Two-dimensional β -In₂S₃ Nanosheets-MoS₂ Nanoflowers Heterostructures: A Novel Sunlight-induced Photocatalyst for Pollutant Removal in Water

Jaspal Singh (✉ jaspal2125@gmail.com)

Indian Institute of Technology Delhi

R. K. Soni

Indian Institute of Technology Delhi

Research Article

Keywords: Nanoflowers, nanosheets, MoS₂, In₂S₃, methylene blue

Posted Date: May 26th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-544180/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Scientific Reports on July 28th, 2021. See the published version at <https://doi.org/10.1038/s41598-021-94966-z>.

Abstract

Visible light-sensitive photocatalytic systems have readily relied on metal oxide semiconductors' functionalization with plasmonic nanostructures to improve their activity. Here, we report a non-metal, visible light (sunlight) sensitive photocatalytic 2D-layered based nanohybrid system capable of efficient degradation of organic contaminants with huge efficiency. MoS₂ nanoflowers decorated β -In₂S₃ nanosheets heterostructure hybrid has been prepared by using a facile hydrothermal method. 2D-layered-based semiconductor heterostructure (In₂S₃-MoS₂) effectively improves the lifetime of the charge carriers by minimizing their rate of recombination, allowing enough time for surface reactions such as photocatalysis to take place. UV-DRS results reveal a significant improvement in the optical absorbance in the visible region. X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy results confirm the appearance of 2H-MoS₂ and β -In₂S₃ in the grown heterostructures. Chemical mapping confirms uniform distribution of Mo, In, and S atoms in the heterostructure, affirming sample uniformity. Modified optical properties of In₂S₃-MoS₂ heterostructure samples reveal efficient charge separation while incrementing the light absorption ability, indicative of its enhanced photocatalytic activity in solar light. The photocatalytic decomposition efficiency of the In₂S₃-MoS₂ heterostructure is compared with pristine In₂S₃ nanosheets. For 8 minute exposure in sunlight, *ca* 97.67% degradation for methylene blue dye has been estimated for a sample load of 0.025 mg/ml. The improved photocatalytic degradation efficiency of the In₂S₃-MoS₂ heterostructure is ascribed to its efficient charge separation mechanism.

1. Introduction

Visible light sensitive photocatalyst has been extensively studied due to their tremendous performance for energy production and environmental remediation applications [1–5]. Visible light-sensitive photocatalyst indicated the capability and usage of engineered nanostructures into the light-harvesting capability from natural sunlight. For more advanced and practical applications, photocatalyst material should be highly sensitive towards the visible light, which can strongly absorb the visible spectrum from sunlight. Semiconductor-based photocatalysts have been proven to be one of the best ways to decomposed organic waste using light exposure after the outstanding discovery of water splitting by Fujishima in 1972 [6–10]. The efficiency of semiconductor-based photocatalyst, however, is limited by insufficient light utilization and poor effective surface area. To overcome these issues, two dimensional (2D) layered structured transition metal chalcogenides (TMDC) based photocatalyst have been developed, which tremendously absorb the visible light and also provide sufficient effective surface area [11–13]. In addition, layered structured TMDC based photocatalyst exhibits outstanding chemical, optical and electronic properties which make them unique for environmental remediation and energy production applications [14, 15]. Among various layered structured Indium sulfide (In₂S₃) has received significant attention recently in the field of visible light photocatalyst because of low toxicity, high photo-stability, and narrow bandgap (2.0-2.3 eV) ability [16, 17]. On the other hand, the photocatalytic nature of In₂S₃ is found to be low due to high recombination rate and poor mass transfer [18]. Several parameters such as modulation in morphology, a surface area strongly influenced the photocatalytic activity of the In₂S₃

nanostructures by efficient charge separation, the improved lifetime of charge carriers, and high rate of mass transfer [18, 19]. Apart from this, various efforts, such as phase optimization [20, 21], heterostructures creation [22, 23], and noble metal nanoparticle functionalization [24, 25], have been devoted to improve the photodegradation capability of In_2S_3 nanostructures. 2D-TMDCs based heterostructures-based photocatalyst is one of the advanced and effective strategies to control the recombination rate and improve the photodegradation ability through synergistic effect among between two layered nanostructures [26]. Nanostructured MoS_2 (bandgap ~ 1.9 eV) is extensively explored and employed for several applications such as sensing [27], energy production [28], optoelectronic devices [29], and antibacterial activity [30]. Due to its fascinating optical, electronic, and chemical properties. MoS_2 modified In_2S_3 based heterostructures can effectively enhance the lifetime of photoinduced charge carries through synergistic effect among them [31]. In_2S_3 nanosheets combined with MoS_2 nanoflowers is expected to increase the photoinduced catalytic activity [32–34] due to sharing of the similar 2D layered structures by MoS_2 and In_2S_3 , which inferred the creation of high-quality, intimate heterojunction, and exhibits preferential band gap alignments that help to generate the unsaturated radicals to enhance the rate of photocatalytic reactions. It has been found that the existence of MoS_2 can initiate the formation of superoxide radicals which is beneficial for the decomposition of organic molecules under light exposure [35, 36]. Moreover, MoS_2 presence in In_2S_3 can further enhance the active sites, which can effectively interact with the pollutant molecules. Li et al. [18] fabricated hierarchical $\text{In}_2\text{S}_3/\text{MoS}_2$ nanosheets using the exfoliation method with the hydrothermal method. The prepared $\text{In}_2\text{S}_3/\text{MoS}_2$ nanohybrids were embraced for the photocatalytic application through the Aza-Henry reaction. They have demonstrated that $\text{In}_2\text{S}_3/\text{MoS}_2$ nanohybrids attained superior photocatalytic activity compared to pure MoS_2 and In_2S_3 . Sun et al. [26] prepared $\text{MoS}_2/\text{In}_2\text{S}_3$ flakes-based photoanode by using one-pot synthesis process and applied it for the H_2 production application. In their study, they have significantly demonstrated the effective charge separation in $\text{MoS}_2/\text{In}_2\text{S}_3$ flakes for a high H_2 production rate.

2D-layered-based heterostructures are emerging as the new material for the environmental remediation application and rarely reported in the literature. In this report, we highlighted the synergistic effect in 2D-layered-based heterostructures for pollutant removal. To employ the proposed strategy, 2D-layered-based $\text{In}_2\text{S}_3\text{-MoS}_2$ nanoheterostructures were engineered using a hydrothermal method and determined their photodegradation capability to decompose the variety of organic pollutant molecules like methylene blue and oxytetracycline under sunlight illumination. Chemical surface states, optical profile, and modulation in the morphologies are explored and assured in the hierarchical heterostructures of In_2S_3 and MoS_2 . $\text{In}_2\text{S}_3\text{-MoS}_2$ nanoheterostructures exhibit a significantly superior photocatalytic nature as compared to pristine In_2S_3 nanostructures. We have tuned the heterojunction density by varying the amount of MoS_2 over In_2S_3 for a superior photodegradation process which provides the insight understanding to design the efficient photocatalyst. Apart from this, $\text{In}_2\text{S}_3\text{-MoS}_2$ nanoheterostructures revealed significant reusability and stability, which indicate their possible applications for other sunlight-driven processes.

2. Experimental

2.1. Materials

Indium chloride, Hexaammonium heptamolybdate tetrahydrate, and thiourea were purchased from Sigma-Aldrich, while oxytetracycline (OTC HCl) and methylene blue (MB) were obtained from SRL, and Merck, respectively. All chemical reagents were employed as purchased.

2.2. Formation of β - In_2S_3 -2H- MoS_2 heterostructures photocatalyst

In the current reaction process, initially, 20 mL of Hexaammonium heptamolybdate tetrahydrate (0.8 mM) was dropwise added into the 20 mL thiourea (0.18mM) under constant stirring. Similarly, another solution contained 20 mL of indium chloride (0.24 mM) was dropwise added into the 20 mL thiourea solution. In the next step, both solutions were mixed in a conical flask under vigorous stirring, after confirming the formation of uniform mixture, it was transferred to a Teflon container of 100 mL. The pH of the obtained solution was set at 6 by using 0.5M NaOH solution. In the next step, the Teflon-lined stainless steel autoclave contained sample was held at 180°C for 18 hours. The obtained sample was treated with ethanol and DI water and collected by centrifugation process, and finally, placed at 80°C in the oven. The pristine In_2S_3 and In_2S_3 - MoS_2 samples with tunable MoS_2 density (0.16 mM and 0.24 mM) were generated by the above-mentioned process. For better understanding, pristine In_2S_3 and In_2S_3 - MoS_2 heterostructures (0.8 mM, 0.16 mM and 0.24 mM) hereafter reported as IP, IPM1, IPM2 and IPM3, respectively. Cite Scheme 1 in the text.

2.3. Characterization techniques and photocatalysis reaction

Surface morphologies of pristine In_2S_3 and MoS_2 modified In_2S_3 samples were explored through scanning electron microscopy (ZEISS, EVO) combined with the elemental mapping facility, while transmission electron microscopy (JEOL-2100 F, Japan) was employed to determine the crystal structure of In_2S_3 - MoS_2 nanohybrids. Powder X-ray diffraction technique (Rigaku Ultima IV, Ri) was employed to investigate the diffraction patterns of In_2S_3 - MoS_2 nanohybrids. Optical studies of synthesized samples were explored by the UV-DRS (Shimadzu UV-2450) method, photoluminescence spectroscopy (RF-6000 Shimadzu), and Raman spectroscopy (Renishaw inVia). The chemical composition of In_2S_3 - MoS_2 nanohybrids was investigated through X-ray photoelectron spectroscopy (ESCA + Omicron Nano Technology). The photodegradation ability of MoS_2 functionalized In_2S_3 and pure In_2S_3 samples were explored by the breakdown of 10 μM MB solution and oxytetracycline (OTC-HCl) molecules in sunlight exposure (800 W/m^2). Modulations in the intensity of the targeted pollutant molecules solutions with different photocatalyst samples for the same exposure time intervals (2, 4, 6, and 8 minutes) were measured using UV-Visible absorption spectroscopy (Perkin Elmer). In photocatalytic reaction, the used amount of each photocatalyst sample is 2.5 mg/L.

3. Results And Discussion

Figure 1 illustrates the X-ray diffraction patterns of pristine In_2S_3 and MoS_2 modified In_2S_3 . XRD for sample IP indicating ten reflections (220), (311), (222), (400), (422), (511), (440), (531), (553), and (622), which assured the presence of β -phase of In_2S_3 (JCPDS-500814). XRD spectra for sample IPM1, IPM2, and IPM3 show two additional minor peaks compared to the XRD spectrum of sample IP. These two peaks (100) and (106) confirm the presence of the 2H phase of MoS_2 in sample IPM1, IPM2, and IPM3 (JCPDS-371492). Raman spectra of sample IP, IPM1, IPM2, and IPM3 are presented in Fig. 2. Raman spectrum for sample IP indicating the four distinct peaks at 181 cm^{-1} , 249 cm^{-1} , 306 cm^{-1} , and 369 cm^{-1} which attributed to the fingerprint vibrations of β -phase of In_2S_3 [37]. Raman result for sample IPM1 indicates the slight shift in the Raman peaks corresponds to the β -phase of In_2S_3 . The observed peaks are 196 cm^{-1} , 223 cm^{-1} , 286 cm^{-1} and 347 cm^{-1} implies the formation of MoS_2 - In_2S_3 nanohybrids [18, 33]. Apart from this, two distinct peaks at 379 cm^{-1} and 405 cm^{-1} arise in the Raman curve of sample IPM1 further confirmed the existence of MoS_2 . Raman spectrum for sample IPM2, the peaks correspond to the β - In_2S_3 and 2H- MoS_2 are found slightly shifted compared to Raman spectrum of sample IPM1. The observed peaks for sample IPM2 are 197 cm^{-1} , 230 cm^{-1} , 343 cm^{-1} , 378 cm^{-1} and 403 cm^{-1} . Interestingly, It can be seen that the intensity of peaks at 378 cm^{-1} and 403 cm^{-1} is higher as than sample IPM1, which suggested the high-density MoS_2 in sample IPM2 as compared to sample IPM1. For sample IPM3, the Raman studies reveals the six peak at 196 cm^{-1} , 232 cm^{-1} , 298 cm^{-1} , 347 cm^{-1} , 378 cm^{-1} and 405 cm^{-1} . The intensity of two peaks for MoS_2 at 378 cm^{-1} and 405 cm^{-1} in sample IPM3 is higher than that of sample IPM1 and IPM2. The significant shift in the Raman peaks of sample IPM1, IPM2, and IPM3 compared to sample IP affirms the attachment of MoS_2 with In_2S_3 [33]. The shift in the Raman spectra of MoS_2 modified In_2S_3 can be ascribed due to the lattice vibrations enable through the variation in the bond force constant of Mo-S and In-S bond. Modulation in bond force constant generated due to the modification of Mo^{4+} atom in In_2S_3 [18, 33, 38].

Figure 3(a-d) depicts the modulations in the morphologies of sample IP, IPM1, IPM2, and IPM3. For sample IP, 2D- nanosheets can appear with an average width of 162 nm (Fig. 3(a)). FESEM result for sample IPM1 illustrates the functionlization of 2D-layered structured aggregates on sheet-like nanostructures Fig. 3(b). With the increment in the concentration of MoS_2 , a more distinct flower-like morphology can be seen in the FESEM image of sample IPM2. Apart from this, a 2D-layered sheet can also be seen attached to the surface of flowers-like morphology (Fig. 3(c)). To further increase the Mo^{+4} ions concentration in In_2S_3 , the 2D sheet mediated flowers-like structures attached with the sheet-like nanostructures can be observed for sample IPM3 (Fig. 3(d)). To confirm the formation of MoS_2 - In_2S_3 nanohybrids, elemental mapping for sample IPM3 was carried out and illustrated in Fig. 4. The broader view of surface morphologies of sample IPM3 has been presented in Fig. 4(a), while elemental mapping of the specific atom and corresponding nanohybrid is depicted in Fig. 4(b-e). Elemental mapping studies affirm the uniform spreading of Mo, In, and S atoms in sample IPM3. Surface morphology results confirm

the formation of $\text{MoS}_2\text{-In}_2\text{S}_3$ nanohybrids. To explore the crystal structures and the attachment of In_2S_3 and MoS_2 , TEM studies were employed. Figure 4(f) shows the addition of MoS_2 nanoparticles in In_2S_3 nanosheets in sample IPM1. The computed average size of MoS_2 nanoparticles in sample IPM1 is 24 nm. TEM images for sample IPM3 (Fig. 4(g-h)) reveal the growth of MoS_2 flakes on the surface of the In_2S_3 sheets. The assembly of MoS_2 nanosheets formed the flowers-like nanostructures on the surface of In_2S_3 sheets (Fig. 4(h)).

The optical profile of pristine In_2S_3 nanosheets and MoS_2 modified In_2S_3 is illustrated in Fig. 5(a). The optical absorption curve of sample IP reveals a broad peak from 250–600 nm. With the modification of MoS_2 in In_2S_3 , the optical absorption enhanced significantly (sample IPM1). For sample IPM2, the optical absorption is further increased and found higher than IP and IPM1. The optical absorption spectrum for sample IPM3 indicates the highest absorption compared to sample IP, IPM1, and IPM2. Optical absorption studies manifest a remarkable improvement in $\text{MoS}_2\text{-In}_2\text{S}_3$ nanohybrids as compared to pristine In_2S_3 . To explore the bandgap engineering in $\text{MoS}_2\text{-In}_2\text{S}_3$ nanohybrids Tauc plots, studies were carried out and presented in Fig. 5 (b). Tauc plots suggest the narrowing in the bandgap in $\text{MoS}_2\text{-In}_2\text{S}_3$ nanohybrids as compared to pristine In_2S_3 . The computed bandgap for sample IP, IPM1, IPM2 and IPM3 are 2.25 eV, 1.94 eV, 1.89 eV and 1.82 eV, respectively.

The valance state and surface chemical composition of $\text{MoS}_2\text{-In}_2\text{S}_3$ nanohybrids were determined through the XPS and illustrated in Fig. 6. Gaussian fitted XPS spectra for $\text{In}3d$, $\text{S}2p$ and $\text{Mo}3d$ were presented in Fig. 6(a-c), respectively. Figure 6(a) reveals that the XPS spectrum for $\text{In}3d$ consists of two distinct peaks at 444.6 eV and 452.2 eV, which can be assigned to the $\text{In}3d_{5/2}$ and $\text{In}3d_{3/2}$, respectively [39]. Gaussian fitted $\text{S}2s$ spectrum reveals the three peaks at 161.8 eV, 164.3 eV and 168.2 eV (Fig. 6(b)). The peaks at 161.8 eV and 164.3 eV can be attributed to the $\text{S}2p_{3/2}$ and $\text{S}2p_{1/2}$ sequentially and affirms the presence of the $\text{S}2p$ state of the sulfur atom [33, 34]. Apart from this, a broad peak at 168.2 eV assured the existence of the S-O bond [40]. The fitted spectrum of $\text{Mo}3d$ shows the distinct four peaks at 228.3 eV, 231.0 eV, 232.1 eV, and 234.5 eV. The major peaks at 228.4 eV and 231.3 eV corresponds to the $\text{Mo}3d_{5/2}$ and $\text{Mo}3d_{3/2}$, respectively [41]. The peaks at 232.1 eV and 234.5 eV can be attributed to the existence of Mo^{+6} states in the $\text{Mo}3d$ spectrum [41, 42]. XPS studies indicate the presence of Mo, In, and S in the state of Mo^{+4} , In^{+3} , and S^{-2} state in the $\text{MoS}_2\text{-In}_2\text{S}_3$ nanohybrids, respectively. XPS results explicitly suggest that no shift takes place in the recombination process of $\text{MoS}_2\text{-In}_2\text{S}_3$ nanohybrids.

We investigated the sunlight-induced photodegradation ability of the In_2S_3 nanosheets and MoS_2 modified In_2S_3 samples by the degradation of MB molecule solution. Figure 7(a-d) depicts the optical absorption spectrum of MB molecule solution employing sample IP, IPM1, IPM2, and IPM3. A UV-visible absorption study implies that sample IPM3 exhibits the highest photocatalytic efficiency compared to sample IP, IPM1, and IPM2. Sample IPM3 is found 96.8% efficient for the breakdown of 10 μM MB molecule solution in 8 minutes, while sample IP, IPM1, and IPM2 are found capable of decomposing 35.3%, 77.7%, and 95.3% of 10 μM MB molecule solution in 8 minutes (Fig. 8(a)). Figure 7(e) shows the

modulations among the photodegradation kinetics of sample IP, IPM1, IPM2, and IPM3. Photodegradation rate kinetics reveals the higher photodegradation performance of sample IPM3 as compared to other photocatalyst samples. In order to found out the rate constant value of each photocatalyst sample, linear fitting of logarithm value of C/Co as a function of exposure time were plotted. The rate constant value for sample IP, IPM1, IPM2, and IPM3 is depicted in Fig. 7(f). The calculated k values for sample IP, IPM1, IPM2, and IPM3 are 0.0475/ min, 0.1724/min, 0.357/min, and 0.3421/min, sequentially. Photocatalytic studies affirm that sample IPM3 attain 2.7 times better photodecomposition performance as compared to pristine sample IP. The rate constant value for sample IPM3 is 7.2 times the K value of sample IP. Photodecomposition results assure the improved degradation nature of the IPM3 sample as compared to other prepared photocatalyst samples. The stability of the most efficient synthesized sample (IPM3) was explored through the usage of sample IPM3 for three cycles of the photocatalytic reaction process. After three runs of photodegradation reaction, the efficiency of sample IPM3 is constant, which indicates their stable nature (Fig. 8(b)). To reveal the high photodegradation capability of the most efficient sample IPM3, the photodecomposition of OTC-HCl molecules was explored. Figure 9(a-b) indicates the optical absorption results of photodegradation results of OTC-HCl molecule solution using sample IP and IPM3, respectively. Photodegradation rate kinetics assures the high photodecomposition performance of sample IPM3 as compare to sample IP. It has been computed that sample IP can decompose the 27.1% efficient while sample IPM3 shows the decomposition of 76.3% of 0.3mg/mL of OTC-HCl solution in sunlight (Fig. 9(c)). The k-values for sample IP and IPM3 are 0.00621/min and 0.0308/min sequentially (Fig. 9(d)).

To determine the charge transfer profile in $\text{In}_2\text{S}_3\text{-MoS}_2$ nanohybrids during the photocatalytic reaction, a schematic diagram has been presented (Fig. 10). Under sunlight irradiation, In_2S_3 sheets and MoS_2 flakes are get activated and generate the electron-hole pair in their respective conduction and valence bands. In the next step, the photoinduced electron exists in the conduction band of In_2S_3 move towards the conduction band of MoS_2 due to the band alignment positions, which in turn maintain the synergistic effect and control the recombination rate in In_2S_3 nanosheets. The VB and CB positions for In_2S_3 nanosheets and MoS_2 nanoflakes are obtained through the following relation (1).

$$E_{CB} = \chi - E^e - 0.5E_g \quad (1)$$

Where E_g indicates the bandgap value of the 2D layered materials (In_2S_3 and MoS_2) while E^e stands for the energy on the hydrogen scale (4.5 eV), and χ shows the electronegativity of the 2D layered nanostructures ($\text{In}_2\text{S}_3 \sim 4.7$ eV and $\text{MoS}_2 \sim 5.32$ eV). The computed VB and CB values for In_2S_3 nanosheets are 1.32 eV and - 0.92 eV, sequentially, while CB and VB values for MoS_2 nanoflakes are - 0.13 eV and 1.77 eV, sequentially.

Apart from the efficient charge separation process, the density of electrons in CB of MoS₂ enhanced remarkably; consequently, the formation rate of superoxide radicals concentration increased. The high concentration of superoxide radicals primarily affects the photocatalytic reaction and accelerates it significantly. Similarly, due to the synergistic effect among In₂S₃ and MoS₂, the enhanced production of holes interacted with the water molecule and created the hydroxyl radicals with high concentration. The high density of hydroxyl radicals interacts with the MB molecule and degrades it. Thus the synergistic effect in In₂S₃ sheets - MoS₂ flakes control the charge separation and improve the photodegradation ability.

In the present report, an In₂S₃-MoS₂ nanohybrids with an effective charge separation effect is successfully fabricated. The density of MoS₂ nanostructures over In₂S₃ nanosheets was precisely varied and used for the decomposition of MB molecules under solar light illumination. Sample IP consists of the sheet-like structures of In₂S₃. Pristine In₂S₃ sheets interact with the pollutant molecules and degrade only 35.3% of 10 µM of MB molecule solution in solar light illumination. For sample IPM1 MoS₂ nanoparticles functionalized In₂S₃ sheets with effective charge separation effect decompose 77.7% of MB molecule solution. In sample IPM2, the density of MoS₂ nanostructures enhanced, which further increases the density of interface among In₂S₃ and MoS₂; consequently, charge separation increase significantly. Therefore sample IPM2 can decompose 95.3% of 10 µM methylene blue (MB) molecules solution in 8 minutes of sunlight irradiation. At the highest density of MoS₂ in sample IPM3, the MoS₂ flakes were assembled on the surface of In₂S₃ nanosheets and significantly improve the charge separation and reduce the recombination rate. UV-DRS results also indicate that sample IPM3 indicates the highest optical absorption compared to sample IP, IPM1, and IPM2.

Moreover, the highest bandgap narrowing occurs in sample IPM3, which also indicates the efficient charge separation. Raman and XRD studies also reveal that the density of MoS₂ over In₂S₃ nanosheets was increased from sample IPM1 to IPM3. For sample IPM3, high numbers of heterojunction of MoS₂ and In₂S₃ are responsible for the extremely high sunlight-induced photodegradation capability towards MB molecules solution. Thus sample IPM3 decomposes 96.8% 10 µM of MB and 76.3% of 0.3 gm/mL OTC molecules solution in 8 minutes and 40 minutes sequentially under solar light illumination. Liu et al. [33] reported the formation of MoS₂ nanodots functionalized In₂S₃ nanoplates and used them for the photoelectrochemical application. They have found that MoS₂/In₂S₃ heterojunction with effective charge exhibited better performance as compared to pristine MoS₂ and In₂S₃. Wang et al. [34] synthesized MoS₂ functionalized In₂S₃ nanostructures for the Cr⁶⁺ removal using a photocatalysis process. They have demonstrated that MoS₂ functionalized In₂S₃ nanostructures exhibit 3.2 times better photocatalytic activity than pristine In₂S₃.

Conclusions

We have successfully engineered In_2S_3 - MoS_2 nanohybrids using a simple hydrothermal method. The density of MoS_2 flakes was tuned over the surface of In_2S_3 nanosheets. Modulation in the optical properties and significant bandgap narrowing tremendously contribute to reducing the recombination rate. Optimized In_2S_3 - MoS_2 nanohybrids reveal the outstanding sunlight-driven photodecomposition performance for MB and OTC pollutant molecules solution. In_2S_3 nanosheets combined with the MoS_2 nanoflakes decompose the 96.8% 10 μM of MB and OTC (0.3 mg/mL) solution in 8 minutes and 40 minutes, respectively. These results are very significant and unique provide the outstanding photocatalytic activity of 2D layered nanoheterostructures

Declarations

Acknowledgments

Jaspal Singh gratefully acknowledges the financial support of IIT Delhi through the IPDF fellowship.

References

1. Singh, J., Rishikesh, Kumar, S. & Soni, R. K. Synthesis of 3D- MoS_2 nanoflowers with tunable surface area for the application in photocatalysis and SERS based sensing. *J. Alloys Compd.* **849**, 156502 (2020).
2. Singh, J., Kumar, S., Rishikesh, Verma, H. K. & Soni, R. K. Cost-effective scalable synthesis of few layers MoS_2 based thin film for sunlight enforced photocatalytic activity. *Opt. Mater.* **110**, 110506 (2020).
3. Singh, J., Juneja, S., Soni, R. K. & Bhattacharya, J. Sunlight mediated enhanced photocatalytic activity of TiO_2 nanoparticles functionalized CuO - Cu_2O nanorods for removal of methylene blue and oxytetracycline hydrochloride. *J. Coll. Interface Sci.* **590**, 60–71 (2021).
4. Singh, J. & Soni, R. K. Two-dimensional MoS_2 nanosheet-modified oxygen defect-rich TiO_2 nanoparticles for light emission and photocatalytic applications. *New J. Chem.* **44**, 14936–14946 (2020).
5. Rengaraj, S. *et al.* Self-assembled mesoporous hierarchical-like In_2S_3 hollow microspheres composed of nanofibers and nanosheets and their photocatalytic activity. *Langmuir*. **27**, 5534–5541 (2011).
6. Fujishima, A. & Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*. **238**, 37–38 (1972).
7. Lin, G. & Xu, X. Ba-Modified LaTiO_2N as an efficient visible light active photocatalyst for water oxidation. *ACS Sus. Chem. Eng.* **8**, 9641–9649 (2020).
8. Xu, X., Wang, R., Sun, X., Lv, M. & Ni, S. Layered perovskite compound NaLaTiO_4 modified by nitrogen doping as a visible light active photocatalyst for water splitting. *ACS Catal.* **10**, 9889–9898 (2020).

9. Shen, Q. *et al.* Hollow dodecahedral structure of In₂O₃-In₂S₃ heterojunction encapsulated by N-Doped C as an excellent visible-light-active photocatalyst for organic transformation. *Inorg. Chem.* **59**, 17650–17658 (2020).
10. Zhang, J. *et al.* Defect engineering in atomic-layered graphitic carbon nitride for greatly extended visible-light photocatalytic hydrogen evolution. *ACS Appl. Mater. Interfaces.* **12**, 13805–13812 (2020).
11. Xiang, Q., Cheng, F. & Lang, D. Hierarchical layered WS₂/graphene-modified CdS nanorods for efficient photocatalytic hydrogen evolution. *ChemSusChem.* **9**, 996–1002 (2016).
12. Fu, S. *et al.* Few-layer WS₂ modified BiOBr nanosheets with enhanced broad-spectrum photocatalytic activity towards various pollutants removal. *Sci. Total Environ.* **694**, 133756 (2019).
13. Fu, S. *et al.* A novel 0D/2D WS₂/BiOBr heterostructure with rich oxygen vacancies for enhanced broad-spectrum photocatalytic performance. *J. Coll. Interface Sci.* **569**, 150–163 (2020).
14. Wang, Y. H., Huang, K. J. & Wu, X. Recent advances in transition-metal dichalcogenides based electrochemical biosensors: A review. *Biosens. Bioelectro.* **97**, 305–316 (2017).
15. Liu, Y., Duan, X., Huang, Y. & Duan, X. Two-dimensional transistors beyond graphene and TMDCs. *Chem. Soc. Rev.* **47**, 6388–6409 (2018).
16. Batabyal, S. K., Lu, S. E. & Vittal, J. J. Synthesis, characterization, and photocatalytic properties of In₂S₃, ZnIn₂S₄, and CdIn₂S₄ nanocrystals. *Cryst. Growth. Des.* **16**, 2231–2238 (2016).
17. Mughal, M. A., Engelken, R. & Sharma, R. Progress in indium(III) sulfide(In₂S₃) buffer layer deposition techniques for CIS, CIGS, and CdTe-based thin film solar cells. *Sol. Energy.* **120**, 131–146 (2015).
18. Li, Z. *et al.* Hierarchical photocatalyst of In₂S₃ on exfoliated MoS₂ nanosheets for enhanced visible-light-driven Aza-Henry reaction. *Appl. Catal. B: Environ.* **237**, 288–294 (2018).
19. Yang, S. *et al.* Ca(II) doped β -In₂S₃ hierarchical structures for photocatalytic hydrogen generation and organic dye degradation under visible light irradiation. *J. Coll. Interface Sci.* **491**, 230–237 (2017).
20. Sharma, R. K. *et al.* Adsorption-driven catalytic and photocatalytic activity of phase tuned In₂S₃ nanocrystals synthesized via ionic liquids. *ACS Appl. Mater. Interfaces.* **9**, 11651–11661 (2017).
21. Nayak, A. K., Lee, S., Sohn, Y. & Pradhan, D. Synthesis of In₂S₃ microspheres using a template-free and surfactant-less hydrothermal process and their visible light photocatalysis. *CrystEngComm.* **16**, 8064–8072 (2014).
22. Baral, B., Mansingh, S., Reddy, K. H., Bariki, R. & Parida, K. Architecting a double charge-transfer dynamics In₂S₃/BiVO₄ n–n isotype heterojunction for superior photocatalytic oxytetracycline hydrochloride degradation and water oxidation reaction: unveiling the association of physicochemical, electrochemical, and photocatalytic properties. *ACS Omega.* **5**, 5270–5284 (2020).
23. Yang, M. Q., Weng, B. & Xu, Y. J. Improving the visible light photoactivity of In₂S₃–graphene nanocomposite via a simple surface charge modification approach. *Langmuir.* **29**, 10549–10558 (2013).

24. Yan, T. *et al.* Ultra-low loading of Ag₃PO₄ on hierarchical In₂S₃ microspheres to improve the photocatalytic performance: The cocatalytic effect of Ag and Ag. *Appl. Catal. B: Environ.* **202**, 3PO4, 84–94 (2017).
25. Wang, F. *et al.* Probing the charge separation process on In₂S₃/Pt-TiO₂ nanocomposites for boosted visible-light photocatalytic hydrogen production. *Appl. Catal. B: Environ.* **198**, 25–31 (2016).
26. Sun, B., Shan, F., Jiang, X., Ji, X. & Wang, F. One-pot synthesis of MoS₂/In₂S₃ ultrathin nanoflakes with mesh – shaped structure on indium tin oxide as photocathode for enhanced photo-and electrochemical hydrogen evolution reaction. *Appl. Surf. Sci.* **435**, 822–831 (2018).
27. Zhang, W., Zhang, P., Su, Z. & Wei, G. Synthesis and sensor applications of MoS₂-based nanocomposites. *Nanoscale*. **7**, 18364–18378 (2015).
28. Theerthagiri, J. *et al.* Recent advances in MoS₂ nanostructured materials for energy and environmental applications—a review. *J. Solid State Chem.* **252**, 43–71 (2017).
29. Wang, H., Li, C., Fang, P., Zhang, Z. & Zhang, J. Z. Synthesis, properties, and optoelectronic applications of two-dimensional MoS₂ and MoS₂-based heterostructures. *Chem. Soc. Rev.* **47**, 6101–6127 (2018).
30. Pandit, S., Karunakaran, S., Boda, S. K., Basu, B. & De, M. High antibacterial activity of functionalized chemically exfoliated MoS₂. *ACS Appl. Mater. Interfaces*. **8**, 31567–31573 (2016).
31. Fang, Z. *et al.* Dual-defective strategy directing in situ assembly for effective interfacial contacts in MoS₂ cocatalyst/In₂S₃ light harvester layered photocatalysts. *J. Mater. Chem. A*. **4**, 13980–13988 (2016).
32. Sheng, W., Song, Y., Dou, M., Ji, J. & Wang, F. Constructing 1D hierarchical heterostructures of MoS₂/In₂S₃ nanosheets on CdS nanorod arrays for enhanced photoelectrocatalytic H₂ evolution. *Appl. Surf. Sci.* **436**, 613–623 (2018).
33. Liu, F. *et al.* MoS₂ nanodot decorated In₂S₃ nanoplates: a novel heterojunction with enhanced photoelectrochemical performance. *Chem. Comm.* **52**, 1867–1870 (2016).
34. Wang, L. & Zan, L. Noble metal-free MoS₂-modified In₂S₃ for excellent visible-NIR-light-driven photocatalytic of Cr⁶⁺ removal in alkaline wastewater. *J. Nanoparticle Res.* **22**, 1–12 (2020).
35. Li, Z. *et al.* Utilization of MoS₂ and graphene to enhance the photocatalytic activity of Cu₂O for oxidative CC bond formation. *Appl. Catal. B: Environ.* **213**, 1–8 (2017).
36. Jiang, W. *et al.* Photocatalytic hydrogen generation on bifunctional ternary heterostructured In₂S₃/MoS₂/CdS composites with high activity and stability under visible light irradiation. *J. Mater. Chem. A*. **3**, 18406–18412 (2015).
37. Zhao, Y. *et al.* Thickness-Dependent Optical Properties and In-Plane Anisotropic Raman Response of the 2D β-In₂S₃. *Adv. Opt. Mater.* **7**, 1901085 (2019).
38. Feth, S., Gibbs, G. V., Boisen, M. B. & Myers, R. H. Promolecule radii for nitrides, oxides, and sulfides: a comparison with effective ionic and crystal radii. *J. Phys. Chem.* **97**, 11445–11450 (1993).

39. Gao, W. *et al.* In₂S₃ nanomaterial as a broadband spectrum photocatalyst to display significant activity. *Appl. Catal. B: Environ.* **176**, 83–90 (2015).
40. Li, B. *et al.* Preparation of monolayer MoS₂ quantum dots using temporally shaped femtosecond laser ablation of bulk MoS₂ targets in water. *Sci. Rep.* **7**, 1–12 (2017).
41. Wang, H. W., Skeldon, P. & Thompson, G. E. XPS studies of MoS₂ formation from ammonium tetrathiomolybdate solutions. *Surf. Coat. Technol.* **91**, 200–207 (1997).
42. He, G., Zhang, Y. & He, Q. MoS₂/CdS heterostructure for enhanced photoelectrochemical performance under visible light. *Catal.* **9**, 19–21 (2019).

Figures

Figure 1

X-ray diffraction reflections of In₂S₃ nanosheets and In₂S₃-MoS₂ nanohybrids.

Figure 2

Raman results of In_2S_3 nanosheets and In_2S_3 - MoS_2 nanohybrids.

Figure 3

(a-d) FESEM images of sample IP, IPM1, IPM2, and IPM3 indicating the modulations in their morphology.

Figure 4

(a) FESEM image of sample IPM3 revealing the formation of In₂S₃ nanosheet decorated MoS₂ nanoflowers, (b-e) Chemical mapping of sample IPM3 assuring the independent existence of In, Mo, and S atoms in sample IPM3, (f-h) Mapped image of sample IPM3.

Figure 5

(a) UV-DRS studies depicting the variations in the optical absorbance profile for sample IP, IPM1, IPM2, and IPM3, (b) Tauc plots for sample IP, IPM1, IPM2, and IPM3.

Figure 6

(a) Fitted XPS spectrum of In3d, (b) Gaussian fitted XPS of Mo3d, (c) Fitted XPS spectrum of S2s.

Figure 7

(a-d) Optical absorption spectra of MB molecule by employing different photocatalyst sample IP, IPM1, IPM2, and IPM3, (e) Photodegradation rate kinetics of MB molecule degradation by employing sample IP, IPM1, IPM2, and IPM3, (f) Rate constant (k) values of breakdown of MB molecule solution using sample IP, IPM1, IPM2, and IPM3.

Figure 8

(a-b) Photodegradation efficiency of sample IP, IPM1, IPM2, and IPM3 under sunlight, (b) Reusable photocatalyst test for sample IPM3 indicating its stability.

Figure 9

(a-b) Optical absorption spectra of OTC-HCl molecule by embracing IP and IPM3 photocatalyst respectively (c) Degradation rate kinetics of OTC-HCl molecule using sample IP and IPM3, (d) Bar graph revealing the rate constant value for the breakdown of OTC-HCl molecule under sunlight using photocatalyst IP and IPM3.

Figure 10

Energy level schematic diagram of In₂S₃-MoS₂ nanohybrids depicting the synergistic effect among In₂S₃ nanosheets and MoS₂ nanoflowers under sunlight.

Figure 11

Depicts the fabrication process of In₂S₃-MoS₂ nanohybrids.