



Original Research Paper

S-scheme $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101}(\text{Cr})$ composite for dual-function removal of polystyrene microplastics and tetracycline in water

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ARTICLE INFO

Article history:

Received 16 August 2025

Received in revised form 11 December 2025

Accepted 18 January 2026

Keywords:

Microplastics

PSMPs

Tetracycline

TiO_2

In_2S_3

$\text{MIL-101}(\text{Cr})$

Adsorption

Photodegradation

ABSTRACT

The progressive contamination of aquatic environments by microplastics and pharmaceutical residues has emerged as a pressing environmental issue. In the present study, a novel S-scheme $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101}(\text{Cr})$ heterojunction composite was synthesized and evaluated for its capacity to simultaneously eliminate polystyrene microplastics (PSMPs) and tetracycline (TC) from aqueous media. The $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101}(\text{Cr})$ composite exhibited outstanding photocatalytic and adsorptive properties, achieving complete removal of PSMPs (500 mg L^{-1}) within 90 min and 97% removal of TC (30 mg L^{-1}) within 210 min under visible-light irradiation. In a binary pollutant system, the composite enabled full elimination of both PSMPs and TC within 240 min, with PSMPs reaching 100% removal at 180 min and TC at 240 min. The superior performance was attributed to enhanced charge carrier separation and the suppression of electron-hole recombination, facilitated by the engineered heterojunction structure. Reusability tests confirmed the material's stability, with over 94% removal efficiency retained after four consecutive cycles. Moreover, adsorption experiments revealed a pronounced pH dependence, with optimal removal efficiency observed at pH 5. Collectively, these results highlight the dual functionality and robustness of $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101}(\text{Cr})$, underscoring its potential as a promising candidate for large-scale water purification and environmental remediation applications.

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1. Introduction

The co-occurrence of MPs and the antibiotic TC in aquatic environments poses a substantial risk to both ecosystems and public health [1]. MPs (<5 mm), originating from fragmented plastic debris and microbeads, are highly persistent in water systems where they readily adsorb organic contaminants and pathogenic microorganisms. Upon ingestion, MPs can induce physical damage, oxidative stress, immunosuppression, and endocrine disruption, with the potential for trophic transfer and bioaccumulation within food webs [2–4]. In parallel, TC—extensively applied in human medicine, veterinary practices, and agriculture—is predominantly excreted in unmetabolized form. Owing to its poor biodegradabil-

ity (half-life > 100 days), TC accumulates in surface and groundwater, contributing to the proliferation of antibiotic resistance and exerting detrimental effects on microbial and algal communities [5,6]. Notably, the coexistence of MPs and TC exacerbates these hazards, as MPs serve as vectors that concentrate and transport TC through hydrophobic and π - π interactions, thereby amplifying its toxicity by up to an order of magnitude and facilitating biofilm-mediated horizontal transfer of resistance genes [7]. These synergistic interactions highlight the urgent demand for advanced water treatment strategies capable of simultaneously eliminating both particulate and dissolved pollutants.

To tackle these challenges, multifunctional materials that combine photocatalytic degradation with high-capacity adsorption have garnered considerable attention. Photocatalysis offers a sustainable and efficient pathway for mineralizing organic pollutants into CO_2 , H_2O , or other environmentally benign products under light irradiation [8]. Among various photocatalysts, titanium

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dioxide (TiO_2) is one of the most widely investigated, owing to its strong oxidative potential, chemical stability, and non-toxicity [9]. Upon UV excitation, TiO_2 generates electron–hole pairs that subsequently produce reactive oxygen species (ROS), such as hydroxyl and superoxide radicals, capable of degrading a wide range of organic contaminants. However, TiO_2 is limited by its wide bandgap (~ 3.2 eV), which restricts solar energy utilization to $< 5\%$ and results in negligible activity under visible light [10].

To overcome this drawback, visible-light-responsive semiconductors such as indium sulfide (In_2S_3 , bandgap 1.8–2.3 eV) have been explored to extend photocatalytic activity into the visible spectrum [11,12]. Despite this advantage, In_2S_3 suffers from rapid recombination of photogenerated charge carriers, which severely diminishes its catalytic efficiency [13]. In this context, the S-scheme heterojunction concept, first proposed by Yu et al. in 2019 [14], has emerged as a promising strategy to integrate complementary semiconductors. An S-scheme heterojunction typically couples a reduction-type photocatalyst, characterized by higher conduction band (CB), valence band (VB), and Fermi levels, with an oxidation-type photocatalyst exhibiting lower corresponding levels [15]. Upon contact, interfacial charge transfer occurs as electrons migrate from the reduction-type to the oxidation-type photocatalyst due to Fermi level equilibration. This process induces electron depletion in the reduction-type photocatalyst and electron accumulation in the oxidation-type photocatalyst, generating an internal electric field oriented from the reduction-type to the oxidation-type semiconductor.

Under light irradiation, photogenerated electrons in the CB of the oxidation-type photocatalyst tend to recombine with holes in the VB of the reduction-type photocatalyst, driven by Coulombic attraction and the built-in electric field. Conversely, the transfer of electrons from the CB of the reduction-type photocatalyst to the CB of the oxidation-type photocatalyst, as well as hole migration from the VB of the oxidation-type to the VB of the reduction-type photocatalyst, is effectively inhibited by Coulombic repulsion, band bending, and the internal field [16]. As a result, high-energy electrons are retained in the reduction-type photocatalyst and strong oxidative holes are preserved in the oxidation-type photocatalyst, thereby maintaining robust redox potential. Compared to conventional heterojunctions, S-scheme architectures not only suppress charge recombination but also preserve the strong redox capability necessary for pollutant degradation [17], CO_2 reduction [18], and H_2O_2 generation [19]. Thus, the rational construction of S-scheme heterojunction photocatalysts represents a highly effective strategy to achieve efficient charge separation and maximize photocatalytic performance in environmental applications.

In parallel, adsorption has emerged as an effective and low-cost strategy for pollutant removal, particularly for particulate matter such as microplastics (MPs). Conventional carbon-based adsorbents, including activated carbon and doped carbon composites, exhibit moderate MP removal performance [20–25]. Nonetheless, their applicability is often limited by poor selectivity among different plastic types and insufficient efficiency in capturing nanoscale MPs within complex water matrices [26,27]. In contrast, metal–organic frameworks (MOFs), owing to their high surface area, tunable porosity, and diverse chemical functionalities, represent a versatile platform for both adsorption and catalysis. MOFs such as UiO-66 and ZIF-67 have demonstrated notable MP removal efficiencies, while MOF-derived composites have been reported to achieve the simultaneous elimination of MPs and organic pollutants, including pesticides [13,21,28]. More recently, hybrid systems such as $\text{g-C}_3\text{N}_4/\text{FeNi-BTC}$ and $\text{g-C}_3\text{N}_4/\text{CoFe-BTC}$ have highlighted the potential of integrating MOFs with photocatalysts and carbon nanostructures to enable efficient treatment of mixed pollutant systems, particularly those containing MPs and antibiotics [29,30].

Building upon these advances, we report the design of a novel ternary photocatalytic nanocomposite, in which $\text{TiO}_2@\text{In}_2\text{S}_3$ nanoparticles are uniformly assembled and well dispersed on the surface of MIL-101(Cr). The composite is rationally engineered to exploit the synergistic functions of its constituents: (i) TiO_2 provides strong oxidative capability under UV irradiation, (ii) In_2S_3 extends photocatalytic activity into the visible-light region, and (iii) the S-scheme heterojunction formed between TiO_2 and In_2S_3 facilitates efficient charge separation, thereby enhancing photocatalytic degradation. Concurrently, MIL-101(Cr) contributes high surface area, large mesopores for effective microplastic capture, and excellent structural as well as chemical stability in aqueous environments [31]. As a result, the $\text{TiO}_2@\text{In}_2\text{S}_3/\text{MIL-101(Cr)}$ composite exhibits dual functionality, achieving both efficient adsorption of polystyrene microplastics and rapid photocatalytic degradation of tetracycline under simulated solar irradiation. This integrated strategy provides a promising route for advanced water treatment, enabling the simultaneous removal of particulate and dissolved contaminants within a single multifunctional material system.

2. Experimental

2.1. Materials

Chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%), hydrofluoric acid (HF, 48%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99%), dimethylformamide (DMF, 99.8%), thiourea ($\text{CS}(\text{NH}_2)_2$, 99%), indium(III) chloride (InCl_3 , 99.99%), titanium isopropoxide (TTIP, 97%), cetrimonium bromide (CTAB, $\text{C}_{16}\text{H}_{33}\text{N}(\text{Br})(\text{CH}_3)_3$, $\geq 99\%$), and acetic acid (CH_3COOH , 99.8%) were purchased from Sigma–Aldrich and used without further purification. Terephthalic acid (TPA) was recovered from post-consumer PET plastic via our previously reported recycling method [5,32]. Tetracycline (TC, 98%) was obtained from Sigma–Aldrich, while polystyrene microplastics (PSMPs; 2.5% w/v aqueous suspension) were purchased from Polysciences (USA). TC and PSMPs were employed as model organic pollutants in the adsorption and photocatalytic degradation experiments.

2.2. Synthesis of $\text{TiO}_2@\text{In}_2\text{S}_3$

The TiO_2 precursor was synthesized via a sol–gel method. Titanium isopropoxide (TTIP) was dissolved in a mixed solvent of ethanol and acetic acid at a molar ratio of 0.01 $\text{Ti}(\text{OC}_3\text{H}_7)_4$: $\text{C}_2\text{H}_5\text{OH}$: CH_3COOH : $4.5\text{H}_2\text{O}$, followed by magnetic stirring at room temperature for 6 h. Subsequently, 0.2 g of CTAB was gradually added under constant stirring, and the reaction was allowed to proceed for an additional 3 h. The resulting TiO_2 sol was then subjected to hydrothermal crystallization at 100°C for 6 h in a Teflon-lined stainless-steel autoclave. After cooling to room temperature, the precipitate was collected by centrifugation, washed repeatedly with distilled water and ethanol, and dried in air at 100°C overnight. The dried gel was finally calcined at 450°C for 3 h under air flow to obtain crystalline TiO_2 powder.

The $\text{TiO}_2@\text{In}_2\text{S}_3$ nanocomposite was prepared via a one-step hydrothermal process. Specifically, 6.15 mmol of the pre-synthesized TiO_2 was dispersed in an aqueous solution of InCl_3 (4 mmol) by ultrasonication for 30 min. A separate aqueous solution containing thiourea (6 mmol) was then added dropwise to the $\text{TiO}_2\text{--InCl}_3$ suspension, followed by continuous stirring for 1 h. The mixture was subsequently transferred into a Teflon-lined stainless-steel autoclave and heated at 150°C for 6 h. The resulting yellowish precipitate was collected by centrifugation, washed thoroughly with distilled water and ethanol, and dried at

80 °C overnight to yield the $\text{TiO}_2/\text{In}_2\text{S}_3$ nanocomposite. For comparison, pure In_2S_3 was synthesized under identical conditions in the absence of TiO_2 .

2.3. Synthesis of $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101}(\text{Cr})$ nanocomposite

The $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101}(\text{Cr})$ heterojunction material was synthesized via a direct hydrothermal method. Typically, 0.5 g of $\text{TiO}_2/\text{In}_2\text{S}_3$ was dispersed in an aqueous solution of chromium (III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 10 mmol in 60 mL of distilled water) by ultrasonication for 30 min. Separately, a solution of terephthalic acid (TPA, 7 mmol) and HF (0.43 mL, 48%) in 75 mL of distilled water was prepared and subsequently added to the $\text{TiO}_2/\text{In}_2\text{S}_3\text{-Cr}(\text{NO}_3)_3$ suspension. The mixture was stirred vigorously at 500 rpm for 1 h to obtain a homogeneous precursor solution.

The precursor was then transferred into a Teflon-lined stainless-steel autoclave and heated at 180 °C for 12 h. After natural cooling to room temperature, the solid product was collected by filtration, washed thoroughly with DMF, ethanol, and distilled water at 80 °C to remove residual organic linkers and impurities, and finally dried in an oven at 80 °C overnight. The resulting material was denoted as the $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101}(\text{Cr})$ (TIM) nanocomposite photocatalyst.

2.4. Characterization

The crystal structure and phase composition of the synthesized materials were characterized by X-ray diffraction (XRD) using a D8 Advance diffractometer (Bruker, Germany) equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at a scanning rate of 0.2° s^{-1} . The surface morphology and microstructural features were examined by scanning electron microscopy (SEM, HITACHI S-4800-3000F) and transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). Fourier-transform infrared (FT-IR) spectroscopy (Jasco 4700 spectrometer) was employed to identify functional groups and chemical bonds in both the synthesized materials and polystyrene microplastics before and after adsorption. Elemental composition and spatial distribution were determined using energy-dispersive X-ray spectroscopy (EDX) and EDX mapping (JEOL JED-2300) with gold coating. The optical properties were analyzed through UV-visible diffuse reflectance spectroscopy (DRS, UV-2600, Shimadzu) and photoluminescence (PL) spectroscopy (Cary Eclipse fluorescence spectrophotometer, Varian). Specific surface area, pore size distribution, and pore volume were measured by nitrogen adsorption-desorption isotherms at 77 K using the Brunauer-Emmett-Teller (BET) method on a Tristar 3030 analyzer (Micromeritics, USA). X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALab 250 spectrometer (Thermo VG, UK) to determine the surface elemental composition and chemical states. Electrochemical impedance spectroscopy (EIS) was performed in 0.1 M KCl electrolyte containing 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ as a redox couple. The particle size distribution of PSMPs was further determined by dynamic light scattering (DLS, Nano Zetasizer, Malvern Instruments Ltd., UK).

2.5. Photodegradation of tetracycline

Photocatalytic degradation experiments were performed in batch mode using 100 mL of TC solution ($30 \text{ mg}\cdot\text{L}^{-1}$) with 40 mg of photocatalyst. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium. The photocatalytic reactions were then carried out under a 150 W xenon lamp ($\lambda = 420\text{--}800 \text{ nm}$) for varying durations (30–210 min). At designated time intervals, 3 mL aliquots were withdrawn, centrifuged, and filtered to remove the

catalyst. The residual TC concentration was quantified spectrophotometrically by measuring the absorbance at $\lambda_{\text{max}} = 365 \text{ nm}$.

2.6. Adsorption of polystyrene microplastics

A stock solution of PSMPs ($1000 \text{ mg}\cdot\text{L}^{-1}$) was prepared by diluting a commercial aqueous suspension of polystyrene (2.5% w/v) with deionized water, followed by ultrasonication in a bath sonicator for 30 min. Adsorption experiments were conducted at room temperature (25 °C) using TiO_2 , In_2S_3 , MIL-101(Cr), and TIM as adsorbents. The influence of adsorption time, solution pH, initial PSMPs concentration, and adsorbent reusability was systematically examined. In a typical experiment, 40 mg of adsorbent was added to 40 mL of PSMPs solution and stirred at 300 rpm. The solution pH was adjusted in the range of 3–11 using 0.1 M HCl or 0.1 M NaOH. At predetermined intervals, aliquots were withdrawn, filtered through a syringe filter, and analyzed by UV-Vis spectrophotometry at 254 nm to determine the residual PSMPs concentration. The adsorption efficiency (η , %) was calculated using the following equation:

$$\eta(\%) = \left(1 - \frac{C_f}{C_o}\right) \times 100 \quad (1)$$

where C_o ($\text{mg}\cdot\text{L}^{-1}$) is the initial PSMPs concentration and C_f ($\text{mg}\cdot\text{L}^{-1}$) is the concentration at time t .

2.7. Simultaneous removal of tetracycline and polystyrene microplastics

In binary pollutant systems, a mixed suspension containing 25% PSMPs and 75% TC by volume was prepared. Specifically, 10 mL of PSMPs suspension ($500 \text{ mg}\cdot\text{L}^{-1}$) and 30 mL of TC solution ($30 \text{ mg}\cdot\text{L}^{-1}$) were combined to obtain 40 mL of mixed-pollutant suspension. The mixture was treated with 40 mg of the TIM nanocomposite at room temperature and neutral pH, under continuous stirring at 400 rpm for 240 min. At predetermined intervals, aliquots were withdrawn, filtered to remove solid residues, and analyzed using a Shimadzu UV-2450 UV-Vis spectrophotometer in the range of 200–800 nm. The characteristic absorption peaks of TC and PSMPs were monitored at 365 nm and 250–295 nm, respectively.

3. Results and discussion

3.1. Structural, surface morphology and physicochemical properties

Fig. 1a shows the XRD patterns of the In_2S_3 , TiO_2 , MIL-101(Cr) and TIM samples. The diffraction peaks of the synthesized In_2S_3 match well with the standard JCPDS 65-0459, confirming the formation of the cubic $\beta\text{-In}_2\text{S}_3$ phase. Specifically, the peaks at $2\theta = 14.5^\circ$, 27.5° , 33.2° , 43.6° and 47.8° correspond to the (101), (331), (400), (511) and (440) crystal planes, respectively [33]. The XRD pattern of TiO_2 shows characteristic peaks at $2\theta = 25.5^\circ$, 37.8° , and 47.9° , which are indexed to the (101), (004), and (200) planes of the anatase phase, consistent with previous reports [34]. For MIL-101(Cr), distinct diffraction peaks appear at $2\theta = 5.8^\circ$, 8.3° , 9.1° , 10.2° , 16.5° and 19.1° , corresponding to the (220), (222), (400), (331), (511/333), and (440) planes, confirming the formation of the MIL-101(Cr) framework [35].

In the TIM composite, the diffraction peaks of MIL-101(Cr) show a slight decrease in intensity, indicating the presence of structural defects in the MIL-101(Cr) lattice due to the incorporation of In_2S_3 and TiO_2 . Nevertheless, the characteristic peaks of both In_2S_3 and TiO_2 are retained in the composite, indicating that their original crystalline structures are preserved after hybridiza-

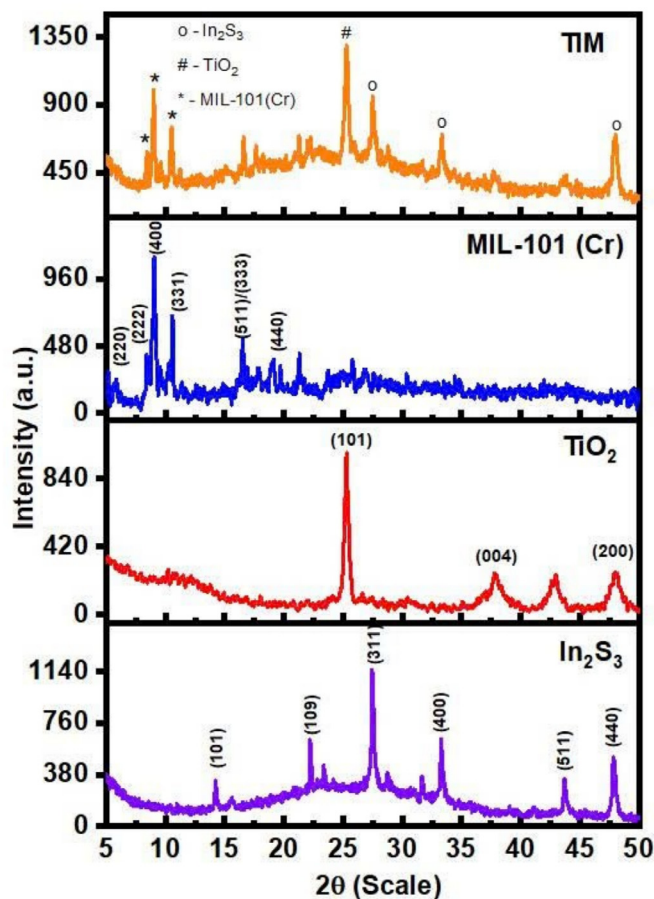


Fig. 1. (a) XRD patterns and (b) FT-IR spectra of In_2S_3 , TiO_2 , MIL-101(Cr), and TIM samples.

tion. The lack of extra peaks confirms that the synthesized materials exhibit high phase purity. The average crystallite sizes of In_2S_3 , TiO_2 , MIL-101(Cr), and TIM were estimated using the Debye-Scherrer equation and found to be approximately 27 nm, 20 nm, 31.4 nm, and 46 nm, respectively.

FT-IR spectra of the In_2S_3 , TiO_2 , MIL-101(Cr), and TIM samples are shown in Fig. 1b. A broad absorption band in the range of $3200\text{--}3400\text{ cm}^{-1}$ is observed in all samples and can be attributed to the stretching vibrations of surface hydroxyl groups or intermolecular hydrogen bonds [30]. In the FT-IR spectrum of In_2S_3 , the peak observed at 806 cm^{-1} is attributed to the stretching vibrations of the In-S bond, whereas the band at 500 cm^{-1} corresponds to the In-O vibration mode. The presence of the In-O bond likely results from the interaction between In^{3+} ions and oxygen-containing surface functional groups [36]. For TiO_2 , characteristic Ti-O stretching vibrations are observed at 690 cm^{-1} and 1623 cm^{-1} [37]. The FT-IR spectrum of MIL-101(Cr) displays distinct vibrational features in the range of $600\text{--}1600\text{ cm}^{-1}$, confirming the presence of aromatic ligands. Specifically, C=C stretching vibrations are seen at 1399 and 1518 cm^{-1} , and C-H deformation vibrations appear at 750 , 887 , 1017 , and 1171 cm^{-1} [35,38]. A peak at 580 cm^{-1} is attributed to the Cr-O stretching vibration, characteristic of the metal-ligand coordination in MIL-101(Cr) [39]. The FT-IR spectrum of the TIM nanocomposite exhibits characteristic features from all three components, indicating successful hybridization. The presence of vibrational bands corresponding to In_2S_3 , TiO_2 , and MIL-101(Cr) suggests strong interfacial interactions and the formation of a homogeneous nanocomposite.

The morphology of the synthesized materials was investigated using SEM and TEM. As shown in the SEM image (Fig. 2a), In_2S_3 exhibits a spherical morphology composed of flower-like crystallites. The corresponding TEM image (Fig. 3a) further reveals that the In_2S_3 structure consists of two-dimensional (2D) nanosheets with rough surfaces and embedded small, irregular nanoparticles. The TiO_2 nanoparticles (Figs. 2b and 3b) display a typical spherical shape with good dispersion, characteristic of anatase-phase TiO_2 . However, some degree of agglomeration is observed, which can be attributed to the high calcination temperature promoting the fusion of primary particles and enhancing crystal growth [40]. MIL-101(Cr) displays a well-defined octahedral morphology with particle sizes ranging from 100 to 200 nm, as evidenced in Figs. 2c and 3c, consistent with previous reports [41]. The SEM and TEM images of the TIM nanocomposite (Figs. 2d and 3d) demonstrate that the In_2S_3 @ TiO_2 nanoparticles, which exhibit a nanosheet morphology, are uniformly distributed around the well-defined octahedral framework of MIL-101(Cr). This arrangement forms a closely integrated interface conducive to efficient direct electron transfer [17]. As shown in Fig. 5e and 5f, the nanosheets are orderly assembled and homogeneously dispersed across the MIL-101(Cr) surface. Moreover, the encapsulating “wrapping” structure of the TIM composite effectively suppresses the aggregation of In_2S_3 @ TiO_2 nanoparticles and enhances their adsorption capacity toward target pollutants [42,43].

Elemental composition and distribution in the TIM nanocomposite were examined using EDX and elemental mapping (Fig. 4). The presence of C, O, Cr, Ti, In, and S confirms the successful incorporation of all constituent components into the composite structure. EDX analysis revealed that the TIM material contains 19.10 wt% C, 34.68 wt% O, 7.85 wt% Cr, 18.64 wt% Ti, 13.92 wt% In, and 5.81 wt% S, corresponding to atomic percentages of 34.59%, 47.10%, 3.28%, 8.46%, 2.63%, and 3.94%, respectively. In comparison, XPS analysis yielded elemental atomic percentages of 33.08% C, 49.79% O, 3.19% Cr, 8.57% Ti, 2.04% In, and 3.32% S. The differences in elemental composition as determined by EDX and XPS are minor, indicating good consistency between the two techniques. Notably, the In:S atomic ratio is approximately 2:3, in good agreement with the stoichiometric composition of In_2S_3 . Furthermore, EDX elemental mapping demonstrates a uniform distribution of all elements throughout the composite matrix, supporting the successful formation of a well-integrated heterojunction structure.

The oxidation states and interactions between components in the TIM nanocomposite were examined using XPS (Fig. 5). The survey spectrum of the TIM (Fig. S1) displayed characteristic peaks corresponding to C, O, Cr, Ti, In, and S, confirming the presence of these elements in the nanocomposite.

High-resolution In 3d and S 2p XPS spectra for the TIM sample revealed energy levels at In $3d_{5/2}$ (444.77 eV) and In $3d_{3/2}$ (452.32 eV), as well as S $2p_{3/2}$ (161.58 eV) and S $2p_{1/2}$ (162.82 eV), indicating the presence of In^{3+} and S^{2-} oxidation states in the nanocomposite [44,45]. Notably, the core-level binding energies of In 3d and S 2p in the TIM shifted to lower (more negative) values compared to those in pure In_2S_3 phase (In $3d_{5/2}$ at 444.96 eV , In $3d_{3/2}$ at 452.51 eV , S $2p_{3/2}$ at 161.38 eV , and S $2p_{1/2}$ at 162.62 eV), indicating the formation of new electronic interactions within the composite.

Additionally, the bonding energies of Ti 2p, Cr 2p, C 1s, and O 1s in the TIM nanocomposite exhibited positive shifts compared to the pure TiO_2 and MIL-101(Cr) phases. Specifically, the Ti $2p_{3/2}$ (458.92 eV) and Ti $2p_{1/2}$ (464.65 eV) peaks confirmed the presence of Ti^{4+} , while the Cr $2p_{3/2}$ (577.81 eV) and Cr $2p_{1/2}$ (587.15 eV) peaks indicated Cr^{3+} . The C 1s spectrum showed peaks at 284.94 eV (C=C/C-C), 285.79 eV (C=O), 288.68 eV (C-O) and 290.04 eV (O-C=O), while the O 1s XPS spectrum exhibited peaks

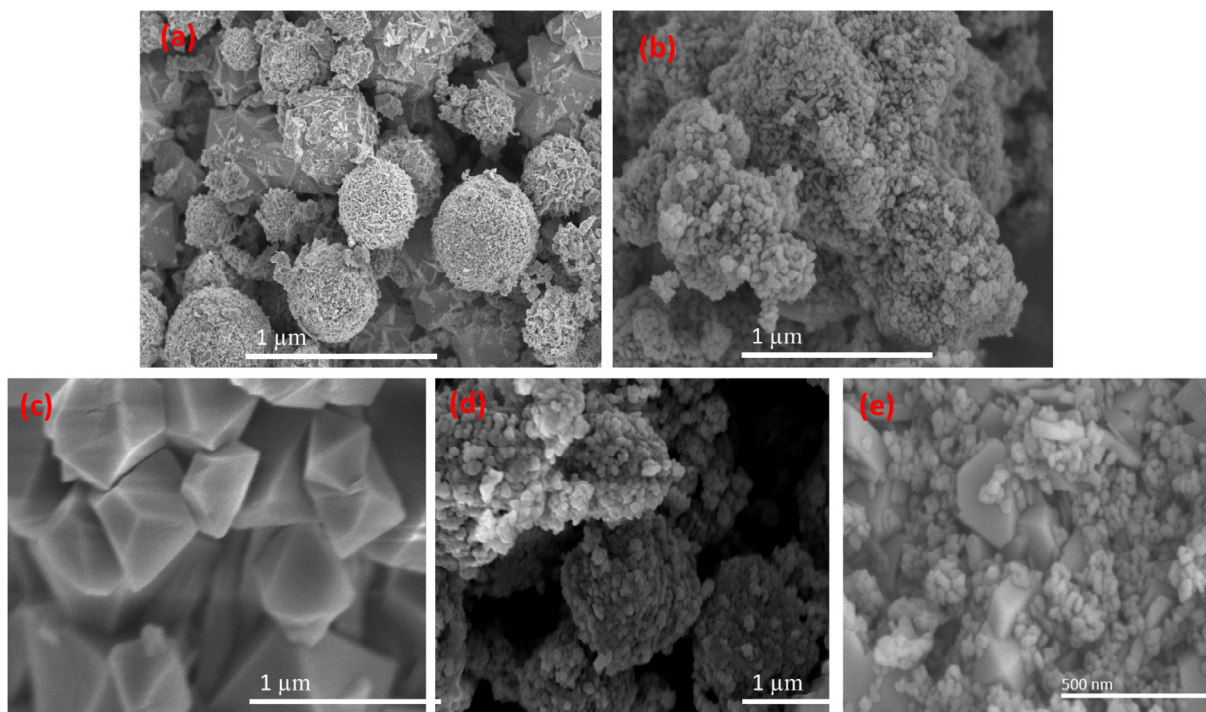


Fig. 2. SEM images of (a) In_2S_3 , (b) TiO_2 , (c) MIL-101(Cr) and (d,e) TIM samples.

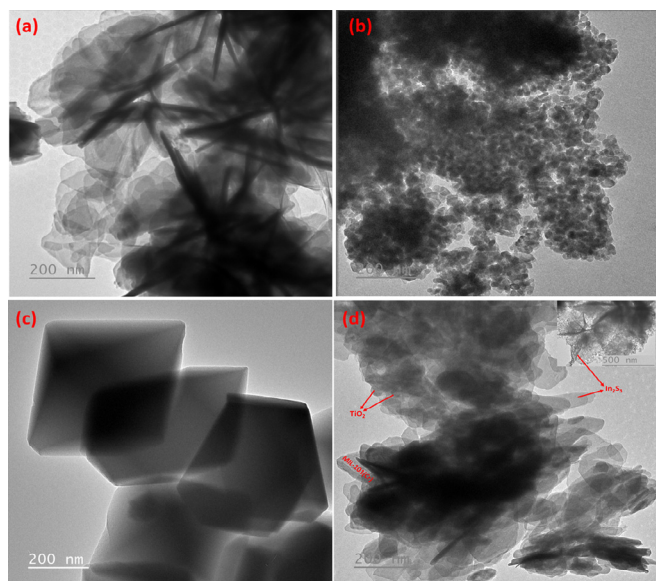


Fig. 3. TEM images of (a) In_2S_3 , (b) TiO_2 , (c) MIL-101(Cr), and (d) TIM samples ((inset, 500 nm of size).

at 530.32 eV (O–C=O), 531.02 eV (oxygen in the crystal lattice), and 532.72 eV (chemisorbed oxygen) [46–49]. These observations suggest that electron density is transferred from the TiO_2 and MIL-101 (Cr) phases to the In_2S_3 phase, leading to an increase in the electron density of In_2S_3 and a decrease in that of TiO_2 and MIL-101(Cr) in the TIM composite.

This electron transfer between components indicates efficient charge carrier separation and migration, which is further supported by changes in binding energy positions [50]. The bond formation between $\text{TiO}_2@/\text{In}_2\text{S}_3$ and MIL-101(Cr) establishes a heterojunction with a S-scheme, enhancing photocatalytic activity by improving charge carrier transport and separation.

The nitrogen adsorption–desorption isotherms and calculated textual characteristics are shown in Fig. 6 and Table 1. The isotherms of the obtained samples correspond to type I and IV, according to the IUPAC classification. The BET surface area of pure In_2S_3 and TiO_2 was found to be $108 \text{ m}^2\cdot\text{g}^{-1}$ and $96 \text{ m}^2\cdot\text{g}^{-1}$, respectively. In contrast, the TIM composite material exhibits a decrease in both specific surface area and total pore volume ($S_{\text{BET}} = 956 \text{ m}^2\cdot\text{g}^{-1}$, $V_{\text{pore}} = 0.60 \text{ cm}^3\cdot\text{g}^{-1}$) compared to pristine MIL-101 (Cr) ($S_{\text{BET}} = 1965 \text{ m}^2\cdot\text{g}^{-1}$, $V_{\text{pore}} = 0.96 \text{ cm}^3\cdot\text{g}^{-1}$). Nevertheless, these values remain relatively high, providing the composite with a considerable number of active sites, which are advantageous for adsorption processes and photocatalytic activity. Furthermore, the pore size, with diameters ranging from 2.09 to 2.22 nm, shows no significant change following the incorporation of $\text{TiO}_2@/\text{In}_2\text{S}_3$. These findings, in conjunction with XRD and SEM analyses, confirm that the TIM nanocomposite retains the structural characteristics of the MIL-101(Cr) framework.

The optical absorption behavior and electronic properties of the TIM heterostructure were systematically examined to elucidate the relationship between structural features and photocatalytic performance. As illustrated in Fig. 7A, the absorption spectrum of MIL-101(Cr) (blue curve) exhibits two distinct peaks, which can be attributed to $\pi \rightarrow \pi$ and $n \rightarrow \pi$ electronic transitions associated with the organic linker (terephthalic acid), as well as ligand-to-metal charge transfer (LMCT) processes and possible d–d transitions involving Cr^{3+} centers within the MOF framework [51]. These characteristic spectral features are indicative of the well-defined and highly ordered electronic structure of MIL-101(Cr). In contrast, the absorption spectrum of the TIM composite (orange curve) no longer displays the characteristic peaks of MIL-101(Cr), indicating substantial alterations in the electronic structure. This spectral modification is likely a result of strong interfacial interactions among the three constituents of the composite, which can induce significant changes in the electronic band structure and facilitate efficient interfacial charge transfer. Such interfacial effects are consistent with previously reported observations in MOF–semiconductor hybrid systems, where the formation of intermediate

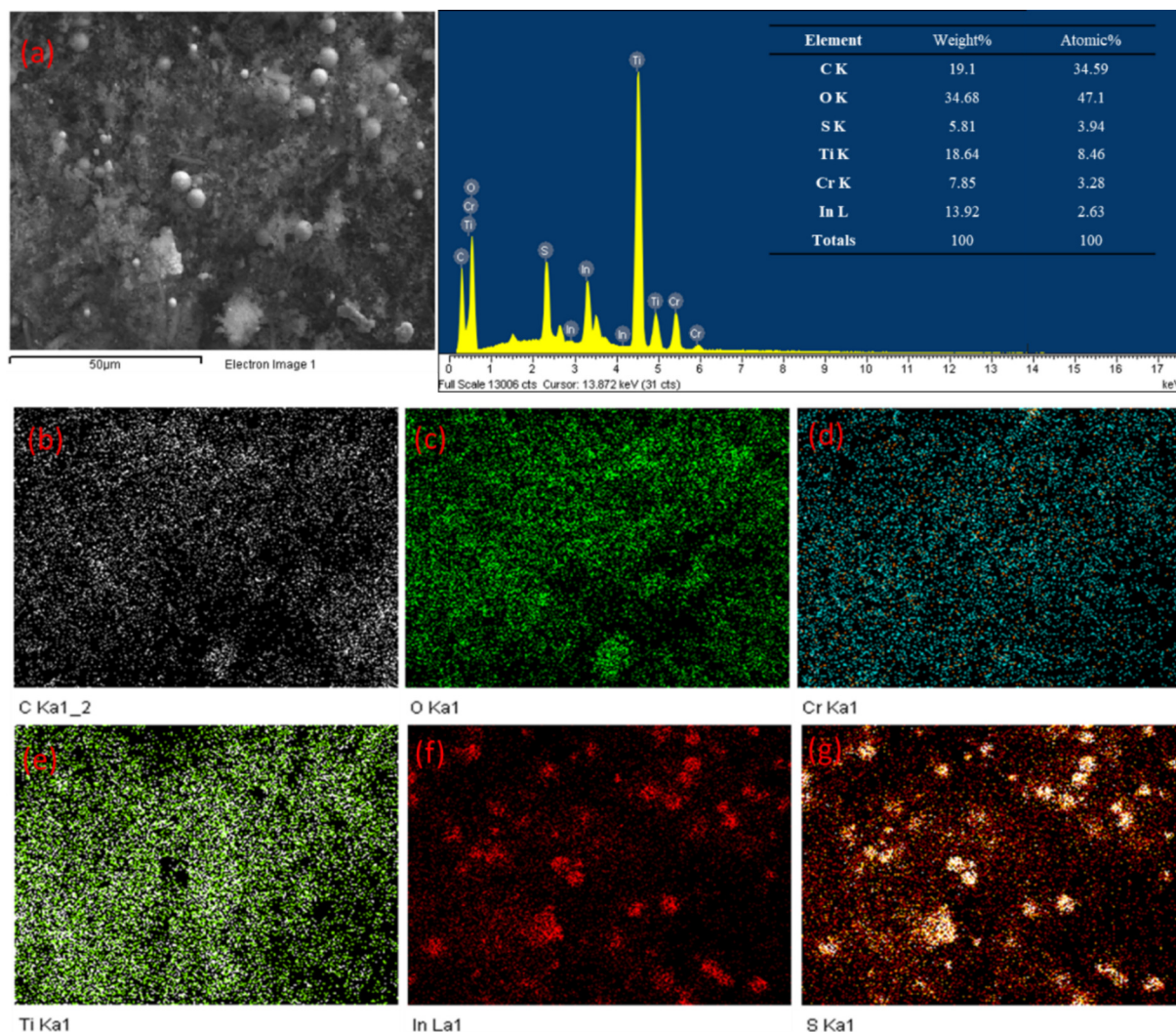


Fig. 4. (a) EDX spectrum and SEM micrograph with elemental mapping of (b) carbon, (c) oxygen, (d) chromium, (e) titanium, (f) indium, and (g) sulfur of TIM nanocomposite.

energy states, hybridized conduction bands, and extended absorption edges has been documented [52]. These changes not only broaden the optical absorption range but also suppress the individual absorption features of the pristine components. This synergistic interaction is expected to play a crucial role in enhancing charge separation and transport processes, ultimately contributing to the improved photocatalytic performance of the TIM heterostructure. Corresponding Tauc plots (Fig. 7B) reveal that the TIM composite possesses a reduced optical band gap of approximately 2.70 eV, suggesting strong electronic coupling and effective interfacial interaction between the semiconductor constituents [53]. Such narrowing of the band gap is beneficial for promoting visible-light-driven photocatalysis.

To gain further insight into the band structure alignment and charge separation behavior, Mott-Schottky analysis was conducted (Fig. 7C). The results confirm that MIL-101(Cr) possesses conduction band characteristics conducive to favorable band alignment when coupled with TiO_2 and In_2S_3 . This configuration facilitates a S-scheme charge transfer mechanism, wherein photogenerated electrons from the conduction band of In_2S_3 migrate through MIL-101(Cr) to TiO_2 , while holes are transferred in the opposite direction. This bidirectional transfer pathway effectively suppresses electron-hole recombination, a key factor limiting photocatalytic efficiency in single-component systems [54,55].

Electrochemical impedance spectroscopy (EIS) results further corroborate the improved interfacial charge dynamics of the TIM composite. As illustrated in the Nyquist plots (Fig. 7D), the TIM sample exhibits the smallest semicircular diameter among all tested materials, indicating the lowest charge transfer resistance. Although In_2S_3 alone shows a relatively small arc, its narrow band gap (1.86 eV) leads to severe recombination of charge carriers. In contrast, the TIM composite achieves a balance between efficient charge transport and enhanced carrier separation, attributed to the synergistic effects among its components.

3.2. Photocatalytic degradation of tetracycline

To evaluate the catalytic performance of the synthesized materials, the degradation of TC was initially examined in individual systems. The results indicated that TiO_2 and In_2S_3 exhibited limited photocatalytic activity, with each material achieving less than 40% TC removal ($30 \text{ mg}\cdot\text{L}^{-1}$) after 30 min of irradiation. In comparison, MIL-101(Cr) demonstrated superior efficiency, removing over 50% of TC within the same time frame and reaching a removal rate of 76.16% after 210 min (Fig. 8a). In contrast, the TIM composite exhibited markedly enhanced performance, removing approximately 55% of TC within the first 30 min and achieving up to 97% removal after 210 min of irradiation. This significant improvement

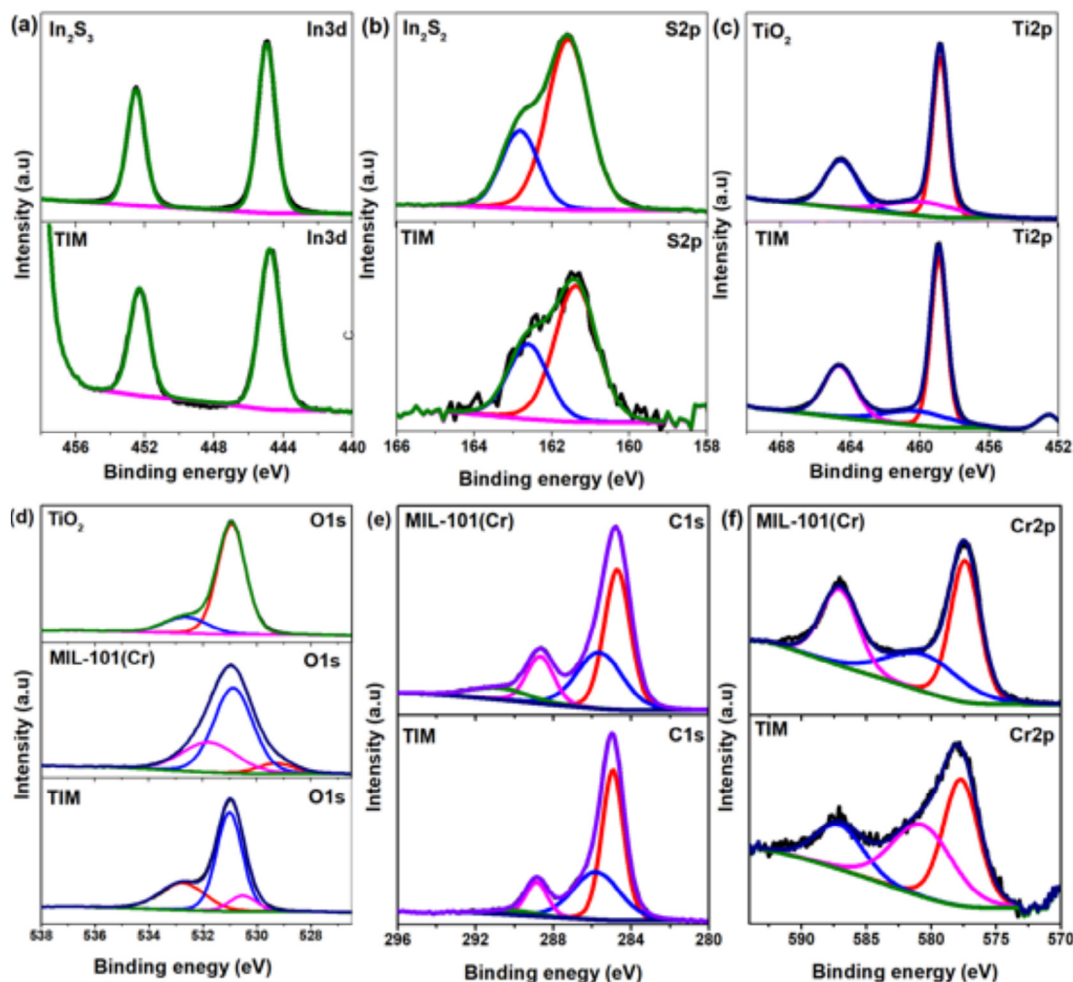


Fig. 5. High-resolution In 3d, S 2p, Ti 2p, Cr 2p, O 1s and C 1s XPS spectra of In_2S_3 , TiO_2 , MIL-101(Cr) and TIM nanocomposite.

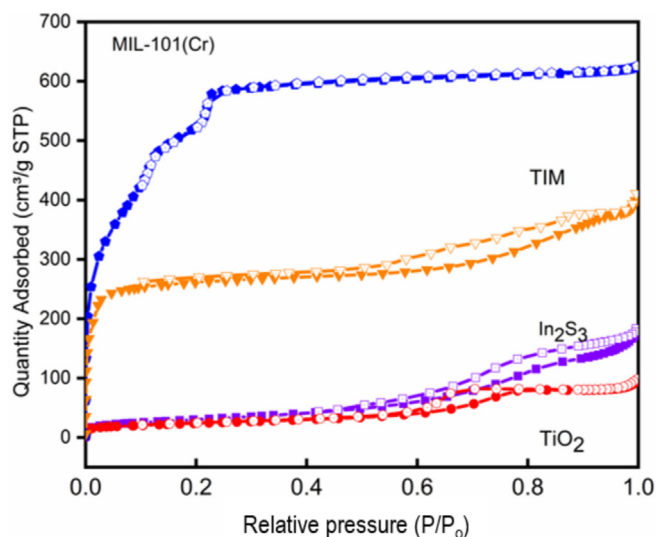


Fig. 6. Nitrogen adsorption-desorption isotherms of TiO_2 , In_2S_3 , MIL-101(Cr) and TIM samples.

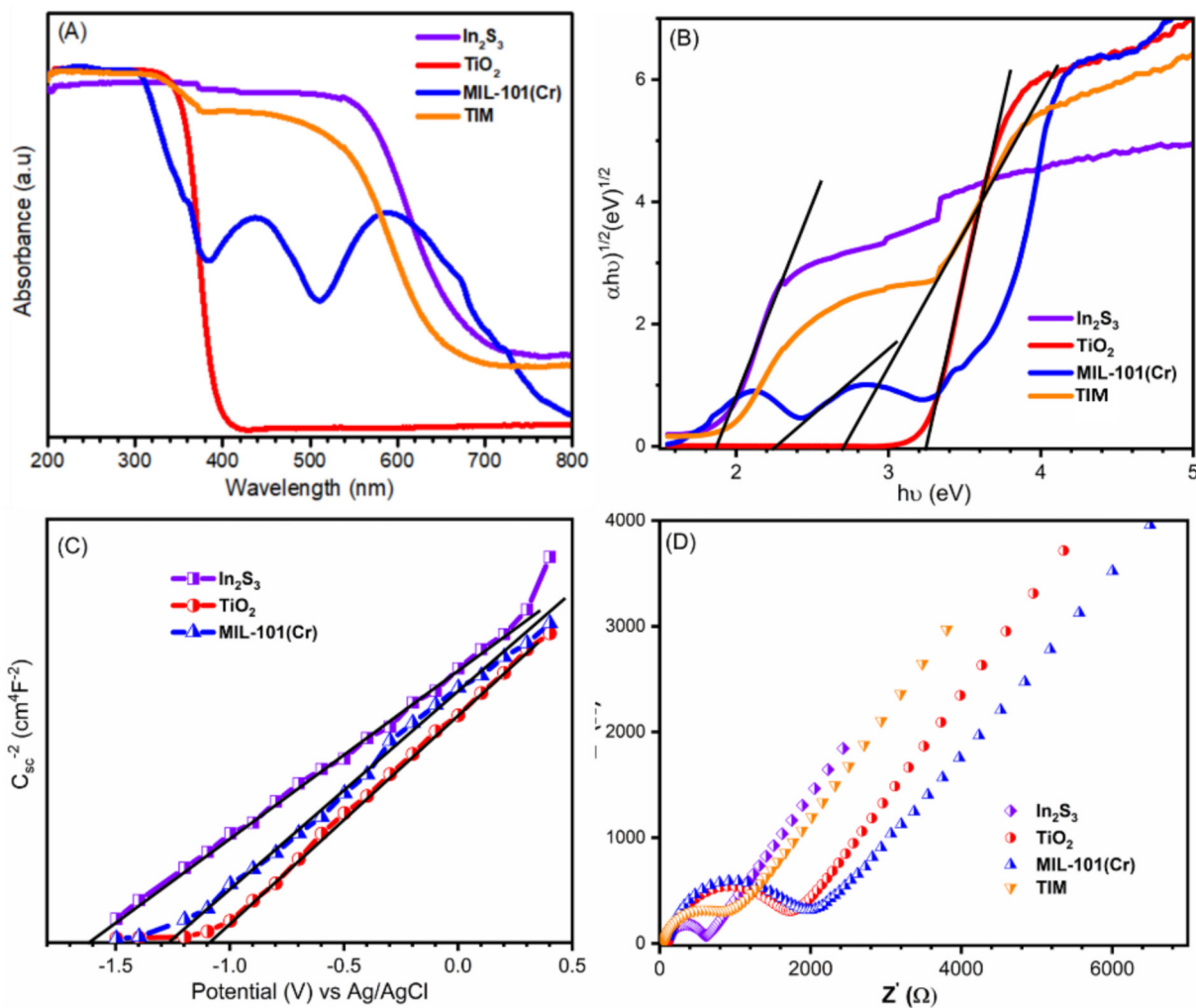
highlights the superior photocatalytic efficiency of the TIM nanocomposite relative to the individual components. The enhanced activity is primarily attributed to the unique architecture

of the composite, which incorporates spherical anatase-phase TiO_2 and microspherical In_2S_3 assembled from interconnected two-dimensional nanosheets. The formation of a heterojunction structure – confirmed by XPS – facilitates more rapid and efficient charge transfer, as further supported by EIS measurements. Moreover, the TIM nanocomposite exhibits a remarkably increased specific surface area ($956 \text{ m}^2 \cdot \text{g}^{-1}$), significantly higher than that of pure In_2S_3 ($108 \text{ m}^2 \cdot \text{g}^{-1}$) and TiO_2 ($95.97 \text{ m}^2 \cdot \text{g}^{-1}$), owing to the structural support provided by MIL-101(Cr). Importantly, MIL-101(Cr) does not merely act as a passive support but plays an active role in facilitating charge transport through its metal-oxo cluster framework. The observed enhancement in charge mobility suggests that MIL-101(Cr) provides conductive pathways that aid in the efficient migration of photogenerated carriers within the composite [56]. This behavior is critical for sustaining long-lived charge carriers and continuous redox activity during photocatalytic reactions. Collectively, these findings highlight the multifunctional role of MIL-101(Cr) in the TIM heterostructure: (i) improving light absorption, (ii) promoting directional charge transfer via favorable band alignment, and (iii) reducing interfacial charge transfer resistance. The integration of TiO_2 , In_2S_3 , and MIL-101(Cr) into a coherent S-scheme system results in a highly synergistic architecture with markedly enhanced photocatalytic performance compared to individual or binary systems.

Environmental conditions play a crucial role in influencing pollutant treatment efficiency. In this study, we investigated the effect of different pH values (3, 5, 7, and 9) at room temperature (30°C)

Table 1Textual characteristics and band gap energies of TiO₂, In₂S₃, MIL-101(Cr) and TIM samples.

Samples	S _{BET} (m ² .g ⁻¹)	V _{pore} (cm ³ .g ⁻¹)	D _{BHJH} (nm)	E _g (eV)
In ₂ S ₃	108	0.26	8.85	1.86
TiO ₂	96	0.19	6.94	3.24
MIL-101(Cr)	1965	0.96	2.09	2.28
TIM	956	0.60	2.22	2.70

**Fig. 7.** (A) UV-Vis DRS spectrum, (B) band gap energies, (C) Mott-Schottky, and (D) EIS of In₂S₃, TiO₂, MIL-101(Cr), and TIM samples.

on the removal of TC. The results showed that the TIM photocatalyst removed 72.82%, 98.67%, 92.90%, and 82.83% of TC after 180 min at pH 3, 5, 7, and 9, respectively (Fig. 8b). The lower removal efficiency at strongly acidic (pH = 3) and basic (pH = 9) conditions is attributed to the repulsive forces between the photocatalyst and the pollutant, as they carry the same charge. In contrast, at neutral or slightly acidic pH, electrostatic interactions are observed between the negatively charged TC pollutant and the positively charged photocatalyst surface [57,58].

To determine the active species participating in the photoredox reaction during TC degradation, we used 4 mmol.L⁻¹ of ammonium oxalate monohydrate, isopropyl alcohol, and 1,4-benzoquinone as scavengers for holes (h⁺), hydroxyl radical (*OH), and superoxide radical anion (*O₂⁻), respectively. As shown in Fig. 9, a significant

decrease in TC degradation was observed in the presence of isopropyl alcohol and ammonium oxalate monohydrate. This suggests that superoxide radical anions and holes are the primary active species responsible for the photocatalytic degradation of TC in visible light using the TIM photocatalyst.

Experiments were carried out to quench the reactive radicals, aiming to better understand the photocatalytic mechanism of the TIM photocatalyst in the TC treatment process. When p-BQ was added to capture the superoxide radical (*O₂⁻), the TC treatment efficiency of the TIM photocatalyst decreased to 58.3%. Similarly, the addition of isopropyl alcohol (IPA), a scavenger for holes (h⁺), and ammonium oxalate (AO), a scavenger for hydroxyl radicals (*OH), resulted in TC treatment efficiencies of 74.46% and 76.50%, respectively, after 180 min of visible light irradiation. These results

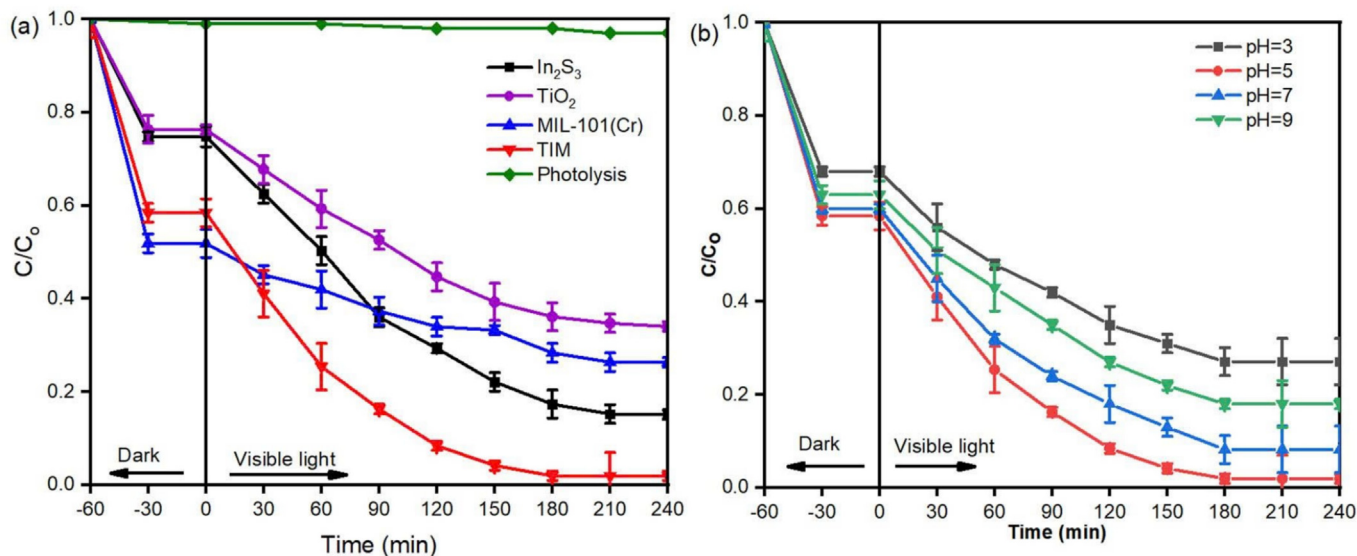


Fig. 8. (a) Effect of the different photocatalysts, and (b) effect the initial pH of TC using TIM as photocatalyst on removal efficiency of tetracycline (photocatalyst loading 40 mg, and 30 $\text{mg}\cdot\text{L}^{-1}$ TC).

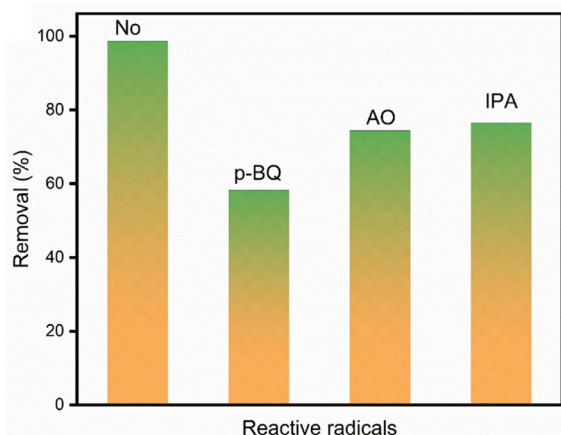


Fig. 9. Photodegradation of TC using TIM with different quenching radical agents (p-BQ, AO, and IPA).

suggest the following order of contribution to the degradation of TC: $\cdot\text{O}_2^- > \text{h}^+ > \cdot\text{OH}$. This finding aligns well with the band potential calculations based on Mott-Schottky plots.

To gain a more comprehensive understanding of the optical properties of the semiconductors, Mott-Schottky analysis was employed to determine their flatband potentials at a frequency of 500 Hz (Fig. 7C). Based on the conversion between the Ag/AgCl reference electrode and the standard hydrogen electrode (SHE), the VB and CB edge positions of the materials were estimated. For In_2S_3 , the VB and CB positions were determined to be 0.84 eV and -1.02 eV, respectively. In the case of TiO_2 , the corresponding values were 2.77 eV and -0.47 eV, while for MIL-101(Cr), the VB and CB positions were 1.63 eV and -0.65 eV, respectively.

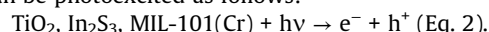
In the S-scheme heterojunction photocatalytic composite system $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101(Cr)}$ (Fig. 10), photogenerated electrons in the reduction-type photocatalyst In_2S_3 migrate to the oxidation-type photocatalyst TiO_2 and/or MIL-101(Cr) at the interface. As a result, In_2S_3 becomes electron-deficient, while TiO_2 and/or MIL-101(Cr) gain electrons, leading to the formation of an internal electric field directed from In_2S_3 to TiO_2 and/or MIL-101(Cr). Upon light irradiation, photogenerated electrons in the conduction

band of TiO_2 and/or MIL-101(Cr) recombine with photogenerated holes in the valence band of In_2S_3 due to Coulombic attraction. Consequently, the high-energy electrons in In_2S_3 and the photo-generated holes in TiO_2 and/or MIL-101(Cr) are preserved, thereby maximizing the redox capability of the S-scheme heterojunction photocatalytic system.

As illustrated in Fig. 10A, the CB potentials of TiO_2 , MIL-101(Cr), and In_2S_3 are all more negative than the reduction potential of O_2/O_2^- ($E^0 = -0.33$ eV vs. NHE) [59], enabling the photogenerated electrons in these materials to reduce adsorbed molecular oxygen on the photocatalyst surface to generate superoxide radicals ($\cdot\text{O}_2^-$) (Eq. 3). In contrast, the VB potentials of In_2S_3 (0.84 eV) and MIL-101(Cr) (1.63 eV) are insufficient to oxidize H_2O to hydroxyl radicals ($\cdot\text{OH}$), since the oxidation potential of $\text{H}_2\text{O}/\cdot\text{OH}$ is 2.40 eV [60]. However, TiO_2 , with a VB position at 2.77 eV, is thermodynamically capable of oxidizing surface-adsorbed water or hydroxide ions to form $\cdot\text{OH}$ radicals (Eq. 4).

During the photocatalytic degradation of TC using the $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101(Cr)}$ composite, the formation of $\cdot\text{OH}$ radicals is confirmed and found to play a significant role in the degradation process. If the photocatalyst were to operate via a conventional n-n type heterojunction, photogenerated holes from TiO_2 and MIL-101(Cr) would migrate to the VB of In_2S_3 . However, due to the lower VB potential of In_2S_3 (0.84 eV), these holes would lack sufficient oxidation potential to generate $\cdot\text{OH}$ radicals from H_2O , rendering the n-n transfer pathway ineffective for this reaction. Furthermore, XPS results reveal a decrease in electron density for the TiO_2 and MIL-101(Cr) phases, alongside an increase in the electron density of In_2S_3 . This observation supports the hypothesis that electrons are transferred from In_2S_3 and MIL-101(Cr) to TiO_2 , suggesting a directional electron flow across the heterojunction.

Based on the band alignment and radical generation evidence, a S-scheme charge transfer mechanism is proposed for the $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101(Cr)}$ photocatalyst, as illustrated in Fig. 10B. Under visible light irradiation (with photon energy > 2.70 eV), electrons (e^-) and holes (h^+) are photoexcited in all components of the composite can be photoexcited as follows:



MIL-101(Cr) can act either as an electron donor or acceptor depending on the direction of the energy level difference. The conduction band of MIL-101(Cr) lies between those of TiO_2 and In_2S_3 ,

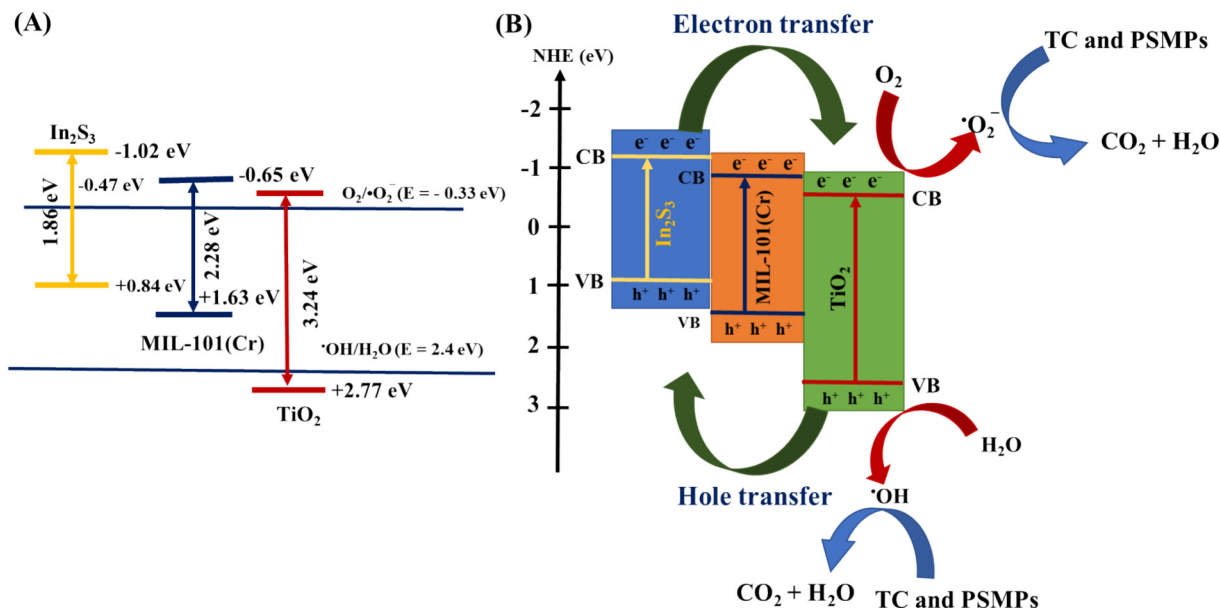


Fig. 10. S-scheme charge transfer mechanism in $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101}(\text{Cr})$ composite: (A) Before and (B) After interfacial contact under visible light irradiation.

suggesting that MIL-101(Cr) functions as an electron mediator. When photogenerated electrons are produced in In_2S_3 , they can transfer successively through MIL-101(Cr) to TiO_2 . Conversely, holes from TiO_2 (with a higher valence band) can migrate to the VB of MIL-101(Cr).

As a result, a three-dimensional charge transport network is formed, rather than a unidirectional transfer path as in the binary $\text{TiO}_2/\text{In}_2\text{S}_3$ heterojunction. The possible charge transfer pathways can be described as follows: Electron transfer from $\text{In}_2\text{S}_3 \rightarrow \text{MIL-101}(\text{Cr}) \rightarrow \text{TiO}_2$; hole transfer from $\text{TiO}_2 \rightarrow \text{MIL-101}(\text{Cr}) \rightarrow \text{In}_2\text{S}_3$. Thus, in this study, the proposed mechanism is more likely to follow the electron-mediated mechanism, where MIL-101(Cr) serves as an efficient charge transfer bridge. This assumption is also consistent with previous studies [61,62].

The remaining electrons in the In_2S_3 CB can react with molecular oxygen to form superoxide radicals (O_2^-): $\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$ (Eq. 3), while the holes in the TiO_2 VB (2.77 eV) can oxidize H_2O and OH^-

to generate hydroxyl radicals ($\text{OH}^\bullet$): $\text{TiO}_2 (\text{h}^+) + \text{H}_2\text{O}/\text{OH}^- \rightarrow \text{OH}^\bullet$ (Eq. 4). These reactive species— O_2^- , $\text{OH}^\bullet$, and h^+ —collectively contribute to the effective photocatalytic degradation of TC, ultimately leading to its mineralization into harmless end-products.

3.3. Polystyrene microplastic adsorption process

The Z-average particle size of the obtained PSMPs was measured using dynamic light scattering (DLS). The particle size distribution, based on intensity measurements at pH 5 and 25 °C, revealed that the PSMPs had a particle size in the range of 400 nm (Fig. 11).

As shown in Fig. 12a, the adsorption of PSMPs was lower for In_2S_3 (25.82%) and TiO_2 (28%) compared to MIL-101(Cr) (96.32%) and TIM (95%). This behavior can be explained by the strong π - π interactions between the aromatic ring structure of terephthalic acid in MIL-101(Cr) and the polystyrene. Additionally, the surface

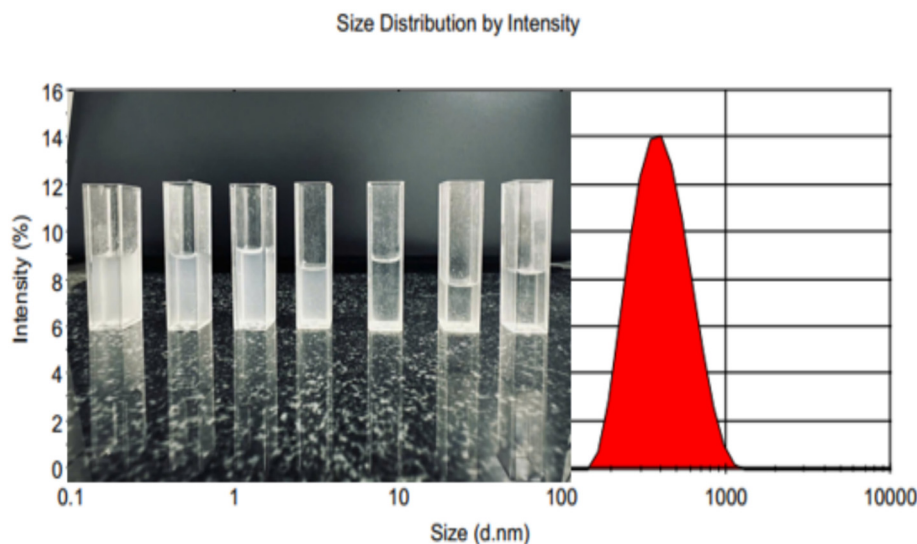


Fig. 11. Suspension imaging and DLS particle size quantification of PS microplastics.

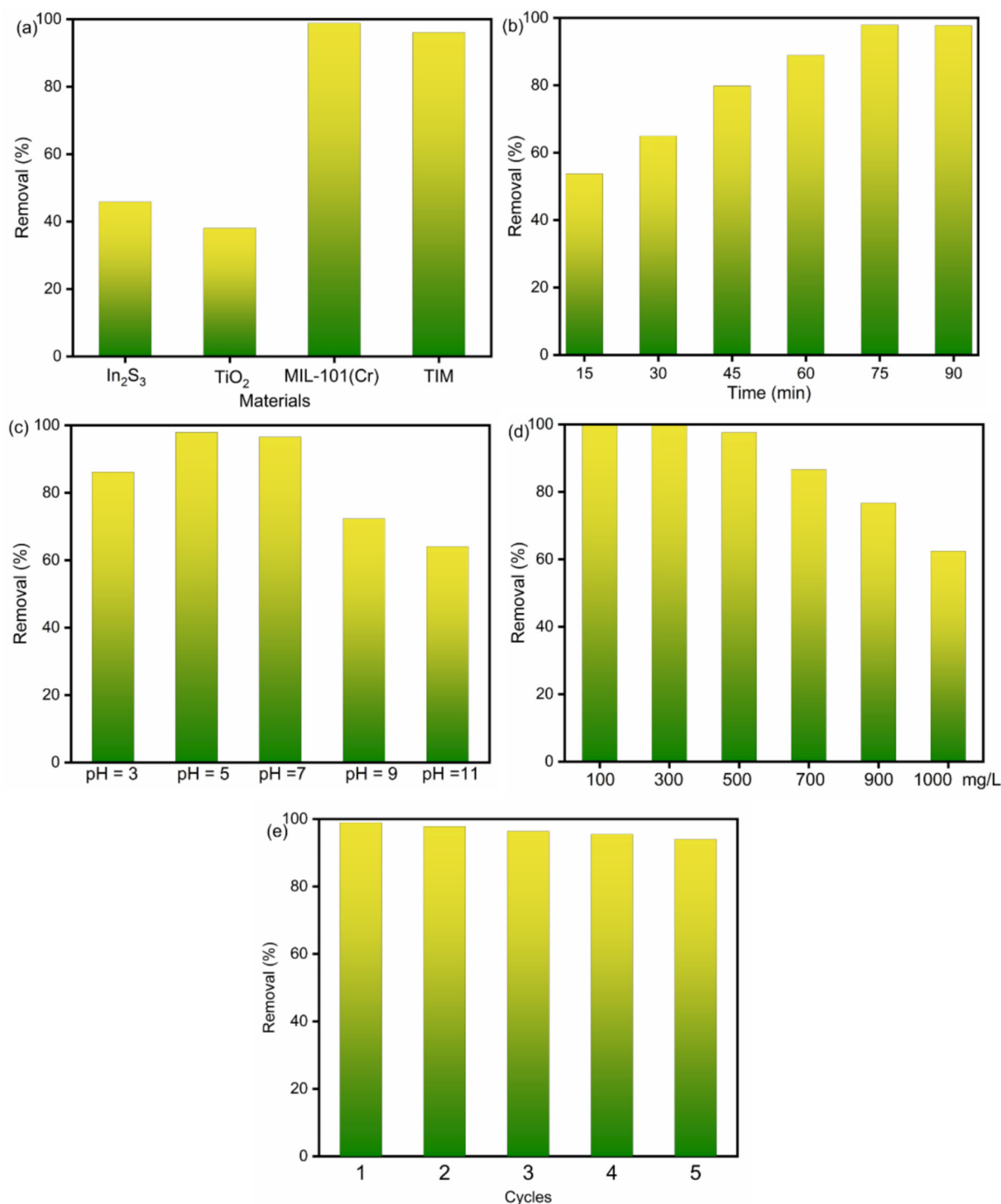


Fig. 12. (a) PS microplastic adsorption performance of In₂S₃, TiO₂, MIL-101(Cr) and TIM samples; Effects of adsorption time (b), pH value (c), PS microplastic concentration (d) and durability after five reaction cycles (e) on TIM sample.

areas of In₂S₃ (108 m².g⁻¹) and TiO₂ (96 m².g⁻¹) are lower than those of MIL-101(Cr) (1965 m².g⁻¹) and TiO₂@In₂S₃/MIL-101(Cr) (956 m².g⁻¹). Notably, the adsorption of PSMPs by TIM was slightly reduced compared to MIL-101(Cr), likely due to differences in surface area and pore volume. This emphasizes how crucial surface area and pore volume are for the mass transfer of pollutants from the bulk liquid to the adsorbent's surface (external mass transfer) and their diffusion into the pores.

The adsorption of PSMPs was strongly dependent on the solution pH (Fig. 12c). At pH 5, the adsorption efficiency exceeded 95% for both MIL-101(Cr) and TIM. The adsorption efficiency increased in the acidic range from pH 3 to pH 5, but decreased significantly as the pH became more basic, from pH 5 to pH 11. At pH 3 and 5, the negatively charged PSMPs and the positively charged TIM promoted electrostatic interactions, thus enhancing the adsorption capacity. At pH 7–11, the adsorption efficiency

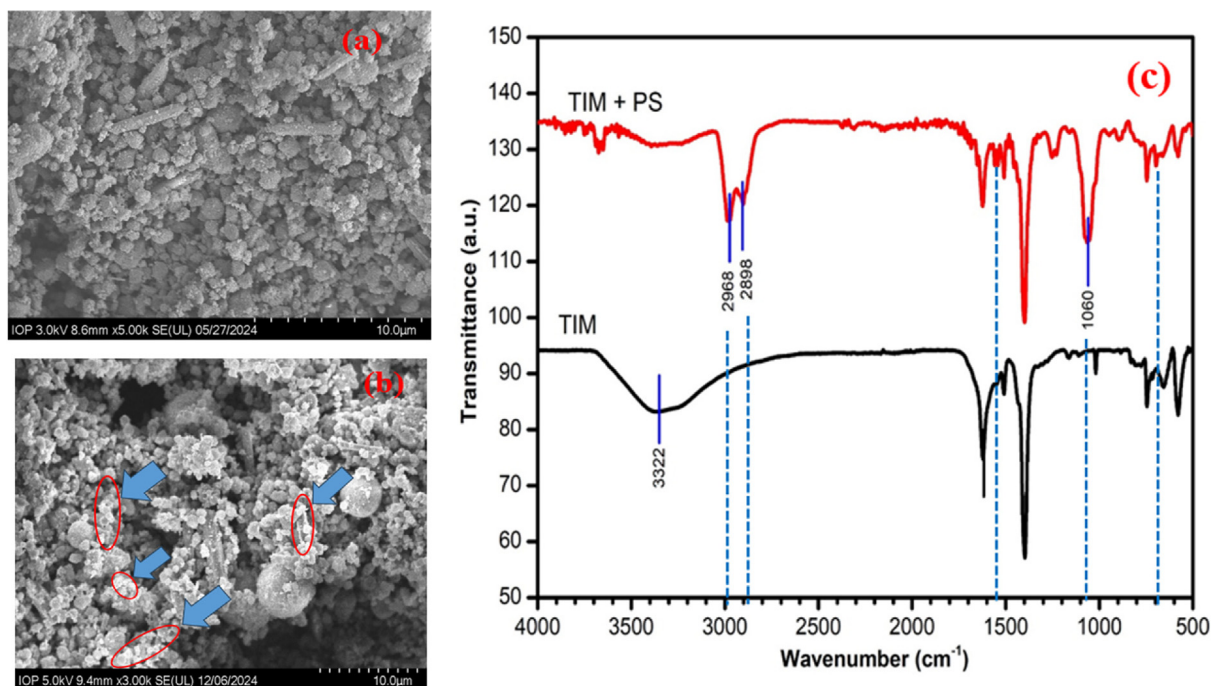


Fig. 13. Ex situ SEM image of (a) TIM and (b) PS microplastic adsorption over TIM; (c) Ex situ FT-IR spectra of TIM and PS microplastic adsorption on TIM.

decreased, likely due to the reduction in the positive charge on the TIM surface under basic conditions. A sharp decrease in adsorption efficiency was observed at pH 11, where the surface charge of TIM became negative, leading to repulsive interactions with the negatively charged PSMPs.

Fig. 12d demonstrates that the initial concentration of PSMPs impacts the adsorption efficiency using TIM. The data shows a negative correlation between the initial concentration of microplastics and their removal efficiency. As the concentration increased from 500 to 1000 mg.L⁻¹, the removal efficiency decreased significantly from 100% to 60%, respectively, after 90 min of adsorption. However, at concentrations between 100 and 300 mg.L⁻¹, the material effectively removed up to 100% of the microplastics in the same time period. These results underscore the excellent adsorption capacity of the TIM material, which is approximately 500 mg.g⁻¹ under atmospheric pressure and ambient temperature (30 °C). This

shows the material's effective adsorption at lower concentrations of PSMPs.

SEM and FT-IR analyses were employed to examine the PSMPs loading capacity of the TIM material after 90 min of the adsorption process, providing more detailed insights into the adsorption mechanism. SEM imaging of TIM after adsorption revealed that the PSMPs were spherical in shape and exhibited a uniform distribution across the material surface, as shown in Fig. 13b.

The FT-IR spectrum of TIM after adsorption reveals characteristic vibration peaks corresponding to PSMPs (Fig. 13c). Specifically, a peak at 695 cm⁻¹ is observed, which corresponds to the out-of-plane phenyl ring vibration [63]. The peak at 1060 cm⁻¹ is attributed to in-plane C-H vibrations, while peaks at 2968 cm⁻¹ and 2898 cm⁻¹ correspond to aliphatic C-H stretching vibrations. A band at 1560 cm⁻¹ indicates C-C bond stretching vibrations of aromatic compounds [52]. These features align with the styrene

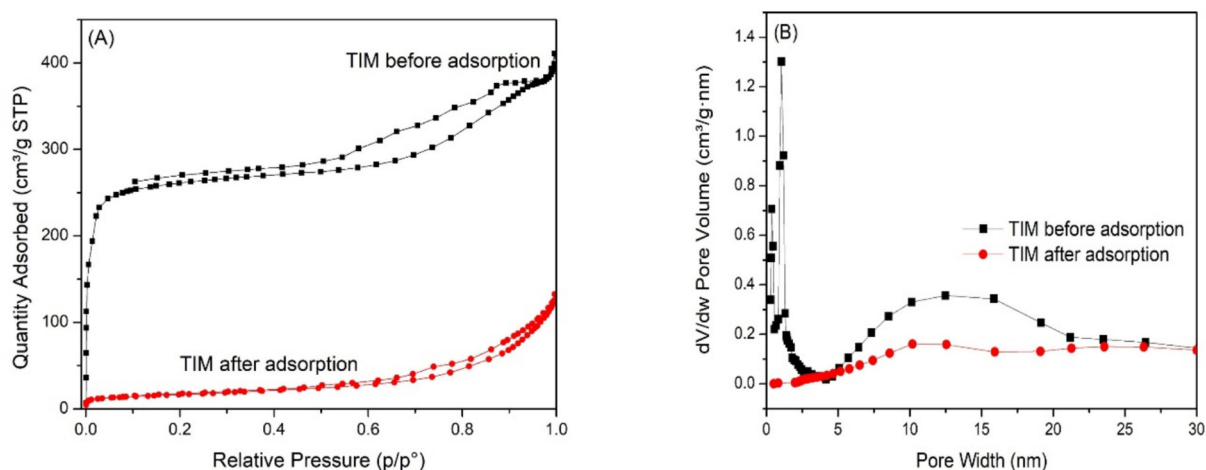


Fig. 14. (A) Nitrogen adsorption-desorption isotherms, and (B) pore size distributions of TIM before and after PSMPs adsorption.

structure, verifying that PSMPs were successfully adsorbed onto the TIM surface.

In addition, the pore characteristics of the composite TIM after saturated adsorption of PSMPs were analyzed. As shown in Fig. 14, the BET surface area and pore volume of the TIM after PSMPs adsorption were found to be $949.2 \text{ m}^2\cdot\text{g}^{-1}$ and $0.578 \text{ cm}^3\cdot\text{g}^{-1}$, respectively. Meanwhile, the BET surface area and pore volume of the original TIM were $956 \text{ m}^2\cdot\text{g}^{-1}$ and $0.60 \text{ cm}^3\cdot\text{g}^{-1}$, respectively. This difference between the TIM samples before and after adsorption indicates that PS microplastics had occupied the pore structure of the TIM after adsorption.

3.4. Stability and reusability of $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101}(\text{Cr})$

To assess the stability and reusability of the adsorbent, TIM was regenerated after saturated adsorption of PSMPs using anhydrous ethanol as the solvent. The adsorbent was separated, dispersed into the solvent, and shaken for 30 min on a shaker, then filtered using a $0.1 \mu\text{m}$ filter. Subsequently, the adsorbent was thoroughly rinsed multiple times with distilled water to eliminate any remaining solvent. Once fully eluted, TIM was dried at 70°C for 3 h and reused in subsequent adsorption cycles.

Ethanol was chosen for the regeneration process due to its ethoxide groups, which enhance the solubility of PSMPs without compromising the structure and active sites of the adsorbent. The adsorption efficiency of the regenerated TIM decreased slightly from 97% in the first cycle to 96% in the second, 95% in the third, and finally 94% in the fourth cycle, as shown in Fig. 12e. This gradual decrease is likely attributable to the use of ethanol, which

effectively dissolves PSMPs while exerting minimal impact on the performance of the adsorbent.

To assess the material's structural stability, XRD and BET analyses were conducted on the sample after five consecutive adsorption cycles (Fig. 15). The results showed that the BET surface area was $951.4 \text{ m}^2\cdot\text{g}^{-1}$, which is very similar to the original surface area of TIM ($956 \text{ m}^2\cdot\text{g}^{-1}$). Additionally, XRD analysis confirmed that the material's structural characteristics remained intact, further supporting its excellent stability over multiple cycles.

Table 2 demonstrates the superiority of the heterostructure in TIM, which not only exhibits superior adsorption efficiency but also requires shorter adsorption times while effectively removing both pollutants. This makes it a promising candidate for large-scale industrial applications.

3.5. Simultaneous removal of polystyrene microplastic and tetracycline

TIM was further tested in a binary system containing both PSMPs and TC. In the simultaneous removal experiment, PSMPs were removed by 78% after 90 min and completely removed (100%) after 180 min, while TC reached 100% removal efficiency after 240 min under visible light irradiation (Fig. 16). This improved performance is due to the combination of active phases that boost charge separation, reduce the recombination of photo-generated holes and electrons, and enable efficient charge carrier transfer. These results are corroborated by UV-Vis DRS and EIS data, as presented in Fig. 7. Consequently, the TIM material has demonstrated excellent simultaneous treatment of PSMPs and TC

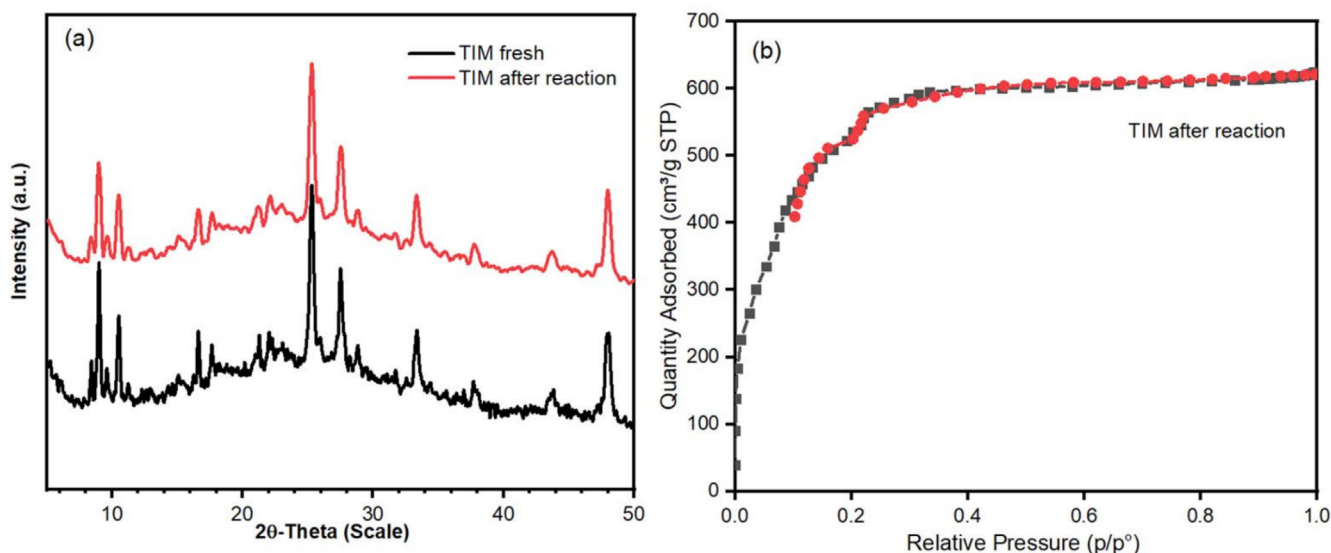


Fig. 15. (a) *Ex situ* XRD of TIM fresh and after PS microplastic adsorption, (b) nitrogen adsorption-desorption isotherm of TIM after PS microplastic adsorption.

Table 2

Comparison of the adsorption efficiency of PS microplastics on various materials.

Materials	MP type	MP conc. ($\text{mg}\cdot\text{L}^{-1}$)	Adsorbent dosage ($\text{g}\cdot\text{L}^{-1}$)	Removal time (min)	Removal efficiency (%)	Refs.
ZIF-67 MOF	PS	0.5	0.4	19.8	92.1	[21]
Zn loaded biochar	PS	100	1.0	300	99	[64]
$\text{g-C}_3\text{N}_4/\text{CQD}/\text{Fe}_8\text{Ni}_2\text{BTC}$	PS	1200	2.5	45	100	[29]
2D MOF@C@FeO	PS	1000	3.0	60	100	[20]
Nano-Fe@ZIF-8	PS	25	0.02	5	≥ 98	[65]
$\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101}(\text{Cr})$	PS	500	0.3	90	100	This study

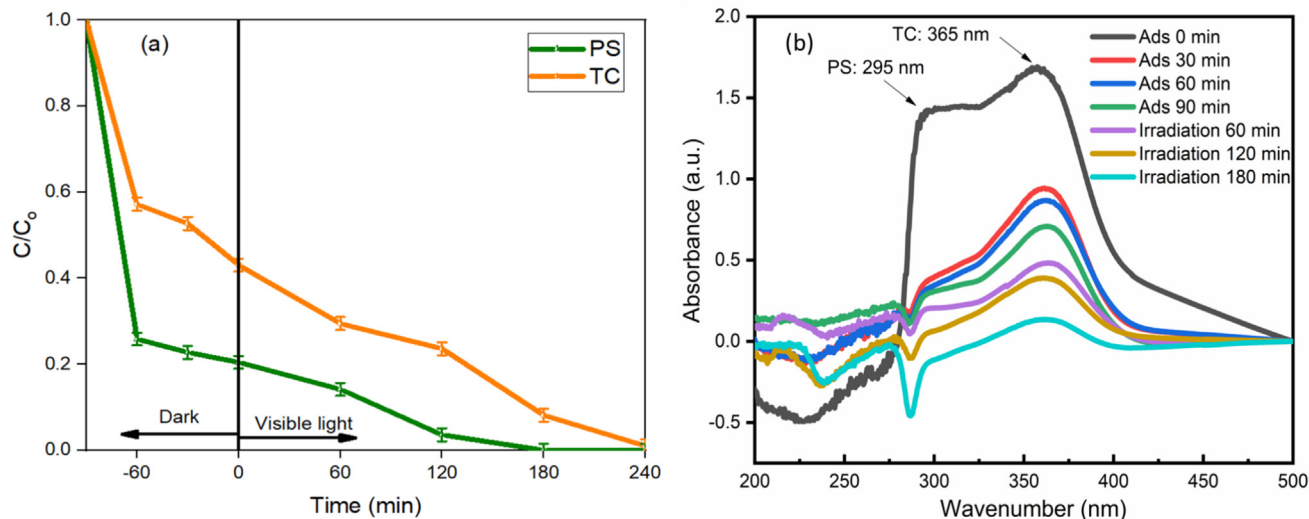


Fig. 16. (a) Removal efficiency and (b) UV-vis spectroscopy for the simultaneous removal of TC ($30 \text{ mg}\cdot\text{L}^{-1}$) and PSMPs ($500 \text{ mg}\cdot\text{L}^{-1}$) from water using TIM sample.

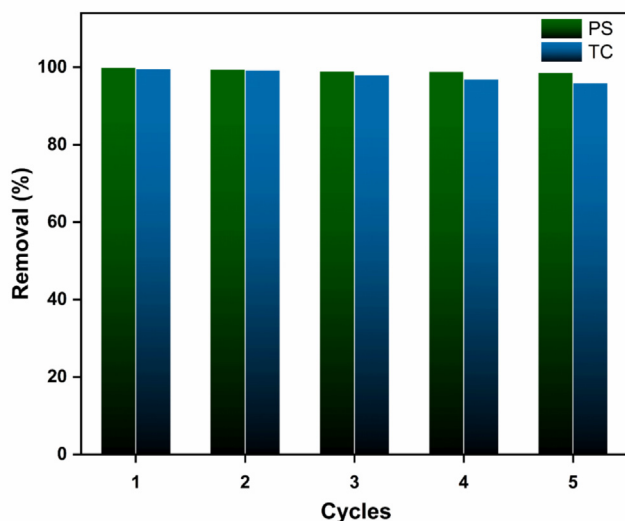


Fig. 17. Recycling tests of TIM composite for simultaneous removal of PSMPs and TC.

in water via a combination of adsorption and photocatalytic processes.

To evaluate the reusability of the TIM composite after the simultaneous removal of PSMPs and TC, the composite was collected by centrifugation, washed, and reused in subsequent cycles under the same reaction conditions. As shown in Fig. 17, the TIM composite demonstrated good reusability in PSMPs removal, with the removal efficiency remaining nearly unchanged after five reaction cycles. Moreover, the photocatalytic activity for TC degradation was also maintained, with the degradation efficiency slightly decreasing from 100% in the first cycle to 96% in the fifth cycle. These results indicate that the TIM composite exhibits good stability and reusability for the simultaneous removal of PSMPs and TC, which is crucial for its potential practical applications.

4. Conclusion

This study demonstrated the successful synthesis of a ternary $\text{TiO}_2/\text{In}_2\text{S}_3/\text{MIL-101}(\text{Cr})$ nanocomposite with outstanding multi-

functional performance in water purification. The composite achieved complete removal of polystyrene microplastics ($500 \text{ mg}\cdot\text{L}^{-1}$) within 90 min and 97% degradation of tetracycline ($30 \text{ mg}\cdot\text{L}^{-1}$) within 210 min under visible-light irradiation, while in mixed-pollutant systems it achieved 100% removal of both contaminants within 240 min. Such superior activity is attributed to the synergistic integration of TiO_2 and In_2S_3 within the MIL-101 (Cr) framework, which promotes efficient charge separation, extended light absorption, and high surface area for adsorption. In addition, TIM exhibited excellent reusability, retaining 94% efficiency after four cycles, as well as structural stability and effective performance across a broad pH range. These results highlight TIM as a promising candidate for advanced water treatment, providing a versatile and robust platform for the simultaneous elimination of microplastics and pharmaceutical pollutants under environmentally relevant conditions.

CRediT authorship contribution statement

Xuan N. Pham: Writing – original draft, Methodology, Data curation. **Hong Van T. Nguyen**: Writing – original draft, Methodology, Data curation. **Manh B. Nguyen**: Writing – original draft, Software, Formal analysis, Data curation. **T.-Thanh-Bao Nguyen**: Formal analysis, Data curation. **Quang Vinh Tran**: Writing – review & editing. **Huan V. Doan**: Writing – review & editing, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to express their sincere gratitude to the Ministry of Education and Training of Vietnam for the financial support provided through grant No. B2024.MDA-10.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ap.2026.105183>.

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