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1 Introduction

Molybdenum disulfide (MoS_2) 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,

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Molybdenum disulfide (MoS_2) 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, MoS_2 has drawn attention due to its excellent solar spectral response and its notable electrical, optical, mechanical and magnetic properties. MoS_2 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, MoS_2 has gained synthetic utility in chemical transformations. In this review, we will discuss MoS_2 properties, structure, synthesis techniques, and photochemistry along with modifications of MoS_2 to enhance its photocatalytic activity with a focus on its applications and future challenges.

methylene blue, methyl orange and novacron red Huntsman), pesticides and herbicides. It also employed for photocatalytic evolution of oxygen, nitrogen fixation, ammonia synthesis and water electrolysis.¹⁻⁷

In recent years, MoS_2 has received much attention due to its unique electrical and optical properties.^{8a} MoS_2 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, MoS_2 is one of the few with a natural layered structure, indicating that MoS_2 can be stripped to obtain high-quality 2D MoS_2 without complicated chemical synthesis.^{8b} Therefore, the cost of preparing 2D MoS_2 is much lower than other 2D TMDs due to



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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.^{8c} These make 2D MoS₂ get more attention among 2D TMDs.

Several characteristics of MoS₂ such as high absorbance in the visible region,⁹ high carrier mobility,¹⁰ stability,¹¹ preferable catalytic activity,¹² good photostability,¹³ outstanding electrochemical properties,¹⁴ strong surface adsorption capacity and higher specific surface area¹⁵ 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.⁷ Currently, semiconductor photocatalysts with controllable morphologies are gaining significant attraction in applications associated with environmental remediation process.¹⁶ Phase engineering, defect engineering, doping of external materials, interlayer engineering, surface modification, and heterojunction^{17a,b} construction make MoS₂ more flexible in terms of tuning its properties during synthesis.

Molybdenum disulfide (MoS₂)^{17c} 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.^{17d} Applications for MoS₂-based materials are said to include energy storage,^{17e} hydrogen production,^{17f} pollutant degradation,^{17g} disinfection,^{17h} etc. Numerous studies have recently provided a summary of photocatalytic properties of MoS₂ for numerous application areas.¹⁷ⁱ⁻ⁿ

In continuation of our work on photocatalysed organic synthesis^{18,19} 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



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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,²⁰ thiourea,²¹ thioacetamide,²² and L-cysteine.²³ 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 synthesize MoS₂ materials alongside the applications of the synthesized materials. The most used methods are solid-state,²⁴ hydrothermal,^{25,26} solvothermal,²⁷ and hybrid methods.^{28,29}

The benefits and drawbacks of synthesis techniques⁴⁴ 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 X⁴⁵ with three hexagonal planes (S-Mo-S), which is bonded to each other via ionic-covalent interactions.⁴⁶ 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.⁴⁷ 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.¹¹ The narrow band gap facilitates its high absorption of light in the visible region.



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Table 1 Synthesis Methods and Applications of MoS₂

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 ₂₄ ·4H 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 ·2H ₂ O)	Thioacetamide (C ₂ H ₅ NS)	Nano flowers with average size ~100 nm	Photocatalytic degradation of rhodamine B	3
4	Hydrothermal Sodium molybdate dihydrate (Na ₂ MoO ₄ ·2H ₂ O)	L-cysteine	Quantum dots with ~2.5 nm particle size	Detection of methyl parathion (pesticide)	4
5	Hydrothermal (NH ₄)MoS ₄	(NH ₄)MoS ₄		Fluorescent probe for hyaluronidase detection	5
6	Chemical Exfoliation Commercially available MoS ₂ powder		Nanosheets	Photocatalytic oxidation of benzyl halides	6
7	Chemical vapor Deposition Ammonium heptamolybdate	Sulfur	Not mentioned		30
8	Colloidal Ammonium tetrathiomolybdate [(NH ₄) ₂ MoS ₄]	Ammonium tetrathiomolybdate [(NH ₄) ₂ MoS ₄]	Spherical quantum dots with average size ~5 nm	Bioimaging	32
9	Heating Mo(acac) ₂	1-Dodecanethiol	Nanosheet	Electrical bistability performance	9
10	Hot injection Molybdenum(v) chloride (MoCl ₅)	N,N'-diphenylthiourea	Nanosheets		33
11	Hydrothermal Sodium molybdate dihydrate (Na ₂ MoO ₄ ·2H ₂ O)	Thioacetamide (CH ₃ CSNH ₂)	Coral-like	Lubrication additive; photocatalytic degradation of liquid paraffin	11
12	Hydrothermal Na ₂ MoO ₄ ·2H ₂ O	Cysteine	Quantum dots with 2 ~3.5 nm particle size	Fluorescent probe for sensing of hydroquinone and bioimaging	36
13	Solid state (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	Sulfur	Nanosheets, thinner than 5 nm	Photocatalytic degradation of rhodamine B	24
14	Hydrothermal Na ₂ MoO ₄ ·2H ₂ O	Thiourea (H ₂ CSNH ₂)	Irregular with average size in the range 12–25 nm	Electrochemical studies	25
15	Hydrothermal Ammonium hepta molybdate tetrahydrate [(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O]	Ammonium polysulfide	Ammonium polysulfide as the sulfur source: Uniform MoS ₂ nanospheres with average size of ~100 nm	Lubrication additive	27
16	Hydrothermal MoO ₃	Potassium thiocyanate	Flowerlike MoS ₂ spheres with average diameter of 1–2 nm	Photocatalytic degradation with average diameter of 1–2 nm of methylene blue	37
17	Hydrothermal Na ₂ MoO ₄ ·2H ₂ O	L-cysteine	Microspheres comprising crossed-linked nanorods ~100 nm in length	Photocatalytic degradation of thiocarbamate herbicides	38
18	Hydrothermal Ammonium tetrathiomolybdate [(NH ₄) ₂ MoS ₄]	Thiourea (H ₂ CSNH ₂)	Flowerlike microsphere	Photocatalytic degradation of rhodamine B and methylene blue	39
19	Hydrothermal (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	Thiourea	Nanosheets	Detection of dopamine	40
20	Hydrothermal (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	Na ₂ S	Hierarchical porous with the thickness of ~20–40 nm	Detection of phenol sulphite oxidase, nicotinamide adenine dinucleotide oxidase and superoxide dismutase mimicking activities	41
21	Microwave Ammonium tetrathiomolybdate [(NH ₄) ₂ MoS ₄]	Ammonium tetrathiomolybdate [(NH ₄) ₂ MoS ₄]	Quantum dots with average diameter of ~1.72 nm	Determination of terramycin	42
22	Solid state (NH ₄) ₂ MoS ₄	Thiourea	Sheetlike structure and ultrathin layers	Electrochemical measurement	43

Crystal lattices of MoS₂ exists 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).¹¹ MoS₂ is synthesized in various morphologies (Fig. 2e) which includes nanoflowers (Fig. 2e₁, Fig. 2e₂),⁴⁸ nanosheets (Fig. 2e₃, Fig. 2e₄),⁴⁹ nanoflakes,⁵⁰ nanocrystals, nanospheres,⁵¹ nanoribbons,⁵² nanotubes (Fig. 2e₅),⁵³ nanoworms (Fig. 2e₆),⁵⁴



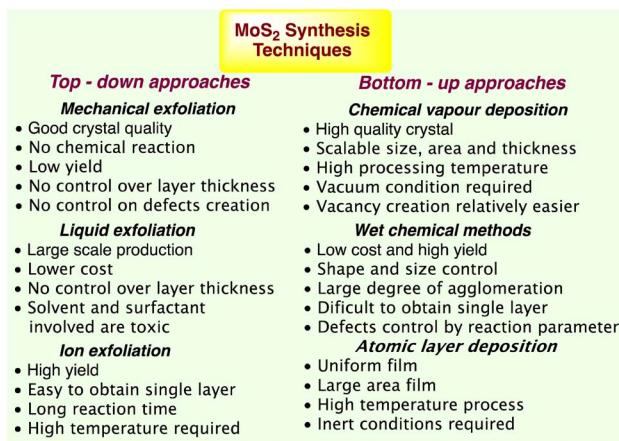


Fig. 1 MoS₂ synthesis techniques with their advantages and disadvantages.⁴⁴

coral-like structures (Fig. 2e₇),⁴⁹ nanodots and quantum dots (Fig. 2e₈).⁵⁵

Due to the 2D nature of MoS₂, 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,^{56a-g} tunable optoelectronic behaviour,^{56h-l} and nanomechanical properties,^{56m-p} all of which are fascinating on their own. The size, surface area, and surface energy of the MoS₂ 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, MoS₂ nanoflowers are more effective for absorption of visible light, which improves their photocatalytic efficacy. The shape of MoS₂ nanoflowers determines their surface area, which in turn determines how well they operate as photocatalysts. MoS₂ is anisotropic, piezocatalytic,⁵⁶ hydrophobic and low-toxic, which has high specific surface area with high surface energy,⁵⁷ high surface to volume ratio, high e⁻ mobility, high optical absorption, high catalytic activity, good tribological properties,⁵⁸ good thermal stability and free sulfur groups.⁵⁹ Due to its low price and a wealth of earth reserves, it is commercially viable. As a result, MoS₂'s characteristics are largely in favour of its application as a photocatalyst.

Unfortunately, the catalytic activity of MoS₂ is greatly inhibited due to its low dispersion ability which can be attributed to its hydrophobicity and low electrical conductivity.⁶⁰ The formation of composites using MoS₂ may be a viable and efficient way to get around this problem and maximise the benefits of MoS₂ as a photocatalyst in aqueous bodies because the

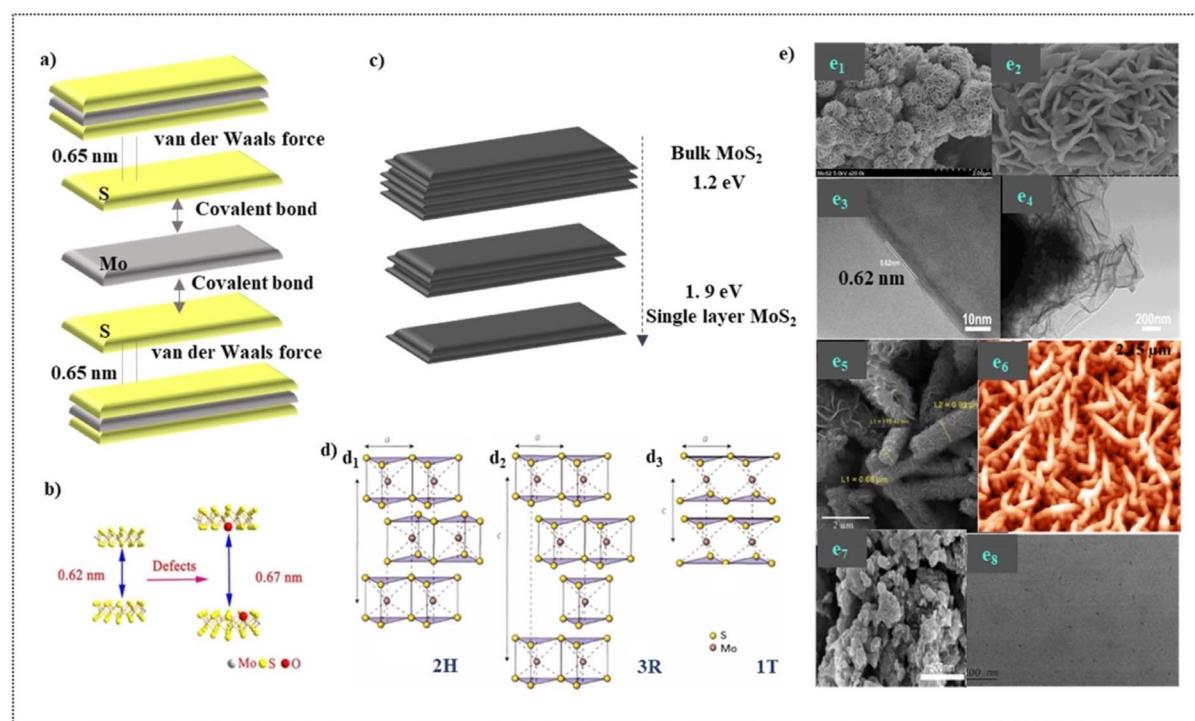


Fig. 2 (a) Visualization of the layered structure of MoS₂ and the forces responsible for its layered structure. (b) Pictorial illustration of the increased interlayer distance due to the presence of impurities. Adapted with permission from ref. 47, Copyrights 2022 Elsevier. (c) Graphical illustration of the tunable band gap exhibited by MoS₂. (d) Crystal structures of MoS₂. (d₁) 2H, (d₂) 3R and (d₃) 1T. Adapted with permission from ref. 11, Copyrights 2022 Elsevier. (e) Different morphologies portrayed by MoS₂ (through synthesis) (e₁). Nanoflowers at the resolution of 2 μm (e₂). Nanoflowers at the resolution of 500 nm Adapted with permission from ref. 48, Copyrights 2022 Elsevier (e₃). TEM image of the nanosheets at 10 nm (e₄). TEM image of the nanosheets at 200 nm Adapted with permission from ref. 49, Copyrights 2022 Elsevier (e₅). Nanotubes Adapted with permission from ref. 53, Copyrights 2022 Elsevier (e₆). Nanoworms. Adapted with permission from ref. 54, Copyrights 2022 Elsevier (e₇). Coral-like structure. Adapted with permission from ref. 49 Copyrights 2022 Elsevier (e₈). Quantum dots. Reproduced from ref. 55 with permission from [Elsevier], Copyright [2022].



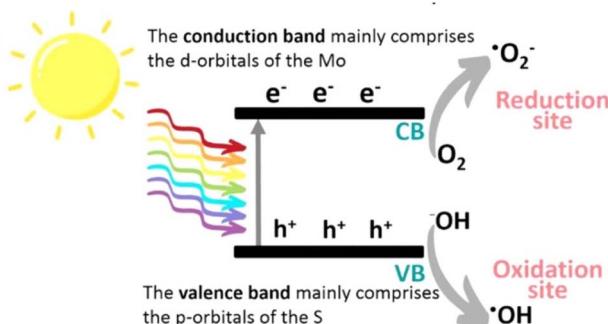


Fig. 3 Schematic illustration of the photocatalytic mechanism of MoS₂. Reproduced from ref. 29 with permission from [American Chemical Society], copyright [2022].

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 photo-generated 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 photo-generated 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,

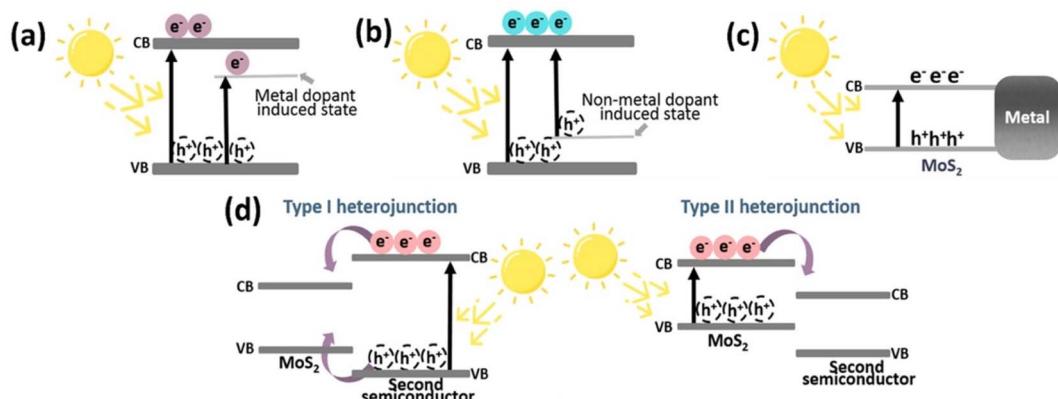


Fig. 4 Modifications of MoS₂ to improve its photocatalytic activity; (a) metal doping of MoS₂, (b) nonmetal doping of MoS₂, (c) metal deposited on MoS₂, and (d) formation of a heterojunction with a second semiconductor. Reproduced from ref. 29 with permission from [American Chemical Society], copyright [2022].



allowing both electrons and holes to pass from the second semiconductor to the MoS_2 . In contrast, a type II heterojunction is created when the VB of MoS_2 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 MoS_2 , acting as an electron sink.⁶⁵ For example, Hu *et al.* reported that an optimized Co-doped $\text{MoS}_2/\text{g-C}_3\text{N}_4$ heterojunction exhibited the highest activity for the photocatalytic reduction of water, with a H_2 evolution rate of $0.31 \text{ mmol g}^{-1} \text{ h}^{-1}$.⁶⁶ According to these authors, Co-doped MoS_2 has an edge-enriched 1T phase with more active sites than pristine MoS_2 , as well as a heterojunction with $\text{g-C}_3\text{N}_4$ to expedite charge transfer and separation and these factors contribute to the enhanced photocatalytic activity. Additionally, the creation 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 $\text{ZnMoS}_4/\text{ZnO}/\text{CuS}$ p-n heterojunction photo-catalyst that results in a hydrogen evolution rate 97% higher than an unoptimized $\text{ZnMoS}_4/\text{CuS}$ p-n structure.⁶⁷

A hydrothermal and calcination technique is used to successfully create a Z-scheme MoS_2/CuO photocatalyst that degrades 2-mercaptopbenzothiazole (MBT) with excellent activity (96 percent) when exposed to visible light⁶⁸ (Fig. 5a–e).

MoS_2 nanosheets and flower-shaped CuO combine to form a Z-scheme heterostructure, which significantly boosts the separation effectiveness of photogenerated carriers. CuO and MoS_2 '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 MoS_2/CuO heterojunction under visible light irradiation and the results are shown in Fig. 5f. Electron–hole pairs are generated by the excitation of both MoS_2 and CuO . The electrons on the CB of CuO migrate to the VB of MoS_2 and combine with holes on the VB of MoS_2 . The photogenerated holes assembled by CuO can degrade MBT molecules in large quantities. In addition, due to the CB position of MoS_2 is much more negative than the potential of O_2/O_2^- , the electrons on the CB of MoS_2 will further undergo a reduction reaction to generate abundant O_2^- , 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 O_2^- . The Z-scheme charge transfer mechanism for MoS_2/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 MoS_2/CuO heterojunction is in Fig. 5f.

A S-scheme $\text{MoS}_2/\text{g-C}_3\text{N}_4$ photocatalyst is developed⁶⁹ a one-pot solid-state reaction of thiourea and sodium molybdate as precursors at different temperatures under N_2 gas was

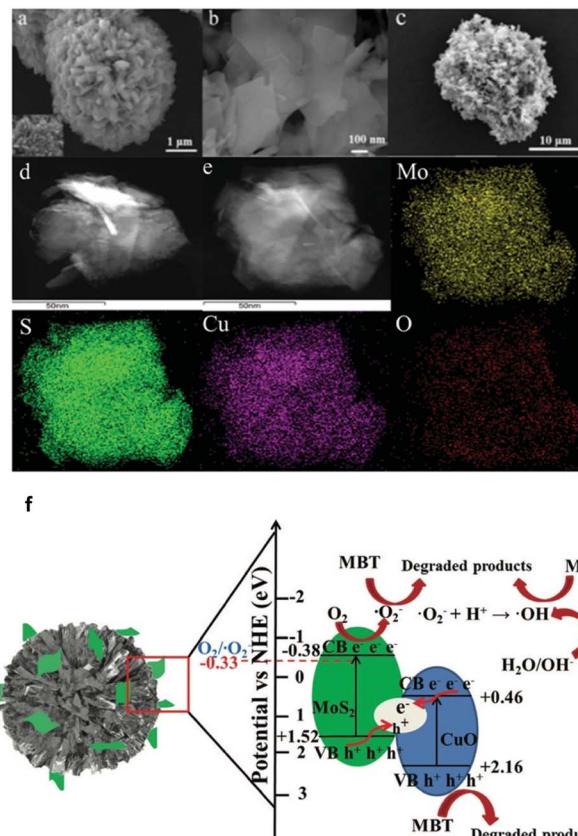


Fig. 5 (a) SEM images of CuO, (b) MoS₂, (c) MoS₂/CuO, (d) TEM image of MoS₂/CuO, (e) elemental mapping of MoS₂/CuO, (f) photocatalytic degradation mechanism of MBT over the Z-scheme MoS₂/CuO heterojunction under visible light irradiation. Reproduced from ref. 68 with permission from [Royal Society of Chemistry], copyright [2020].

applied. The variation in component contents (MoS_2 and $\text{g-C}_3\text{N}_4$) 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 $\text{MoS}_2/\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$. 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).

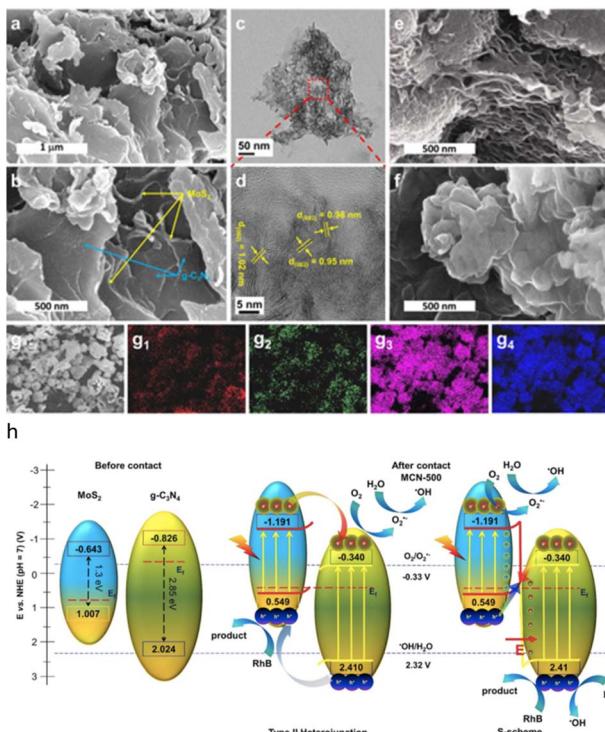


Fig. 6 (a and b) FE-SEM; and (c and d) HR-TEM images of MCN-500; FE-SEM images of (e) MCN-600; and (f) CN-500; EDS mapping images of (g) mapping area, (g₁) carbon, (g₂) nitrogen, (g₃) sulfur, and (g₄) molybdenum, (h) schematic diagram of band alignment of heterojunction and S-scheme charge transfer on interface of MoS₂ and g-C₃N₄. Reproduced from ref. 69 with permission from [Springer Nature], copyright [2021].

6 Applications of MoS₂ based nano-photocatalyst for chemical transformations

The MoS₂ 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 MoS₂-based materials are tabulated in Table 2.

6.1 Cross-dehydrogenative coupling reaction

De *et al.* developed^{77a} a methodology targeted for the utilization of sacrificial amine donors for C–H functionalization with MoS₂ 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 H₂ 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 MoS₂ QDs (Fig. 7). An electron is excited from the valence band (VB) to the conduction band (CB) by radiation. In presence of O₂, 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 H₂. 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 H₂O 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 H₂.

De *et al.* also demonstrated^{77b} 1T (metallic)-2H (semiconducting) phase boundaries intrinsic to individual sheets of chemically exfoliated 2D-MoS₂ that can serve as heterojunctions for enhanced photocatalysis compare to only semiconducting phase. Due to the abundance of heterojunctions in these multiphasic materials, chemically exfoliated 2D-MoS₂ 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-MoS₂ 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.*^{77c} have developed an efficient method for Cross Dehydrogenative Coupling (CDC) reaction by using mixed phase 2D-MoS₂ 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-MoS₂ 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.* demonstrated⁷⁸ the incorporation of MoS₂ nanosheets with Pd nanodots is a promising way for promoting the visible-light-induced Suzuki–Miyaura C–C coupling reaction. The MoS₂ 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 MoS ₂ /g-C ₃ N ₄	2D nanosheet morphology with curly stripes		80 W LED lamp	Benzaldehyde production rate of 0.48 mmol g ⁻¹ h ⁻¹	66
2	Photocatalytic oxidative coupling of thiols	Pd@Cu/MoS ₂	Spherical	64.5 nm	300 W Xe lamp	~99% conversion under 400–800 nm irradiation	70
3	Photocatalytic reduction of 4-nitrophenol	TiO ₂ hollow spheres/ crumpled MoS ₂ nanosheet	Hollow sphere	~200 nm	500 W Xe lamp	99.35% photocatalytic reduction of 4-nitrophenol	71
4	Photocatalytic conversion of CO ₂ to methane	MoS ₂ /Cu	MoS ₂ 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 CO ₂ to methanol	MoS ₂ grown on hexagonal boron nitride nanoplatelets	MoS ₂ nanosheets are uniformly grown over the hexagonal boron nitride nanoplatelets	Each MoS ₂ 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 CO ₂ to methane and CO	In ₂ S ₃ /MoO ₃ @MoS ₂	Distorted hexagonal nanorods		300 W Xe lamp	Yield ~29.4 and ~35.6 μmol g ⁻¹ h ⁻¹ for CH ₄ and CO, respectively	74
7	Photocatalytic selective oxidation of benzyl alcohols to benzaldehyde	Ag ₃ PO ₄ nanoparticle@MoS ₂ quantum dot/few-layered MoS ₂ 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	CdS-MoS ₂ /rGO composite	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.* developed⁷⁹ 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^{80,81}.

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.*⁸² 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 localised 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



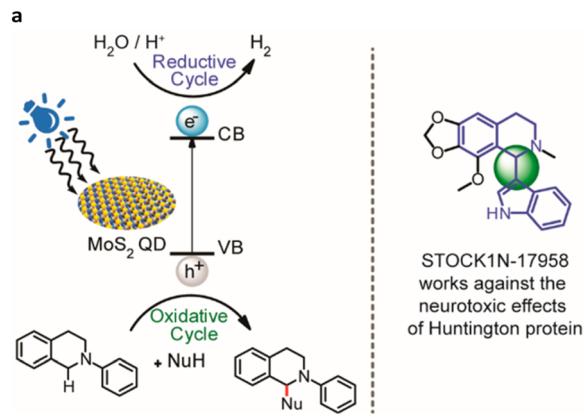


Fig. 7 (a) Photomediated oxidation and reduction cycle of MoS₂ QDs. (b) Proposed mechanism for the catalytic activity of MoS₂ blue QDs in CDC reaction synchronized with HER. Reproduced from ref. 77a with permission from [American Chemical Society], copyright [2022].

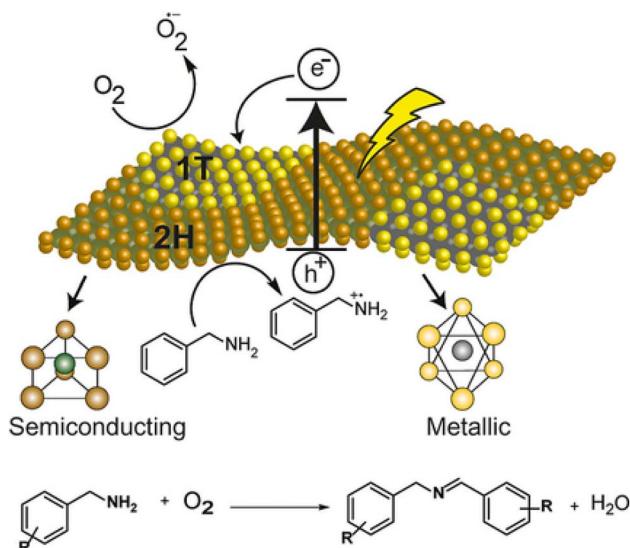


Fig. 8 Plausible mechanism for the oxidative coupling of benzylamine to imine photocatalyzed by mixed-phase 2D-MoS₂ nanosheets. Reproduced from ref. 77b with permission from [John Wiley & Sons, Inc.], copyright [2018].

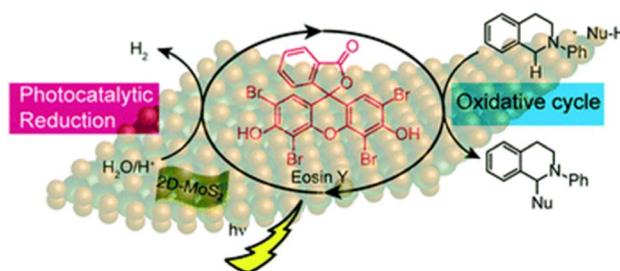


Fig. 9 Schematic illustration of the 2D-MoS₂ photocatalyzed oxidation and reduction cycles in presence of Eosin Y as photosensitizer. Reduction cycle produces H₂ from water as reported earlier, whereas oxidative cycle is responsible for CDC Reaction and formation of additional H₂. Reproduced from ref. 77c with permission from [Royal Society of Chemistry], copyright [2019].

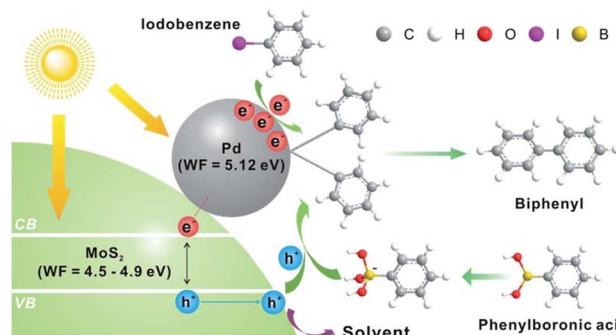


Fig. 10 The Pd-nanodot decorated MoS₂ micro/nanosheet for an efficient visible light induced photocatalytic Suzuki-Miyaura coupling reaction. Reproduced from ref. 78 with permission from [Royal Society of Chemistry], copyright [2017].

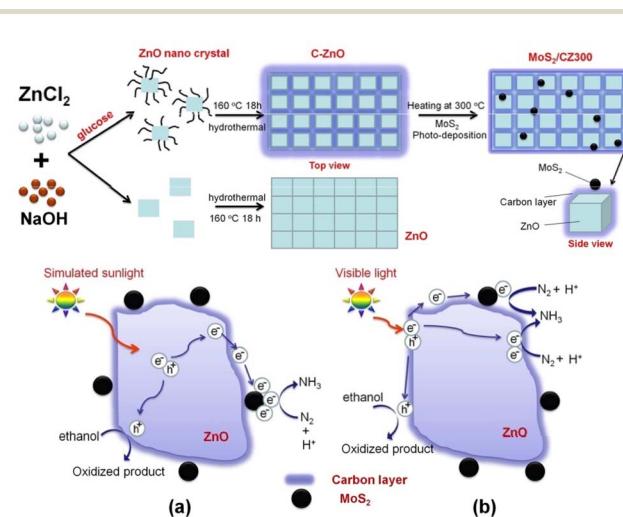


Fig. 11 Preparation of MoS₂/CZ300 photocatalyst and the suggested charge transfer mechanism of MoS₂/CZ300 composite (a) under simulated sunlight (b) and visible light irradiation. Reproduced from ref. 79 with permission from [American Chemical Society], copyright [2018].

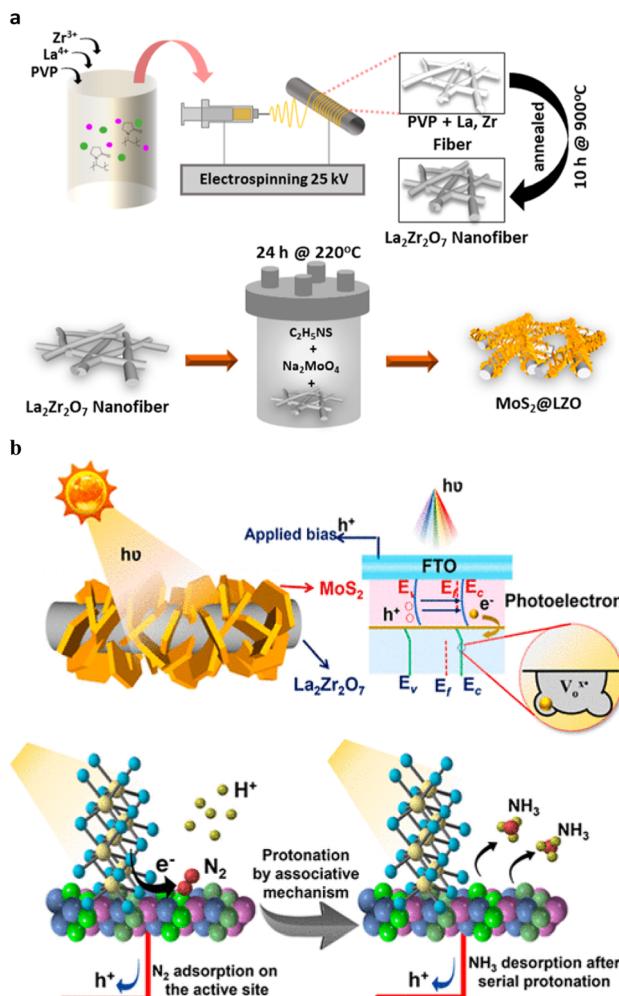


Fig. 12 (a) Schematic illustration of the electrospun LZO nanofibers, followed by hydrothermal synthesis of MoS_2 @LZO. (b) The band structure demonstrating the type II heterojunction for MoS_2 @LZO heterostructures with a reduced Fermi level under applied bias and solar illumination and schematic illustration of the PEC-NRR mechanism following the associative pathway for ammonia production. Reproduced from ref. 82 with permission from [American Chemical Society], copyright [2022].

active site for these reactions. The MoS_2 @LZO PEC catalyst exhibits a maximum ammonia yield rate of approximately $10.4 \mu\text{g h}^{-1} \text{cm}^{-2}$ and a higher faradaic efficiency of approximately 2.25% compared to pristine MoS_2 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 MoS_2 catalysts, MoS_2 @LZO demonstrates a higher ammonia yield, selective N_2 adsorption, and excellent stability. The 2D- MoS_2 nanoflakes, the $\text{La}_2\text{Zr}_2\text{O}_7$ 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.* reported⁸³ the photocatalytic oxidation rate of NO_2^- under simulated solar irradiation, which can reach 62% by the $\text{MoS}_2/\text{TiO}_2$ composite synthesized in a hydrothermal system with a $\text{C}_2\text{H}_5\text{NS}/\text{Na}_2\text{MoO}_4$ molar ratio of 1 : 0.6 : under 200 °C for 24 h, which is significantly higher than that by pristine TiO_2 NFs, P25 and pure MoS_2 . The photocatalytic oxidation process of NO_2^- 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} . MoS_2 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 CO_2 and H_2O to CO , CH_4 and H_2 products

Ray *et al.* reported,⁸⁴ the integration of photoabsorber MoS_2 and N-containing conducting polymer polypyrrole (PPy) over reduced graphene oxide improved CO_2 photoreduction and H_2 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 /PPy nanocomposite was found to exhibit a remarkable production of CO ($3.9 \mu\text{mol g}^{-1} \text{h}^{-1}$), CH_4 ($1.50 \mu\text{mol g}^{-1} \text{h}^{-1}$), and H_2 ($4.19 \mu\text{mol g}^{-1} \text{h}^{-1}$) in the photocatalytic reduction of CO_2 in an aqueous suspension (Fig. 14).

The synergistic effect of the MoS_2 , rGO, and PPy nanostructures, which encouraged the separation and migration of the photogenerated charges through the heterojunction interfaces and decreased electron–hole recombination, was

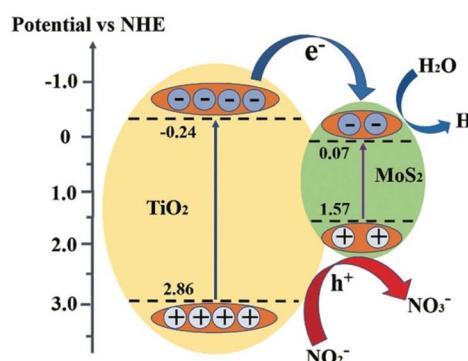


Fig. 13 Schematic illustration of the energy band structure and electron–hole separation of $\text{MoS}_2/\text{TiO}_2$ composites. Reproduced from ref. 83 with permission from [Royal Society of Chemistry], copyright [2021].



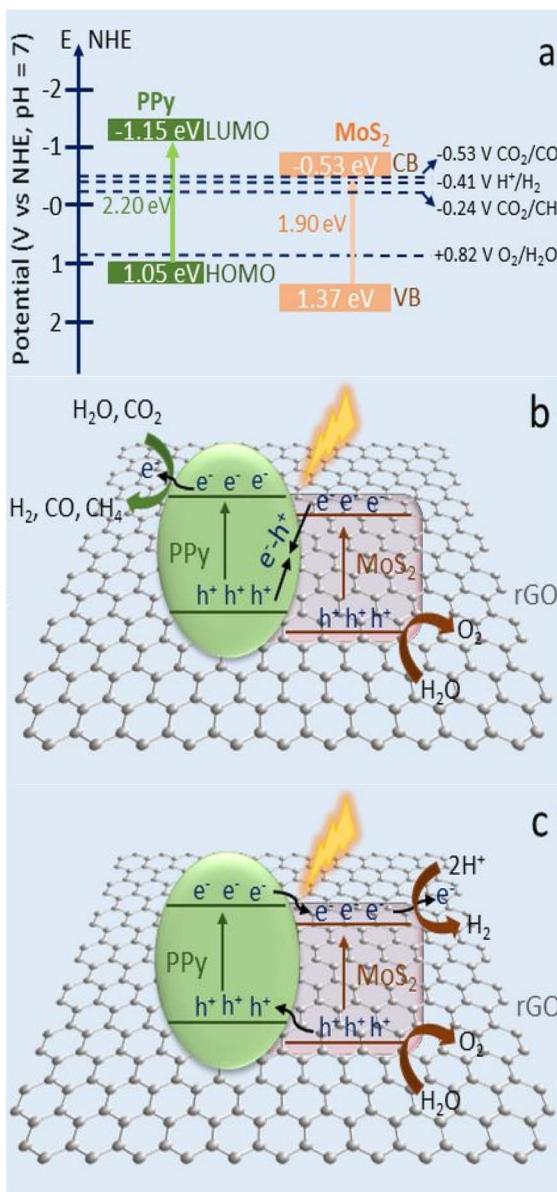


Fig. 14 (a) Schematic representation of the band positions and potentials of PPy and MoS₂. (b) Photocatalytic CO₂ conversion into CH₄ and CO gas via Z-scheme mechanism with rGO as redox mediator on the rGO-MoS₂/PPy nanocomposite. (c) The conventional type II electron transfer for H₂ production on the rGO-MoS₂/PPy nanocomposite. Reproduced from ref. 84 with permission from [American Chemical Society], copyright [2020].

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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