and stability). The works conducted thus far have reached some solutions such as using MoS\textsubscript{2} composites [132] or heterostructures or using specific structures to enhance the efficiency and decrease the production cost. Still, there is a lot of work to be conducted to completely substitute other materials, but it will be worth it, since the MoS\textsubscript{2} will be an economic, easy, and efficient solution compared to other 2D nanomaterials [133–141].

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