

Review on Synthesis and Applications of Nanomaterial Molybdenum Disulphide (MoS_2) and Photocatalysis Process

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Abstract: Research on the creation and use of nanomaterials has been done for a long time. Because of the contrasts between the two chemical elements-Sulphur, an oxygen family element, and molybdenum, the base element—they have a range of desirable qualities. There are still a number of obstacles to overcome despite significant advancements in our understanding of the mechanisms underlying the biological characteristics and catalytic activity of molybdenum disulphide nanoparticles, as well as the procedures involved in their nucleation, development, and structure. The evolution of nano-materials has made it possible to modify a material's structure and form at the nano-scale level to achieve specific uses. To discriminate between metallic phases and semiconducting, also layered transition metal chalcogenides (TMDs), such as molybdenum disulfide (MoS_2), and quasi two-dimensional (2D) materials like graphene and 2D honeycomb silicon were developed.. Because it can display a broad variety of properties as it moves from the bulk to the nano-scale. Among these, molybdenum disulfide (MoS_2) is an intriguing multifunctional substance. MoS_2 is a great material for post-silicon electronics on a single sheet because of its straight band-gap value of 1.9 eV. Its mobility is around $200\text{cm}^2(\text{Vs}^{-1})$ at room temperature, and it has high on/off current ratio. MoS_2 's structure also contributes to two of its properties. It is a useful instrument for gas sensing because of its hexagonal structure, covalent connections between S-Mo-S atomic layers, and Van der Waals interactions between neighboring MoS_2 layers.

Because of its promising characteristics, MoS_2 can be used in a variety of practical applications. Our goal in this work is to talk about the most recent synthesis techniques and how they can be used to create 2D MoS_2 materials. Photocatalytic materials that react to visible light have numerous significant uses, from energy storage and conversion to the processing of industrial waste. For all photocatalytic applications, molybdenum disulfide (MoS_2) and its derivatives are ideal because they have good stability and recyclability, when exposed to visible light it has more photocatalytic activity. Because of their superior physicochemical characteristics, MoS_2 -based materials have found extensive application in a variety of sectors, including organic transformation processes, environmental remediation, and wastewater treatment. This review centres on the basic characteristics of molybdenum Disulphide (MoS_2), its current applications and unresolved issues, as well as important approaches to address problems pertaining to MoS_2 use in photo catalysis. There is also a critical discussion of the use of MoS_2 -based materials in visible-light-induced catalytic processes for the treatment of various pollutants, such as industrial, pharmaceutical, environmental, and agricultural waste. The review concludes by outlining MoS_2 's potential applications in both established and developing photo catalysis fields.

Keywords: Molybdenum disulphide (MoS_2), transition metal dichalcogenides (TMDs), Photocatalysis.

1. Introduction

Due to population expansion and the fast industrialization of developing countries, there is an increasing demand for energy worldwide, which is driving up the usage of fossil fuels and perhaps causing irreversible anthropogenic climate change. Photocatalytic technologies have shown a lot of promise in recent years for reducing environmental pollution and the energy issue [1]. The capacity of visible-light driven photo catalysis to efficiently harness the vast energy of solar radiation as a clean, inexpensive, and renewable driving force[2] is one of its primary advantages. Visible-light-active photo catalysts have attracted a lot of interest because they are very easy to create and recycle using fundamental chemical processes [3].



Figure 1: Benefits of utilizing photo catalysts to remove contaminants

A few advantages of employing photo catalysts for pollutant removal are illustrated in Figure 1. These photo catalysts' band gap energy determines how much light they can absorb. Among those used as photo catalysts, semiconductors referred to as metal oxides and metal chalcogenides have piqued the most attention. Since metal oxides are stable, environmentally benign, and readily available, they have been used in photo catalysis. Nevertheless, the majority of the only light that metal oxide photo catalysts can detect is ultraviolet (UV) light that makes up approximately 8% of the solar spectrum's energy, compared to 43% for visible light [4]. On the other hand, metal chalcogenides, having higher visible light sensitivity, smaller band gaps than metal oxides, and the ability to function as visible light-active photo catalysts [5]. The use of metal chalcogenides in photocatalytic systems is becoming more and more common due to their among other advantageous features, large surface area, configurable form, and band gap energies [6-7]. Molybdenum disulfide (MoS_2) is one of the chalcogenides that has drawn the attention of scientists due to its remarkable properties, [8-9] that includes, and more of locations that are catalytically have hardness, high stability and, active strong oxidizing activity, and non-toxicity [10]. Among the principal uses for MoS_2 [11-12] are the oxidative desulfurization, photocatalytic evolution of hydrogen, and the photocatalytic destruction of organic contaminants. One- or few-layered MoS_2 has been compared to graphene due to its hexagonal Mo and S atom arrangement; [13] but MoS_2 With a smaller band gap than graphene, MoS_2 is a good option for photo catalysis driven by visible light because it can produce electron/hole pairs (e^-/h^+) when excited by light. MoS_2 's superior light absorption capacity and strong chemical stability have garnered a lot of interest in photo catalysis. Previous studies have demonstrated that doping MoS_2 with metal or nonmetal elements or modifying it with a second semiconductor or metal are efficient methods for increasing its photocatalytic activity. A $\text{C}_3\text{N}_4/1\%\text{Ni}_2\text{P}/\text{MoS}_2$ hetero junction, for example, demonstrated a high H_2 generation of $532.41 \mu\text{mol g}^{-1} \text{h}^{-1}$, according to Lu et al. [14]. In comparison with the $\text{g-C}_3\text{N}_4/1.5\% \text{MoS}_2$ and $\text{g-C}_3\text{N}_4/1\% \text{Ni}_2\text{P}$, respectively, this was 2.47 and 5.15 times higher.

Using several sulfur sources and molybdenum precursors, such as elemental sulfur powder [15], thiourea [16], thioacetamide [17], and L-cysteine [18], there are several approaches to manufacture MoS_2 . By varying the reaction solvent, temperature, pH, length of the reaction, and the addition of ligands or surfactants—all of which are essential for controlling the synthesis to yield the intended chalcogenide—a variety of intriguing morphologies can be created. A review of the literature demonstrates the many techniques employed in the synthesis of MoS_2 materials as well as their uses. The most popular techniques are hybrid, solvothermal, hydrothermal, solid-state [20-23].

The structure, characteristics, and synthetic techniques pertaining to MoS_2 and MoS_2 -based materials are the main topics of this review. A succinct summary of the challenges addressed by researchers in the field is still missing, despite an exponential growth in publications over the previous five years pertaining to the photo-catalytic uses of MoS_2 -based materials. Therefore, the purpose of this study is to provide an overview of the major issues and essential tactics for resolving the issues that have been discovered. Furthermore discussed will be the most current advancements in the agricultural waste and photocatalytic degradation of pharmaceutical, environmental, industrial using materials based on molybdenum disulfide (MoS_2). Lastly, the prospects for this quickly developing topic will be discussed, along with some specific recommendations for future research.

2. Challenges Facing Chalcogenide-Based Photo-catalysis:

The majority of metal oxides have broad band gaps, which restricts their use as photocatalysts in visible light. Since most metal chalcogenides have band gap energies than metal oxides, they are more suitable for photocatalysis triggered by visible light. Although, as will be discussed in more detail below, some adjustments are needed to enhance their photocatalytic activity. Another difficulty confronted by researchers is the stability of chalcogenides that have been synthesized in photocatalytic settings. The photocatalytic efficacy of chalcogenides has been demonstrated to be impacted by challenging conditions such as photocorrosion and a brief excited-state lifespan [39]. For example, Cai et al. showed that photo corrosion produced significant levels of Cd^{2+} in solution⁴⁰ when pure CdS was used for photocatalytic rhodamine B degradation [40].

Because of its exceptional photo stability in solution, MoS_2 does not suffer from photo corrosion. This is because the interaction between the sulfur pz and molybdenum dz² orbitals at the top of the valence band (VB) leads to the development of the antibonding state [41]. In addition, there may be issues with the photo catalyst's recovery following the conclusion of the photocatalytic activity. Finally, but just as importantly, a major problem with the majority of metal chalcogenides is their limited ability to transfer and segregate the photo generated charge carriers to active catalytic sites. This can be attributed to low carrier mobility, short carrier lifetimes, or a mix of the two [42].

2.1 Realistic Approaches to Address the Difficulties in Chalcogenide-Based Photocatalysis:

Although MoS_2 is a visible light-responsive photocatalyst, its wide applicability to photocatalysis is restricted due to a common restriction shared by narrow band gap photocatalysts: e^-/h^+ pairs' high recombination efficiency. Consequently, a variety of materials, including metals[43], metal oxides[11], and carbon-based compounds, have been doped and combined with MoS_2 , in order to increase charge carrier separation[44]. $Ag@MoS_2$'s increased H_2 evolution activity under visible light irradiation was demonstrated by Cheah et al.[45].

The authors discovered that the e^- and h^+ separation was aided by the deposition of Ag onto MoS_2 , It also enhanced the total photocatalytic efficacy by preventing charge recombination. Additionally, the SPR effect of the nanosized Ag particles enhanced the photocatalyst's ability to harvest light. These findings showed that MoS_2 has higher photocatalytic activity than pure MoS_2 , suggesting that material modification through composite creation represents a viable tactic for enhancing MoS_2 's photocatalytic efficacy.

2.2 MoS_2 's optical and structural characteristics:

Attractive van der Waals forces hold MoS_2 's layered S-Mo-S atomic layers a multilayer transition metal dichalcogenide, together [51]. The characteristics of MoS_2 change dramatically as it goes from bulk to nanoscale, which makes it a material with multiple functions. Two aspects of MoS_2 's structure are: 1) a S-Mo-S atomic layer configuration arranged hexagonally, with the Mo and S atoms having strong covalent connections 2) Van der Waals forces hold together the constituent layers [35,36].

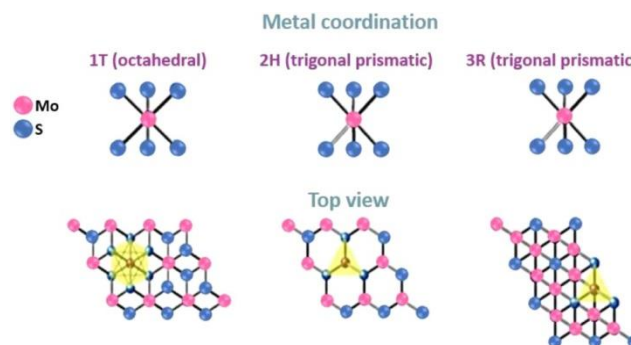


Figure 2: MoS_2 three different phases' crystal structures and metal coordination.

Figure 2 , MoS₂ shows many phases. We can see 1T, 2H, and 3R. 2H-MoS₂ or 3R-MoS₂, H- hexagonal and R- rhombohedral symmetries, In nature MoS₂ is present in Crystalline form. Each Mo atom is bound covalently with six S₂ is in centre in a trigonal prismatic coordination sphere . A new trigonal symmetry metastable metallic phase known as 1T Figure 2 shows the distinct phases of MoS₂, specifically 1T, 2H, and 3R. Natural forms of crystalline MoS₂ are 2H-MoS₂ or 3R-MoS₂, where the letters "H" and "R" denote, respectively, rhombohedral and hexagonal symmetry. In these figures, every Mo atom is covalently connected to six S₂⁻ ions and centered in a each S atom has coordination which is pyramidal and is connected to three Mo atoms [26]. A brand-new, trigonal symmetry metastable metallic phase known as 1T -MoS₂ is produced when alkali metals are intercalated with 2H-MoS₂. This phase is not found in the natural world [29].

2.3 The Use of MoS₂ and MoS₂-Based Materials as Photocatalysts:

MoS₂ has garnered a lot of interest, and a number of advantageous photocatalytic characteristics, including low toxicity and cost, have been documented. These characteristics include good optical absorptivity, a small band gap energy and strong charge carrier mobility. However, photocorrosion, edge activity effect, and photogenerated e⁻/h⁺ recombination limit the performance of MoS₂. Controlling the morphology, doping to modulate energy bands, band alignment via carbon nanostructure alteration, heterojunction creation, and conjunction with surface plasmon resonance-exhibiting metal particles have all been tried in the past to improve the photocatalytic properties of MoS₂. The generation charge carrier pairs photoexcited (e⁻/h⁺) is the first step in the photocatalytic redox reactions.

2.4 Using MoS₂ and MoS₂-based materials, photocatalytic treatment of microorganisms, organic pollutants, and inorganic pollutants:

Inadequate wastewater treatment, coupled maintaining both human health and the natural ecology, remain major global issues as a result of industrialization's impact on the environment. Water bodies are contaminated by both organic and inorganic pollutants, such as wastes from industry, the environment, pharmaceuticals, and agriculture, making the efficient treatment of wastewater essential. Figure 3 illustrates the uses of MoS₂ and MoS₂-based materials under visible-light irradiation.

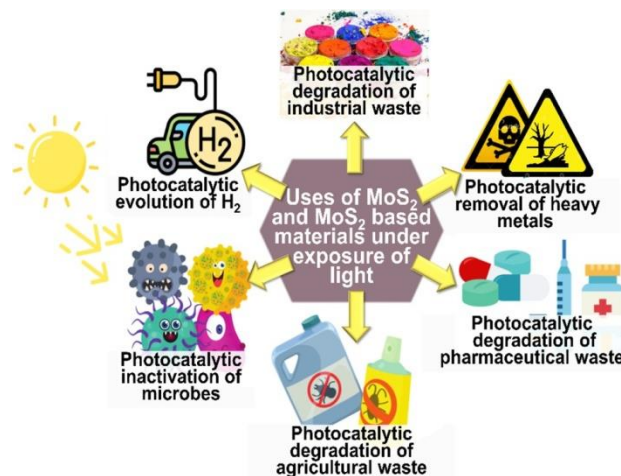


Figure 3. MoS₂ and MoS₂-based materials exposed to visible light [courtesy from google]

3. Photocatalytic Treatment of Industrial Waste:

One of the main causes of environmentally dangerous water contamination is industrial waste effluents. Wastewater pollutants have been removed via coagulation, adsorption, precipitation, and biodegradation, among other treatment methods. An additional potentially effective technique for eliminating contaminants that are incapable of being broken down by physical or biological processes is photocatalysis. Even at low quantities, dyes containing coloured pigments that are not biodegradable are hazardous to living organisms and present in water. Therefore, it is essential to remove colours from waste water. Using hydrothermally produced flowerlike MoS₂, In just ninety minutes, Sheng et al. were able to demonstrate

the photocatalytic breakdown of dye methylene blue with a degradation activity of 95.6% when exposed to visible light [31]. In a different study, Zhang et al. used a hydrothermal technique using CTAB as the surfactant to effectively construct MoS₂ nanosheet petals with 2.05 eV band gap energy [34].

3.1 Photocatalytic Treatment of Environmental Waste:

One well-known way to prevent environmental problems brought by releasing of industrial effluents directly or indirectly into the environment is to remove heavy metals from the ecosystem. The precipitation method, membrane separation, activated carbon adsorption, and activated carbon adsorption are some of the commonly utilized heavy metal removal techniques²⁵. In addition to these more well-established techniques, photocatalysis is becoming more significant as a heavy metal pollution cleanup strategy. Growing concern is being expressed about the expanding usage of chromium in modern civilization, which can contaminate land and water. There are various oxidation states in which Cr can exist. Cr(VI) is dangerous due to its high mobility, while Cr(III) is less toxic due to its lower mobility²⁸. Using a MoS₂/ZnS/ZnO composite, Zhao et al. effectively demonstrated photocatalytic Cr(VI) reduction with a 98.7% reduction in 90 minutes³⁰. In order to create high efficiency of Mo-based photocatalysts and the capacity to optimise the heavy metal treatment effect, various methods for enhancing the photocatalytic activity of MoS₂ materials should be further researched. Moreover, additional procedures, including electrocatalysis and photocatalysis, adsorption and photocatalysis, etc., might be combined to remove heavy metals more effectively.

4. Prospects for the future:

Many studies have addressed the synthesis of MoS₂ and MoS₂-based nanomaterials as well as their many uses nevertheless; a number of obstacles still need to be overcome.

- 1) Because of their exceptional physical and chemical properties, materials based on molybdenum will find extensive application in a various fields and may even become commercially viable in the future. This will make it possible to apply MoS₂ on different types of media and release it into the environment, which could have an impact on human health and environmental safety. As such, a thorough assessment of the toxicity of MoS₂-based materials is needed.
- 2) Up until now, the application of MoS₂-based photocatalysts has only been possible in laboratory settings. Real-world environmental applications for MoS₂ have not yet been investigated, and there is currently no perfect photocatalyst that can be utilized commercially or on a large scale.
- 3) Major issues still include the short life of charge carriers, rapid recombination, and catalyst recovery after use. Because of these inherent issues with MoS₂, it is imperative to find a new class of materials to improve its photocatalytic properties.
- 4) Because of its exceptional optical characteristics, the photocatalytic activity of MoS₂ in a variety of model systems has been thoroughly investigated. Nevertheless, a key goal continues to be the creation of reasonably priced MoS₂-based products that can specifically target the pollutants found in wastewater.
- 5) When exposed to visible light Some MoS₂ composites become unstable. Thus, additional research is needed to create photostable MoS₂-based material.
- 6) Information on the variables that influence photocatalytic activity, such as temperature, pH, and the presence of many pollutants, is scarce. Thus, a greater variety of experimental circumstances should be used to study photo-catalytic degradation.
- 7) One of the main challenges is coming up with workable ways to prepare MoS₂ in large enough amounts for industrial use. Therefore, additional study is required to determine how to scale up synthetic processes for large-scale production.

5. Conclusion:

A lot of research is now being done on MoS₂ and MoS₂-based nanomaterials as possible photocatalysts for the destruction of organic and inorganic contaminants and the eradication and/or inactivation of microorganisms. Due to their exceptional physicochemical characteristics, MoS₂ and MoS₂-based materials can be prepared using a variety of synthetic techniques, and they find use in a wide range of industries. This paper examined the latest developments in MoS₂ modification, such as the use

of carbon-based supports, coupling with other semiconductors or metals, and doping with metals and nonmetals. Additionally, a summary of the synthesised materials' photocatalytic capabilities towards the breakdown of particular contaminants was provided. Lastly, the prospects for employing MoS₂-based materials for effective visible-light-induced photocatalysis were explored.

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