Molybdenum disulfide (MoS₂) based photoredox catalysis in chemical transformations

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Photoredox catalysis has been explored for chemical reactions by irradiation of photoactive catalysts with visible light, under mild and environmentally benign conditions. Furthermore, this methodology permits the activation of abundant chemicals into valuable products through novel mechanisms that are otherwise inaccessible. In this context, MoS₂ has drawn attention due to its excellent solar spectral response and its notable electrical, optical, mechanical and magnetic properties. MoS₂ has a number of characteristic properties like tunable band gap, enhanced absorption of visible light, a layered structure, efficient photon electron conversion, good photostability, non-toxic nature and quantum confinement effects that make it an ideal photocatalyst and co-catalyst for chemical transformations. Recently, MoS₂ has gained synthetic utility in chemical transformations. In this review, we will discuss MoS₂ properties, structure, synthesis techniques, and photochemistry along with modifications of MoS₂ to enhance its photocatalytic activity with a focus on its applications and future challenges.

1 Introduction

Molybdenum disulfide (MoS₂) is an inorganic compound of the transition metal dichalcogenide (TMD) series. It is one of the most used photocatalysts that has a wide range of applications in different fields. It is applicable to degrade pharmaceutically active compounds (PhACs), synthetic dyes (rhodamine B, methylene blue, methyl orange and novacron red Hunts-man), pesticides and herbicides. It also employed for photocatalytic evolution of oxygen, nitrogen fixation, ammonia synthesis and water electrolysis.1–7

In recent years, MoS₂ has received much attention due to its unique electrical and optical properties.8a MoS₂ is a two-dimensional (2D) transition metal dichalcogenide, a narrow band semiconductor with a band gap of 1.9 eV which can be altered by adjusting the number of layers. Among all 2D TMDs, MoS₂ is one of the few with a natural layered structure, indicating that MoS₂ can be stripped to obtain high-quality 2D MoS₂ without complicated chemical synthesis.8b Therefore, the cost of preparing 2D MoS₂ is much lower than other 2D TMDs due to...
the simple synthesis conditions. More importantly, 2D MoS₂ is a 2D semiconductor with a direct band-gap, which has the best electric performance among 2D TMDs. These make 2D MoS₂ get more attention among 2D TMDs.

Several characteristics of MoS₂ such as high absorbance in the visible region, high carrier mobility, stability, preferable catalytic activity, good photostability, outstanding electrochemical properties, strong surface adsorption capacity and higher specific surface area favours its application as a photocatalyst as well as a co-catalyst and also, it is capable of addressing the limitations faced by typical photocatalysts. Additionally, MoS₂ is found to be abundant and cheap. Currently, semiconductor photocatalysts with controllable morphologies are gaining significant attraction in applications associated with environmental remediation process. Phase engineering, defect engineering, doping of external materials, interlayer engineering, surface modification, and heterojunction construction make MoS₂ more flexible in terms of tuning its properties during synthesis.

Molybdenum disulfide (MoS₂) has emerged as one of the most important two-dimensional functional materials, popular new co-catalysts due to their excellent photocatalytic activity, substantial adsorptivity, great value and its non-toxicity. The visible region of electromagnetic spectrum exhibits the absorption spectrum of 2D MoS₂, providing a plethora of opportunities for widespread applications. Applications for MoS₂-based materials are said to include energy storage, hydrogen production, pollutant degradation, disinfection, etc. Numerous studies have recently provided a summary of photocatalytic properties of MoS₂ for numerous application areas.

In continuation of our work on photocatalysed organic synthesis, this review aims to provide a comprehensive report on the current research, especially the role of MoS₂ in the chemical transformation.

2 Synthesis of MoS₂

For the most part, two different synthetic procedures are used to create MoS₂: (1) a top-down strategy that involves exfoliating bulk MoS₂ to create materials with one or two monolayers, and (2) a bottom-up strategy that uses techniques like hydrothermal or chemical vapour deposition. Several methods exist for the preparation of MoS₂ using different molybdenum precursors and sulfur sources, like elemental sulfur powder, thiourea, thioacetamide, and L-cysteine. By regulating variables such as the reaction solvent, temperature, pH, reaction time, and the application of surfactants or ligands, which are essential for managing the synthesis to create the desired chalcogenide, a variety of fascinating morphologies can be created. Table 1 exhibits the different methods that have been used to synthesise MoS₂ materials alongside the applications of the synthesised materials. The most used methods are solid-state, hydrothermal, solvothermal, and hybrid methods.

The benefits and drawbacks of synthesis techniques such as thermal annealing, plasma-assisted synthesis, magnetron sputtering-based synthesis, atomic layer deposition (ALD), and wet chemical processes are summarised in Fig. 1.

3 Properties of MoS₂

MoS₂ is a typical and stable 2D transition metal dichalcogenide which reveals that it is a semiconductor of MX₂ type where the transition metals denote M and the chalcogen denotes X²⁻. MoS₂ is bonded to each other via ionic–covalent interactions. The sandwiched MoS₂ is brought together to form sheets with an interlayer distance of 0.65 nm by the weak van der Waals force, which assumes responsibility for creating a 2D layered structure. Fig. 2a depicts the MoS₂ structure as described. In addition, Fig. 2b reflects the fact that the presence of impurities in MoS₂ alters its interlayer distance. As an n-type semiconductor, MoS₂ has an indirect band gap of 1.2 eV in the bulk. The band gap of this semiconductor is inversely proportional to its number of layers. As a result, a direct band gap of 1.9 eV is obtained by almost reducing the number of layers to just one (Fig. 3c), making it a suitable photocatalyst in the visible region. The narrow band gap facilitates its high absorption of light in the visible region.

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Crystal lattices of MoS2 exist in four polymorphic forms namely 1H, 2H, 1T and 3R (H- Hexagonal, T-Tetragonal and R- Rhombohedral) which are classified based on the stacking arrangement and the co-ordination between Mo and S atoms (Fig. 2d).\(^{13}\) MoS2 is synthesized in various morphologies (Fig. 2e) which includes nanoflowers (Fig. 2e1, Fig. 2e2),\(^{48}\) nanosheets (Fig. 2e3, Fig. 2e4),\(^{49}\) nanoflakes,\(^{38}\) nanocrystals, nanospheres,\(^{31}\) nanoribbons,\(^{52}\) nanotubes (Fig. 2e5),\(^{51}\) nanoworms (Fig. 2e6),\(^{54}\)

| Synthesis No. | Method            | Metal precursor used | Source of sulfur used | Morphology and particle size | Applications                          | Ref. |
|---------------|-------------------|----------------------|-----------------------|------------------------------|---------------------------------------|------|
| 1             | Colloidal         | Mo(CO)\(_6\)         | Sulfur powder         | Nanosheets                   | Electrochemical studies               | 1    |
| 2             | Hydrothermal      | (NH\(_4\))Mo\(_7\)O\(_4\)\(_4\)H\(_2\)O | Thiourea (H\(_2\)CSNH\(_2\)) | Layered MoS\(_2\) nanoflowers with ∼0.1 μm particle size | Photocatalytic degradation of methylene blue and crystal violet dyes | 2    |
| 3             | Hydrothermal      | Sodium molybdate dihydrate | (Na\(_2\)MoO\(_4\)\(_2\)H\(_2\)O) | Nano flowers with average size ∼100 nm | Photocatalytic degradation of rhodamine B | 3    |
| 4             | Hydrothermal      | Sodium molybdate dihydrate | (Na\(_2\)MoO\(_4\)\(_2\)H\(_2\)O) | \(\ell\)-cysteine | Quantum dots with ∼2.5 nm particle size | 4    |
| 5             | Hydrothermal      | (NH\(_4\))Mo\(_4\)S\(_4\) | (NH\(_4\))Mo\(_4\)S\(_4\) | | Fluorescent probe for hyaluronidase detection | 5    |
| 6             | Chemical Exfoliation | Commercially available MoS\(_2\) powder | | | Nanosheets | 6    |
| 7             | Chemical vapor deposition | Ammonium heptamolybdate | Sulfur | | Not mentioned | 7    |
| 8             | Colloidal         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | | Spherical quantum dots with average size ∼5 nm | 8    |
| 9             | Heating | Mo(acac)\(_2\) | 1-Dodecanethiol | Nanosheet | Electrical bistability performance | 9    |
| 10            | Hot injection     | Molybdenum(v) chloride | MoCl\(_3\) | | | 10    |
| 11            | Hydrothermal      | Sodium molybdate dihydrate | (Na\(_2\)MoO\(_4\)\(_2\)H\(_2\)O) | Thiourea (H\(_2\)CSNH\(_2\)) | Coral-like | 11    |
| 12            | Hydrothermal      | Na\(_2\)MoO\(_4\)\(_2\)H\(_2\)O | Cysteine | | Quantum dots with 2 ∼3.5 nm particle size | 12    |
| 13            | Solid state       | (NH\(_4\))Mo\(_7\)O\(_4\)\(_4\)H\(_2\)O | Sulfur | | Nanosheets, thinner than 5 nm | 13    |
| 14            | Hydrothermal      | Na\(_2\)MoO\(_4\)\(_2\)H\(_2\)O | Thiourea (H\(_2\)CSNH\(_2\)) | Irregular with average size in the range 12–25 nm | Electrochemical studies | 14    |
| 15            | Hydrothermal      | Ammonium hepta molybdate tetrahydrate | [NH\(_4\)]\(_4\)Mo\(_4\)O\(_4\)\(_4\)H\(_2\)O | | Ammonium polysulfide as the sulfur source: Uniform MoS\(_2\) nanospheres with average size of ∼100 nm | 15    |
| 16            | Hydrothermal      | MoO\(_3\) | Potassium thiocyanate | | Flowerlike MoS\(_2\) spheres with average diameter of 1–2 nm | 16    |
| 17            | Hydrothermal      | Na\(_2\)MoO\(_4\)\(_2\)H\(_2\)O | \(\ell\)-cysteine | | Microspheres comprising crossed-linked nanorods ∼100 nm in length | 17    |
| 18            | Hydrothermal      | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea (H\(_2\)CSNH\(_2\)) | Flowerlike microsphere | 18    |
| 19            | Hydrothermal      | (NH\(_4\))Mo\(_7\)O\(_4\)\(_4\)H\(_2\)O | Thiourea | | | | 19    |
| 20            | Hydrothermal      | (NH\(_4\))Mo\(_7\)O\(_4\)\(_4\)H\(_2\)O | Na\(_2\)S | | Nanasheets | Detection of dopamine | 20    |
| 21            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | Quantum dots with average diameter of ∼1.72 nm | 21    |
| 22            | Solid state       | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | Sheetlike structure and ultrathin layers | 22    |
| 23            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 23    |
| 24            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 24    |
| 25            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 25    |
| 26            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 26    |
| 27            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 27    |
| 28            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 28    |
| 29            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 29    |
| 30            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 30    |
| 31            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 31    |
| 32            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 32    |
| 33            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 33    |
| 34            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 34    |
| 35            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 35    |
| 36            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 36    |
| 37            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 37    |
| 38            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 38    |
| 39            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 39    |
| 40            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 40    |
| 41            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 41    |
| 42            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 42    |
| 43            | Microwave         | Ammonium tetrathiomolybdate | [NH\(_4\)]\(_4\)Mo\(_4\)S\(_4\) | Thiourea | | | 43    |

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coral-like structures (Fig. 2e).\textsuperscript{49} nanodots and quantum dots (Fig. 2e).\textsuperscript{55}

Due to the 2D nature of MoS\textsubscript{2}, its intrinsic properties are greatly influenced by the surrounding environment on the nanoscale. The suspended structures in these systems are hybrid systems with transport performance,\textsuperscript{56-58} tunable optoelectronic behaviour,\textsuperscript{58} and nanomechanical properties,\textsuperscript{58} all of which are fascinating on their own. The size, surface area, and surface energy of the MoS\textsubscript{2} particles are determined by its morphology, which has a significant impact on how it executes in photocatalytic applications. Due to their large surface area and narrow band gap, MoS\textsubscript{2} nanoflowers are more effective for absorption of visible light, which improves their photocatalytic efficacy. The shape of MoS\textsubscript{2} nanoflowers determines their surface area, which in turn determines how well they operate as photocatalysts. MoS\textsubscript{2} is anisotropic, piezocatalytic,\textsuperscript{56} hydrophobic and low-toxic, which has high specific surface area with high surface energy,\textsuperscript{57} high surface to volume ratio, high $e^-$ mobility, high optical absorption, high catalytic activity, good tribological properties,\textsuperscript{58} good thermal stability and free sulfur groups.\textsuperscript{59} Due to its low price and a wealth of earth reserves, it is commercially viable. As a result, MoS\textsubscript{2}’s characteristics are largely in favour of its application as a photocatalyst.

Unfortunately, the catalytic activity of MoS\textsubscript{2} is greatly inhibited due to its low dispersion ability which can be attributed to its hydrophobicity and low electrical conductivity.\textsuperscript{60} The formation of composites using MoS\textsubscript{2} may be a viable and efficient way to get around this problem and maximise the benefits of MoS\textsubscript{2} as a photocatalyst in aqueous bodies because the

Fig. 1 MoS\textsubscript{2} synthesis techniques with their advantages and disadvantages.\textsuperscript{44}
properties of other compounds in the composite may enhance the electrical conductivity and dispersion of MoS2 and thereby facilitate the exhibition of its full potential and surplus advantages.

4 Photochemistry of MoS2

MoS2 has attracted significant attention, and a wide range of desirable photocatalytic properties have been reported, such as narrow band gap energy, excellent optical absorptivity, and high mobility of charge carriers, in addition to low toxicity and cost. However, the performance of MoS2 is limited by photogenerated e−/h+ recombination, the edge activity effect, and photocorrosion. Past efforts to enhance the photocatalytic properties of MoS2 have involved controlling the morphology, modulation of energy bands through doping, band alignment through heterojunction formation, modification with carbon nanostructures, and combining with metal particles exhibiting surface plasmon resonance.

The photocatalytic redox processes begin with the production of photoexcited charge carrier pairs (e−/h+). As illustrated in Fig. 3, upon irradiation the MoS2 simultaneously generates e− and h+, where the photogenerated e− is promoted to the CB, leaving behind the hole (h+) in the VB. Subsequently, these photogenerated carriers migrate to the surface of the MoS2 to participate in reduction (e−) and oxidation (h+) processes. Photoexcited e− may react with adsorbed O2 to produce ‘•O2− radicals and, simultaneously, the h+ remaining in the VB can abstract an e− from hydroxyl ions or adsorbed H2O molecules to produce ‘•OH radicals, which are powerful oxidizing agents that can react with harmful organic, inorganic, and biological compounds.

5 Modifications of MoS2 to improve its photocatalytic activity

The high e−/h+ pair recombination efficiency of MoS2 prevents it from being widely used in photocatalysis, despite the fact that it is a visible-light sensitive photocatalyst. This is a frequent problem with narrow band gap photocatalysts. Hence, to improve charge carrier separation, MoS2 has been doped and coupled with many varied materials such as metals,61 metal oxides,62 and carbon-based materials.63 Fig. 4 exhibits some of the modifications of MoS2. The doping of MoS2 with metal or non-metal dopants, as shown in Fig. 4a and b, can generate defects and change the optical band gap of MoS2. Charge separation can be enhanced when associated with metals due to the existence of the metal–MoS2 interface, as depicted in Fig. 4c. For instance, Cheah et al. reported an improved H2 evolution activity of Ag@MoS2 under irradiation by visible light.64 They reported that the deposition of Ag onto MoS2 assisted e− and h+ separation, prevented charge recombination, and hence, enhanced the overall photocatalytic performance. By creating a band offset and/or an electric field across the space-charge area at the junction between the two materials, a heterojunction enables the separation of e−/h+ pairs instantly. Fig. 4d shows the formation of two types of heterojunctions. A type I heterojunction results when the VB of MoS2 is greater than the VB of the second semiconductor and the conduction band (CB) of MoS2 is lower than the CB of the second semiconductor,
allowing both electrons and holes to pass from the second semiconductor to the MoS₂. In contrast, a type II heterojunction is created when the VB of MoS₂ is above the VB of the second semiconductor, acting as a hole sink, while the CB of the second semiconductor is below the VB of MoS₂, acting as an electron sink. For example, Hu et al. reported that an optimized Co-doped MoS₂/g-C₃N₄ heterojunction exhibited the highest activity for the photocatalytic reduction of water, with a H₂ evolution rate of 0.31 mmol g⁻¹ h⁻¹. According to these authors, Co-doped MoS₂ has an edge-enriched 1T phase with more active sites than pristine MoS₂, as well as a heterojunction with g-C₃N₄ to expedite charge transfer and separation and these factors contribute to the enhanced photocatalytic activity. Additionally, the addition of ternary and quaternary chalcogenides by including one or more additional elements into binary chalcogenides is a potential method for increasing the effectiveness of charge separation and interfacial charge transfer through the addition of additional surfaces. For example, Lim et al. fabricated a ZnMoS₄/ZnO/CuS p-n heterojunction photocatalyst that results in a hydrogen evolution rate 97% higher than an unoptimized ZnMoS₄/CuS p-n structure.

A hydrothermal and calcination technique is used to successfully create a Z-scheme MoS₂/CuO photocatalyst that degrades 2-mercaptobenzothiazole (MBT) with excellent activity (96 percent) when exposed to visible light (Fig. 5a–e). MoS₂ nanosheets and flower-shaped CuO combine to form a Z-scheme heterostructure, which significantly boosts the separation effectiveness of photogenerated carriers. CuO and MoS₂’s oxidation and reduction characteristics are enhanced by the Z-scheme electron transfer process that gives significant accumulation of photogenerated electrons and holes.

The authors proposed a possible Z-scheme charge transfer process and the reaction mechanism of MBT degradation by MoS₂/CuO heterojunction under visible light irradiation and the results are shown in Fig. 5f. Electron–hole pairs are generated by the excitation of both MoS₂ and CuO. The electrons on the CB of CuO migrate to the VB of MoS₂ and combine with holes on the VB of MoS₂. The photogenerated holes assembled by CuO can degrade MBT molecules in large quantities. In addition, due to the CB position of MoS₂ is much more negative than the potential of O₂/O₂⁻, the electrons on the CB of MoS₂ will further undergo a reduction reaction to generate abundant O₂, which will be further involved in the degradation process. Although CuO has a higher negative VB potential than OH, it is theoretically impossible to form OH; yet, some OH has been found using the ESR technique, which may be the result of further reducing O₂. The Z-scheme charge transfer mechanism for MoS₂/CuO significantly increases the separation efficiency of photogenerated carriers and positively influences the oxidizability and reducibility of the photocatalysts. Finally, the detailed photocatalytic reaction process of the Z-scheme MoS₂/CuO heterojunction is shown in Fig. 5f.

A S-scheme MoS₂/g-C₃N₄ photocatalyst is developed by a one-pot solid-state reaction of thiourea and sodium molybdate as precursors at different temperatures under N₂ gas was applied. The variation in component contents [MoS₂ and g-C₃N₄] is determined by the physicochemical characterization of the final products via an increase in synthesis temperature. The morphology and elemental composition of representatives were investigated using field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HR-TEM), along with energy dispersive X-ray spectroscopy (EDS) mapping (Fig. 6a–g).

The degradation of Rhodamine B in an aqueous solution under visible light was used to evaluate the enhanced photocatalytic activity of the MoS₂/g-C₃N₄ composites. The best photocatalytic performance there was demonstrated by composites created at 500 °C, with a degradation efficiency of 90%, which was significantly better than that of a single g-C₃N₄. The improvement in light harvesting and the extension in the lifetime of photoinduced charge carriers of composites, which are the result of the synergistic interaction between the components, are credited with the significant improvement in photocatalytic performance. Besides, the photocatalytic mechanism is demonstrated to well-fit into the S-scheme pathway with apparent evidences (Fig. 6h).
6 Applications of MoS$_2$ based nanophotocatalyst for chemical transformations

The MoS$_2$ photocatalysis visible-light irradiation is considered a green alternative to traditional synthetic methodologies. As only mild conditions are needed and the formation of undesirable byproducts is decreased, it is a viable path for organic transformation processes. Summary of previous studies on photocatalytic organic transformation reactions using MoS$_2$-based materials are tabulated in Table 2.

6.1 Cross-dehydrogenative coupling reaction

De et al. developed a methodology targeted for the utilization of sacrificial amine donors for C–H functionalization with MoS$_2$ quantum dots (QDs) as the catalyst as well as the photosensitizer. Infact, QDs has emerged to be an active participant in the heterogeneous electron transfer process. This approach brings up new opportunities for photomediated organic transformations using nanomaterials without the need for external photosensitizers using a non-toxic, long-lasting procedure. The reduction cycle produces H$_2$ from water, and the oxidative cycle culminates in the CDC product. (Fig. 7).

The authors proposed a mechanistic pathway for the CDC reaction parallel to the photochemical HER mediated by MoS$_2$ QDs (Fig. 7). An electron is excited from the valence band (VB) to the conduction band (CB) by radiation. In presence of O$_2$, 2-Aryl-1,2,3,4-tetrahydroisoquinoline 1 is oxidized to radical cation 1$^{+*}$ via transferring an electron to the VB to regenerate the ground state of the QD. There is no need of any external photosensitizer for the oxidation of 1. The radical cation of 1 results the formation of iminium intermediate 1$^{+}$ by losing a H. The nucleophile 2 attacks the iminium intermediate 1$^{+}$ to give the targeted cross-coupled product 3 with simultaneous evolution of H$_2$. Thus, QDs act as a photosensitizer as well as a catalyst that also transfer electron for the water-splitting process and further regenerated in the process. In the proposed mechanism, they have stated that the source of H can be from H$_2$O as well as the nucleophile NuH. As their target was to design a methodology for the CDC reaction, they did not carry out any deuterated experiments to confirm the source of H$_2$.

De et al. also demonstrated 1T (metallic)-2H (semiconducting) phase boundaries intrinsic to individual sheets of chemically exfoliated 2D-MoS$_2$ that can serve as heterojunctions for enhanced photocatalysis compare to only semiconducting phase. Due to the abundance of heterojunctions in these multiphase materials, chemically exfoliated 2D-MoS$_2$ provides improved stability as well as transfer of photogenerated charges to the reactants, giving better yield. Significantly, they proved that this simple synthesize material works well as a photocatalyst for the aerobic oxidative coupling of amines to imines when subjected to visible light. Given its broad applications, they believe mixed phase 2D-MoS$_2$ can be of interest to several industrial synthetic applications related to semiconductor-based photocatalysis. An additional benefit is that this heterogeneous photocatalyst can be regenerated up to five times without significant loss in the activity (Fig. 8).

Further De et al. have developed an efficient method for Cross Dehydrogenative Coupling (CDC) reaction by using mixed phase 2D-MoS$_2$ nanosheets and Eosin Y alongside the photochemical Hydrogen Evolution Reaction (HER). The reaction has been carried out at room temperature under visible light irradiation and results in good to excellent yields. It is an example of a CDC reaction using mixed phase 2D-MoS$_2$ nanosheets as a catalyst regenerator and Eosin Y as photosensitizer. Due to incomplete recovery of the catalyst, the material can be reused with slight loss in the yields. Additionally, the scope of this protocol can be used to create various C–C coupled products. This could be an illustration of how to completely utilise the oxidation and reduction cycles of several semiconductor-based photocatalysts. (Fig. 9).

6.2 Suzuki–Miyaura coupling reaction

Lim et al. demonstrated the incorporation of MoS$_2$ nanosheets with Pd nanodots is a promising way for promoting the visible-light-induced Suzuki–Miyaura C–C coupling reaction. The MoS$_2$ nanosheets decorated with Pd nanodots showed excellent photocatalytic activity. The turnover frequency for the biphenyl product was $>1600$ h$^{-1}$ even under sunlight illumination at...
Table 2  Summary of previous studies on photocatalytic chemical transformation reactions using MoS2-based materials

| S. N. | Application | Photocatalyst used | Morphology | Particle size | Light source | Performance | Ref. |
|-------|-------------|--------------------|------------|---------------|--------------|-------------|------|
| 1     | Photocatalytic oxidation of benzyl alcohol to benzaldehyde | Co-doped MoS2/g-C3N4 | 2D nanosheet morphology with curly stripes | 6.45 nm | 80 W LED lamp | Benzaldehyde production rate of 0.48 mmol g⁻¹ h⁻¹ | 66 |
| 2     | Photocatalytic oxidative coupling of thiols | Pd@Cu/MoS2 | Spherical | 64.5 nm | 300 W Xe lamp | ~99% conversion under 400–800 nm irradiation | 70 |
| 3     | Photocatalytic reduction TiO2 hollow spheres/crumpled MoS2 nanosheet | MoS2/Cu | Hollow sphere | ~200 nm | 500 W Xe lamp | 99.35% photocatalytic reduction of 4-nitrophenol | 71 |
| 4     | Photocatalytic conversion of CO2 to methane | MoS2 grown on hexagonal boron nitride nanoplatelets | MoS2 nanosheets are coated on the surface of Cu nanorods | About 50–700 nm | 300 W Xe lamp | Maximum yield of methane ~23 mmol g⁻¹ h⁻¹ | 72 |
| 5     | Photocatalytic reduction of CO2 to methanol | MoS2 grown on hexagonal boron nitride nanoplatelets | Each MoS2 nanosheet is composed of 2–6 molecular lamellae | 20 W white LED lamp | Maximum yield of methanol 5994 µmol g⁻¹ | 73 |
| 6     | Photocatalytic reduction of CO2 to methane and CO | In2S3/MoO3@MoS2 | Distorted hexagonal nanorods | | 300 W Xe lamp | Yield ~29.4 and ~35.6 µmol g⁻¹ h⁻¹ for CH4 and CO, respectively | 74 |
| 7     | Photocatalytic selective oxidation of benzyl alcohols to benzaldehyde | Ag3PO4 nanoparticle@MoS2 quantum dot/few-layered MoS2 nanosheet | Nanosheet | | 300 W Xe lamp | ≤92% conversion of benzyl alcohol and ~87% yield of benzaldehyde after 3 h of irradiation | 75 |
| 8     | Photocatalytic reduction of 4-nitrophenol to 4-aminophenol composite | Cds-MoS2/rGO | Flowerlike morphology | | 500 W Xe lamp | ≤70% reduction of 4-nitrophenol after 60 min of irradiation | 76 |

room temperature. Mechanistic researches revealed that the high catalytic activity of MoS2 originated from the efficient electron–hole pair generation mechanism under visible-light (Fig. 10).

6.3 Photocatalytic NH3 synthesis

He et al. developed the efficient photoreduction of N2 to NH3 over ternary MoS2/C–ZnO composite, that was prepared via a combination of hydrothermal and photodeposition method (Fig. 11).

Several methods were employed to characterise the produced composite, and the results displayed that carbon was loaded onto the surface of ZnO instead of doped into the lattice in order to prevent charge carrier recombination. By thermal processing, the carbon content of C–ZnO can be altered by which enhances the effectiveness of charge separation. For calcination, the most favourable temperature of 300 °C determined. The separation of electron–hole pairs can be further improved by photodepositing MoS2 nanoparticles on the C–ZnO–300 sample, which traps electrons on the carbon layer. The ideal 1% MoS2/C–ZnO–300 composite exhibits the fastest NH3 generation rate under simulated sunlight irradiation at 245.7 µmol L⁻¹ g⁻¹ h⁻¹, which is 9.3 and 4.0 times higher than that of ZnO and C–ZnO, respectively. However, when exposed to visible light, C–ZnO performs best, producing NH3 at a rate of 28.8 µmol L⁻¹ g⁻¹ h⁻¹, indicating that the composite employs a different process. The carbon layer was thought to act as a photosensitizer by transferring electrons to ZnO or MoS2. The processes proposed have been confirmed by EIS and PC evaluations. The addition of a carbon layer and MoS2 nanoparticles to the ZnO increases the BET area. The increased surface area might be partially responsible for the higher photocatalytic performance. (Fig. 11a and b). There is another way to reduce N2 to NH3 via photocatalysis.

6.4 Photoelectrochemical nitrogen reduction

The photoelectrochemical (PEC) technique, which uses both solar energy as well as electricity efficiently synthesize ammonia under ambient conditions. Han et al. have been synthesized MoS2@LZO heterostructures by assembling 2D-MoS2 nanoflakes on La2Zr2O7; nanofibers via a facile hydrothermal method (Fig. 12a).

Due to the electrical dispersion in LZO, the homogeneous assembly of MoS2@LZO prevents the photogenerated electron hole pair from recombining more quickly. Superior PEC-NRR performances can be seen as a result of the interaction between the localized electronic distribution in the MoS2@LZO heterostructures, oxygen vacancies in La2Zr2O7; excellent conductivity of the nanofibers, and increased exposure of surface sites for electron–hole generation in MoS2. The trapped photoelectron during N2 activation is donated by the reduction of N2 to NH3 at the oxygen vacancy, which serves as the stimulation of the photocatalyst.
Fig. 7 (a) Photomediated oxidation and reduction cycle of MoS$_2$ QDs. (b) Proposed mechanism for the catalytic activity of MoS$_2$ blue QDs in CDC reaction synchronized with HER. Reproduced from ref. 77a with permission from [American Chemical Society], copyright [2022].

Fig. 8 Plausible mechanism for the oxidative coupling of benzylamine to imine photocatalyzed by mixed-phase 2D-MoS$_2$ nanosheets. Reproduced from ref. 77b with permission from [John Wiley & Sons, Inc.], copyright [2018].

Fig. 9 Schematic illustration of the 2D-MoS$_2$ photocatalyzed oxidation and reduction cycles in presence of Eosin Y as photosensitizer. Reduction cycle produces H$_2$ from water as reported earlier, whereas oxidative cycle is responsible for CDC Reaction and formation of additional H$_2$. Reproduced from ref. 77c with permission from [Royal Society of Chemistry], copyright [2019].

Fig. 10 The Pd-nanodot decorated MoS$_2$ micro/nanosheet for an efficient visible light induced photocatalytic Suzuki–Miyaura coupling reaction. Reproduced from ref. 78 with permission from [Royal Society of Chemistry], copyright [2017].

Fig. 11 Preparation of MoS$_2$/CZ300 photocatalyst and the suggested charge transfer mechanism of MoS$_2$/CZ300 composite (a) under simulated sunlight (b) and visible light irradiation. Reproduced from ref. 79 with permission from [American Chemical Society], copyright [2018].
active site for these reactions. The MoS2@LZO PEC catalyst exhibits a maximum ammonia yield rate of approximately 10.4 μg h⁻¹ cm⁻² and a higher faradaic efficiency of approximately 2.25% compared to pristine MoS2 and LZO. The heterostructure interface, which is rich in oxygen vacancies and offers a stable design with effective active sites, can be used to confirm this remarkable performance. Compared to the current MoS2 catalysts, MoS2@LZO demonstrates a higher ammonia yield, selective N₂ adsorption, and excellent stability. The 2D-MoS2 nano flakes, the La₂Zr₂O₇ pyrochlore/fluorite structured nanofibers, and their heterostructure interfaces for enhanced ammonia production are presented with PEC-NRR mechanisms under ambient conditions. For various additional catalysis techniques to efficiently drive photoelectrocatalytic activity, the design strategy of inserting an n-type semiconductor over rich oxygen-vacant stable nanostructures to establish an interface can be used. (Fig. 12b).

6.5 Photocatalytic oxidation of nitrite
Zheng et al. reported the photocatalytic oxidation rate of NO₂⁻ under simulated solar irradiation, which can reach 62% by the MoS2/TiO2 composite synthesized in a hydrothermal system with a C₂H₅NS/Na₂MoO₄ molar ratio of 1 : 0.6 : under 200 °C for 24 h, which is significantly higher than that by pristine TiO2 NFs, P25 and pure MoS2. The photocatalytic oxidation process of NO₂⁻ follows the Langmuir–Hinshelwood kinetic model (pseudo-first order reaction), and the reaction rate constant (k) of the as-prepared composite is about 0.19194 h⁻¹. MoS2 considerably increases the ability of catalyst ability to absorb visible light, which promotes the production of electrons and holes and ensures the strong photoactivity of catalyst. The composite has an about 2.2 eV band gap, which indicates improved visible light absorption. The titanium substrate is permanently attached to the composite using this straightforward, low-consumption approach, enabling recycling and ecologically responsible implementation possible (Fig. 13).

6.6 Photocatalytic conversion of CO₂ and H₂O to CO, CH₄ and H₂ products
Ray et al. reported, the integration of photoabsorber MoS2 and N-containing conducting polymer poly pyrrole (PPy) over reduced graphene oxide improved CO₂ photoreduction and H₂ production (rGO). A variety of rGO-MoS/PPy nanocomposites were created and morphologically, structurally, and optically studied using various methods. Under pretend sunlight the optimal rGO-MoS /PPynanocomposite was found to exhibit a remarkable production of CO (3.9 μmol g⁻¹ h⁻¹), CH₄ (1.50 μmol g⁻¹ h⁻¹), and H₂ (4.19 μmol g⁻¹ h⁻¹) in the photocatalytic reduction of CO₂ in an aqueous suspension (Fig. 14).

The synergistic effect of the MoS2, rGO, and PPy nanostructures, which encouraged the separation and migration of the photogenerated charges through the heterojunction interfaces and decreased electron–hole recombination, was
attributed to the improvement in the photocatalytic performance of the highly active surface material rGO-MoS2/PPy-150. The PPy in the rGO-MoS2/PPy nanocomposite played multiple roles in improving the photocatalytic reduction of CO due to its superior conductivities, CO2 adsorption capabilities via its amine groups, and electron storage qualities. Better catalytic performance is possible due to the reduced PPy concentration in nanocomposite. Importantly, the strong recycling performance of rGO-MoS2/PPy-150 nanocomposite revealed the robustness and stability of photocatalyst (Fig. 14a–c).

7 Future outlook

Although many studies have focused on the synthesis of MoS2 and MoS2-based nanomaterials and their different uses, there are still a plethora of challenges:

1. MoS2-based materials will be extensively used in a variety of disciplines and could one day become commercially feasible because of their unique physical and chemical qualities. With this, MoS2 will be applied to various media and released into the environment, potentially posing risks to both human health and the ecosystem. Therefore, a detailed evaluation of the toxicity of MoS2-based compounds is required.

2. The application of MoS2-based photocatalysts has so far been confined to laboratory-based research; it has not yet been investigated how well MoS2 performs in real-world environments, and a perfect photocatalyst that can be used on a wide scale and in industry has not yet been developed.

3. Certain MoS2 composites become unstable when exposed to visible light. Therefore, more investigation is required to design materials based on MoS2 that are photosensitive.

4. A significant challenge pertains for the development of practical techniques for the generation of MoS2 in quantities appropriate for industrial applications. For large-scale production, additional research into the scaling up of synthetic approaches is therefore needed.

8 Conclusion

In this review, we highlighted the different MoS2 structures, their synthesising techniques and properties. The primary benefits and drawbacks of synthesis approaches were also summarised. MoS2 is a promising material with a wide range of applications. MoS2 and MoS2-based nanomaterials are currently the topic of extensive research as promising photocatalyst for the photocatalytic degradation and inorganic and organic chemical transformation. MoS2 and MoS2-based materials have exceptional physicochemical features, due to which they exhibit wide range of synthetic applications like coupling reaction, oxidation, reduction as well as organic and inorganic compound production. This review relies on recent developments regarding the application of MoS2 in chemical transformations. The prospects for successful visible-light-induced photocatalysis using MoS2 based materials are finally discussed.

Conflicts of interest

There are no conflicts to declare.

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