Transition Metal Dichalcogenides in Photocatalytic Hydrogen Evolution

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Transition metal dichalcogenides (TMDCs) is an emerging class of two-dimensional (2-D) materials that have exhibited great potential in photocatalytic applications owing to their intrinsic properties. They are normally used as cocatalysts together with other semiconductor materials and the junction created between them facilitates charge transfer of the photogenerated electrons and holes. The photocatalytic H₂.evolution systems can be enhanced by lengthening the parts of uncovered surface of photocatalyst and delaying the recombination of electron-hole pairs.

Keywords: transition metal dichalcogenides ; water splitting ; photocatalysis ; co-catalyst

1. Introduction

Society at large is prospecting for carbon-free fuel alternatives to purvey an unfailing panacea to the present energy plight of the world. Research efforts into the development of alternate clean and renewable energy sources have been at a steady rise in the last few decades. Hydrogen is credited to be an unpolluted, robust, environmentally safe, and emerging fuel, efficient to curb total reliance on petroleum-based fuels. Currently, methane reforming accounts for the largest production of hydrogen fuel, where methane gas is converted to carbon monoxide and hydrogen. This process is energy inefficient and has a negative environmental impact. Consequently, it is desirable generating hydrogen through unexhausted resources such as water and solar power. Solar light-assisted water decomposition is an emerging method for sustainable hydrogen production. Producing hydrogen through solar simulated light, water and photocatalyst is a desired technology not only because water and solar energy are abundant on the earth but also because it is environmentally friendly and economically viable. Hydrogen is attributed to have the maximum energy content per weight in comparison to other combustion fuels, the by-products are environmentally friendly which are water vapour and ^{[1][2][3]}

To a consumer, similar to natural gas serves many purposes, hydrogen gas could be used to heat homes and as a fuel for automobiles. Environmentally, hydrogen is exceptional among other fuels, being a carbon-free fuel, it will generate zero carbon dioxide during combustion. To the scientists, hydrogen is the most simplified and most abundant element in the world. The hydrogen atom (H) is made of one electron and one proton but as a molecule (H₂), it has a favourable physical feature. In terms of energy, it is the highest carrier of energy, having 2.4 folds higher energy content than that of natural gas. This can be put to use using fuel cell to generate electricity or by combustion to produce heat for homes use. It is also a carbon neutral energy carrier. With many countries till date still dependent on energy from fossil fuel sources which is a major source of environmental pollution, there is a dire need for cleaner energy to meet CO_2 emission reduction targets. The Asian countries are the major players in realising the hydrogen economy. Commitment is a vital key to attain the regulatory CO_2 emission targets, as it is very costly to achieve. Japan has keyed into the Paris climate agreement of 2016 and has made much commitment to be a large-scale hydrogen user for energy. Most countries in Europe have signed an agreement based on the European Green Deal to ensure zero-emissions for cars and vans and to achieve zero net emissions of greenhouse gases in Europe by 2050 ^{[1][5]}. Little work has been carried out or reported on hydrogen economy in Africa. In South Africa, the telecommunication industry is already using hydrogen fuel. This is used as support system power for petrol or diesel generators in military, hospitals and mines in case of intermittent power supply.

With water and sunlight being free and abundant in nature, this method of generating hydrogen gas is beneficial, environmentally safe, and renewable avenue which could serve as valuable resource to tackle both the energy plight and environmental pollution. Photocatalytic processes have been considered as one of the most promising methods to split water into hydrogen and oxygen. For an effective photocatalytic process, there is a need to use a sturdy and very active photocatalyst to produce good yields of hydrogen gas. Since Fujishima and Honda ^[6] used TiO₂ electrodes for photocatalytic water splitting, a large array of other photocatalysts have been studied for solar driven water splitting; for

instance, CdS, CuS, C₃N₄, ZnO, BiVO₄, MoS₂ ^{[Z][8][9][10][11][12][13]}. So far, numerous semiconductor photocatalysts are being explored and used for photocatalytic water splitting. Photocatalysts can be subdivided into three categories namely: metal oxides, metal chalcogenides, and metal–free photocatalysts. Despite the progress made so far on these photocatalysts, they still have some deficiencies. The metal oxide makes use of ultraviolet region of the spectrum because of their large band gap energy. Some semiconductors favour either water reduction or oxidation activity, hence they are not appropriate for effective water splitting. These semiconductors undergo quick charge co-existence of the electron-hole pair resulting in inefficient charge separation and finally, the active sites must not be covered, but in bulk they are not available to partake in photocatalytic processs [Z][14][15].

Transition metal dichalcogenides (TMDCs) is an emerging class of two-dimensional (2-D) materials that have exhibited great potential in photocatalytic applications owing to their intrinsic properties. They are normally used as cocatalysts together with other semiconductor materials and the junction created between them facilitates charge transfer of the photogenerated electrons and holes. TMDCs have the general formula MX₂, where M is a transition metal (Mo, W, Ti, Zr, Hf, Nb, etc.) and X is a chalcogen element (S, Se, or Te). While TMDCs of groups V and VI elements have been extensively studied for applications in photocatalysis, in the open literature, not much information is currently available on the group IV TMDCs ZrS₂ and HfS₂ especially synthesized by colloidal methods as these are very unstable and are easily oxidized in mono or few-layers.

2. Application of Transition Metal Dichalcogenides in Photocatalytic Hydrogen Evolution

2D layered transition metal dichalcogenides have received an enormous amount of attention for their magnificent catalytic activities, narrow band gap, crystallinity, excellent properties and their use in catalysis for production of hydrogen gas $[I]_{14}]_{[16][17][18]}$. They are being sought for in recent time as a result of their low cost, earth abundance and excellent catalytic activities as a possible replacement for scarce and expensive noble metals $[I]_{[14][12][18]}$. The transformation that occurred in the material from 3D to 2D paved the way for their novel electronic and mechanical properties. There are many active sites in 2D chalcogenides which participate during catalytic reaction and the possibility of harnessing solar energy by the atoms of the semiconductor. The chalcogenides possess right and adjustable band gap depending on the number of layers they possess. To illustrate this, the band gap of ZrS_2 may be increased from 1.5 to 2.0 eV if the bulk ZrS_2 is exfoliated to single layer of ZrS_2 , hence, there is changes in the band gap energy as it moved from an indirect to a direct band gap by reason of quantum confinement ^[18]. A lot of these 2D chalcogenides have been proven to be good photocatalysts for water splitting, including MoSe₂, MoS₂, WS₂, NiS, NiSe, Wse₂, SnS₂, and ReS₂ ^{[11][16][17][19][20][21]}. Some other semiconductors, the likes of HfS₂, ZrS₂, TcSe₂, and TaS₂ are being anticipated as photocatalysts to be considered for decomposition of water ^{[14][12][13]}.

Composite photocatalysts have been used to improve photocatalytic processes by reason of their excellent configuration. To enhance the properties of these, TMDCs are integrated with other photocatalysts such as TiO₂, ZnO, CdS, CuS, g- C_3N_4 etc. There must be an intimate interface between the semiconductor and the co-catalyst which will accelerate electron transfer within the interface of the semiconductor to the co-catalyst. The design and assembly of an exclusive junction between the photocatalyst and the co-catalyst plays a vital role for enhanced photocatalytic performance [14][24]. There are reports on the utilization of MoS₂ as co-catalyst by several researchers to greatly enhance the activity of photocatalysts. Table 1 shows a summary of composite photocatalysts that have been employed in hydrogen evolution reactions. Ma et al. ^[25] constructed a CdS-MoS₂ hybrid catalyst for photocatalytic production under visible light, by ultrasonication treatment. The presence of MoS₂ greatly boosted the production of hydrogen which was about two times greater than when CdS alone was used. However, due to weak interface between them, the photocatalytic activity decreased (about 35%) after four cycles which was attributed to ease of separation of MoS₂ from CdS. CdS is a wellknown photocatalyst, but it has the drawbacks of photo corrosion and great toxicity of Cd to the environment. Chang et al. ^[26] demonstrated that the number of layers of TMDCs played a key role in a catalytic reaction. In their study for photocatalytic hydrogen evolution reaction using MoS₂ loaded on CdS in the presence of NaS-Na₂SO₃ and lactic acid as sacrificial agents, the yield of hydrogen with lactic acid was higher than with NaS-Na₂SO₃, however the catalyst was more stable in Na₂S-Na₂SO₃ compared to lactic acid. This was expected since lactic acid solution contains abundant H⁺ to Na₂S-Na₂SO₃. The researchers do not report on the number of cycles conducted on the catalyst to determine its stability. They revealed that mono, or few layer(s) of MoS₂ produced maximum generation of hydrogen compared to higher numbers (7–122) of layers. The yield of monolayer was the optimum generating 0.00259 mmolh⁻¹ and 0.00201 mmolh⁻¹ H₂, respectively, and this was associated to the following 3 factors: (a) the mono layer displayed a more negative conduction band minimum to H^+/H_2 potential (b) the edge sites are very pivotal to the hydrogen production and the monolayer has plethora exposed active sites arising from the unsaturated (S) atom to the other layers (bulk) and (c) delayed rate of recombination of photogenerated carriers was observed in mono-layer compared to bulk which was attributed to

good interface contact between mono MoS₂ and CdS. The yield of MoS₂/CdS was 5.89 times higher than Pt/Cds conducted in lactic acid. However, there is possibility of carbon monoxide generation which may lead to Pt catalyst poisoning, thus a reduced production using Pt/Cds in lactic solution. Very recently, Zong et al. [27] fabricated CdS-MoS₂ by conventional impregnation method. The H₂-evolution rate was 36 times higher when 0.2 wt% MoS₂ was loaded on CdS. The enhanced photocatalytic activity was attributed to the tight junction formed between MoS₂ and CdS and the excellent H₂ activation property of MoS₂. In similar work, Zong et al. ^[28] also fabricated CdS-WS₂ by impregnation method. The loading of 1% weight of WS₂ increased hydrogen evolution rates by 28 times attributed to the interface formed between CdS and WS₂ and the excellent performance of WS₂ as a co-catalyst in catalysing H₂ evolution. CdS is a well-known photocatalyst, but it has the drawbacks of photo corrosion and great toxicity of Cd to the environment. In a recent work, Reddy et al. [29] accounted for the outstanding HER activity of a nanohybrid which was reported to be highest using a ternary catalyst compared to the one available in literature. The group constructed heterostructures by loading fewlayered ultrathin MoS₂-WS₂ on CdS and applied the catalyst for photocatalytic water splitting using lactic acid as holes acceptor. The HER performance of 209.79 mmolg⁻¹ h⁻¹ was obtained which was 1.70 folds greater than Cds-MoS (123.31 mmolh⁻¹), 1.70 folds higher than Cds-WS₂ (169.82 mmolh⁻¹), 6 folds higher than CdS-Pt and 83 times higher than bare CdS (2.54 mmolh⁻¹). The 6 wt% MoS₂-WS₂ loading was the most effective which showed robust activity, durability, and stability even up to 2.5 days. The high-level activity was attributed to the following reasons: (i) more actives sites were available by MoS₂-WS₂ cocatalyst in contrast with a single cocatalyst (ii) proper band gap of the nanohybrid (iii) tight heterojunction between the catalyst and cocatalyst which promoted ultrafast electron transfer to the cocatalyst, as well tardy re-joining of the photogenerated carriers. Swain et al. ^[30] synthesized MoS₂ nanoflowers and used them to decorate Caln₂S₄ microflowers using double step hydrothermal method. The experiment showed that hybrid catalyst generated higher H₂ production (19 times) compared when the Caln₂S₄ was used in a visible light irradiation. The catalyst showed a band gap of 2.11 eV which enabled the reaction to be conducted in visible region of light compared to UVvisible light. The MoS₂ provided more edge sites having plethora of unsaturated sulphur ions which facilitate quick capture of the H⁺ ions at the interface of the p-n heterojunction of the catalyst. This activity enhancement was as a result of adequate prevention of quick reoccurrence of electron-hole pair at interface of the hybrid catalyst. This work showed that MoS₂ is a possible replacement to other promoter on a semiconductor catalyst with just 0.50% loading. With increasing loading as low as 1% the output of H₂ production declined due to the black colour of MoS₂ which prevented the transfer of photons. The catalyst also generated H₂ even in the absence of sacrificial agent though with a lower yield. Stability study showed the catalyst to be stable even after 4 cycles. The rate of H₂ production generated in the research was a great improvement over previous studies on Caln₂S₄ based composite for photocatalytic water splitting as the yield is far higher compared to when other catalysts that were loaded on the semiconductor photocatalyst. Nguyen et al. [31] decorated Zn_xCd_{1-x}S with MoS₂ via a photo-assisted deposition. The 3% decoration of Zn_{0.2}Cd_{0.8}S/MoS₂ gave H₂ evolution 210 times higher than the undecorated photocatalyst. Huang et al. [32] constructed 2D/2D ZnIn₂S₄/MoS₂ nanohybrid using electrostatic self-assembly method. Generally, due to the possibility of shading effect as a result of excess loading of the co-catalyst on the catalyst, low loadings of MoS₂ are required. The 0.75% loading gave the maximum hydrogen yield which was almost 50 times higher than the raw ZnInS₄. Only traces (0.099 mmol h^{-1}) of hydrogen were generated when pristine ZnIn₂S₂ was used for the photocatalytic reaction. However, when MoS₂ was loaded on it, the hydrogen yield increased linearly with increase amount of the promoter until 0.75% after which the yield deceases due to the shading effect. The result was also compared to 0.75% Pt/Znl₂S₄. The production of H₂ was 2.2 lesser with noble metal as a promoter. The reaction was visible light-driven possibly due to its band gap that is proper for visible light, however the researchers did not report on the adsorption edges or band gap of any of the catalyst used. The structure of a catalyst determines its efficiency in a photocatalytic reaction. The high yield could be as a result of the ultrathin structure of both MoS₂ nanosheet and ZnIn₂S₄ nanosheet, and the robust and close contact interface in the hetero layered enhanced the photocatalytic hydrogen generation. The fabrication of ultra-thin 2D/2D structure performs better compared to 0D/2D and 1D/2D counterparts. The catalyst was reported to be stable until fourth cycle of use in which a decrease in the activity was noticed. Pudkon et al [33] synthesized ZnIn₂S₄ using different sulphur sources and loaded it on WS₂ using microwave method of synthesis. The L-cysteine not just being a sulphur source but played the dual purpose as a reducing agent and as capping agent and helped in growth direction for the formation of flower-like nanomaterials. The HER activity of the hierarchical (flower-like) catalyst (145.3 µmolh⁻¹) was far more than the non-hierarchical (81.6 µmolh⁻¹) catalyst. The former provides diverse reflections of the incident light via its shape thus a lengthy lifetime of the incident light in its structures. This can be credited to the surface area as well, surface area is an important factor in a catalytic reactions, the higher the surface the more active site will be available for reactions to take place. The nanomaterial with flower-like morphology had a surface area 1.6 folds higher than non 3D nanomaterials fabricated. The 40%wt loading of WS₂ on flower-like catalyst was most suitable for HER with activity 2 times higher (293.3 μ molh⁻¹) than the pure ZnIn₂S₄ and 6.67 folds than raw WS_2 . The close contact contributed to good separation of charge and injection at the interface of the catalysts whereas the composite formed by mere grinding of the two catalysts gave activity of (101.3 µmolh⁻¹) which was even less than activity of untreated flower-like $ZnIn_2S_4$ alone. Both $ZnInS_4$ and WS_2 are photocatalysts that absorb within the visible region of solar spectrum. The researchers did not report on the band gap of the composite however, the band edge obtained from the UV-absorption showed a slight shift to higher wavelength which is an indication of a better response of the composite to visible light. However, in their report the composite catalyst activity for H2-evolution was more favoured in UV-visible compared to visible region up to about four folds. This may be accounted for by the band gap of the semiconductor synthesized; it had a band gap of 2.81 eV, close to that of a material that absorbs in the UV region, and the promoter did not significantly improve the response of the composite to visible light. The output of hydrogen obtained was slightly lower than previously reported on ZnInS₄ based heterostructure demonstrated for H₂ production. Photocatalysts that absorb in the visible region are required for visible light driven photocatalysis and they have their band gap very close to 2.0 eV [34]. Zeng et al. [35] in a manner similar to constructed metal-sulphide -metal-selenide hybrid (Znln₂S₄-MoSe₂) system for HER using a one-pot polyol method. The synthesized Znln₂S₂ had hierarchical structures which contributed to the increased HER activity of the untreated catalyst of 1023 µmolh⁻¹ in contrast with previous work in which pristine $ZnIn_2S_4$ was used for photocatalytic water splitting. The 2 wt% loading on the hierarchical structure $ZnIn_2S_4$ improved the activity by a multiple of 2.2 times. The stability test on the catalyst showed good stability even after five cycles. The result obtained with MoSe₂ as cocatalyst on a ternary chalcogenide is very comparable to results from previous researchers with MoS₂ loaded on the same material. This is an indication the activity of MoSe₂ as a promoter is as well good as MoS₂ in photocatalytic water splitting.

A lot of work has also been reported on the improvement of the photocatalytic activity of TiO₂ with TMDCs. Li et al. ^[36] synthesized MoS₂/TiO₂ hybrid by hydrothermal treatment and found the MoS₂/TiO₂ hydrogen evolution yield was 2.19 and 3.15 times higher than TiO₂ and MoS₂, respectively. The yield was still good after 4 cycles of use, this as a result of close interaction between the co-catalyst and the photocatalyst. Recently, Zhang et al. [37] fabricated novel mesoporous anatase titania with high photoconductivity and photocatalytic attributes compared to nanocrystal TiO₂ such as P25 using hydrothermal method. MoS₂ nanosheets was loaded on the 3D TiO₂ using same hydrothermal process and evaluated for hydrogen evolution reaction under UV light source for irradiation. The composite showed higher photocatalytic activity for hydrogen evolution compared to undecorated TiO₂ and MoS₂. The mesocrystal of the TiO₂-MoS₂ composite produced an H₂-evolution rate of 0.55 mmolh⁻¹ which was 4 times greater than MoS₂-TiO₂ (P25) hybrid. The performance of MoS₂ as a promoter on the semiconductor in work is an indication of possible replacement over precious metal such as Pt and Pd. The 1% MoS₂ loading resulted in 200 times higher H₂ evolution compared to the bare mesocrystal TiO₂. However, previous reports showed that a maximum loading of about 2% MoS₂ on semiconductor resulted in enhanced photocatalytic water splitting contradict the report in this work where up to 10% of MoS₂ was the optimal loading for high hydrogen production. The main factor was identified as annealing process. Annealing the catalyst at about 160 °C greatly improved its performance towards HER since phases of TMDCs contributes immensely to the catalyst activity towards HER. The annealing caused some phase transition of the MoS₂ from metallic phase to mostly hexagonal phase. Moreover, at annealing temperatures exceeding 240 °C the activity of the composite declined possibly due to the sulphur active sites being oxidized or loss of the metallic phase. The catalyst also showed good stability after five test cycles. In another report, Zhou et al. [38] fabricated MoS₂-TiO₂ heterostructures by hydrothermal method. MoS₂ loaded on TiO₂ nanobelts and the resulting photocatalyst exhibited outstanding H_2 -evolution to a value of 1600 µmolh⁻¹ compared with pure TiO₂.

Dong et al. ^[39] also made TiO₂.MoS₂ heterojunction via annealing impregnation deposition method. The hybrid generated H₂ evolution with activity 7.2 times and 17.6 higher than the bare TiO₂ and MoS₂, respectively, ascribed to that the heterojunction between TiO₂ and MoS₂ quantum dots which could suppress the recombination of electron-hole pairs efficiently and that the hollow TiO₂ nanospheres and MoS₂ quantum dots with high specific surface area and pore diameter could supply plenty of active sites. Moreover, the researchers did not experiment on different loading to determine the optimal loading and the percent of co-catalyst used was not reported and more so, the recyclability test was not reported. Feng et al. [40] fabricated guaternary nanocomposite of Mn-Cds-MoS₂-TiO₂ by hydrothermal method. The quaternary nanocomposite gave outstanding H₂-evolution up to a level of 408.27 mmolh⁻¹ which was 30.08 folds that of TiO₂, 5.18 folds of TiO₂-MoS₂ and 2.52 folds for CdS-Mn-TiO₂, respectively. The photocatalyst performance was greatly improved which was attributed mainly to the synergetic effects of CdS-Mn, MoS₂ and TiO₂, forming a Z-scheme system in the CdS-Mn/MoS₂/TiO₂ electrode, which not only accelerates the interfacial charge transfer efficiency but also preserves the strong redox ability of the photogenerated electrons and holes. This is one of the highest activities reported so far for a catalyst for photocatalytic water decomposition. MoS₂ has also been used to improve the photocatalytic properties of ZnO. Yuan et al. [41] loaded MoS₂ on ZnO via hydrothermal route. The loading of MoS₂ as cocatalyst on ZnO elevated its H_2 -evolution rate up to 14.8 folds than the pristine ZnO. The optimum loading of 1% MoS₂/ZnO generated 768 μ molh⁻¹ of H₂. The activity enhancement was due to the suppression of the recombination of electron hole pairs of ZnO. Li et al. ^[42] constructed the nanohybrid of MoS₂-ZnO by dispersion method. The deposition of MoS₂ enhanced the hydrogen evolution 5 times compared to pure ZnO because of the production of more electrons and holes and reducing their

recombination. The hydrogen output activity was 27.69 mmolh⁻¹. The method used to prepare to prepare the nanostructure did not produce a thorough interface between the two catalysts thus a reduced activity was noticed, and the recyclability of this catalyst was very difficult. Very recently similar research was conducted by Chang et al. ^[43] in which they constructed p-n MoS₂-ZnO heterostructures with large surface area using hydrothermal method. The nanohybrid with 0.03 g of MoS₂ yielded the highest activity (145.6 μ molh⁻¹) after which the performance declined with further loading. However, the activity reported was 5.3 times less than what Yuan et al. obtained ^[41]. Chang's group ^[44] also investigated the photocatalytic water splitting activity of MoS₂-SnO₂ core-shell sub microsphere using Na₂S as hole collector, the yield was slightly lower when compared to MoS₂-ZnO (117.2 μ molh⁻¹). Oxides of bismuth are good semiconductors which find application in photocatalytic processes. Khalid et al. ^[45] constructed nano composite of Bi₂O₃-MoS₂ by hydrothermal method with varying composition from 0–15 wt% of MoS₂. The highest HER was obtained with 11 wt% with activity (10 μ molh⁻¹) which was ten folds higher than raw Bi₂O₃ and pure MoS₂. The ability of the catalyst to absorb much visible light and delayed recombination of electrons and holes led to higher production of H₂.

The use of CeO₂ has not been explored in photocatalytic water splitting until Swain et al. ^[46] successfully constructed MoS_2 -CeO₂ using hydrothermal approach. The best output was when 2 wt% of the promoter was deposited on CeO₂ to form p-n junction with large intimate and close junction with performance of 508.44 µmolh⁻¹ which is far higher (57 times) than unloaded CeO₂. The catalyst still showed good stability even after 3 cycles.

Hollow graphitic carbon nitride (g-C₃N₄) has been a photocatalyst widely used in hydrogen evolution. Both g-C₃N₄ and MoS₂ have comparable layered structures which should help to reduce the lattice mismatch and ease the planar growth of MoS_2 layers on the g-C₃N₄ surface. Hou et al. ^[47] loaded MoS_2 on mesoporous g-C₃N₄ by impregnation method followed by sulfurization. The nanohybrid played a vital role in boosting the photocatalytic activity to 310 µmolh⁻¹ with 0.5 wt% compared to when pristine $g-C_3N_4$ (108 μ molh⁻¹) and untreated MoS₂ (0.25 μ molh⁻¹) were used where the activities were much lower. The group [47] in a similar reaction also formed heterostructure of WS2-C3N4 using impregnation system followed by sulfurization. The 3 wt% loading gave the highest activity (20.60. μ molh⁻¹) while with unloaded C₃N₄ the activity was very minimal. In a related research, Ge et al. [48] synthesized composite of MoS₂-g-C₃N₄ by impregnation route. The 0.5 wt% MoS₂-g-C₃N₄ gave the maximum catalytic activity with H₂ evolution of 23.10 μ molh⁻¹ which was 11.3 times higher to unwrapped g- C_3N_4 . Wang et al. ^[49] performed density functional theory calculations on hybrid g- C_3N_4 . MoS_2 and found that photo-generated electrons migrate easily from the $g-C_3N_4$ monolayer to the MoS_2 sheet leading to a high hydrogen evolution activity of the hybrid over g-C₃N₄ or MoS₂ singly. Recently, Liu et al. [50] synthesized 3D/2D nanojunction of flower-like MoS₂ on graphitic carbon nitride using ultrasonication and thermal treatment method. The optimum loading of 5 wt% of MoS₂ was also used by this group to generate 867.6 μ molh⁻¹ of hydrogen which exceeded that of untreated g-C₃N₄ by 2.80 times. The activity observed with 3D MoS₂ and g-C₃N₄ and was reported to be higher than other dimensions of MoS₂ composite with g-C₃N₄. The enhanced HER activity was attributed to tight interface between the catalysts which facilitated higher light harnessing, quicker bond charge separation, faster electron transport and the increased electrical conductivity of the materials. The catalysts also showed good electrocatalytic HER activity with reduced overpotential and high current densities. Zhang et al. [51] used hydrothermal method to prepare heterostructure of nitrogen doped carbon tube molybdenum disulphide (TNCT@MoS2) for photocatalytic water splitting in the absence of electron donor. The microcomposite displayed increased performance with activity of 120 µmolh⁻¹ which was several times greater than untreated MoS_2 . The generation of H_2 without the use of a sacrificial agent which plays the function of acceptance of the hole suggested the micro-heterostructure catalyst to be effective in water splitting. The achieved result was attributed to higher absorption of visible light, creation of more active sites, possibly the power of the xenon lamp used (1000 W); the maximum of power of xenon lamp that was reported in literature was 400 W, as well as the nitrogen dopant which could help in fast electron transfer to the active sites of the MoS₂. The group also observed similar activity when the pH of the water used was varied from 5-11. The gas chromatography used could not detect any O₂ generated during the reaction which was later probed by fluorescence method in which the intermediate OH was picked up. The O_2 produced during reaction was reported to be absorbed by the metal of the cocatalyst to form a peroxide complex.

Gupta and Rao ^[52] highlighted the use of dye with TMDCs in photocatalytic water splitting. The dyes have capacity to absorb light. Common dyes that are used are noble-metal-centred and metal-free dyes. Noble metal dyes that are often used are Ru(ii) tris bipyridine (Ru(bpy)₂³⁺) and hydrated iridium oxide (IrO₂.nH₂O). The metal free dyes such as Eosin Y or Rose Bengal are commonly used. The noble metal-centred dyes are being reported to be more effective in generation of hydrogen over the metal free dyes because they give more photocurrent upon irradiation with visible light over the metal free dye. They play a dual role as oxidizing catalyst and photosensitizer ^[53]. Upon excitation it undergoes some transformation to inject an electron to TMDC (MoS₂). In 2009 Zong et al. ^[54] conducted photocatalytic hydrogen generation in visible light using composite of dye Ru(ii) tris bipyridine (Ru(bpy)₂³⁺) which play the role of an organic photosensitizer and colloidal MoS₂ in presence of ascorbic acid. Upon irradiation in a visible light source, the dye

transferred electrons to MoS_2 which has many active sites, which in turn reduce the protons to $H_2(g)$. It was observed an increase in the concentration of the dye used led to a corresponding increase in the amount of $H_2(g)$ formed. It was also noted the amount of the $H_2(g)$ produced increased with temperature employed in the synthesis of colloidal MoS_2 using solvothermal method. When the reaction was performed in a mixture of acetonitrile and methanol solution while ascorbic acid serves as the sacrificial agent, the hybrid catalyst gave rise to 210 mmolh⁻¹ of hydrogen gas, but this got diminished after some hours due to the decomposition of the organic photosensitizer dye. The use of the dye has the drawback of photo-instability.

Other dyes that have been employed as organic photosensitizer is the metal–free dye such as Eosin Y and Rose Bengal. Min and Lu et al. ^[55] synthesized nano composite of MoS_2 and graphene {G} using hydrothermal method. The nano composite was sensitized by Eosin y dye during photocatalytic reaction using triethanolamine (TEOA) as sacrificial agent, showing an activity of 83.8 µmolh⁻¹. However, when EY-RGO was tested the activity was very low < 0.5 µmolh⁻¹ and activity of 37.7 µmolh⁻¹ with MoS_2/RGO was obtained.

Catalyst	Synthesis Method	Sacrificial Agent	Light Source	Activity	Ref.
MoS ₂ -TiO ₂	Hydrothermal	0.35 M Na_2SO_3 and Na_2S	Xe Lamp 300 W	1600 µmolh ⁻¹	[<u>38]</u>
MoS ₂ -Caln ₂ S ₄	Two-step hydrothermal	$0.025M$ Na_2SO_3 and Na_2S	Xe Lamp 150 W	602 µmolh ^{−1}	[30]
MoS ₂ -CdS	Sonication and stirring	Na_2SO_3 and Na_2S	Xe Lamp 300 W	1750 µmolh ⁻¹	[<u>25</u>]
MoS ₂ -CdS	Impregnation	Methanol and 10% Lactic acid	Xe Lamp 300 W	532.8 µmolh ⁻¹	[<u>26]</u>
MoS ₂ -CdS	Centrifugation	Lactic acid	Xe Lamp 300 W	259 µmolh ⁻¹	[<u>27]</u>
WS ₂ -CdS	Impregnation	10% Lactic acid	Xe Lamp 300 W	420 µmolh ^{−1}	[<u>28]</u>
CdS-MoS ₂ -WS ₂	Hydrothermal	10% Lactic acid	-	209.790 µmolh ⁻¹	[<u>29]</u>
MoS ₂ -Zn _{0.2} Cd _{0.8} S	Photo deposition	$0.25~M~Na_2SO_3$ and $0.25~Na_2S$	Xe Lamp 300 W	2 µmolh ^{−1}	[<u>31</u>]
MoS ₂ -ZnIn ₂ S ₄	Electrostatic self-assembly	Lactic acid	Xe lamp	4974 µmolh ⁻¹	[<u>32]</u>
WS ₂ -ZnIn ₂ S ₄	Micro wave	Na_2SO_3 and Na_2S	Xe lamp 150 W	293.3 µmolh ⁻¹	[<u>33]</u>
MoSe ₂ -ZnInS ₄	One polyol	$0.35~M~Na_2SO_3$ and $0.25~Na_2S$	Xe Lamp 300 W	2228 µmolh ⁻¹	[<u>35]</u>
MoS ₂ -TiO ₂	Hydrothermal	Methanol	Xe Lamp 350 W	75 µmolh ^{−1}	[<u>36]</u>
MoS ₂ -TiO ₂	Hydrothermal	10% Lactic acid	-	550 µmolh ⁻¹	[<u>37]</u>
MoS ₂ -TiO ₂	Annealing and impregnation	Triethanolamine	Xe Lamp 350 W	391.1 µmolh ⁻¹	[<u>39]</u>
Mn-CdS-MoS ₂ - TiO ₂	Hydrothermal	Methanol	Xe Lamp 300 W	408.370 µmolh ⁻¹	<u>[40]</u>
MoS ₂ -ZnO	Hydrothermal	0.5M Na ₂ SO ₄	Xe Lamp 1000 W	768 µmolh ^{−1}	<u>[41]</u>
MoS ₂ -ZnO	Hydrothermal	0.10M Na ₂ S	Xe Lamp 300 W	27,690 µmolh ^{−1}	[<u>42]</u>
MoS ₂ -ZnO	Hydrothermal	0.10 Na ₂ SO ₄	Xe Lamp 100 W	145.6 µmolh ⁻¹	[<u>43]</u>
MoS ₂ -SnO ₂	Hydrothermal	0.10 Na ₂ SO ₄	Xe Lamp 400 W	117.2 µmolh ⁻¹	[44]
Bi ₂ O ₃ -MoS ₂	Two steps hydrothermal	-	Xe Lamp 300 W	10 µmolh ⁻¹	[45]

Table 1. Role of TMDC as a good promoter of catalysts in hydrogen evolution reaction.

Catalyst	Synthesis Method	Sacrificial Agent	Light Source	Activity	Ref.
MoS ₂ -CeO ₂	Hydrothermal	Methanol	-	508.44 µmolh ⁻¹	<u>[46]</u>
MoS ₂ -g-C ₃ N ₄	Impregnation and sulfidation	10% lactic acid	Xe Lamp 300 W	108 µmolh ⁻¹	[47]
WS_2 -g- C_3N_4	Impregnation and sulfidation	10% lactic acid	Xe Lamp 300 W	20.6 µmolh ⁻¹	[47]
MoS ₂ -g-C ₃ N ₄	Impregnation	Na ₂ SO ₄	Xe Lamp 300 W	23.10 µmolh ⁻¹	<u>[48]</u>
MoS ₂ -g-C ₃ N ₄	Sonication and treatment	Triethanolamine	Xe Lamp 300 W	887.6 µmolh ^{−1}	<u>[50]</u>
MoS ₂ -C	Hydrothermal	Na_2SO_3 and Na_2S	Xe Lamp 1000 W	120 µmolh ⁻¹	[<u>51]</u>
MoS ₂ -RGO	Hydrothermal	Triethanolamine	Xe Lamp 400 W	42,000 µmolh ^{−1}	[55]

The presence of graphene also contributed to the enhanced performance of the catalyst. On excitation of the dye with visible light, the dye injected electron (EY^{-1}) into the RGO after which to the active edge sites of the MoS₂ which reduces the proton to H₂. The Eosin was proposed to first move to single state (EY^{1*}) on excitation, which later descended to low-lying triple state (EY^{3*}) by inter system crossing and later reduced to (EY^{-1}) in company of sacrificial agent (TEOA). EOSIN Y is preferred over other metal-free dyes due to the prolonged lifetime during excitation state because of bulky (Br) atom in the molecule. High activity was accounted for by the tight p-n junction of the composite. The graphene being heavily doped with the heteroatom nitrogen (15%) boosted electron injection capability of the graphene thus better HER activity. The intensity (power) and kind of lamp used could as well contribute the amount of H₂ produced. The amount of H₂ generated was a magnitude of four-fold higher (42 mmolh⁻¹) when 400 W xenon lamp to when 100 W Halogen lamp was used (10.5 mmolh⁻¹).

Deployment of phase-engineering has greatly help to elevate the catalytic output of MoS₂ by making both the edge sites and basal plane available for HER thus improving on the performance of the catalyst. This method helps to tune the electronic structure of the semi-conductor nanomaterial to a metallic 1T-phase. New research has proved that phaseengineered metallic 1T-MoS₂ was more effective in water splitting over 2H-MoS₂ since both the edge sites and basal plane active sites participated in the catalytic reaction. Maitra's group [56] demonstrated the use of mono 1T-MoS₂ for photocatalytic water splitting in the presence of dye (EOSIN Y) the yield was 30 mmolh⁻¹ of H₂ which was several folds (600) higher compared to few-layer 2H-MoS₂ (0.05 mmolh⁻¹). With prolonged time (3 h) 1T MoS₂ generated 250 mmolh⁻¹ of H₂. However, when the catalyst was dried, the activity was minimized, and observable reduction was noticed in the performance when annealed sample was applied. The H₂ yield was comparable to that of 1H-MoS₂.This suggested possible transformation to 1H-MoS₂ upon annealing the sample. The group also did further study on the metallic group VI TMDC by working with other chalcogens. When metallic 1T MoSe₂ was tested for HER performance was 900 times higher than 1H-MoSe₂. A similar observation was also recorded for 1T MoTe₂ which showed far better activity when compared to 1H MoTe₂. In related research applying phase engineering the group ^[52] also produced 1T MoSe₂ which showed high performance for hydrogen evolution using visible light. The reaction was conducted using EOSIN as a sensitizer and TEOA as holes acceptor. It was observed that the HER activity of 7500 mmolh⁻¹ was far higher than for the semiconducting phase (1H-MoSe₂) by almost 100 times, as well more superior to both 2H and 1T- MoSe₂. This was attributed to ultra-fast electron transport to the active sites of the material upon excitation with photon. DFT using theoretical calculation also proved 1T-MoSe₂ to have a lower work function than both 1T and 2-H MoSe₂.

Other methods that are employed to make the basal plane of TMDC active apart from phase engineering include introducing sulphur vacancies and doping with active metal ions charge. Common methods used in introducing chalcogenide deficiencies are contact with argon (Ar) plasma, annealing in H_2 and electrochemical reduction. Doping with active metals such as Cu, Zn, Ag, Pt and Co can increase the active sites and conductivity of TMDC. Recent Investigations have shown that the basal plane of TMDC become active by activating the catalytic activity of Se atoms in the basal plane [57].

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