Enhanced sunlight driven photocatalytic activity of In$_2$S$_3$ nanosheets functionalized MoS$_2$ nanoflowers heterostructures

Jaspal Singh & R. K. Soni

Visible light-sensitive 2D-layered based photocatalytic systems have been proven one of the effective recent trends. We report the preparation of a 2D-layered based In$_2$S$_3$–MoS$_2$ nanohybrid system through a facile hydrothermal method, capable of efficiently degrading of organic contaminants with remarkable efficiency. Transmission electron microscopy (TEM) results inferred the attachment of 2D-layered In$_2$S$_3$ sheets with the MoS$_2$ nanoflakes. Field emission SEM studies with chemical mapping confirm the uniform distribution of Mo, In, and S atoms in the heterostructure, affirming sample uniformity. X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy results confirm the appearance of 2H-MoS$_2$ and β-In$_2$S$_3$ in the grown heterostructures. UV-DRS results reveal a significant improvement in the optical absorbance and significant bandgap narrowing (0.43 eV) in In$_2$S$_3$–MoS$_2$ nanohybrid compared to pristine In$_2$S$_3$ nanosheets in the visible region. The effective bandgap narrowing facilitates the charge transfer between MoS$_2$ and In$_2$S$_3$ and remarkably improves the synergistic effect. Effective bandgap engineering and improved optical absorption of In$_2$S$_3$–MoS$_2$ nanohybrids are favorable for enhancing their charge separation and photocatalytic ability. The photocatalytic decomposition efficiency of the pristine In$_2$S$_3$ nanosheets and In$_2$S$_3$–MoS$_2$ nanohybrids sample is determined by the decomposing of methylene blue and oxytetracycline molecules under natural sunlight. The optimized In$_2$S$_3$–MoS$_2$ nanohybrids can decompose 97.67% of MB and 76.3% of OTC-HCl molecules solution in 8 min and 40 min of exposure of sunlight respectively. 2D-layered In$_2$S$_3$–MoS$_2$ nanohybrids reveal the tremendous remediation performance towards chemical contaminations and pharmaceutical waste, which indicates their applicability in industrial and practical applications.

Visible light-sensitive photocatalyst has been extensively studied due to their tremendous performance for energy production and environmental remediation applications. 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 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. 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 photocatalysts have been developed, which tremendously absorb the visible light and also provide sufficient effective surface area. 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. Among various layered structures Indium sulfide (In$_2$S$_3$) has received significant attention recently in the field of visible light photocatalyst because of its low toxicity, high photo-stability, and narrow bandgap (2.0–2.3 eV). On the other hand, the photocatalytic nature of In$_2$S$_3$ is found to be low due to the high recombination rate and poor mass transfer. Several parameters such as modulation in morphology, a surface area strongly influenced the photocatalytic activity of the In$_2$S$_3$ nanostructures by efficient charge separation, the improved lifetime of charge carriers, and high rate of mass transfer. Apart from this, various efforts, such as phase optimization, heterostructures creation, and noble metal nanoparticle functionalization, have been devoted to improving remediation performance towards chemical contaminations and pharmaceutical waste, which indicates their applicability in industrial and practical applications.

Laser Spectroscopy Lab, Department of Physics, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India. *email: jaspal2125@gmail.com
the photodegradation capability of In$_2$S$_3$ nanostructures. 2D-TMDs based heterostructures-based photocatalyst is one of the advanced and effective strategies to control the recombination rate and improve the photodegradation ability through synergetic effect between two layered nanostructures. Nanostructured MoS$_2$ (band-gap = 1.9 eV) is extensively explored and employed for several applications such as sensing, energy production, optoelectronic devices, and antibacterial activity. Due to its fascinating optical, electronic, and chemical properties, MoS$_2$ modified In$_2$S$_3$ based heterostructures can effectively enhance the lifetime of photoinduced charge carriers through synergetic effect among them. In$_2$S$_3$ nanosheets combined with MoS$_2$ nanowalls is expected to increase the photoinduced catalytic activity due to 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. Moreover, MoS$_2$ presence in In$_2$S$_3$ can further enhance the active sites, which can effectively interact with the pollutant molecules. Li et al. fabricated hierarchical In$_2$S$_3$/MoS$_2$ nanosheets using the exfoliation method with the hydrothermal method. The prepared In$_2$S$_3$/MoS$_2$ nanohybrids were embraced for photocatalytic application through the Aza-Henry reaction. They have demonstrated that In$_2$S$_3$/MoS$_2$ nanohybrids attained superior photocatalytic activity compared to pure MoS$_2$ and In$_2$S$_3$. Sun et al. prepared MoS$_2$/In$_2$S$_3$ flakes-based photoanode by using a one-pot synthesis process and applied it for the H$_2$ production application. In their study, they have demonstrated the effective charge separation in MoS$_2$/In$_2$S$_3$ flakes for a high H$_2$ production rate.

2D-layered-based heterostructures are emerging as the new material for environmental remediation applications and are rarely reported in the literature. Removal of pharmaceutical and chemical waste has not been reported by using the 2D-layered In$_2$S$_3$-MoS$_2$ nanohybrids-based photocatalyst. This study also highlights the contribution of improvement in the optical absorption and significant bandgap narrowing on the photodegradation nature of In$_2$S$_3$-MoS$_2$ nanoheterostructures.

In this work, we highlight the synergetic effect due to the effective bandgap narrowing in 2D-layered-based heterostructures for pollutant removal. To employ the proposed strategy, 2D-layered-based In$_2$S$_3$-MoS$_2$ nanoheterostructures were engineered using a hydrothermal method and determined their photodegradation capability to decompose the variety of organic pollutants molecules 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$_2$S$_3$ and MoS$_2$. In$_2$S$_3$-MoS$_2$ nanoheterostructures exhibit a significantly superior photocatalytic nature as compared to pristine In$_2$S$_3$ nanostructures. We have tuned the heterojunction density by varying the amount of MoS$_2$ over In$_2$S$_3$ for a superior photodegradation process which provides the insight understanding to design the efficient photocatalyst. Apart from this, In$_2$S$_3$-MoS$_2$ nanoheterostructures revealed significant reusability and stability, which indicate their possible applications for other sunlight-driven processes.

**Experimental Materials.** Indium chloride, Hexaammonium hexamolybdate 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.

**Formation of β-In$_2$S$_3$-2H-MoS$_2$ heterostructures photocatalyst.** In the reaction process, initially, 20 mL of Hexaammonium hexamolybdate tetrahydrate (0.08 mM) was dropwise added into the 20 mL thiourea (0.18 mM) 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 a uniform mixture, it was transferred to a Teflon container of 100 mL. The pH of the obtained solution was set at 6 by using 0.5 M NaOH solution. In the next step, the Teflon-lined stainless steel autoclave contained sample was held at 180 °C for 18 h. 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$_2$S$_3$ and In$_2$S$_3$-MoS$_2$ samples with tuneable MoS$_2$ density (0.16 mM and 0.24 mM) were generated by the above-mentioned process. For better understanding, pristine In$_2$S$_3$ and In$_2$S$_3$-MoS$_2$ heterostructures (0.08 mM, 0.16 mM and 0.24 mM) hereafter reported as IP, IPM1, IPM2 and IPM3, respectively. The reaction process is depicted in Fig. 1.

**Characterization techniques and photocatalysis reaction.** Surface morphologies of pristine In$_2$S$_3$ and MoS$_2$, modified In$_2$S$_3$ 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$_2$S$_3$-MoS$_2$ nanohybrids. Powder X-ray diffraction pattern (Rigaku Ultima IV, Ri) was employed to investigate the diffraction patterns of In$_2$S$_3$-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$_2$S$_3$-MoS$_2$ nanohybrids was investigated through X-ray photoelectron spectroscopy (ESCA + Omicron Nano Technology). The photodegradation ability of MoS$_2$ functionalized In$_2$S$_3$ and pure In$_2$S$_3$ samples were explored by the breakdown of 10 mM 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 min) were measured using UV–Visible absorption spectroscopy (Perkin Elmer). In the photocatalytic reaction, the used amount of each photocatalyst sample is 2.5 mg/L. In order to explore the active species in the photodegradation reaction charge trapping studies were
performed. To trap the superoxide radicals, electrons, hydroxyl radicals, and holes four scavengers namely benzoquinone (BQ), copper nitrate (CN), formic acid (FA), and Isopropanol alcohol (IPA) were employed, respectively.

Results and discussion

Figure 2 illustrates the X-ray diffraction patterns of pristine \( \text{In}_2\text{S}_3 \) and \( \text{MoS}_2 \) modified \( \text{In}_2\text{S}_3 \). XRD for sample IP indicates nine reflections (311), (222), (400), (422), (511), (440), (531), (553), and (622), which assured the presence of \( \beta \)-phase of \( \text{In}_2\text{S}_3 \) (JCPDS-500814). XRD spectrum for sample IPM1 shows eight diffraction patterns (311), (222), (400), (511), (440), (531), (533), and (622) corresponds to \( \text{In}_2\text{S}_3 \) while two peaks with reflection (100) and (106) assures the existence of 2H phase of MoS\(_2\) (JCPDS-371492). XRD spectrum for sample IPM2 indicates similar diffraction peaks compared to the XRD curve of sample IPM1. Interestingly, the peak intensity of (100) and (106) peaks are found enhanced in sample IPM2 compared to sample IPM1 which inferred the high concentration of \( \text{MoS}_2 \) in \( \text{In}_2\text{S}_3–\text{MoS}_2 \) nanohybrids. For sample IPM3, nine diffraction peaks (100), (311), (400), (511), (440), (531), (553), and (622) can be appeared. Among them, seven peaks (311), (400), (511), (440), (531), (553), and (622) inferred the formation of \( \text{In}_2\text{S}_3 \) while (100) and (106) indicate the presence of \( \text{MoS}_2 \). XRD results assure the formation of \( \text{In}_2\text{S}_3–\text{MoS}_2 \) nanohybrids in samples IPM1, IPM2 and IPM3.

Raman spectra of sample IP, IPM1, IPM2, and IPM3 are presented in Fig. 3. Raman spectrum for sample IP indicating the four distinct peaks at 183 cm\(^{-1}\), 249 cm\(^{-1}\), 306 cm\(^{-1}\) and 369 cm\(^{-1}\) which are attributed to the fingerprint vibrations of \( \beta \)-phase of \( \text{In}_2\text{S}_3 \). Raman result for sample IPM1 indicates the slight shift in the Raman peaks corresponds to the \( \beta \)-phase of \( \text{In}_2\text{S}_3 \). The observed peaks are 195 cm\(^{-1}\), 223 cm\(^{-1}\), 305 cm\(^{-1}\) and 347 cm\(^{-1}\) implies the formation of \( \text{MoS}_2–\text{In}_2\text{S}_3 \) nanohybrids. 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 \( \text{MoS}_2 \). Raman spectrum for sample IPM2, the peaks correspond to the \( \beta \)-\( \text{In}_2\text{S}_3 \) and 2H-MoS\(_2\) are found slightly shifted compared to Raman spectrum of sample IPM1. The observed peaks for sample IPM2 are 197 cm\(^{-1}\), 221 cm\(^{-1}\), 303 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 \( \text{MoS}_2 \) in \( \text{In}_2\text{S}_3–\text{MoS}_2 \) nanohybrids. For sample IPM3, the observed peaks for sample IPM3 are 197 cm\(^{-1}\), 221 cm\(^{-1}\), 304 cm\(^{-1}\), 343 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 \( \text{MoS}_2 \) with \( \text{In}_2\text{S}_3 \). The shift in the Raman spectra of \( \text{MoS}_2 \) modified \( \text{In}_2\text{S}_3 \) 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 \( \text{In}_2\text{S}_3 \).

Figure 4a–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. 4a). FESEM result for sample IPM1 illustrates the functionalization of 2D-layered structured aggregates on sheet-like nanostructures (Fig. 4b). With the increment in the concentration of \( \text{MoS}_2 \), 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. 4c). To further increase the Mo\(^{4+}\) ions concentration in \( \text{In}_2\text{S}_3 \), the 2D sheet mediated flowers-like structures attached with the sheet-like nanostructures can be observed for sample IPM3 (Fig. 4d). To confirm the formation of \( \text{MoS}_2–\text{In}_2\text{S}_3 \) nanohybrids, elemental mapping for sample IPM3 was carried out and illustrated in Fig. 4e–i. The broader view of surface morphologies of sample IPM3 has been presented in Fig. 4e, while elemental mapping of the specific atom and corresponding nanohybrid is depicted in Fig. 4f–i. Elemental mapping
studies affirm the uniform spreading of Mo, In, and S atoms in sample IPM3. Surface morphology results confirm the formation of MoS$_2$–In$_2$S$_3$ nanohybrids. The EDX spectrum for sample IPM3 is presented in (Fig. 1) supporting information. To explore the crystal structures and the attachment of In$_2$S$_3$ and MoS$_2$, TEM and HRTEM studies were employed. Figure 5a–d shows the TEM images for sample IPM3 which inferred the presence of MoS$_2$ nanoflakes were attached with the In$_2$S$_3$ nanosheets. Figure 5c,d reveals the heterojunction creation among the MoS$_2$ nanoflakes and In$_2$S$_3$ sheets. TEM studies affirm that the assembly of MoS$_2$ nanosheets formed the flowers-like nanostructures on the surface of In$_2$S$_3$ sheets. To further assured the formation of In$_2$S$_3$–MoS$_2$ nanoheterojunction, high-resolution TEM studies were performed and depicted in Fig. 5e,f. The evaluated distance among the inter-planer lattice fringes is 0.61 nm and 0.32 nm which implies the existence of MoS$_2$ (002) and In$_2$S$_3$ (311) in sample IPM3. Thus HRTEM results assured the creation of In$_2$S$_3$–MoS$_2$. The information regarding the structural profile of the pristine MoS$_2$ sample is represented in Fig. 2 supporting information).

The optical profile of pristine In$_2$S$_3$ nanosheets and MoS$_2$ modified In$_2$S$_3$ is illustrated in Fig. 6a. The optical absorption curve of sample IP reveals a broad peak form 250–600 nm. With the modification of MoS$_2$ in In$_2$S$_3$, 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

![Figure 2. X-ray diffraction reflections of In$_2$S$_3$ nanosheets and In$_2$S$_3$–MoS$_2$ nanohybrids.](image-url)
improvement in MoS$_2$–In$_2$S$_3$ nanohybrids as compared to pristine In$_2$S$_3$. To explore the bandgap engineering in MoS$_2$–In$_2$S$_3$ nanohybrids, Tauc plots were carried out and presented in Fig. 6b. Tauc plots suggest the narrowing in the bandgap in MoS$_2$–In$_2$S$_3$ nanohybrids as compared to pristine In$_2$S$_3$. 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 valence state and surface chemical composition of MoS$_2$–In$_2$S$_3$ nanohybrids were determined through XPS and illustrated in Fig. 7. Gaussian fitted XPS spectra for In3d, S2p and Mo3d were presented in Fig. 7a–c, respectively. Figure 7a reveals that the XPS spectrum for In3d consists of two distinct peaks at 444.6 eV and 452.2 eV, which can be assigned to the In3d$_{5/2}$ and In3d$_{3/2}$, respectively. Gaussian fitted S2s spectrum reveals the three peaks at 161.8 eV, 164.3 eV and 168.2 eV (Fig. 7b). The peaks at 161.8 eV and 164.3 eV can be attributed to the S2P$_{3/2}$ and S2P$_{1/2}$ sequentially and affirms the presence of the S2p state of the sulfur atom. Apart from this, a broad peak at 168.2 eV assured the existence of the S–O bond. This bond inferred the partial oxidation of sulfur in the hydrothermal process. The fitted spectrum of Mo3d shows the distinct four peaks at 228.3 eV, 231.0 eV, 232.1 eV, and 234.5 eV (Fig. 7c). The major peaks at 228.4 eV and 231.3 eV corresponds to the Mo3d$_{5/2}$ and Mo3d$_{3/2}$, respectively. The peaks at 232.1 eV and 234.5 eV can be attributed to the existence of Mo$^{6+}$ states in the Mo3d spectrum. Both peaks arise due to the incomplete reduction of Mo precursors in hydrothermal reaction. Zou et al. reported the formation of MoS$_2$/RGO nanocomposites through the hydrothermal method.

Figure 3. Raman results of In$_2$S$_3$ nanosheets and In$_2$S$_3$–MoS$_2$ nanohybrids.
In their XPS study, they have also observed the Mo$^{+6}$ peaks due to incomplete reduction of Mo precursors. Moreover, it is possible that edges of the MoS$_2$ or defect state are bonded with oxygen and give rise to the peaks corresponds to the Mo$^{+6}$ states$^{49}$. XPS studies indicate the presence of Mo, In, and S atoms in sample IPM3. (i) Mapped image of sample IPM3 assuring the formation of In$_2$S$_3$–MoS$_2$.

Figure 4. (a–d) FESEM images of sample IP, IPM1, IPM2, and IPM3 indicating the modulations in their morphology, (e) FESEM image of sample IPM3 revealing the formation of In$_2$S$_3$ nanosheet decorated MoS$_2$ nanoflowers, (f–h) Chemical mapping of sample IPM3 assuring the independent existence of In, Mo, and S atoms in sample IPM3.
and S$^2$ state in the MoS$_2$–In$_2$S$_3$ nanohybrids, respectively. XPS results explicitly suggest that no shift takes place in the recombination process of MoS$_2$–In$_2$S$_3$ nanohybrids.

We investigated the sunlight-induced photodegradation ability of the In$_2$S$_3$ nanosheets and MoS$_2$ modified In$_2$S$_3$ samples by the degradation of MB molecule solution. Figure 8a–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 min, 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 min (Fig. 9a). Figure 8e shows the modulations among the photodegradation kinetics of sample IP, IPM1, IPM2, and IPM3. The photodecomposition capability of pristine MoS$_2$ nanoflowers for MB pollutant molecules

Figure 5. (a–d) TEM image of sample IPM3 revealing the formation of In$_2$S$_3$ nanosheet decorated MoS$_2$ nanoflowers, (e, f) High-resolution TEM images indicating fringes distance for MoS$_2$ and In$_2$S$_3$.
Figure 6. (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 7. (a) Fitted XPS spectrum of In3d, (b) Fitted XPS spectrum of S2s, (c) Gaussian fitted XPS of Mo3d.
was measured and presented in (Fig. 3a supporting information). The calculated photodegradation efficiency of pristine MoS$_2$ is 62.2%. 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
The rate constant value for sample IP, IPM1, IPM2, and IPM3 is depicted in Fig. 8f. 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 while the k value for pristine MoS2 nanoflowers is found to be 0.1673/min (Fig. 3b supporting information). Photocatalytic studies affirm that sample IPM3 attain 2.70 times better photodecomposition performance as compared to pristine sample IP. The rate constant value for sample IPM3 is 7.2 times and 2.04 times the k value of sample IP and pristine MoS2. 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. 9b). To reveal the high photodegradation capability of the most efficient sample IPM3, the photodecomposition of OTC-HCl molecules was explored. Figure 10a,b indicates the optical absorption results of photodegradation results of OTC-HCl molecule solution using sample IP and IPM3, respectively. Photo-degradation 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 0.3 mg/mL of OTC-HCl solution in sunlight (Fig. 10c). The k-values for sample IP and IPM3 are 0.00621/min and 0.0308/min sequentially (Fig. 10d).

To determine the charge transfer profile in In2S3–MoS2 nanohybrids during the photocatalytic reaction, a schematic diagram has been presented (Fig. 11). Under sunlight irradiation, In2S3 sheets and MoS2 flakes are activated and generate the electron–hole pair in their respective conduction and valence bands. In the next step, the photoinduced electron in the conduction band of In2S3 moves towards the conduction band of MoS2 due to the band alignment positions, which in turn maintain the synergistic effect and control the recombination rate in In2S3 nanosheets. The VB and CB positions for In2S3 nanosheets and MoS2 nanoflakes are obtained through the following relation (1).

\[
E_{CB} = \chi - E^e - 0.5E_g
\]

where \( E_{CB} \) indicates the bandgap value of the 2D layered materials (In2S3 and MoS2) while \( E^e \) stands for the energy on the hydrogen scale (4.5 eV), and \( \chi \) shows the electronegativity of the 2D layered nanostructures (In2S3 ~ 4.7 eV and MoS2 ~ 5.32 eV). The computed VB and CB values for In2S3 nanosheets are 1.32 eV and −0.92 eV, sequentially, while CB and VB values for MoS2 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 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 concentrations. 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. To recognize the active species responsible for the improved photocatalytic activity of In2S3–MoS2 nanohybrids, charge trapping studies were embraced and presented in Fig. 4 (supporting information) Scavenger studies inferred that BQ and CN largely quench the rate of photocatalytic reaction kinetics of sample IPM3. Thus it can be concluded that superoxide and electrons majorly influence the photocatalytic reaction kinetics. In order to further determine the stability of sample IPM3 during the reusable photodegradation process, their structural characterization was explored and depicted in Fig. 5 (supporting information). Raman studies and TEM images assure the high stability of sample IPM3.
In the present report, an In$_2$S$_3$–MoS$_2$ nanohybrids with an effective charge separation effect is successfully fabricated. The density of MoS$_2$ nanostructures over In$_2$S$_3$ nanosheets was precisely varied and used for the decomposition of MB and OTC molecules under solar light illumination.

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 MoS$_2$ over In$_2$S$_3$ nanosheets was increased from sample IPM1 to IPM3. For sample IPM3, high numbers of heterojunction of MoS$_2$ and In$_2$S$_3$ 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 min and 40 min sequentially under solar light illumination. Liu et al.\textsuperscript{33} reported the formation of MoS$_2$ nanodots functionalized In$_2$S$_3$ nanoplates and used them for the photoelectrochemical application. They have found that MoS$_2$/In$_2$S$_3$ heterojunction with effective charge exhibited better performance as compared to pristine MoS$_2$ and In$_2$S$_3$. Wang et al.\textsuperscript{34} synthesized MoS$_2$ functionalized In$_2$S$_3$ nanostructures for the Cr$^{6+}$ removal using a photocatalysis process. They have demonstrated that MoS$_2$ functionalized In$_2$S$_3$ nanostructures exhibit 3.2 times better photocatalytic activity than pristine In$_2$S$_3$.

Conclusions
We have successfully engineered In$_2$S$_3$–MoS$_2$ nanohybrids using a simple hydrothermal method. The density of MoS$_2$ flakes was tuned over the surface of In$_2$S$_3$ nanosheets. Improvement in the optical absorption and significant bandgap narrowing tremendously contribute to improving the charge separation in 2D-layered In$_2$S$_3$–MoS$_2$ nanohybrids. Optimized In$_2$S$_3$–MoS$_2$ nanohybrids reveal the outstanding sunlight-driven photodecomposition performance for MB and OTC pollutant molecules solution. In$_2$S$_3$ nanosheets combined with the MoS$_2$ nanoflakes decompose the 96.8% 10 µM of MB and OTC (0.3 mg/mL) solution in 8 min and 40 min, respectively. The photodecomposition capability of 2D-layered In$_2$S$_3$–MoS$_2$ nanohybrids was found 2.7 times higher as compared to pristine In$_2$S$_3$ nanosheets. Charge trapping studies inferred that superoxide radicals and electrons density majorly take part to improve the photodegradation ability of In$_2$S$_3$–MoS$_2$ nanohybrids. These results are very

Figure 10. (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.
significant and unique, which demonstrated the outstanding photocatalytic activity of 2D layered In$_2$S$_3$–MoS$_2$ nanohybrids towards chemical and pharmaceutical waste.

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Author contributions

J.S.: Conceptualization, Investigation, Writing—original draft. R.K.S.: Supervision, Writing—review and editing.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to J.S.

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