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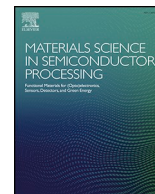
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Visible-light responsive Z-scheme Ti_3C_2 MXene/ In_2S_3 / CeO_2 heterojunction for enhanced photocatalytic water purification

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ABSTRACT

Sun-driven photocatalysis has emerged as a promising and sustainable approach for the degradation of organic pollutants in water, offering a green solution to the global challenge of clean water for everybody. The efficiency of this process is largely determined by advanced photocatalysts. Semiconductor-based heterojunctions play a crucial role by facilitating rapid charge transfer, acting as electron mediators for redox reactions, and accelerating photocatalytic activity through synergistic effects. In this study, we successfully fabricated a novel Ti_3C_2 MXene/ In_2S_3 / CeO_2 (TMIC) Z-scheme heterojunction using a simple in situ synthesis and deposition method. Initially, we determined that the optimal ratio of CeO_2 to In_2S_3 was 15 %. After incorporating Ti_3C_2 MXene, electro-optical measurements, and catalytic activity tests indicated that the Ti_3C_2 MXene_{0.0025}/ In_2S_3 / CeO_2 (TM_{0.025}IC-15 %) heterojunction exhibited the optimal photodegradation performance, degrading over 92 % of methyl orange within 60 min and 99.7 % of diclofenac within 180 min. This performance was superior to both the individual components and other reported heterojunctions. Additionally, the TMIC heterojunction demonstrated excellent stability under our testing conditions and maintained satisfactory activity in a real municipal wastewater treatment plant effluent. This research presents a novel approach to advancing Z-scheme heterojunction photocatalyst design, demonstrating significant potential for practical wastewater treatment.

1. Introduction

Water pollution is one of the most pressing environmental challenges worldwide, impacting ecosystems, human health, and economic development [1–3]. The growing demand for water in industrial, agricultural, and domestic sectors has intensified the release of pollutants into the environment, degrading water quality and threatening both aquatic life and human populations [4]. Conventional primary (physical) treatment methods, such as sedimentation [5], aeration [6], and filtration [7] have proven effective in separating suspended solids and particulates. However, they are limited in their ability to eliminate dissolved pollutants or pathogens. For this reason, Secondary (biological) treatments, such as activated sludge, biofilm and sequencing batch reactor [8,9], are applied to degrade the remaining dissolved and suspended organic matter by microorganisms to significantly reduce the chemical and biochemical oxygen demand and achieve an effluent suitable discharge. However, an increasing number of chemicals are found to be recalcitrant to

biodegradation. These contaminants of emerging concern require advanced purification methods (tertiary treatment). Particularly, advanced oxidation processes (AOPs) [10,11] use strong oxidants, such as reactive oxygen species (ROS), to degrade pollutants, making them suitable for both industrial wastewater and municipal water treatment. Despite their effectiveness, AOPs can be costly and when not completely effective can result in secondary contamination and excessive disinfection, which hinders their widespread use [11,12]. On the contrary, an ideal water purification technology should be scalable, adaptable, environmentally friendly, and sustainable [12,13].

A promising solution to water pollution lies in the development of processes that can exploit renewable energy sources such as solar energy [14]. Photocatalysis presents a green strategy capable of eliminating toxic contaminants and inactivating pathogens by harnessing light to activate a photocatalyst, which generates redox radicals [15,16]. However, conventional semiconductor photocatalysts face significant challenges, including poor utilization of visible light and the rapid

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recombination of photogenerated carriers [17,18], which limits their efficiency under visible light. Ongoing research is exploring various strategies to overcome these limitations, such as doping [19], manufacturing defects [20], and coupling with other semiconductors to provide more active sites [21], increase specific surface area, and extend light absorption. Notably, constructing heterogeneous structures offers a promising approach to enhancing photocatalytic performance by creating a built-in electric field at the heterojunction interface [22,23], which facilitates the separation and transfer of photogenerated electron-hole pairs [23,24]. In recent years, two-dimensional MXene has been proposed to assemble Mott-Schottky junctions with semiconductors due to their excellent conductivity and abundant hydrophilic functional groups [25]. The close integration of semiconductors with MXene significantly improves the transfer and separation of photogenerated carriers [25,26], thus enhancing photocatalytic performance. This type of 2D/2D semiconductor heterojunction, with its large contact area, closely knit heterointerface, short carrier migration distance, and abundant active sites, is highly effective in promoting efficient photocatalytic reactions [27–29]. So far, limited research has been conducted on the intricate construction of multiple heterointerfaces and their specific contributions to photocatalysis.

In this study, we developed a non-noble all-solid-state Z-scheme Ti_3C_2 MXene/ In_2S_3 / CeO_2 (TMIC) heterojunction through one-step in-situ growth (Fig. 1). The combined analysis of crystallographic structure and bandgap potential confirmed the formation of the Z-scheme heterojunction, which significantly enhanced photocatalytic activity in degrading organic pollutants compared to the individual pristine components. The underlying mechanism of contaminant degradation on the TMIC heterojunction was thoroughly explored using both experimental methods and DFT calculations. Moreover, wastewater from the Aalborg municipal water treatment center was collected to evaluate the performance of the TMIC heterojunction in a real-world natural environment. The design and concept of this work provide valuable insights for the synthesis of high-performance Z-scheme heterojunction catalysts, offering promising applications for photocatalytic wastewater purification.

2. Experimental section

2.1. Materials and reagents

All chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise specified. Analytical-grade methyl orange (MO) was used to screen the performances of the photocatalytic materials, while diclofenac (DCF, purity $\geq 98\%$) was used as a model pollutant in pure water and spiked in a sample from the effluent for the urban wastewater treatment plant in Aalborg East, Denmark.

2.2. Synthesis of Ti_3C_2 MXene nanosheets

In a Teflon-lined container, 2.0 g of LiF was mixed with 40 mL of 9.0 mol L^{-1} HCl. Subsequently, 1.0 g of Ti_3AlC_2 powder was slowly added to the acid solution over a period of 10 min, followed by continuous stirring at room temperature for 48 h. The resulting mixture was then centrifuged and washed with deionized water until the pH of the supernatant reached approximately 6.0. The sediment was redispersed in 150 mL of deionized water and ultrasonicated in an ice-water bath for 3 h under a nitrogen atmosphere. Finally, the suspension was centrifuged at 3000 rpm for 30 min to obtain delaminated Ti_3C_2 MXene nanosheets.

2.3. Synthesis of CeO_2 particles

2 mmol of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.4 g of PVP were dispersed in deionized water and stirred for 60 min. A 0.5 mol L^{-1} sodium hydroxide solution was then added dropwise to the mixture. The solution was subsequently heated to 180°C for 24 h in a hydrothermal reactor. After cooling to room temperature, the resulting samples were washed three times with ethanol and water, followed by centrifugation at 8000 rpm for 10 min. The precipitate was dried overnight at 60°C to obtain CeO_2 particles.

2.4. Synthesis of Ti_3C_2 MXene/ In_2S_3 / CeO_2 (TMIC)

A TMIC heterojunction was synthesized using an in-situ growth and deposition method. In a typical experiment, the calculated amounts of CeO_2 and Ti_3C_2 MXene were ultrasonically dispersed in 100 mL of deionized water and stirred for an additional 60 min under nitrogen gas protection. Then, 2 mmol of $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ and 6 mmol of TAA were

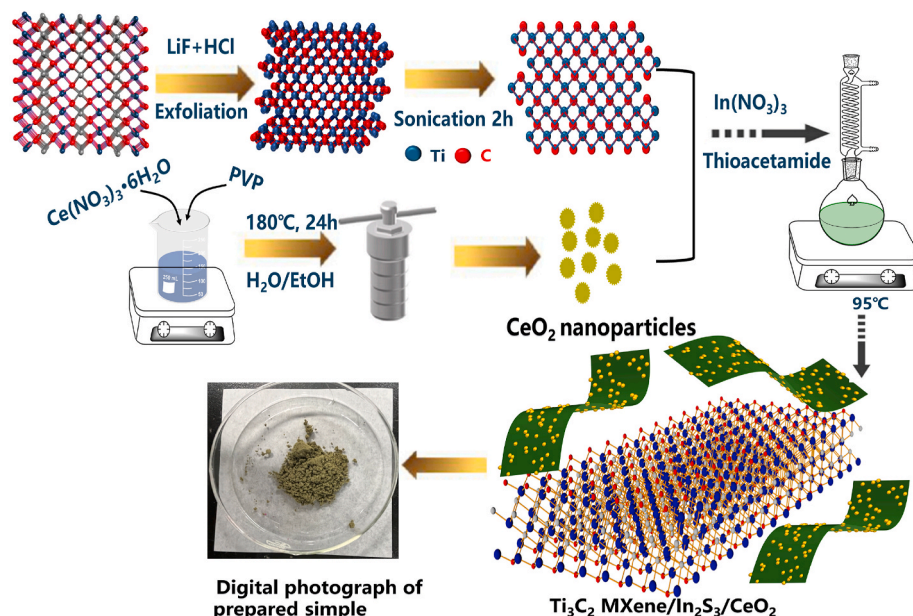


Fig. 1. Illustration of the fabrication procedure for TMIC heterojunctions.

separately added to the mixture. The solution was transferred to a 150 mL three-neck flask and refluxed at 95 °C for 90 min. After the reaction, the flask was rapidly cooled by immersion in ice water, and the product was centrifuged using a water-ethanol mixed solvent. The resulting yellow-brown precipitate was dried under a vacuum at 60 °C for 8 h. The so obtained ternary heterostructures are hereinafter named TMnIC-X%, where n indicates the mass fraction of the Ti_3C_2 MXene in the nanocomposites and $X\%$ designates the CeO_2 mass fraction in the $\text{In}_2\text{S}_3+\text{CeO}_2$ photocatalytic nanocomposite. To further demonstrate the superiority of the ternary heterostructures, binary heterojunctions ($\text{In}_2\text{S}_3/\text{CeO}_2$ -X%) synthesized under identical conditions were used for parallel comparisons. Detailed quantities of the individual components and corresponding nomenclature of the composites are provided in Table S1.

2.5. Characterization of the materials

The morphological characteristics of the catalysts were analyzed using a Zeiss Merlin field emission scanning electron microscope (SEM) from Germany, while element distribution was assessed with high-resolution transmission electron microscopy (HRTEM) and energy-dispersive elemental mapping. Crystal phase and lattice parameters were determined using a PANalytical X-ray powder diffractometer from the Netherlands, equipped with a Cu target X-ray source, operating at a scanning rate of 16.7°/min over a range of 5–80°. Surface composition and chemical states were analyzed using a Thermo Fisher X-ray photoelectron spectrometer (ESCALAB 250), with energy calibration referenced to the C 1s peak at 284.8 eV. Optical absorption properties and bandgap were measured using a UV-Vis DRS Lambda 750s spectrophotometer, with a scanning range of 200–800 nm [30]. Steady-state photoluminescence (PL) spectra were recorded using an Edinburgh FS5 fluorescence spectrophotometer at an excitation wavelength of 350 nm [31]. Electron spin resonance (ESR) spin-trapping studies were conducted using a Bruker A300 instrument from Germany to analyze the intensity of free radical signals.

Density Functional Theory (DFT) calculations were performed based on the CASTEP module [32,33]. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) function was employed to describe the exchange-correlation potential. In all calculations, the cut-off energy of the plane-wave basis set was 500 eV, the geometric structure was optimized until all the residual forces on each atom were smaller than 0.03 eV/Å [33]. For the geometrical optimization setting, the total energy change and displacement were set to 1.0×10^{-5} eV and 0.001 Å, respectively.

2.6. Photocatalytic activity measurements

The tests on the photocatalytic abatement of water pollutants were conducted as illustrated in Fig. S5. The polluted water solution was poured into a double-layered quartz glass reactor, with the temperature maintained by circulating water cooling. A 300 W Xenon lamp (model LS0306, LOT Quantum Design, GmbH) equipped with a 420 nm cutoff filter was used as the light source. The calibration of the equipment (light intensity: 125 W m^{-2}) was carried out with a Si reference solar cell (Model LS0042, ReRa System, Netherlands) before photocatalytic experiments. The typical procedure was as follows: a certain amount of the prepared photocatalyst was dispersed in 80 mL of pollutant solution with an initial concentration of 20 mg L⁻¹. Prior to visible light irradiation, the suspension was placed in the dark and magnetically stirred for 1 h to achieve adsorption saturation. At fixed time intervals, 3–4 mL of the suspension was withdrawn from the reactor, and filtered through a 0.45 µm pore size membrane filter to remove the photocatalyst. In the case of MO, the absorbance was measured at its maximum absorption wavelength (464 nm) on a UV-Vis spectrophotometer (Shimadzu, UV-3600) using ultrapure water as the reference [34]. The residual concentration of DCF was detected using high-performance liquid chromatography (HPLC) equipped with a (specify the detector used) using a

C18 column (250 × 4.6 mm, 5 µm) [35]. The column temperature was set at 35 °C, and the injection volume was 20 µL. The mobile phase consisted of 70 % methanol and 30 % aqueous formic acid solution (0.2 % formic acid concentration), with detection at a wavelength of 276 nm. The calibration curve for diclofenac is presented in Fig. S7d.

The initial concentration of the solution was indicated as C_0 , and the concentration corresponding to the measured signal during the experiment was denoted as C_t ($t = 1, 2, \dots$). The degradation efficiency was then calculated using the following formula [36]:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Additionally, the kinetics rate constants for pollutant degradation were estimated by the pseudo-first-order kinetic model calculated by Eq. (2) [37]:

$$\ln \frac{C_e}{C_t} = Kt \quad (2)$$

Where C_e is the concentration of pollutant at adsorption-desorption equilibrium, and C_t is the concentration of pollutant after catalytic at photoreaction time t min; k represents the kinetics rate constant.

Monitoring of MO degradation by-products was performed by RP-HPLC-HRMS on a Hitachi LaChrome Elite HPLC system where degradation products were separated on a C18 column (150 mm × 4.6 mm XB C18, 5 µm; Phenomenex) at 40 °C. The degradation products were detected with a high-resolution mass spectrometer (compact qTOF, Bruker) with an electrospray source (capillary: 4500 V; end plate offset 500V; dry gas 4.0 L min⁻¹, 200 °C) operated in positive mode. The mobile phase flow was kept constant at 1.2 mL min⁻¹, and the gradient initiated at 5 % solvent A (MeCN HiPerSolv, VWR) and 95 % solvent B (H₂O HiPerSolv, VWR) both supplemented with 0.1 % formic acid. The gradient increased linearly to 100 % A over 19 min and held at 100 % for 2 min. At 0.5 min, 10 µL calibrant solution (1:1 MQ-water: isopropanol with 20 mM of both NaOH and formic acid) was directly injected into the ESI and was used for internal calibration of data.

3. Results and discussion

3.1. Structural characterization

SEM images were obtained to visualize the morphologies of the as-prepared samples. Fig. 2a and b shows that pure Ti_3AlC_2 exhibits a terraced structure composed of several parallel laminated layers. After etching, the MXene nanosheets are ultrathin and exhibit a prominent wrinkled texture (Fig. 2c and d). SEM-EDX analysis indicates that the Al content is negligible, confirming the effective removal of the Al layer from the MAX phase. Pristine In_2S_3 appears as irregular nanosheets (Fig. 2e), the surface of which becomes coarser after coupling with CeO_2 particles (Fig. 2f). Mapping images of In-L, Ce-L, S-K, and O-K demonstrate the coexistence of CeO_2 and In_2S_3 in the composite. With the introduction of Ti_3C_2 MXene, the ternary composite displays a staggered lamellar phase (Fig. S2), with In_2S_3 sheets intercalated into the interlayer spacing of MXene. This observation is supported by the interconnected characteristics of the components. The negatively charged Ti_3C_2 MXene provides abundant open channels and active sites [38], where In^{3+} cations in aqueous solution are immobilized near the edges of the hydrophilic Ti_3C_2 MXene and diffuse into deeper sites, as the interior of particles is reported to have favorable activation energies for In^{3+} ion adsorption [39,40]. During the hydrothermal reaction, S^{2-} anions from thioacetamide promote the heterogeneous nucleation and growth of In^{3+} , resulting in irregular flaky In_2S_3 on the surface of Ti_3C_2 MXene [39]. New mapping images of Ti and C in the ternary compounds (Fig. S2) indicate the presence of Ti_3C_2 MXene and a homogeneous distribution of the corresponding elements.

The crystal structure of the photocatalysts was determined using X-

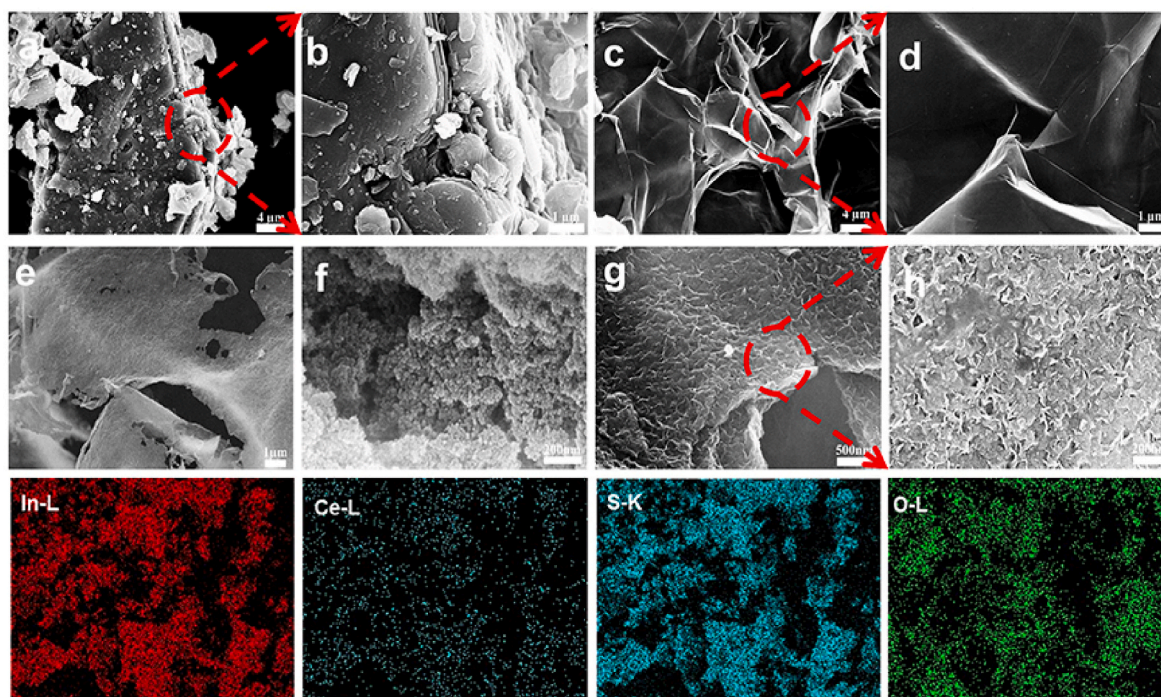


Fig. 2. SEM images of Ti_3AlC_2 (a, b); Ti_3AlC_2 MXene (c, d); In_2S_3 (e); CeO_2 (f); $\text{In}_2\text{S}_3/\text{CeO}_2$ -15 % (g, h); EDX mapping images of indium, cerium, sulfur, and oxygen for the $\text{In}_2\text{S}_3/\text{CeO}_2$ -15 % sample are depicted in the bottom section of the figure.

ray diffraction (XRD). As shown in Fig. 3, the crystalline MAX phase exhibited sharp 2θ characteristic peaks at 9.52° , 19.15° , 33.64° , 36.73° , 38.98° , 41.73° , 48.42° , 52.25° , 56.41° , and 60.17° , corresponding to the (002), (004), (101), (103), (104), (105), (107), (108), (109), and (110) planes of Ti_3AlC_2 , respectively [41]. After chemical etching, these peaks disappeared, and the characteristic peak at 7.27° (002) broadened and shifted to a lower angle, indicating the successful removal of interlayer Al and the formation of crystalline Ti_3C_2 MXene (Fig. 3a) [42]. Additionally, the diffraction peaks of bare In_2S_3 and CeO_2 matched well with the β -tetragonal phase (JCPDS No. 25–0390) and cubic phase (JCPDS No. 43–1002), respectively [43,44], confirming the high purity of these samples, for composites with varying amounts of CeO_2 , the presence of characteristic peaks for both In_2S_3 and CeO_2 was observed, with the intensity of the (111) peak of CeO_2 increasing with its content, confirming the successful integration of CeO_2 with In_2S_3 (Fig. 3b and c). Furthermore, the presence of the Ti_3C_2 MXene (002) peak in the XRD pattern of the TMIC composite verified successful incorporation. However, the diffraction peaks of Ti_3C_2 were initially indiscernible due to its low content and homogenous dispersion within the ternary compound.

XPS spectra were used to investigate the surface chemical composition and electronic valence states of the elements. In the $\text{TM}_{0.025}\text{IC}$ -15 % sample (Fig. 4a), the presence of In, Ce, Ti, S, F, and O elements was confirmed, consistent with previous EDX results. Specifically, the Ti 2p binding energies in Ti_3AlC_2 are at 455.9, 457.3, 460.6, 462.5, and 466.0 eV corresponding to C-Ti-O_x, C-Ti-O_xF_x, Al-Ti-O, C-Ti-F_x, and TiO_2 , respectively [44,45]. The Al-Ti-O peak in Ti_3C_2 MXene is absent, further confirming the successful chemical etching. As shown in Fig. 4c, the Ce 3d spectrum displays two multiplets, with binding energies for Ce $3d_{3/2}$ of the Ce^{4+} ions at 882.4 and 916.5 eV, and peaks at 898.4 eV corresponding to Ce $3d_{5/2}$ for Ce^{4+} [46,47], indicating that Ce^{4+} is predominant valence state in our materials. In the S 2p spectrum (Fig. 4d), characteristic peaks at 161.1 and 162.3 eV are assigned to S $2p_{3/2}$ and S $2p_{1/2}$ of S_2^{2-} respectively [48]. The O 1s spectrum (Fig. 4e) shows a peak at 529.08 eV corresponding to the Ce-O bond and another peak at 531.25 eV attributed to the C-O bond [49]. Additional peaks observed at 533.37 eV in the O 1s spectrum of $\text{TM}_{0.025}\text{IC}$ -15 % are likely due to adsorbed free

oxygen on the surface of MXene. The In 3d peak located at 447.6 eV and 455.2 eV correspond to $\text{In}3d_{5/2}$ and $\text{In}3d_{3/2}$, respectively, affirming the In(III) valence state [48]. The observed shift of peaks in both Ce 3d and O 1s spectra to higher binding energies compared to pristine CeO_2 suggests electron transfer between CeO_2 and Ti_3C_2 MXene, which may result in the formation of a built-in electric field [50,51].

3.2. Surface structure and optical properties

Photocatalytic phenomena typically occur at the atomic layer on the photocatalyst surface [51]. N_2 adsorption-desorption isotherms for $\text{TM}_{0.025}\text{IC}$ -15 % exhibit distinct H₂-type hysteresis loops in the range of 0.45–1.0 P/P₀ [52] and with a specific surface area of $220.173 \text{ m}^2 \text{ g}^{-1}$, significantly higher than that of Ti_3AlC_2 and Ti_3C_2 MXene ($4.0 \text{ m}^2 \text{ g}^{-1}$ and $101 \text{ m}^2 \text{ g}^{-1}$, respectively) (Fig. S3)). This increase is attributed to the addition of In_2S_3 and CeO_2 particles within the interlayer of Ti_3C_2 MXene. Optical properties were assessed using UV-Vis DRS. Ti_3C_2 MXene shows typical metallic behavior with no significant light absorption peaks. Pristine CeO_2 has limited visible light absorption, mainly in the ultraviolet region below 420 nm. However, upon coupling In_2S_3 with CeO_2 , the absorption edges of $\text{In}_2\text{S}_3/\text{CeO}_2$ -X% composites shift significantly to longer wavelengths, ranging from 600 nm to 650 nm (Fig. 5b). Among these, $\text{In}_2\text{S}_3/\text{CeO}_2$ -15 % shows the highest light absorption ability. Moreover, adding an appropriate amount of Ti_3C_2 MXene to $\text{In}_2\text{S}_3/\text{CeO}_2$ -15 % further extends the absorption edges into the near-infrared region. Nevertheless, excessive Ti_3C_2 MXene reduces light absorption due to the “covering effect” (Fig. 5c). Additionally, the bandgap energies (E_g) of the materials were determined using the Tauc plot from Eq. (3) [53]:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (3)$$

where α is the absorption coefficient, h is the Planck constant, ν is the frequency, and A denotes a constant [53,54]. Specifically, a value of n was selected for 1/2 for In_2S_3 and CeO_2 , which are direct transition semiconductors. The nominal bandgap energies determined with this method for CeO_2 , In_2S_3 , $\text{In}_2\text{S}_3/\text{CeO}_2$ -15 %, and $\text{TM}_{0.025}\text{IC}$ -15 % are 2.90,

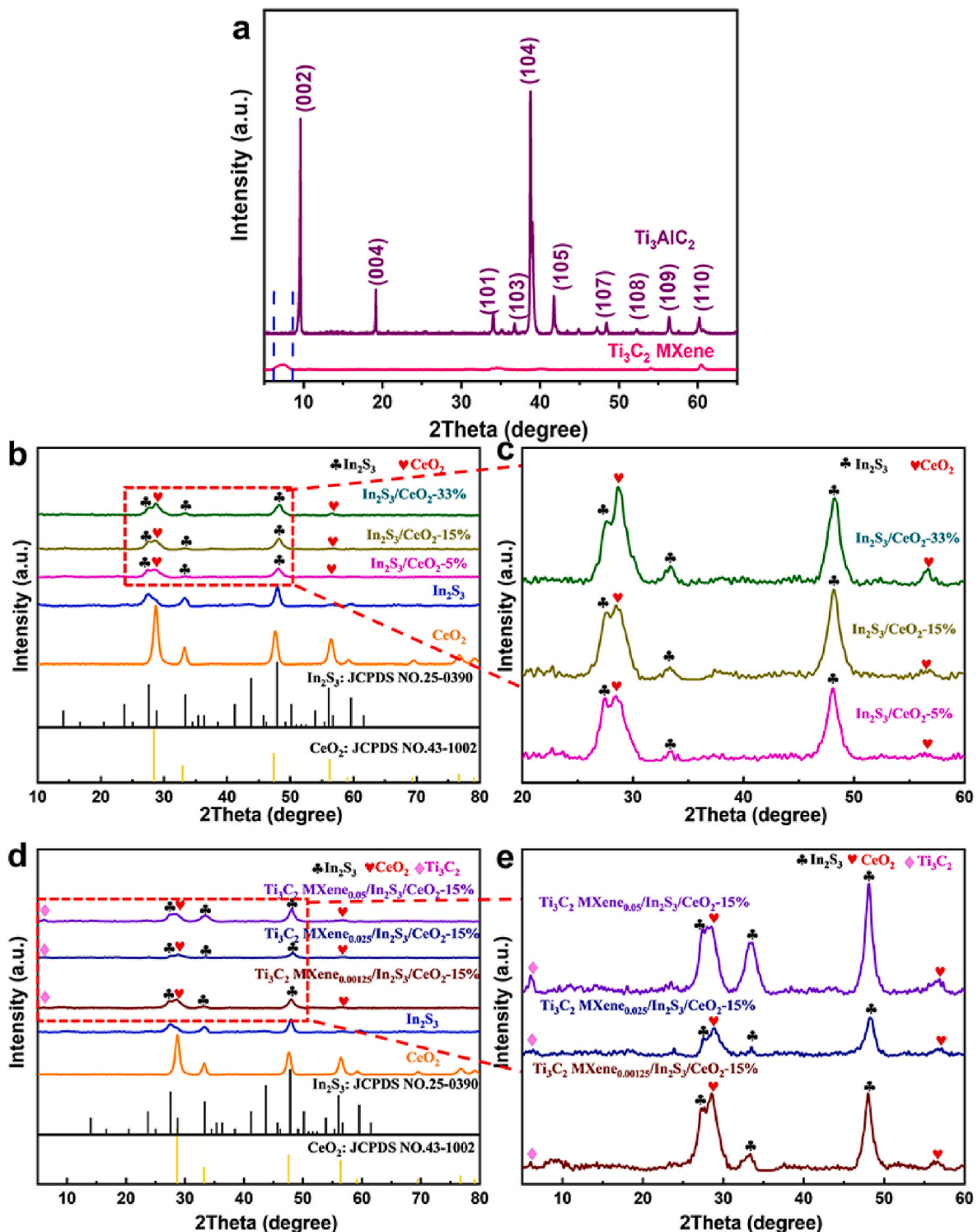


Fig. 3. XRD patterns of Ti_3AlC_2 and Ti_3C_2 MXene (a); $\text{In}_2\text{S}_3/\text{CeO}_2$ -X (b) and partial enlargement (c); Ti_3C_2 MXene n/ $\text{In}_2\text{S}_3/\text{CeO}_2$ -15 % (d) and partial enlargement (e).

2.16, 1.88, and 1.64 eV, respectively (Figs. S4a and b). These results indicate that the inclusion of a moderate amount of Ti_3C_2 MXene significantly shifts the light absorption towards the infrared region, thereby reducing the observed bandgap. To elucidate this point, the band structure of the heterojunction is further investigated using Density Functional Theory calculation, as detailed in Section 3.5.

The recombination velocity of photogenerated carriers across the semiconductor bandgap was determined using photoluminescence (PL) spectroscopy with an excitation wavelength of 350 nm. Fig. 5d shows a

gradient decrease in intensity for $\text{TM}_{0.025}\text{IC-15}$ %, indicating that Ti_3C_2 MXene effectively inhibits the recombination of charge carriers. This improvement is likely due to the well-constructed Z-scheme heterojunction framework facilitated by the doping of Ti_3C_2 MXene.

3.3. Photoelectric properties

Electrochemical impedance spectroscopy (EIS) and transient photocurrent response curves were used to evaluate the electronic

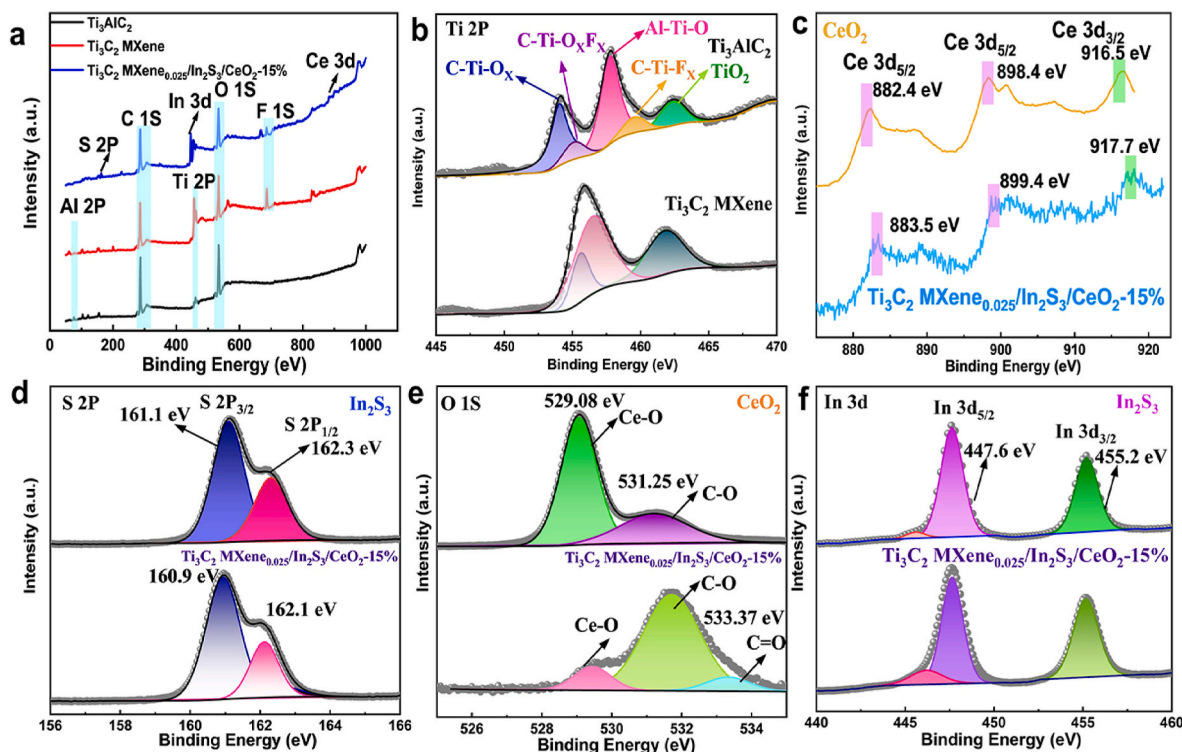


Fig. 4. XPS full region spectra (a); Ti 2p (b); Ce 3d (c); S 2p (d); O 1s (e); In 3d (f).

conductivity and charge carrier transfer capabilities of the photocatalysts [55]. Fig. 6a shows that the photocurrent of TM_{0.025}IC-15 % dropped sharply when the lamp was turned off and rose sharply when illumination resumed, demonstrating the semiconductor-type photocatalyst's intrinsic characteristics. The TM_{0.025}IC-15 % heterojunction exhibited the highest photocurrent intensity compared to the pristine components and binary compounds, indicating a higher efficiency in separating interfacial photoexcited electrons and holes. This suggests that the incorporation of Ti₃C₂ MXene improves the charge carrier separation performance of the heterojunction. Additionally, the Nyquist plots from the EIS spectra revealed that the TM_{0.025}IC-15 % heterojunction has a smaller semicircle radius, indicating that Ti₃C₂ MXene serves as an excellent co-catalyst for accelerating the migration of spatial charge, thereby enhancing photocatalytic activity.

3.4. Water depollution

The proposed Z-scheme heterojunction was initially tested under visible light using model MO solutions to demonstrate its enhanced activity compared to the individual components of the material and the TiO₂-P25 reference. This enhanced activity was subsequently confirmed with effluent from a real wastewater treatment plant. Although there are concerns regarding tests with organic dyes [56,57], this procedure provided a fast and reliable method for comparing the different materials. The results of the MO abatement are summarized in Fig. 7. The experiments performed in dark conditions indicated that continuous stirring for 30 min was sufficient to achieve adsorption-desorption equilibrium between the adsorbates and catalysts (Fig. S6). Initial photocatalytic activity tests were conducted on individual components and benchmarked against TiO₂-P25, a common reference photocatalyst although activated only under UV light [58]. The results showed that MO did not undergo significant direct photolysis under visible light irradiation (black curve in Fig. 7a), confirming literature [59]. Fig. 7a also shows that all pristine photocatalytic materials exhibited limited activity due to their poor response to visible light. However, Ti₃C₂ MXene exhibited relatively high adsorption capacity due to the

electrostatic attraction between its negatively charged oxygen-containing functional groups and positively charged organic contaminant. Compared to the catalytic activity of pure In₂S₃ (49.7 % abatement in 1h), all binary and ternary hybrids showed higher photocatalytic performance, except for CeO₂/Ti₃C₂ MXene, which like failed to enhance light absorption effectively. Notably, photocatalysts with Ti₃C₂ MXene loading exhibited significantly higher degradation efficiencies than other samples. TM_{0.025}/IC-15 % achieved optimal MO degradation within 60 min (92.94 % abatement in 1h), attributed to the synergistic effect of Ti₃C₂ MXene as an electronic mediator, enhancing charge transfer between In₂S₃ and CeO₂. However, excessive Ti₃C₂ MXene proved to be detrimental to the abatement of the pollutants, as the abundance of layered material led to agglomeration, reducing the active contact area between Ti₃C₂ and the two semiconductors and diminishing electron transmission ability. Degradation kinetic studies were performed to quantitatively analyze the photocatalytic process, with all curves presented in Figs. S7a and b. The kinetic constants for TM_{0.025}/IC-15 % were 2.62 and 9.28 times higher than those for In₂S₃ and TiO₂ P25 (Fig. 7c), respectively, consistent with the degradation experiment results. Furthermore, a comparison with photocatalysts containing Ti₃C₂ MXene or metal oxide semiconductors, displayed in Table S2, shows that TM_{0.025}IC-15 % synthesized in this work exhibits superior catalytic efficiency compared to reported heterojunction catalysts, achieving a higher catalysis ratio within a shorter period.

The most promising photocatalyst, namely the Z-scheme TM_{0.025}IC-15 % heterojunction, was further tested by treating the real effluent from an urban wastewater treatment plant, contaminated with diclofenac (DCF). DCF, a commonly used non-steroidal anti-inflammatory drug, represents a concern due to its persistence in aquatic environments and its resistance to biodegradation in wastewater treatment plants (WWTPs) [60]. Moreover, the direct photolysis rate of DCF under solar light is negligible [61]. Therefore, this molecule serves as an ideal probe to test the performance of the newly developed photocatalysts in real WWTP effluent. The effluent was spiked with 10 mg L⁻¹ of DCF to facilitate our investigation. To evaluate the effectiveness of the Z-scheme TM_{0.025}IC-15 % heterojunction in treating real wastewater

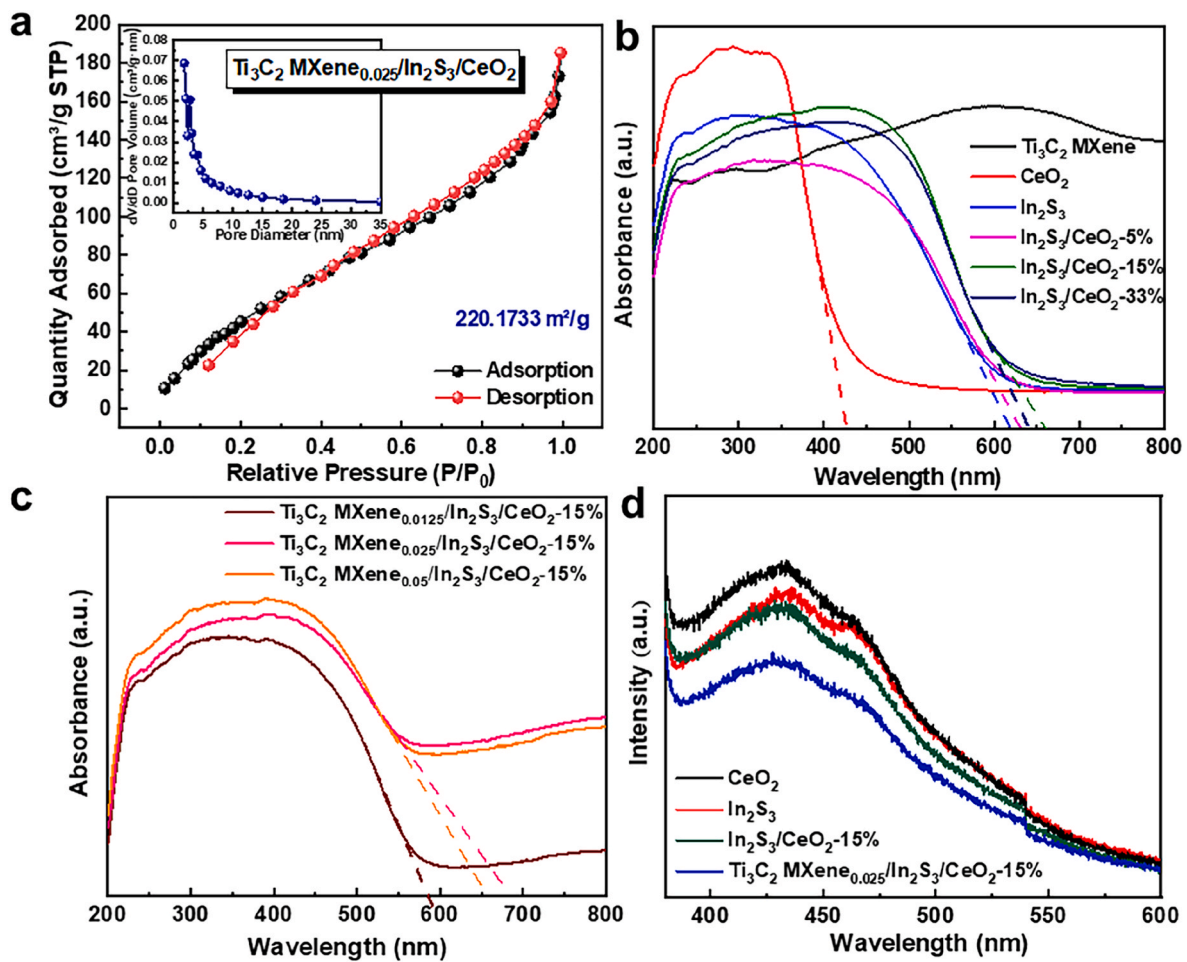


Fig. 5. (a) N₂ adsorption-desorption isotherms of TM_{0.025}IC-15 % and the pore diameters distribution (inset). UV-Vis DRS of samples (b) and (c); PL spectra of In₂S₃; CeO₂; In₂S₃/CeO₂-15 % and TM_{0.025}IC-15 % (d).

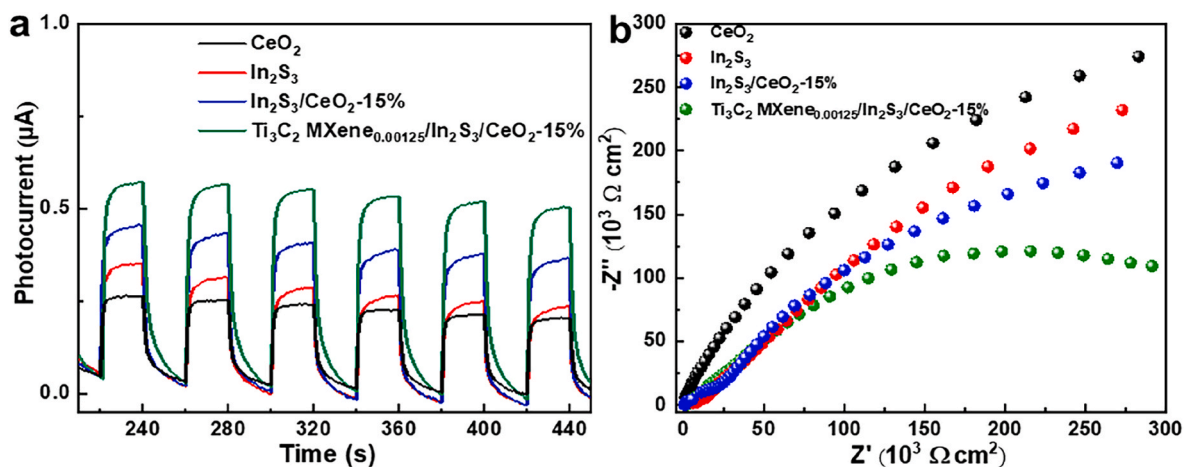


Fig. 6. (a) Transient photocurrent response curves and (b) electrochemical impedance spectra of In₂S₃; CeO₂; In₂S₃/CeO₂-15 % and TM_{0.025}IC-15 %.

samples, two additional tests were performed: the photodegradation of DCF in deionized water in the presence of TM_{0.025}IC-15 % and the photodegradation of DCF in deionized water in the presence of the In₂S₃/CeO₂ binary heterojunction. The experiments were carried out under the same conditions as described in the experimental section, with a target pollutant concentration of 10 mg L⁻¹ and a photocatalyst concentration of 50 mg L⁻¹.

In Fig. 7d, we observe that more than 98 % of DCF was eliminated by the Z-scheme TM_{0.025}IC-15 % heterojunction in pure water within 4 h of visible light irradiation, confirming the effectiveness of this material in the abatement of organic pollutants. Moreover, the Z-scheme TM_{0.025}IC-15 % heterojunction provided a higher DCF abatement than the In₂S₃/CeO₂-15 % binary heterojunction (87.4 % in 4 h). This observation further supports our hypothesis that the introduction of Ti₃C₂ MXene

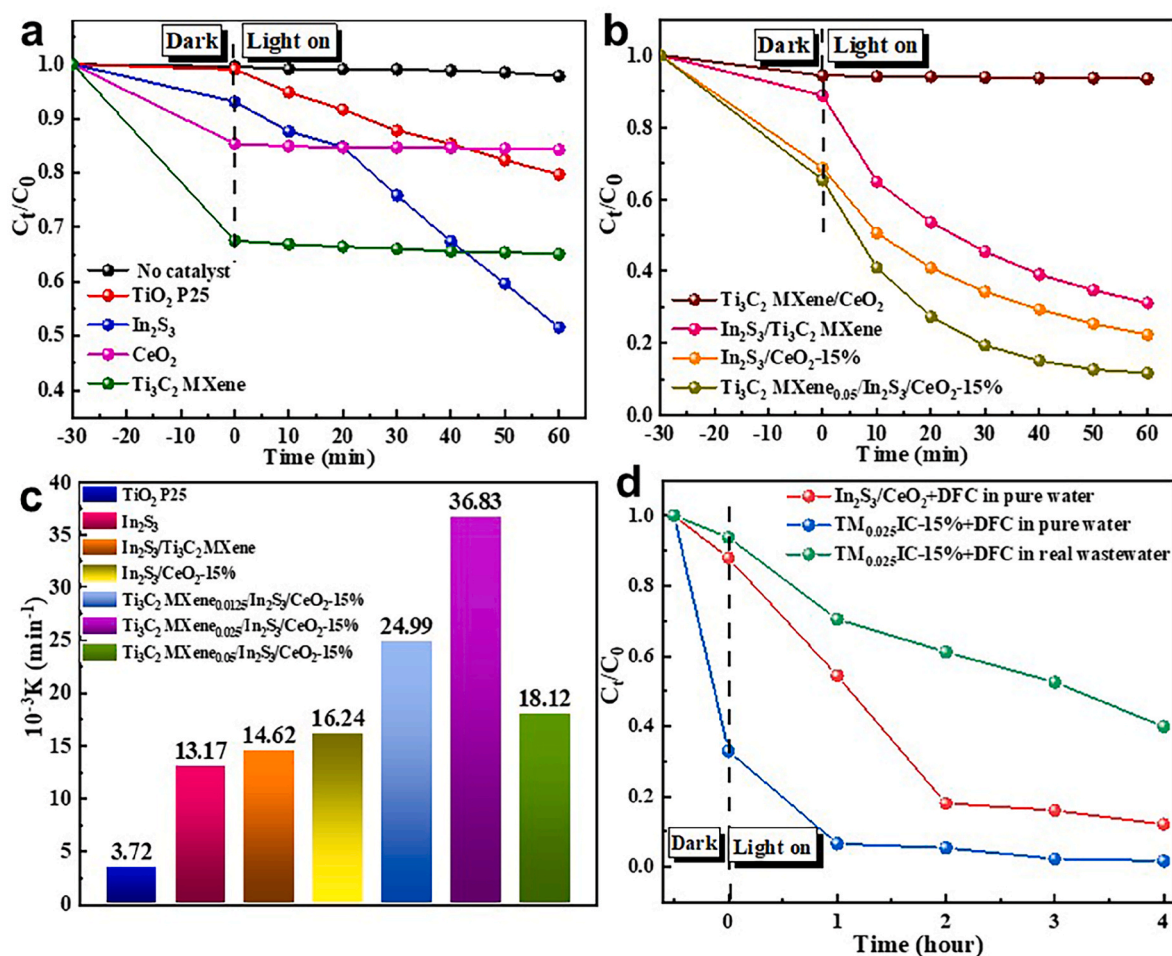


Fig. 7. Photocatalytic abatement of MO as a function of the light exposure time for the studied materials and the TiO₂ P25 reference under visible light (a, b); abatement rate constants of pseudo first-order reaction kinetics (c); photocatalytic abatement of DFC as a function of the light exposure time for TM_{0.025}IC-15 % and In₂S₃/CeO₂ in pure water and WWTP effluent (d).

into the heterojunction can effectively enhance photocatalytic activity towards water purification. This enhancement is attributed to the synergistic interaction between the nanocomposite components, resulting in improved charge separation and transfer.

Fig. 7d also shows that the adsorption of DCF on the TM_{0.025}IC-15 % surface under dark conditions is significantly suppressed when testing real wastewater effluent samples. This phenomenon can be attributed to the complex chemical composition of the matrix, which has a conductivity of $940 \mu\text{S cm}^{-1}$ and a total organic carbon (TOC) of 30 mg L^{-1} . Specifically, the wastewater effluent contained a large amount of dissolved organic matter competing with the model pollutants for adsorption sites [62]. Despite this, the performance of TM_{0.025}IC-15 % in the photocatalytic degradation of DCF remains significant, achieving abatements of 61 %, in 4 h under visible light irradiation. This is attributed to the action of photogenerated charge carriers producing reactive oxygen species (ROS). However, the activity of ROS, which has a short lifetime, is easily affected by external interference. The photogenerated active species can react not only with the target pollutant but also with ions and the dissolved organic matter in real water matrices that inevitably hinder the migration of radicals to reach the target pollutant, explaining the reduced catalytic activity. The catalytic degradation experiments conducted in real wastewater solutions prove the effectiveness of the synthesized heterojunction, highlighting its promising potential for use in treating real wastewater streams.

3.5. Photocatalytic mechanism

The stability and reusability of photocatalysts are crucial evaluation criteria, particularly given the concerns regarding the oxidation tendency of MXene materials [63,64].

Repeated degradation cycle experiments were conducted using recovered catalysts through high-speed centrifugation. TM_{0.025}IC-15 % maintained high degradation efficiency even after five cycles, demonstrating excellent stability under our testing conditions (Fig. 8a). Radical-trapping experiments were performed to identify the active species in the photocatalytic system. To capture specific radicals, 2 mmol of 1,4-benzoquinone (BQ), isopropyl alcohol (IPA), and sodium oxalate (SO) were used to scavenge $\bullet\text{O}_2^-$, $\bullet\text{OH}$, and h^+ , respectively. The addition of BQ resulted in a significant decrease in both degradation efficiency and kinetic constant (Fig. 8b & Fig. S8), inferring that $\bullet\text{O}_2^-$ is a crucial intermediate in the photocatalytic degradation process. Although the addition of SO and IPA also reduced catalysis to some extent, suggesting their involvement in the degradation process, it is evident that multiple active species collaborate in the photocatalytic reaction.

Natural water bodies typically contain various inorganic anions. To assess the interference of these anions, we investigated the effects of adding 1 mmol of NaCO₃, NaCl, and Na₂SO₄ salts to the system [65]. As shown in Fig. 8c and Fig. S9, the presence of these salts inhibited the degradation process. This inhibition is attributed to the competitive adsorption between the anions and the model pollutant, which reduces

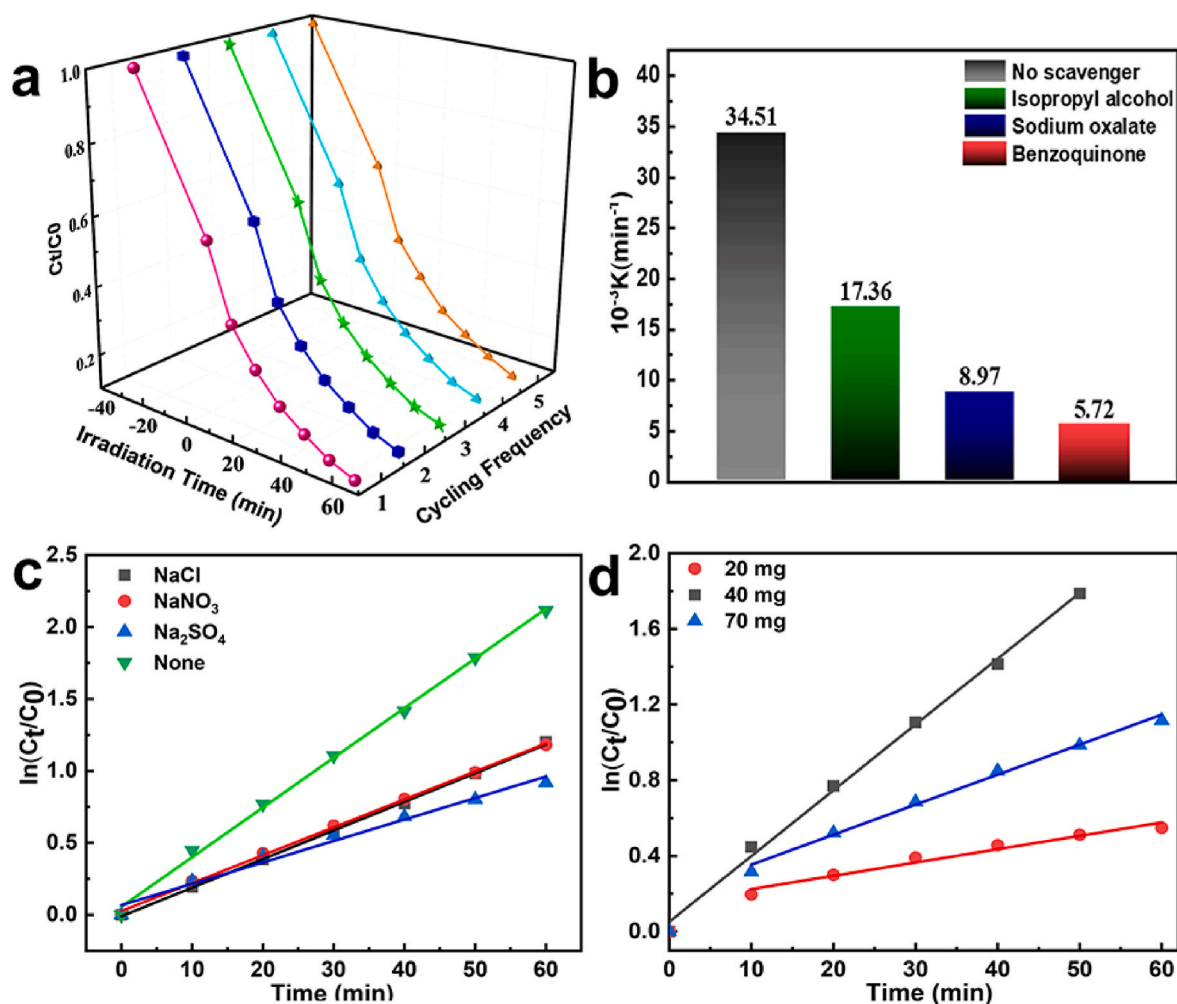


Fig. 8. Cycling runs for MO degradation (a); Effects of a series of radical scavengers (b); Influence of different anions (c); Effect of photocatalyst dosage (d).

the availability of active sites. Among the anions test, sulfate (SO_4^{2-}) had the most pronounced effect, leading to the slowest degradation rate. This is due to sulfate's larger size and higher valence state compared to chloride Cl^- and NO_3^- (Fig. S9a), causing greater blockage on the catalyst surface [66]. Additionally, the amount of catalyst used also influences the effectiveness of the photocatalysis. While an optimal amount of catalyst enhances the catalytic rate (Fig. 8d and Fig. S9c), excessive catalyst leads to increased turbidity in the system, which can shield light and reduce catalytic performance.

Electron paramagnetic resonance (EPR) spectrum confirmed the generation of radicals on $\text{TM}_{0.025}/\text{IC-15}$ %. We used 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the probe molecule to detect $\bullet\text{O}_2^-$ and $\bullet\text{OH}$. As displayed in Fig. 9a and b, neither the signal of $\bullet\text{O}_2^-$ nor $\bullet\text{OH}$ were detected in the dark. However, under visible light irradiation, distinct signals for $\text{DMPO}\cdot\text{O}_2^-$ and $\text{DMPO}\cdot\text{OH}$ were observed, indicating their involvement in the photocatalytic degradation process. In contrast, for h^+ detection, the dark signal corresponds to the paramagnetic resonance of the probe molecule 2,2,6,6-Tetramethylpiperidinoxy (TEMPO), while a decrease in $\text{TEMPO}\cdot\text{h}^+$ signal intensity under light illumination exactly indicates the generation of h^+ (Fig. 9c) [67]. Furthermore, XPS-VB was utilized to determine the band potentials (E_{VB}) of CeO_2 and In_2S_3 (Fig. 9d). However, due to the inherent potential difference introduced by the XPS analyzer, the precise E_{VB} value at the standard hydrogen electrode (VS. NHE) need to be corrected using Eq. (4) [68]:

$$E_{\text{VB}} = E_{\text{VB-XPS}} + \varphi - 0.44 \text{ eV} \quad (4)$$

where φ represents the work function potential of the XPS instrument used in this study (4.6 eV). Consequently, the E_{VB} of In_2S_3 and CeO_2 relative to the NHE are determined to be 2.13 and 1.20 eV, respectively. The corresponding conduction band potentials (E_{CB}) of In_2S_3 and CeO_2 were then calculated to be -0.96 eV and -0.77 eV (vs. NHE), respectively, using the following equation [69]:

$$E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}} \quad (5)$$

Intermediates generated during MO degradation were monitored by LC-MS to gain insight into the possible degradation pathway. Twelve compounds were hypothesized based on a chemical formula with detected m/z values, as summarized in Table S3. The degradation process began with the attack of $\bullet\text{OH}$, which substituted one of the aromatic benzene rings in MO, forming a compound with an m/z value of 320.0707 (MO-C). This was followed by demethylation, where the methyl group was replaced by a hydrogen atom, resulting in the formation of MO-B (m/z 292.0749) and MO-D (m/z 306.0550). Afterward, the electron-rich chromophoric azo bond ($-\text{N}=\text{N}-$) underwent cleavage, leading to the production of various intermediate compounds with smaller molecular sizes, such as MO-F (m/z 136.0773), MO-K (m/z 137.1006), MO-L (m/z 174.0218), MO-M (m/z 123.0914), and MO-N (m/z 150.1026). These findings also explain why the solution's color gradually faded and eventually the solution turned colorless (Fig. S11).

Based on the aforementioned characterization, a mechanism for enhancing the photocatalytic degradation performance of TMIC was proposed. Under visible-light irradiation, e^- are excited from the

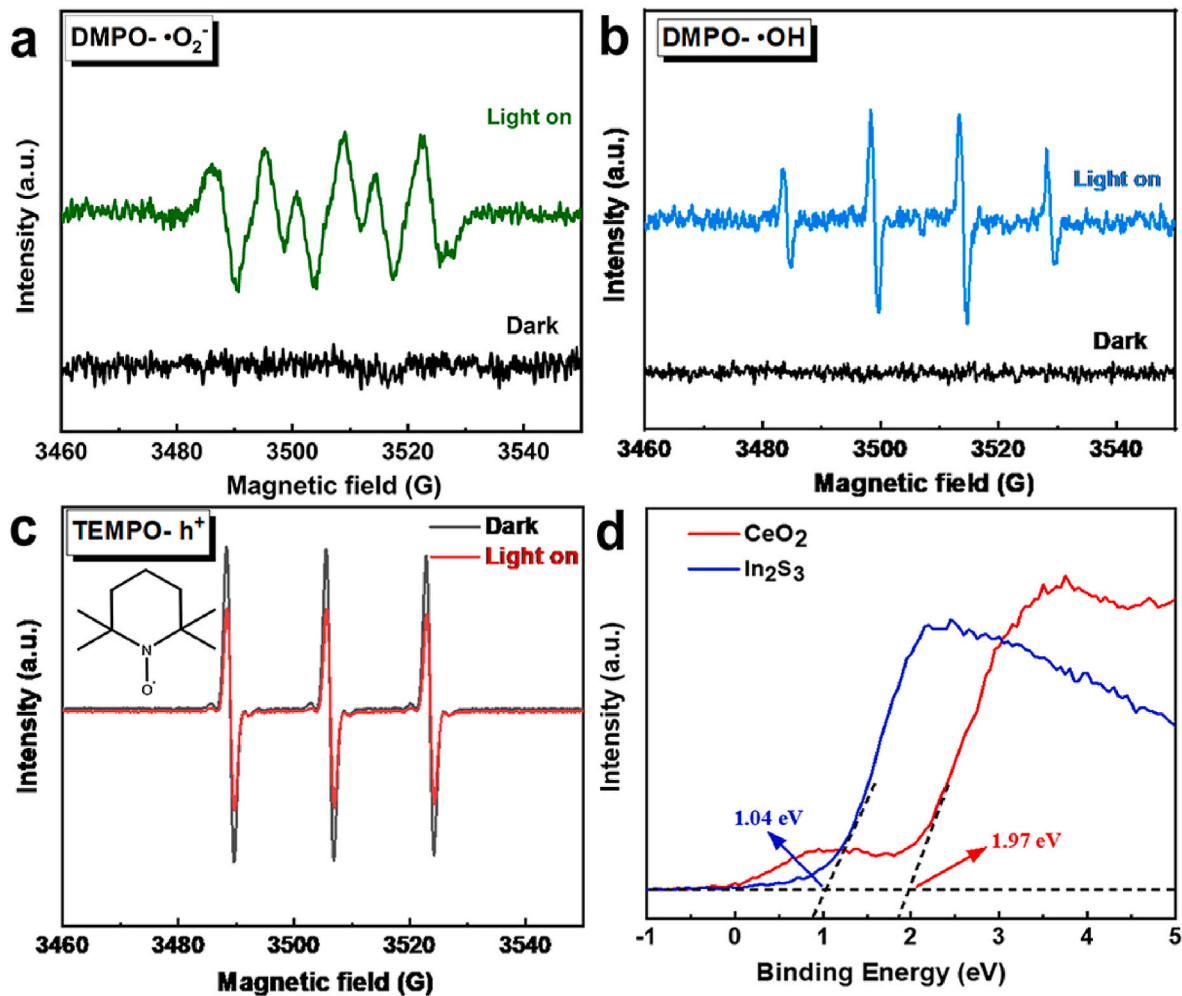


Fig. 9. EPR spectra of DMPO-•O₂⁻ (a), DMPO-•OH (b) and TEMPO-h⁺ (c) under dark and visible light irradiation; (d) XPS-VB curves of In₂S₃ and CeO₂.

valence band (VB) of both In₂S₃ and CeO₂ to their respective conduction bands (CB), leaving h⁺ in both VBs, as illustrated in Fig. 10. Supposing the TMIC heterojunction had a traditional type-II (band-to-band)

scheme, the e_{CB}⁻ of In₂S₃ would migrate to the CB of CeO₂, while the h_{VB}⁺ of CeO₂ would migrate to the VB of In₂S₃ owing to the relatively low potential of the CB and VB of CeO₂ relative to those of bare In₂S₃.

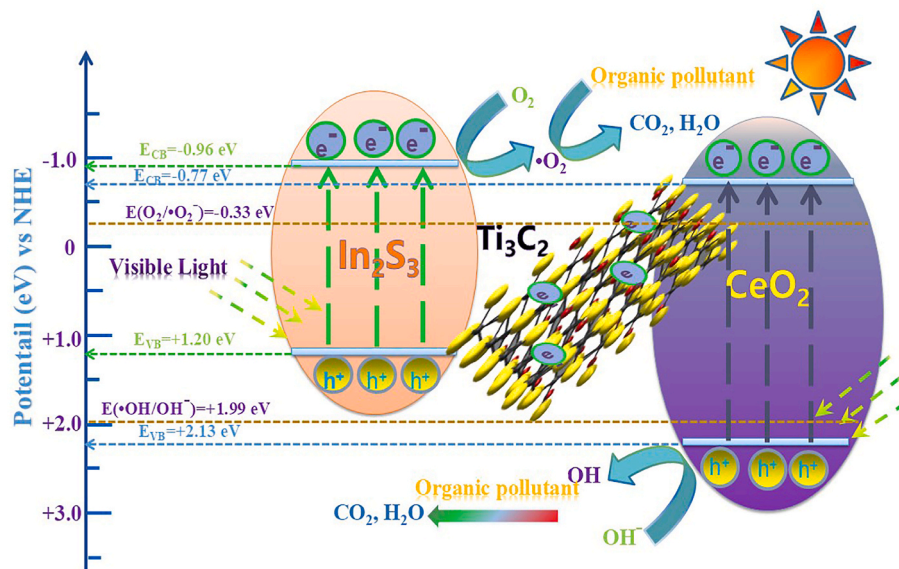
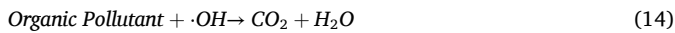
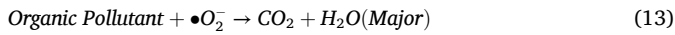
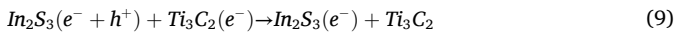
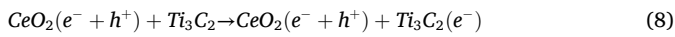


Fig. 10. Schematic diagram of photocatalytic degradation mechanism.

However, radical trapping experiments and EPR analysis revealed that $\bullet\text{O}_2^-$ possesses an indispensable effect on the degradation process, but the potential of the VB of In_2S_3 (+1.20 eV) is lower than the standard oxidation potential of $\text{OH}^-/\bullet\text{OH}$ (+1.99 eV), indicating insufficient oxidation activity for driving the reaction. Therefore, the type II heterojunction hypothesis is incorrect. Instead, the oxidation reaction must occur in the VB of CeO_2 . In this scenario, the e^- on the CB of CeO_2 transfer through the surface of Ti_3C_2 MXene to combine with the h^+ on the VB of In_2S_3 . This arrangement preserves the e^- on In_2S_3 and h^+ on CeO_2 , allowing for stronger reduction and oxidation capabilities, respectively. Notably, Ti_3C_2 MXene acts as an “electronic bridge” between two semiconductors, a mediator to prevent the recombination of photogenerated carriers. Consequently, the accumulated e^- on In_2S_3 and h^+ on CeO_2 lead to the generation of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$, respectively. This charge-transfer pathway in the synthesized heterojunction catalyst presents a typical all-solid-state Z-scheme mechanism, which is capable of fully utilizing the stronger redox ability of both semiconductors, thereby resulting in improved photocatalytic degradation activity compared to the corresponding binary photocatalysts. The specific reaction processes for the degradation of a generic organic pollutant are as follows:



3.6. Density Functional Theory calculation

To further evaluate the formation mechanism of the proposed Z-scheme heterojunction, DFT calculation was adopted to reveal the energy band/density of states and the work function (Φ) of individual components [70]. As shown in Fig. 11a–c, both In_2S_3 and CeO_2 exhibited semiconductor properties, with the Fermi level crossing the valence band. Compared to the results from UV–VIS–DRS, the theoretical band gaps are relatively underestimated. This phenomenon is consistent with previously reported DFT theoretical conclusions due to the limitations in accurately capturing electron correlation effects in semiconductors [70, 71]. The work function (Φ) shows a negative relationship with the Fermi levels (E_F) of semiconductors. Generally, the higher values of Φ (lower values of E_F) can contribute to capturing electrons transferred from another semiconductor [72]. As displayed in Fig. 11d–f, the theoretical Φ of In_2S_3 and CeO_2 are 5.149 and 6.70 eV, respectively, suggesting that electrons tend to migrate from In_2S_3 to CeO_2 until the Fermi level equilibrium is reached. It can be reasonably inferred that the introduction of metallic Ti_3C_2 MXene constructed two internal electrical fields during the heterojunction formation as the E_F was placed between In_2S_3 and CeO_2 . This result can be directly verified by planar-averaged electron density difference calculation.

As demonstrated in Fig. 12a–b, the theoretical models of $\text{In}_2\text{S}_3/\text{Ti}_3\text{C}_2$ and $\text{Ti}_3\text{C}_2/\text{CeO}_2$ binary composites were established. Note the purple and yellow regions distributed around the interface represent areas of electron accumulation and depletion, respectively. This indicates charge redistribution at the heterojunction interface after introducing Ti_3C_2 , which highlights the formation of a built-in electric field and is crucial for enhancing the photocatalytic activity of the material. Those results confirmed that the electron is extracted from In_2S_3 to Ti_3C_2 surface and then flowed into CeO_2 , which is in good agreement with the Φ values. During the process, the energy bands of In_2S_3 bent upward toward the interface on account of losing electrons, leading to the formation of an electron depletion layer that limits the transport of electrons. Conversely, the energy band edge in the CeO_2 with lower E_F value bent downward as a result of electron accumulation, which restricts the movement of holes, as displayed in Fig. 12c. Under light irradiation, the

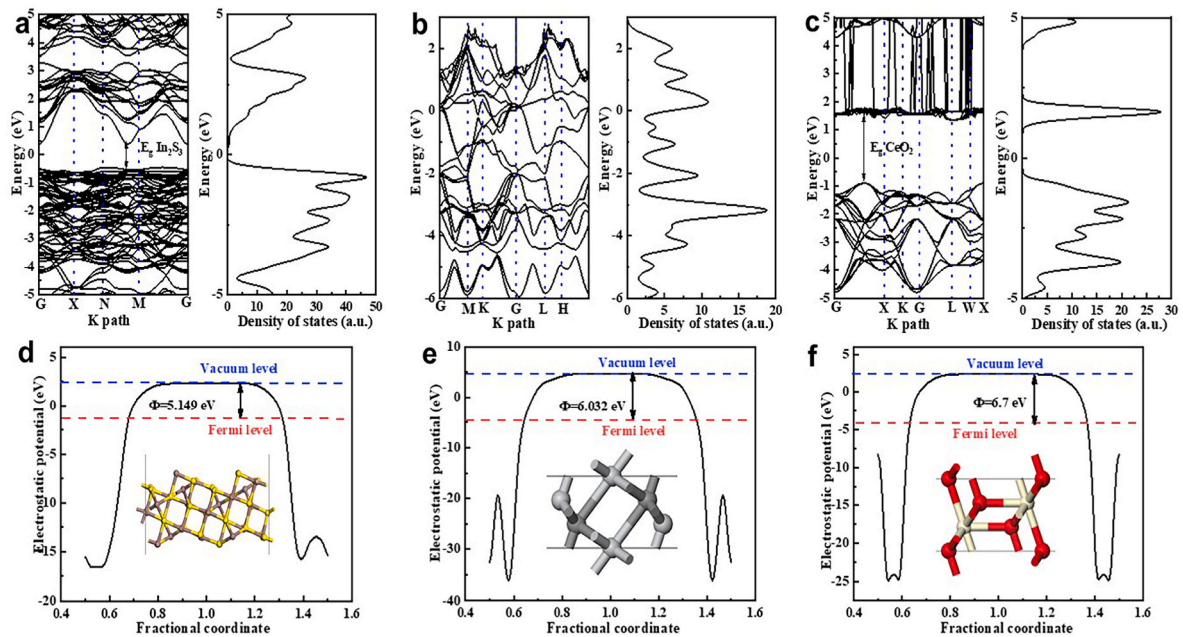


Fig. 11. Adsorption band gap diagram (left) and total state density (right) of In_2S_3 (a), Ti_3C_2 MXene (b), CeO_2 (c). Work function (Φ) of In_2S_3 (110) (d), Ti_3C_2 MXene (001) (e), CeO_2 (111) (f), and the corresponding geometrical structure model (inset). The blue and red dashed lines represent the Vacuum energy level and Fermi energy level, respectively.

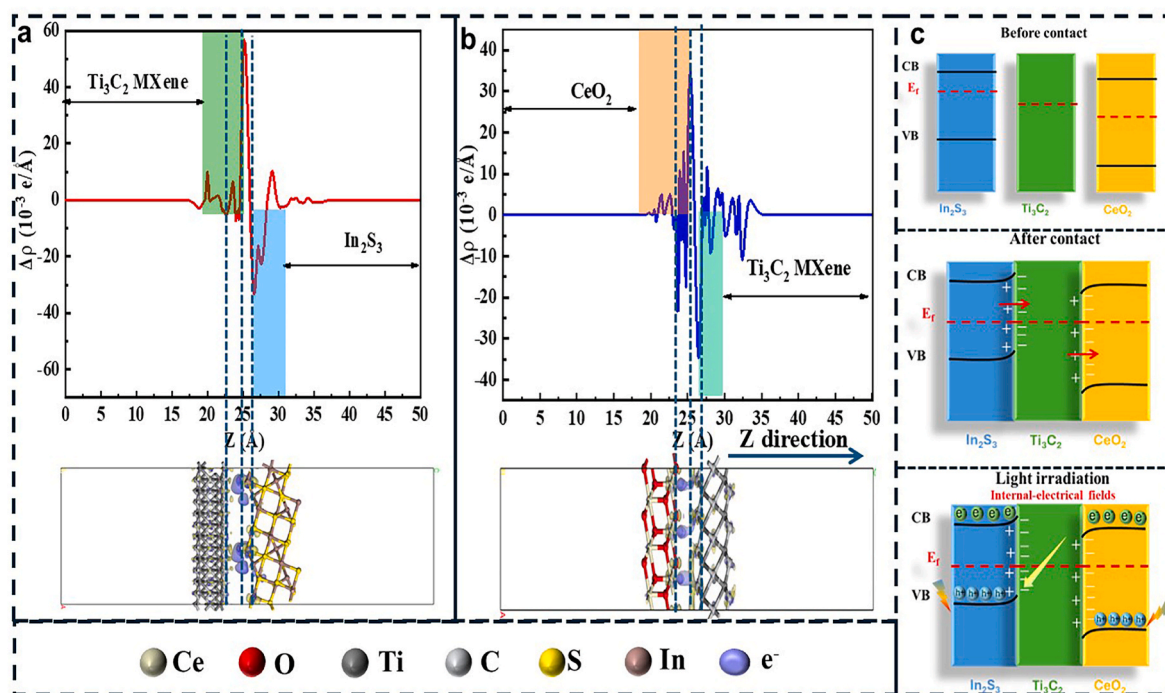


Fig. 12. Planar-averaged electron density difference $\Delta\rho(z)$ for $\text{In}_2\text{S}_3/\text{Ti}_3\text{C}_2$ (a) and $\text{Ti}_3\text{C}_2/\text{CeO}_2$ (b), (c) Schematic diagram of the internal electric field with band bending in Z-scheme TMIC heterojunction and the photoelectrons transfer pathway of under light irradiation.

energy bands of In_2S_3 and CeO_2 are transformed into excited states, the photoelectrons accumulated in the CB of CeO_2 quenched with the photogenerated holes in the VB of In_2S_3 , driven by force of the internal electric field and Coulomb interaction. The Z-scheme transfer pathway in ternary heterojunction not only realized the facilitation of charge separation but also preserved the electron-hole pairs with stronger photoredox ability, thus significantly promoting photocatalytic water purification efficiency.

4. Conclusion

A novel and rationally designed $\text{Ti}_3\text{C}_2 \text{ MXene}_{0.025}/\text{In}_2\text{S}_3/\text{CeO}_2$ -15 % heterojunction was synthesized in this work, demonstrating exceptional photocatalytic degradation activity towards organic pollutants in aqueous solutions. In_2S_3 and CeO_2 contribute a highly reductive conduction band and a highly oxidative valence band in the heterojunction, respectively, while Ti_3C_2 MXene acts as an electron conductor “bridge” between the two semiconductors. This facilitates the transfer of photo-generated electrons from CeO_2 to neutralize the holes in In_2S_3 , thereby preserving a higher concentration of active charge carriers for catalytic reactions. The performance of this heterojunction was further validated through simulated experiments in real wastewater, which highlighted its excellent structural stability and remarkable catalytic activity under harsh experimental conditions and during recycling. However, it was also observed that the catalytic activity of the TMIC heterojunction was less prominent when dealing with complex macromolecular pollutants with heterocyclic structures. Therefore, ongoing work on catalyst screening and optimization will continue to be reported. Comprehensive experimental characterization and theoretical DFT calculation revealed that the enhancement in photocatalytic performance was due to the unique Z-scheme charge transfer mechanism, which effectively utilizes the redox properties of both semiconductors and hinders the recombination of photogenerated carriers. Additionally, the favorable electrical conductivity of Ti_3C_2 MXene facilitated rapid carrier transfer. Based on these findings, further exploration of Ti_3C_2 MXene-modified Z-scheme heterojunctions is anticipated, also considering the potential use of other oxide semiconductors with suitable band structures to further enhance

performance, offering significant promise for developing economical, efficient, and sustainable technologies for real wastewater purification.

CRediT authorship contribution statement

Jingbo Ni: Writing – original draft, Methodology, Data curation. **Vittorio Boffa:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Klaus Westphal:** Resources. **Deyong Wang:** Formal analysis. **Peter Kjær Kristensen:** Investigation. **Paola Calza:** Writing – review & editing, Data curation.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mssp.2025.109379>.

Data availability

Data will be made available on request.

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