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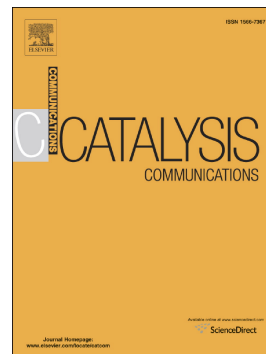
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**Bismuth sulphide-modified molybdenum disulphide as an efficient photocatalyst for
hydrogen production under simulated solar light**

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Abstract

To overcome rapid electron-hole recombination and the need for employing noble metals as co-catalysts for photocatalytic water splitting, the present work reports on the fabrication of bismuth sulphide (Bi_2S_3)-modified molybdenum disulphide (MoS_2) as an efficient hybrid photocatalyst. Under simulated solar light irradiation, the $\text{Bi}_2\text{S}_3/\text{MoS}_2$ photocatalyst with an optimum molar ratio of Mo to Bi of 50% (mol/mol) achieved a H_2 production rate of $61.4 \mu\text{mol/h}$. The photocatalytic enhancement was attributed to an effective charge transfer mechanism between Bi_2S_3 and MoS_2 , as evidenced by photoelectrochemical characterization. A plausible reaction mechanism over the as-prepared $\text{Bi}_2\text{S}_3/\text{MoS}_2$ photocatalyst was also proposed based on the experimental results obtained.

Keywords: hydrogen production; transition metal dichalcogenide; photocatalyst

1.0 Introduction

Due to population and economic growth, particularly in emerging market economies, global demand for energy is increasingly rapidly. Energy security concerns are gradually emerging as more consumers require ever more energy resources. Moreover, high consumption of fossil fuels leads to greenhouse gas emissions, particularly carbon dioxide (CO₂) which contributes to global warming. Therefore, there is an immediate need for alternative renewable fuels to reduce the dependency on fossil fuels. Among the various renewable projects to date, the photocatalytic splitting of water to generate hydrogen (H₂) fuel has garnered interdisciplinary research attention to meet the long-term worldwide energy demands without utilizing further CO₂-generating power resources [1-3]. However, the state-of-the-art technology is far from being optimal due to low overall photoconversion. Hence, breakthroughs in the preparation of efficient photocatalysts which are active under solar light, are necessary towards realizing the process for commercial applications.

Among the studied photocatalysts to date, metal sulphide semiconductors have been widely studied due to their narrow band gaps, high efficiency of light absorption and photocatalytic activity [4-7]. In particular, bismuth sulphide (Bi₂S₃) has garnered incessant research interest due to its narrow band gap of 1.3 – 1.7 eV [8-10]. However, the main drawback with any sulphur-containing catalysts is that their photoactivities are limited due to problems with photocorrosion and rapid charge recombination. Therefore, this leads to our interest in preparing heterostructured Bi₂S₃-based photocatalyst for the photocatalytic splitting of water. The general concept is to reduce rapid electron-hole recombination by merging two semiconductors with different energy levels to prolong the travel pathway of electrons.

Molybdenum disulphide (MoS_2) is a two dimensional material classified as a transition metal dichalcogenide. Previous works have shown that heterostructures of $\text{MoS}_2/\text{Bi}_2\text{S}_3$ are efficient for various applications such as Cr (VI) reduction [11], degradation of rhodamine B, atrazine and phenol red [12, 13]. To the best of our knowledge, there has yet to be a study on the application of $\text{Bi}_2\text{S}_3/\text{MoS}_2$ photocatalyst for solar H_2 generation. In this work, $\text{Bi}_2\text{S}_3/\text{MoS}_2$ photocatalysts were synthesized via an anion-exchange method. The photocatalytic activity of the as-synthesized photocatalyst was evaluated in the photocatalytic splitting of water under simulated solar light irradiation using $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ as sacrificial reagent. The improved performance of $\text{Bi}_2\text{S}_3/\text{MoS}_2$ photocatalyst in H_2 production provides a new pathway towards the goal of attaining clean renewable energy through water-splitting.

2.0 Experimental procedure

2.1 Materials

Bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), thioacetamide ($\text{C}_2\text{H}_5\text{NS}$), sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) were supplied by Sigma Aldrich. Sodium tungstate dehydrate ($\text{Na}_2\text{WO}_4 \cdot 5\text{H}_2\text{O}$) and ethanol were supplied from Merck and Friendemann Schmidt, respectively. All chemicals were of analytical reagent grade and were used as received without further purification. Deionized (DI) water was used in all experiments.

2.2 Synthesis of Bi_2WO_6

Bi_2WO_6 was prepared following modified methods reported from our previous work [14]. In brief, 0.4 mmol of $\text{Na}_2\text{WO}_4 \cdot 5\text{H}_2\text{O}$ first dissolved in DI water after which 0.8 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was then added into the mixture slowly to form a white solution. The mixture

was subsequently stirred for 1 h before being transferred to a Teflon lined autoclave for 15 h at 160°C. The precipitate was washed with DI water and ethanol before drying in an oven.

2.3 Synthesis of MoS₂/Bi₂S₃

For the preparation of MoS₂/Bi₂S₃ photocatalyst, a predetermined amount of Na₂MoO₄·2H₂O was dissolved in DI water before adding C₂H₅NS, the mixture was then stirred for 1 h at ambient condition. The as-prepared Bi₂WO₆ from Section 2.2 and a stoichiometric amount of C₂H₅NS were then added into the mixture with the aid of sonication to ensure a homogeneous mixture. After 1 h of sonication, the mixture was placed in a Teflon lined autoclave for 24 h at 200°C. The photocatalyst was then removed and washed with DI water and ethanol before drying in an oven. Pristine Bi₂S₃ was prepared through an in-situ anion-exchange between Bi₂WO₆ and the sulphur source under similar conditions while pristine MoS₂ was prepared following the method reported elsewhere [15]. MoS₂/Bi₂S₃ samples were prepared based on the molar ratio of Mo to Bi and were denoted as XMBS (X = 10, 30, 50 and 70 mole%).

2.4 Material characterization

The as-synthesized samples were analysed with field-emission scanning electron microscope (FE-SEM) (Hitachi SU8010) with energy dispersive X-ray (EDX) and transmission electron microscope (TEM) (TECNAI G2 F20) with an accelerating voltage of 200 kV. The X-ray diffraction (XRD) patterns of the samples prepared were determined using Bruker D8 Discover X-Ray diffractometer with CuK_α radiation ($\lambda = 0.15406$ nm) at a scan rate of 0.02 s⁻¹. The optical properties of the as-prepared samples were determined using ultraviolet-visible (UV-Vis) spectrometer (Agilent Cary 100) from 200 –800 nm. Photoluminescence (PL) measurements

were analysed using LS 55 PerkinElmer fluorescence spectrometer with the excitation wavelength of 320 nm. The emission spectra were scanned from 610 – 670 nm.

2.5 Photoelectrochemical measurements

Electrochemical impedance spectroscopy (EIS) Nyquist plots, transient photocurrent responses and Mott-Schottky plot were conducted in a three electrode electrochemical quartz cell with CHI6005E electrochemical workstation. 0.5 M Na₂SO₄ was used as the electrolyte for all photoelectrochemical measurements. Drop-casting method was employed to prepare the working electrode whereby slurry was prepared through suspension of samples in ethanol and casted onto fluorine-doped tin oxide (FTO) glass slide. The working electrode has an active area of 1 cm², where Pt and Ag/AgCl were used as counter and reference electrode respectively. The Mott-Schottky plots were measured from -1 to 1 V at 100 Hz frequency while transient photocurrent responses were measured with an applied bias of 0.5 V. EIS was performed over the frequency from 0.1 to 10⁵ Hz with amplitude of 0.01 V.

2.6 Evaluation of photocatalytic activity

The photocatalytic water splitting experiments were conducted at ambient pressure and temperature. MoS₂/Bi₂S₃ (10 mg) was dispersed in 120 mL DI water containing 0.5 M Na₂S and 0.5 M Na₂SO₃ which act as sacrificial reagents. The H₂ production was carried out under the irradiation of 500 W Xe lamp fitted with AM1.5 filter to simulate the solar light spectrum. The product gas was analysed using an online gas chromatography.

3.0 Results and discussion

3.1 Structural and chemical characterization

The crystallographic structures of the as-synthesized photocatalysts were characterised using XRD (see Figure S1). As shown in Figure S1(a), the peaks observed in the diffraction pattern of pristine Bi_2S_3 corresponded to the orthorhombic structure of Bi_2S_3 (JCPDS #017-0320), which verified the successful synthesis of Bi_2S_3 . Comparing the diffraction patterns of Bi_2S_3 (Figure S1(a)) and Bi_2WO_6 (Figure S1(g)), an additional distinct peak at 55.8° was observed for the latter (JCPDS# 039-0256). This unique peak corresponding to Bi_2WO_6 was not observed in other samples as shown in Figure S1(b – e), confirming the formation of Bi_2S_3 from Bi_2WO_6 . Furthermore, the peak observed at 14.4° (marked #) in Figure S1(b – e) can be ascribed to the (002) facet of MoS_2 . In addition, the peaks presented in Figure S1(f) are also in accordance with the hexagonal crystal structure of MoS_2 (JCPDS# 037-1492) [16, 17].

XPS was performed to analyse the surface chemical state of pristine Bi_2S_3 and 50MBS (see Figure 1 and Figure S2). As shown in Figure S2(A), the survey scan of 50MBS revealed the presence of elements Bi and Mo. The representative Bi core level XPS spectrum depicted in Figure 1(A) showed two peaks centered at 158.7 eV and 164.0 eV, which were indexed to Bi $4f_{7/2}$ and Bi $4f_{5/2}$ respectively. This indicated that Bi existed mainly in the chemical state of +3 [18]. Figure 1(B) shows the high resolution XPS spectrum for Mo. The binding energies of 235.6 eV and 232.4 eV corresponded to Mo $3d_{3/2}$ and Mo $3d_{5/2}$ respectively [6, 19]. The results obtained were in agreement with the XRD results presented in Figure S1. The characteristic peaks for S could be observed at 225.8 eV and 161.4 eV. It is to note that W^{6+} peaks at 35.8 and 37.9 eV, corresponding to W $4f_{7/2}$ and W $4f_{5/2}$ respectively, could not be observed in the survey

scan of Bi_2S_3 (Figure S2(B)), further confirming that Bi_2WO_6 were transformed into Bi_2S_3 [14].

The elemental scan for Bi of Bi_2S_3 sample is shown in Figure S2(C).

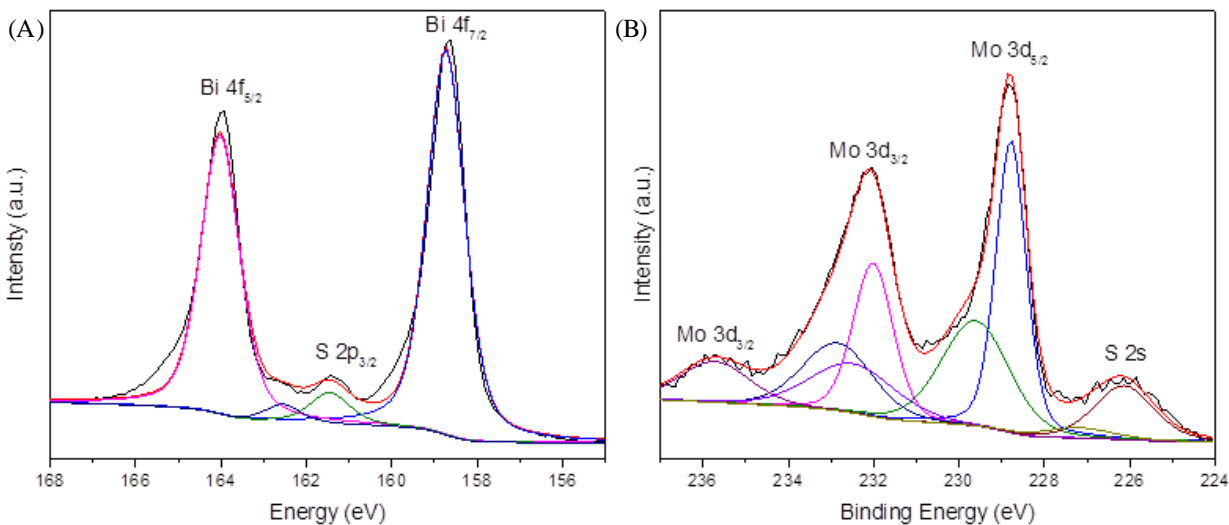


Figure 1: High resolution XPS of (A) Bi4f and (B) Mo 3d spectra of 50MBS.

The surface morphologies and structures of the photocatalysts were studied using FE-SEM and HR-TEM. Figure S3(A) shows the typical 2D structure of Bi_2WO_6 which is generally square in shape. After the anion-exchange reaction, Bi_2WO_6 transformed to Bi_2S_3 as shown in Figure S3 (B). It could be observed that Bi_2S_3 formed a rod-like structure and self-assembled into a disc with an average width of 2 μm . Owing to the lower solubility of Bi_2S_3 ($K_{\text{sp}} = 1 \times 10^{-97}$), the conversion of Bi_2WO_6 into Bi_2S_3 was easily achieved through the reaction with S^{2-} ions generated from thioacetamide [20, 21]. Figure S3(C) shows the FE-SEM image of 50MBS at high magnifications. MoS_2 nanosheets could be seen to have formed onto the surface of Bi_2S_3 , where it acted as a sacrificial site for nucleation and crystallization. Figure S3(D) shows the TEM image of 50MBS. At higher magnification (inset), a lattice spacing of 0.27 nm which corresponded to the MoS_2 (100) facet could be observed. **Figure S4 shows the elemental mapping pattern of Bi, Mo and S with EDX spectrum for 50MBS.**

3.2 Photocatalytic water splitting to produce H₂

The photocatalytic water splitting experiments were conducted over the as-prepared photocatalysts (see Figure 2). Despite being an effective light absorption material, MoS₂ was shown to be inactive in the production of H₂. This could be attributed to the poor electrical conductivity of MoS₂, which resulted in a high recombination rate of photogenerated charge carriers [22]. In addition, Bi₂S₃ exhibited relatively low photoactivity towards water splitting, achieving a H₂ production rate of only 38.6 μmol/h. By combining MoS₂ and Bi₂S₃, the rate of H₂ generation over 10MBS hybrid photocatalyst was shown to have risen by 22% to 47.0 μmol/h. By increasing the amount of MoS₂ in the binary heterostructure, the H₂ production rate gradually increased until it reached an optimum production rate of 61.4 μmol/g.h at 50 mole% MoS₂ loading. However, a further increase in MoS₂ loading led to a reduction in H₂ production rate. This could be due to the crippling of photogenerated electron transfer between Bi₂S₃ and MoS₂ at the presence of excessive MoS₂. In contrast, when the MoS₂ content is too low, there could be inadequate light absorption to promote the excitation of electrons. Therefore, there exists an optimum loading of MoS₂ in the binary composite to achieve most efficient photocatalytic performances. The stability performance of 50MBS was evaluated by subjecting it to 4 consecutive photocatalytic runs under the same reaction condition. The results showed that 50MBS retained almost 90% of its reactivity after its fourth cycle (Figure S5).

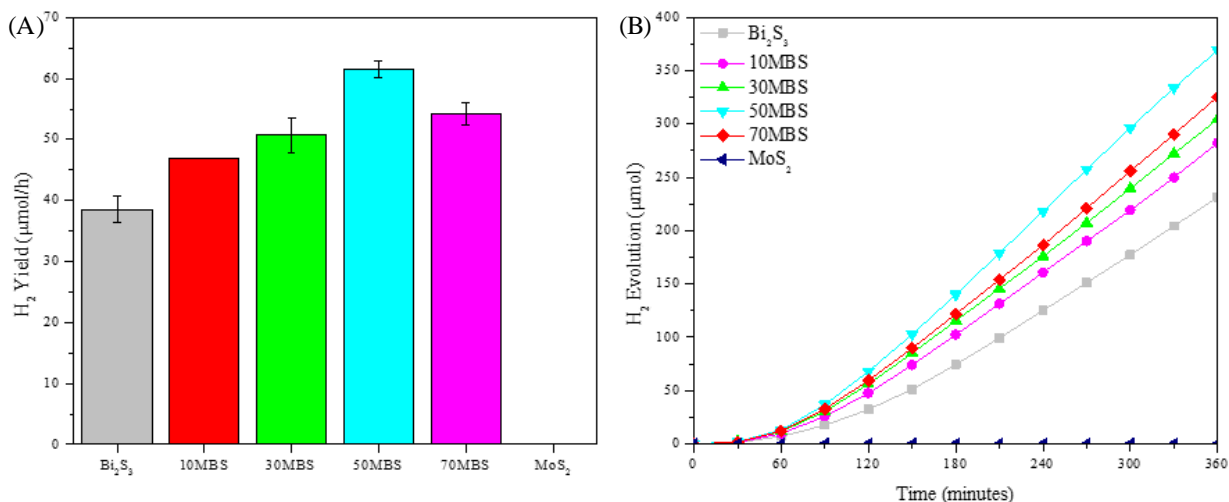


Figure 2: (A) Photocatalytic H₂ production activities and (B) amount of H₂ evolved over 6 h.

3.3 Photocatalytic mechanism over Bi₂S₃/MoS₂ hybrid photocatalyst

To fully elucidate the underlying photocatalytic reaction mechanism of Bi₂S₃/MoS₂ hybrid photocatalyst, the energy structure of Bi₂S₃ and MoS₂ was studied. Firstly, the absorption band energies of Bi₂S₃ and MoS₂ were determined through diffuse reflectance spectra by the modified Tauc plot (see Figure S6(B)). The band energies for Bi₂S₃ and MoS₂ were shown to be 1.20 and 1.38 eV respectively. The Mott-Schottky plot in Figure S6(D) revealed a conduction band potential of approximately -0.5 V/NHE and 0.0 V/NHE for MoS₂ and Bi₂S₃, respectively. Based on the obtained results, a band position diagram for the hybrid photocatalyst was proposed (Figure 3). As the conduction band of MoS₂ is more negative than Bi₂S₃, the diagram resembled a type-II band alignment structure. Upon light irradiation, photoinduced electrons migrated from MoS₂ to Bi₂S₃, thus enhancing the charge separation process. The PL spectrum shown in Figure S6(C) indicated that pristine Bi₂S₃ suffered from high charge recombination rate. The lower peak intensity for the Bi₂S₃/MoS₂ hybrid confirmed a prolonged electron-hole separation rate.

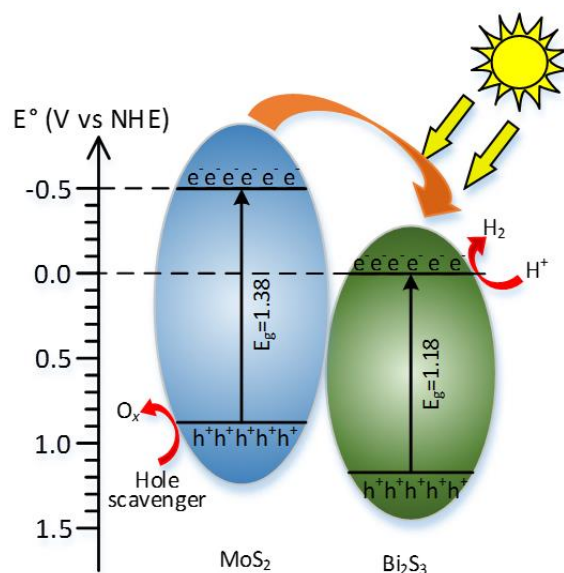


Figure 3: Charge transfer mechanism of MoS₂/Bi₂S₃.

A useful tool to gauge the separation efficiency and lifetime of photogenerated charge carriers can be measured by the transient photocurrent response [23, 24]. Figure 4(A) shows the transient photocurrent responses for 50MBS and Bi₂S₃. 50MBS demonstrated a higher photocurrent density as compared to Bi₂S₃, which showed a rapid decrease in photocurrent density over 20 seconds upon simulated solar light irradiation. The observed phenomenon indicated that the addition of MoS₂ reduced the electron-hole pair recombination rate and extended the activity of charge carriers. Electrochemical impedance spectroscopy Nyquist plot was employed to further investigate the transfer of photogenerated charge carriers as shown in Figure 4(B). A smaller semi-arc shown by 50MBS, under the irradiation of simulated solar light, indicated the decrease in charge transfer resistance and the solid state interface layer resistance on the surface of 50MBS [25]. This signifies that 50MBS has a more efficient charge transfer interface as compared to Bi₂S₃. These findings further solidify the importance of MoS₂ for enhanced photoactivity.

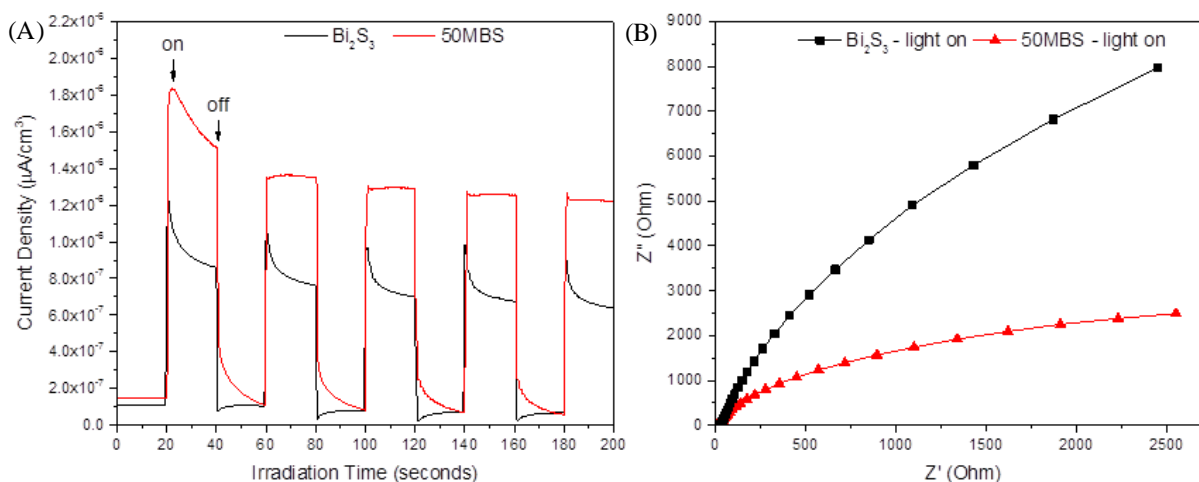


Figure 4: (A) Photocurrent responses of Bi_2S_3 and 50MBS and (B) electrochemical impedance spectroscopy of Bi_2S_3 and 50MBS.

4.0 Conclusions

In conclusion, a noble metal-free MoS_2 modified Bi_2S_3 photocatalyst was successfully synthesized through an anion exchange method. To the best of our knowledge, this is the first report on the use of $\text{Bi}_2\text{S}_3/\text{MoS}_2$ photocatalyst for the photocatalytic production of H_2 . At the optimum of 50% $\text{Mo}:\text{Bi}$ (mol/mol), the H_2 evolution rate was determined to be $61.4 \mu\text{mol}/\text{h}$ under simulated solar light, which was more than 50% higher as compared to pristine Bi_2S_3 ($38.6 \mu\text{mol}/\text{h}$). The enhancement in photoactivity was ascribed to the intimate interface contact between Bi_2S_3 and MoS_2 , which improved the separation of electron-hole pairs. The findings from this work could potentially bring photocatalytic water splitting one step closer to the realization of clean and carbon emission-free energy for the future.

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Highlights

- Bi_2S_3 modified MoS_2 as a highly efficient hybrid photocatalyst under simulated sunlight
- Optimum loading 50% Mo:Bi molar ratio with H_2 production rate of $61.4 \mu\text{mol/h}$
- Improved H_2 production due to effective charge transfer between Bi_2S_3 and MoS_2

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