



Driving S-scheme charge transfer via Fermi level disparity: efficient toluene mineralization over oxygen vacancy engineered Bi₂WO₆ coupled with TiO₂

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Abstract

Photocatalytic degradation is a sustainable strategy for the remediation of stable aromatic volatile organic compounds such as toluene. Yet, the energy-efficient mineralization of these pollutants under ambient conditions remains a critical bottleneck. Herein, an n–n S-scheme heterojunction photocatalyst is constructed via in situ hydrothermal coupling of TiO₂ with oxygen-vacancy-engineered Bi₂WO₆ (TB-x: x represents the TiO₂/Bi₂WO₆ molar ratio). A work function difference of 0.39 eV induces band bending and an internal electric field from Bi₂WO₆ to TiO₂, enabling an efficient S-scheme charge transfer pathway. Consequently, the optimized TB-2 exhibits a longer charge carrier lifetime (21.1 ps) than the pristine components. In a fixed-bed flow system, TB-2 achieves 97.2% degradation of 5 ppm toluene within 60 min under UV irradiation, delivering a high dynamic clean air delivery rate (1940 L h^{−1} g^{−1}) and an apparent quantum yield of 0.1%, with high stability across reuse cycles and under varying humidity conditions. In situ DRIFTS, EPR, and DFT analyses reveal a stepwise oxidation pathway via benzyl alcohol and benzaldehyde intermediates, ultimately forming CO₂ and H₂O. This work highlights the critical role of interfacial band engineering in constructing an efficient air purification system based on direct mechanistic evidence for oxygen-vacancy-assisted S-scheme charge transfer in TiO₂/Bi₂WO₆ heterojunctions.

Keywords Toluene degradation · Charge transfer mechanism · Photocatalysis · TiO₂/Bi₂WO₆ · Oxygen-vacancy-assisted S-scheme

1 Introduction

Aromatic volatile organic compounds (VOCs), such as toluene, are persistent air pollutants present at concentrations often 2–5 times higher indoors than outdoors, where they pose significant risks to human health, especially in vulnerable populations [1]. Current abatement technologies for aromatic VOCs, including filtration, adsorption, and

thermal oxidation, are often limited by incomplete mineralization, high operational costs and energy consumption, the risk of secondary waste generation, and diminishing effectiveness at trace contaminant levels typical of indoor air [2, 3]. In contrast, photocatalytic air remediation has recently emerged as a green and effective technology for the removal of aromatic VOCs under mild operating conditions [4]. Upon light irradiation, photocatalysts are activated to generate charge carriers that participate in the formation of reactive oxygen species (ROS: hydroxyl radicals (•OH) and superoxide anions (•O₂[−])) and oxidative decomposition of aromatic molecules [5]. However, photocatalytic oxidation of aromatics (e.g., toluene) remains challenging due to the high activation energy required for ring-opening reactions (stable chemical structure), leading to slow reaction kinetics, incomplete mineralization, and the risk of catalyst deactivation from the accumulation of intermediate by-products [6]. To address these challenges, the rational selection of photocatalysts, coupled with the careful engineering of their

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electronic structures, is crucial for enhancing charge separation, optimizing redox potential, and maximizing reactive species generation during photocatalysis.

A variety of photocatalysts (e.g., TiO_2 , ZnO , $\text{g-C}_3\text{N}_4$, and CeO_2) have been developed for environmental remediation [7–9]. Among them, TiO_2 remains one of the most widely used and effective materials owing to its commercial availability, chemical stability, strong oxidative capability, low cost, and non-toxicity [10, 11]. Nevertheless, the activation energy for photocatalytic C–H bond activation of toluene over rutile TiO_2 (110) was calculated to be 1.10 eV [12]. This higher energy barrier indicates the intrinsic stability of aromatic VOCs and the kinetic limitation of the active TiO_2 (110) facet, which restricts its ability to rapidly generate ROS and accelerate the photocatalytic mineralization of aromatic VOCs. Additionally, the by-products generated (such as benzaldehyde, benzoic acid, and acid anhydride) limit the long-term stability of TiO_2 in real-world applications [13]. Overcoming the high activation barrier and limited photocatalytic activity of TiO_2 toward aromatic VOCs requires deliberate modification strategies to optimize both surface reactivity and charge separation. One effective approach is to create heterojunctions by coupling TiO_2 with other semiconductors to facilitate efficient separation and mobility of photogenerated charge carriers, thereby promoting radical formation and reducing kinetic constraints on aromatic C–H bond activation [14].

Bismuth tungstate (Bi_2WO_6) is a highly promising semiconductor to pair with TiO_2 due to its distinctive orthorhombic structure and favorable band alignment [15]. Bi_2WO_6 features a scheelite-like orthorhombic framework of alternating BiO_6 octahedra and WO_4 tetrahedra, enabling spatial separation by localizing photogenerated electrons on WO_4 units and holes on BiO_6 units [16]. Its conduction and valence band positions align well with those of TiO_2 , enabling the formation of a heterojunction that promotes directional charge transfer across the interface [15]. Upon coupling with TiO_2 , this intrinsic feature enhances interfacial charge transfer, facilitating efficient heterojunction formation and promoting the generation of reactive oxygen species [17]. Therefore, the rational coupling of TiO_2 with Bi_2WO_6 is mechanistically justified for enhancing charge separation efficiency, optimizing redox capability, and overcoming the kinetic limitations associated in the photocatalytic mineralization of stable aromatic VOCs such as toluene.

Owing to their complementary band structures and interfacial synergy, $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures have been widely investigated for photocatalytic applications, including antibiotic degradation [18], CO_2 reduction [19],

and NO_x conversion [20]. However, their application in the photocatalytic degradation of VOCs, such as toluene, has scantily been made. In particular, complete photomineralization of toluene has not been explored under dynamic gas–solid reaction conditions and/or the influence of varying humidity conditions. Furthermore, the charge-transfer mechanisms at the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ interface are yet debatable with respect to proposed models including II type [21], Z scheme [22, 23], and S scheme [23]. In addition to heterojunction construction, defect engineering, especially the introduction of oxygen vacancies in Bi_2WO_6 , offers an effective strategy to regulate band alignment, promote charge separation, and enhance oxygen activation. Yet, the interplay between such defects and interfacial charge-transfer pathways has been largely overlooked. Therefore, a systematic investigation combining oxygen-vacancy-engineered Bi_2WO_6 with a $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunction is timely and necessary to clarify the optimal charge-transfer mechanism and to maximize photocatalytic degradation and mineralization efficiency of aromatic VOCs under near-ambient conditions.

In this work, a series of $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunctions (at varying molar ratios of $\text{TiO}_2:\text{Bi}_2\text{WO}_6$) was synthesized through an in situ hydrothermal method. The $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunctions were employed as fixed-bed catalysts for the photomineralization of toluene vapor under dynamic flow conditions with UV illumination. The study investigated the photocatalytic performance of $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunctions in both dry and humidified gas streams to elucidate the influence of compositional tuning on charge-carrier separation efficiency, surface reactive species generation, and toluene mineralization rates, thereby optimizing catalyst formulation for practical air-purification applications. This study provided a systematic evaluation of the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ catalytic bed system under realistic conditions, accounting for the often-overlooked influence of variable operational parameters (e.g., photocatalytic bed mass, toluene concentration, and relative humidity) on photocatalytic performance. More importantly, advanced analytical characterization clarified the interfacial electronic interactions and charge migration pathways within the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunction, providing mechanistic insights into the relationship between structure and photocatalytic activity. Additionally, the study comprehensively investigated the photocatalytic degradation pathway of toluene over $\text{TiO}_2/\text{Bi}_2\text{WO}_6$, including the dominant reactive species involved. The outcomes of this study are expected to advance fundamental understanding of TiO_2 -based heterojunction structures and guide the rational design of highly efficient photocatalysts for the remediation of aromatic VOCs.

2 Materials and experimental methods

2.1 Materials and chemicals

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (98%) and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ($\geq 99\%$) were supplied by Sigma-Aldrich (St. Louis, MO, USA). Ethylene glycol (EG) was sourced from Daejung Chemicals & Metals Co., Ltd. (Siheung, South Korea). AEROXIDE® TiO_2 P25 was obtained from Evonik Industries AG (Essen, Germany). High-purity N_2 (99.999%), toluene (500 ppm), and air (99.999%) cylinders were provided by Union Gas Co., Ltd. (Yongin, South Korea).

2.2 Synthesis of $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunction photocatalysts

The $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures were synthesized following previously reported methods with some modifications [24]. 2 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 50 mL of ethylene glycol, and varying amounts of TiO_2 were dispersed in the solution under vigorous stirring for 1 h to form solution A. Separately, 1 mmol of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 10 mL of ethylene glycol to form solution B, which was then added to solution A. The resulting mixture was stirred continuously for an additional 3 h at room temperature. The resulting solution was then transferred to a Teflon-lined autoclave for hydrothermal reaction at 160 °C over 6 h. After cooling, the precipitate was collected by centrifugation, washed with deionized water (three times), and dried in the oven at 80 °C for 12 h to obtain the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunction (at $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ molar ratio of 0.5; coded as TB-0.5) (Fig. S1). A series of TB-x heterojunctions was prepared using the same procedure, with only the amount of TiO_2 nanopowder varied (e.g., 80, 160, 400, and 800 mg). The resulting $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunctions were

labeled as TB-0.5, TB-1, TB-2, TB-5, and TB-10, corresponding to a $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ molar ratio “x” of 0.5, 1, 2, 5, and 10, respectively, as listed in Table 1. Pristine Bi_2WO_6 was synthesized by following the same procedure as that used for TB-x, except that TiO_2 was omitted from the reaction system. In addition, for comparison, a $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunction was prepared by replacing the EG solution with deionized water while keeping all other synthesis conditions identical to those for TB-2. Note that this sample was denoted as TBH-2. Furthermore, a Bi_2WO_6 sample synthesized in aqueous solution under the same conditions as TB-2 but without the addition of TiO_2 , was labeled as BWO-H.

2.3 Characterization techniques

The morphology of all samples was characterized by scanning electron microscopy (SEM, Zeiss Auriga, Germany). Transmission electron microscopy (TEM, Talos F200S S/TEM, Thermo Fisher Scientific, USA) equipped with an energy-dispersive X-ray spectroscopy (EDS) probe was employed for detailed structural and compositional analysis. Their surface chemistry was evaluated using a Fourier-transform infrared spectrophotometer (FTIR: Nicolet iS50, Thermo Scientific, USA). The crystal structure of the catalysts was tested using X-ray diffraction (XRD, Empyrean, Almelo, The Netherlands) with Cu-K α radiation (1.5406 Å). The N_2 adsorption–desorption isotherms were measured using an ASAP 2460 surface area and porosity analyzer (Micromeritics Instrument Corp., USA). Prior to the measurements, the samples were evacuated at 150 °C for 2 h to remove adsorbed gases and moisture. The surface elemental oxidation states of the photocatalysts were investigated by X-ray photoelectron spectroscopy (XPS, AXIS Supra, Manchester, UK). The obtained spectra

Table 1 A list of sample code for the prepared photocatalyst samples used in this research

Order	Sample code ^{b)}	Composite component (mmol) ^{a)}		Molar ratio	Mass ratio	Solvent
		TiO_2 (T)	Bi_2WO_6 (B)	TB	TB	
1	TiO_2	1	-	-	-	EG
2	Bi_2WO_6	-	1	-	-	EG
3	TB-0.5	0.5	1	0.5	0.06	EG
4	TB-1	1	1	1	0.11	EG
5	TB-2	2	1	2	0.23	EG
6	TB-5	5	1	5	0.57	EG
7	TB-10 ^{c)}	10	1	10	1.14	EG
8	BWO-H	-	1	-	-	H_2O
9	TBH-2	2	1	2	0.23	H_2O

a) Composite components of TiO_2 and Bi_2WO_6 are coded as T and B, respectively. The molar weight of T and B are 79.9 and 697.8 g mol⁻¹, respectively

b) The $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ composites are coded as TB-x, where x values are derived from the molar ratio values of $\text{TiO}_2:\text{Bi}_2\text{WO}_6$ as presented in this Table

c) In case of TB-10. 2 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.9702 g) and 1 mmol $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.3299 g) were dissolved in 60 ml ethylene glycol to prepare 1 mmol of Bi_2WO_6 . Next, 10 mmol of TiO_2 (0.799 g) is mixed into the above solution and heated at 160 °C for 6 h to obtain TB-10

were calibrated with respect to the C 1s peak at 284.8 eV and deconvoluted using Gaussian–Lorentzian functions after Shirley background subtraction. Positron annihilation lifetime spectroscopy (PALS, FAST ComTec GmbH, Germany) was utilized to analyze oxygen vacancy characteristics. The optical and electronic features of the prepared photocatalysts were comprehensively investigated using (i) UV–Visible diffuse reflectance spectroscopy (UV-Vis DRS: UV 2600, Shimadzu, Japan) and (ii) photoluminescence spectroscopy (PL: FLS1000, Edinburgh Instruments, UK). Electrochemical properties of the photocatalysts were investigated using an electrochemical workstation (AUTO-LAB PGSTAT302N, Metrohm, Switzerland). Experiments were conducted in a three-electrode quartz cell, with the catalyst-coated FTO glass as the working electrode, Ag/AgCl as the reference, and a Pt wire as the counter electrode. A 0.5 M Na₂SO₄ solution was used as the electrolyte, and illumination was provided by a 100 W UV LED. The effective area of the working electrode was 2 cm × 2 cm. Mott–Schottky measurements were performed at 1.0 kHz, EIS was recorded at an open circuit potential from 0.01 Hz to 100 kHz, and transient photocurrent responses were collected under periodic light on/off cycles.

2.4 Experimental setups for dynamic photocatalytic degradation of gaseous toluene

The photocatalytic toluene degradation experiments were carried out in a flow dynamic tubular reactor packed with fixed-bed catalytic materials (TB-x, TiO₂, or Bi₂WO₆) in ambient air at room temperature and atmospheric pressure. The bed photocatalyst was packed in the center of a quartz tube (90 mm length × 4 mm inner diameter) between two quartz wool plugs, and the packed-bed tube was surrounded by a water-cooling system to maintain a constant reaction temperature at 25 °C. The photocatalytic packed-bed tube system was uniformly irradiated from four directions using four ultraviolet (UV) lamps (8 W each; 32 W in total). The irradiance on the catalyst surface was measured to be 0.742 W using a radiometer (EVO-UA-50, Avantes, Gelderland, Netherlands). The inlet side of the photocatalytic tube was connected to the gaseous phase feed (5 ppm toluene), while the outlet was interfaced with a gas chromatograph-flame ionization detector (GC-FID). The gaseous flow rate through the photocatalyst bed was maintained at 100 mL min⁻¹ using a mini vacuum pump. This setup enabled real-time assessment of toluene degradation efficiency and identification of transient intermediates in the effluent gas stream during photocatalysis under dynamic flow conditions. The GC-FID analytical instrument was calibrated to quantify toluene concentration, as shown in Fig. S2.

Before photocatalysis, the gaseous toluene was continuously flowed through the photocatalytic bed for 40 min in the dark to establish adsorption/desorption equilibrium. Following this equilibration period, the photocatalyst surface was irradiated with UV light, and the toluene concentration was subsequently monitored by the GC-FID system to evaluate photocatalytic degradation efficiency.

2.5 Data analysis

The photocatalytic effectiveness of the TB-x photocatalysts (relative to pristine counterparts) was assessed based on five key performance metrics, including toluene degradation efficiency (X_T ; Eq. 1), steady-state reaction rate (r -value: mmol g⁻¹ h⁻¹; Eq. 2), dynamic clean air delivery rate (D-CADR: L h⁻¹ g⁻¹; Eq. 3), apparent quantum yield (AQY: %; Eq. 4), and mass-normalized apparent quantum yield (MAQY; Eq. 5). X_T is a widely used metric to evaluate the overall efficiency of catalytic bed to remove target pollutant (e.g., toluene). However, it does not consider factors such as reaction time, gas feed concentration, light intensity, or catalyst amount, potentially making it susceptible to bias from the variations in operational conditions. The steady-state r -value also neglects photon utilization efficiency and does not account for variations in light intensity or catalyst mass. AQY normalizes reaction rates by the number of incident photons but often disregards the fraction of light actually absorbed and catalyst surface area, limiting comparability across systems. Therefore, in this study, D-CADR and MAQY are used to provide advanced normalization approaches that integrate airflow, pollutant concentration decay, catalyst mass, and photon flux, thereby enabling more accurate and unbiased comparisons of photocatalytic effectiveness across varying experimental and operational conditions. These metrics guide rational catalyst evaluation and process optimization by bridging lab-scale performance with realistic application scenarios.

$$X_T (\%) = (1 - C_{out}/C_{in}) \times 100 \quad (1)$$

$$r - \text{value} = \frac{X_T \times F_T (\text{mol h}^{-1}) \times 10^3}{m_{\text{cat}} (\text{g})} \quad (2)$$

$$D - \text{CADR} = Q \times (1 - C_{out}/C_{in}) / m \quad (3)$$

$$AQY = \text{number of toluene molecules} / \text{number of incident photons} \quad (4)$$

$$MAQY = AQY / m \quad (5)$$

where C_{in} and C_{out} denote the initial and residual toluene concentrations (ppm) at time (t , h), respectively. F_T and m_{cat} represent the FA molar flow rate (mol h⁻¹) and catalyst mass

(m_{cat} (g)), respectively, and Q is the gaseous flow rate (L h^{-1}) through the catalytic bed. Note that AQY is expressed as a percentage (%) by multiplying the fractional yield in Eq. (4) by 100. Its absolute (integral) form, expressed as molecules photon^{-1} and defined as AQY (%) divided by 100, is used for the calculation of the MAQY in Eq. 5.

Together, these five parameters (i.e., X_T , D-CADR, r -value, AQY, and MAQY) offer a multidimensional framework for evaluating photocatalyst performance. They encompass pollutant removal capacity, reaction kinetics, photon utilization, and mass efficiency under simulated or real solar irradiation.

3 Results and discussion

3.1 Physicochemical characterization of photocatalysts

3.1.1 Morphological features

Figure 1a–c present SEM micrographs of the TB- x heterojunctions in comparison with the pristine components (TiO_2 , BWO-H, and Bi_2WO_6). As shown in Fig. 1a and Fig. S3, pristine TiO_2 is composed of irregularly aggregated spherical nanoparticles with grain sizes of 20–30 nm. When synthesized in an aqueous solvent, the BWO-H sample exhibits a hierarchical nanoflower-like morphology assembled from ultrathin nanosheets (Fig. 1b). In contrast, Bi_2WO_6 synthesized in ethylene glycol (EG) displays a fluffy block-like morphology with a relatively loose and porous structure (Fig. 1c). This morphological evolution indicates that EG plays a crucial role in regulating the crystal growth of Bi_2WO_6 during the hydrothermal process. Specifically, Bi^{3+} ions tend to coordinate with the hydroxyl groups of EG, which effectively reduces the concentration of free Bi^{3+} ions in the solution. This coordination suppresses supersaturation and slows down the nucleation and growth of Bi_2WO_6 crystals, ultimately leading to a loosely assembled nanosheet-based structure. After coupling TiO_2 with Bi_2WO_6 , two distinct interfacial architectures are formed depending on the Bi_2WO_6 morphology. For TBH-2, spherical TiO_2 nanoparticles are uniformly distributed on the surface of the nanosheet-assembled Bi_2WO_6 nanoflowers, as shown in Fig. 1d. In the case of TB-2, benefiting from the loose and open structure of EG-derived Bi_2WO_6 , TiO_2 nanoparticles are more tightly anchored onto the Bi_2WO_6 surface, forming intimate interfacial contact (Fig. 1e). Notably, the agglomeration of TiO_2 is significantly suppressed in the composites compared with pristine TiO_2 , indicating improved dispersion and enhanced interfacial interaction between the two components. This loose Bi_2WO_6

framework facilitates the uniform loading and tight anchoring of TiO_2 nanoparticles, which promotes intimate interfacial contact for efficient charge carrier transfer. The SEM morphologies of $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ composites with different mass ratios are shown in Fig. S4. As the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ ratio increases, a progressively higher density of TiO_2 nanoparticles is observed on the Bi_2WO_6 surface, demonstrating the tunable loading behavior. This controlled distribution is expected to optimize the number of interfacial active sites and further facilitate charge separation and transfer across the heterojunction.

High-resolution TEM (HR-TEM) images further verify the successful construction of the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunction. As shown in Fig. 1f, clear lattice fringes with an interplanar spacing of 0.355 nm are observed, corresponding to the (101) crystal plane of anatase TiO_2 [25]. Meanwhile, a lattice spacing of 0.315 nm is detected for Bi_2WO_6 (Fig. 1g), which can be indexed to the (131) plane of orthorhombic Bi_2WO_6 [26]. In the TB-2 heterostructure (Fig. 1h), the lattice fringes of TiO_2 and Bi_2WO_6 are closely adjacent to each other, providing direct evidence of the formation of a well-defined heterojunction with intimate interfacial contact. Furthermore, EDX elemental mapping (Fig. 1i) reveals a homogeneous distribution of Bi, W, Ti, and O throughout the TB-2 heterojunction, further confirming the uniform integration of TiO_2 and Bi_2WO_6 and the presence of strong interfacial coupling within the heterostructure.

3.1.2 Structural and textural properties

The XRD patterns of TB-2 compared to pristine TiO_2 and Bi_2WO_6 catalysts are shown in Fig. 2a. The diffraction pattern of TiO_2 exhibits multiple peaks, representing anatase (at 2θ of 25.3° (101), 37.8° (004), 48.0° (200), 55.1° (211), and 62.7° (204); JCPDS 21–1272) and rutile (at 2θ of 27.4° (110) and 53.9° (211); JCPDS 21–1276) phases [27]. The pattern for pristine Bi_2WO_6 exhibits characteristic peaks at 28.3° , 32.8° , 47.1° , 55.9° , which is attributed to the (131), (002), (202), and (133) plane of orthorhombic Bi_2WO_6 , respectively [28]. In the TB-2 structure, the presence of diffraction peaks belonging to both TiO_2 and Bi_2WO_6 indicates that their crystal structures remain intact after composite formation.

The surface chemistry and chemical structures of TB-2 (relative to TiO_2 and Bi_2WO_6) were further studied using FTIR spectra in Fig. 2b. For pure TiO_2 , the FTIR spectrum shows a broad absorption band in the $400\text{--}880\text{ cm}^{-1}$ region attributed to Ti–O–Ti lattice vibration, along with bands corresponding to surface hydroxyls at 1633 cm^{-1} (–OH bending) and $3000\text{--}3500\text{ cm}^{-1}$ (–OH stretching) [29]. Bi_2WO_6 , in contrast, displays the characteristic features of Bi–O–Bi/Bi–O stretching ($608/799\text{ cm}^{-1}$), W–O stretching

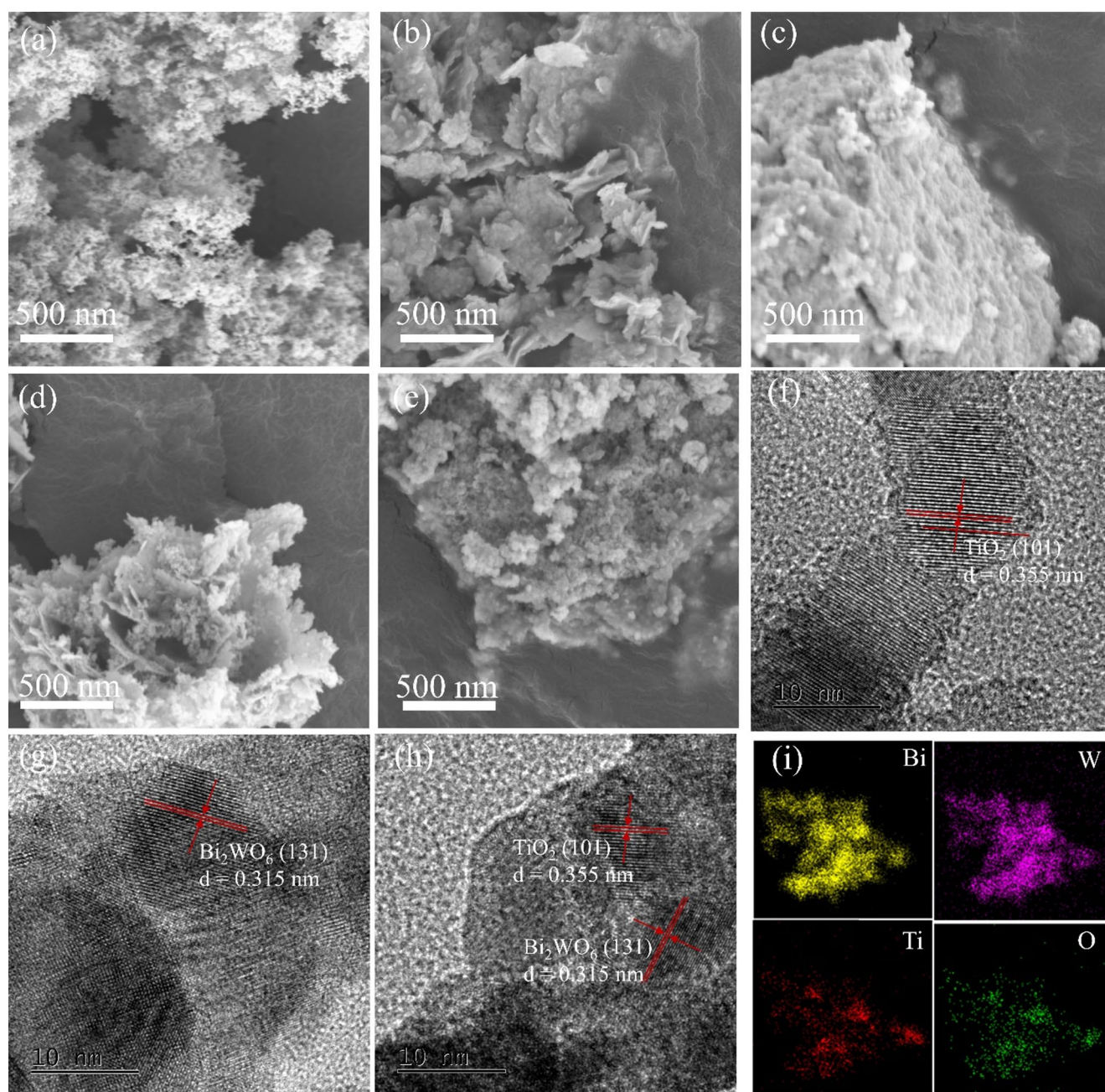


Fig. 1 Surface morphology and microstructure of the as-prepared photocatalysts: (a–e) SEM images of (a) TiO_2 , (b) BWO-H, (c) Bi_2WO_6 , (d) TBH-2, (e) TB-2, (f–h) HRTEM images of (f) TiO_2 , (g) Bi_2WO_6 , (h) TB-2, and (i) EDS elemental mapping of TB-2

modes (706 and 1150 cm^{-1}), and O–H bending/stretching vibrations (1633 and $3000\text{--}3500\text{ cm}^{-1}$), consistent with its layered Aurivillius structure and metal–oxygen bonding motifs [30]. Notably, the FTIR spectrum of TB-2 exhibits characteristic absorption features from both TiO_2 and Bi_2WO_6 , confirming the successful construction of the heterojunction. In the $400\text{--}880\text{ cm}^{-1}$ region, the Ti–O–Ti and Bi–O/W–O stretching vibrations become less distinguishable, which can be attributed to the pronounced broadening of the Ti–O–Ti band originating from TiO_2 , indicating the

dominant presence of the TiO_2 phase within the heterojunction. Nevertheless, the W–O bond stretching vibration at approximately 1150 cm^{-1} remains distinct and well resolved in TB-2, suggesting strong interfacial interactions and effective molecular-level integration between TiO_2 and Bi_2WO_6 .

The nitrogen adsorption–desorption isotherms of TB-2, TiO_2 , and Bi_2WO_6 are shown in Fig. S5a. Notably, all catalysts display type IV isotherms, indicative of mesoporosity, but with distinct hysteresis loop behavior reflecting differences in pore architecture. Pristine Bi_2WO_6 exhibits

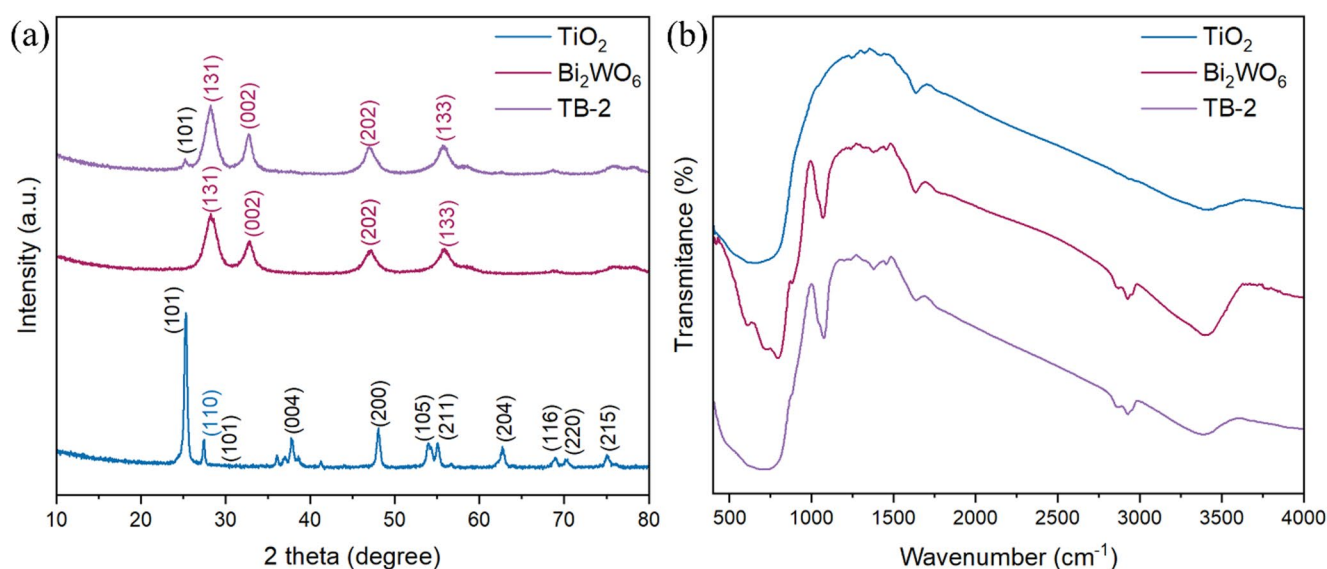


Fig. 2 Crystalline and surface properties of TB-2 with the reference catalysts (e.g., TiO_2 and Bi_2WO_6): (a) XRD patterns and (b) FTIR spectra

an H2-type hysteresis loop, characteristic of disordered mesoporous with “wormhole-like” pore structures, signifying a higher prevalence of interconnected mesopores and some pore-blocking effects [31]. In contrast, TiO_2 and TB-2 reveal H3-type hysteresis loops, implying the presence of narrow slit-like mesopores formed by the aggregation of nanoparticles and interparticle voids [32]. Based on the isotherm analysis, the texture data indicate that Bi_2WO_6 has a higher specific surface area (SSA: $68.26 \text{ m}^2 \text{ g}^{-1}$) than TiO_2 (SSA: $54.10 \text{ m}^2 \text{ g}^{-1}$). The SSA of TB-2 ($54.44 \text{ m}^2 \text{ g}^{-1}$) was closely matched to that of TiO_2 , with only a subtle increase of approximately $0.34 \text{ m}^2 \text{ g}^{-1}$ over pure TiO_2 . This indicates the close integration of Bi_2WO_6 with TiO_2 in the TB-2 composite, without substantially altering the total surface area. The porosity of photocatalysts plays an important role in enhancing the accessibility of active sites for reaction. As shown in Fig. S5b, the average pore diameters of TB-2, Bi_2WO_6 , and TiO_2 were 40.77, 23.65, and 23.25 nm, respectively. The total pore volume of TB-2 was $0.55 \text{ cm}^3 \text{ g}^{-1}$, about 1.78 times higher than that of pristine Bi_2WO_6 ($0.31 \text{ cm}^3 \text{ g}^{-1}$). The higher porosity of TB-2 improved mass transport to catalytically active sites during photocatalysis in dynamic flow conditions [33].

3.1.3 Surface composition analysis

XPS measurements were used to analyze the chemical composition and carrier transfer pathway of TB-2, in comparison with pristine TiO_2 and Bi_2WO_6 catalysts. The detection of Bi, W, Ti, and O elements in TB-2 suggests the successful integration of TiO_2 nanoparticles and Bi_2WO_6 nanosheets, forming a heterostructured composite (Fig. S6). Figure 3a presents the high-resolution Ti 2p XPS spectra. Pure TiO_2

exhibits two characteristic peaks at 458.4 and 464.1 eV, corresponding to $\text{Ti}^{4+} 2p_{3/2}$ and $\text{Ti}^{4+} 2p_{1/2}$, respectively, confirming the Ti^{4+} oxidation state [34]. Notably, upon forming the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunction, the Ti 2p peaks in TB-2 shift to higher binding energies compared with those of pristine TiO_2 , indicating electron depletion on the TiO_2 side. Figure 3b displays the high-resolution XPS spectra of Bi 4f. In Bi_2WO_6 , two distinct peaks at 159.3 and 164.5 eV correspond to the $\text{Bi}^{3+} 4f_{7/2}$ and $\text{Bi}^{3+} 4f_{5/2}$ of Bi^{3+} , respectively [35]. After integration with TiO_2 , both Bi 4f peaks in TB-2 exhibit a noticeable negative shift relative to pure Bi_2WO_6 , suggesting an increased electron density around Bi species. As shown in Fig. 3c, the binding energies at 35.4 and 37.5 eV correspond to $\text{W}^{6+} 4f_{7/2}$ and $\text{W}^{6+} 4f_{5/2}$, respectively, confirming the presence of W^{6+} in Bi_2WO_6 [36]. Similar to Bi 4f, these W 4f peaks shift slightly toward lower binding energies in TB-2, further indicating a modified electronic environment induced by heterojunction formation. These opposite binding-energy shifts provide compelling evidence for interfacial electron transfer from TiO_2 to Bi_2WO_6 , leading to the establishment of an internal electric field at the interface. Such directed charge redistribution is a defining feature of an S-scheme heterojunction and plays a crucial role in promoting spatial charge separation while suppressing carrier recombination [37]. The O 1s XPS spectrum (Fig. 3d) of TB-2 can be deconvoluted into three components at 530.2, 531.6, and 532.6 eV, which are attributed to lattice oxygen, oxygen vacancies, and adsorbed water, respectively. The oxygen vacancies peak at 531.6 eV indicates a high concentration of surface oxygen vacancies. These oxygen vacancies are widely recognized as primary active sites for molecular O_2 adsorption and activation, facilitating electron trapping and promoting the formation

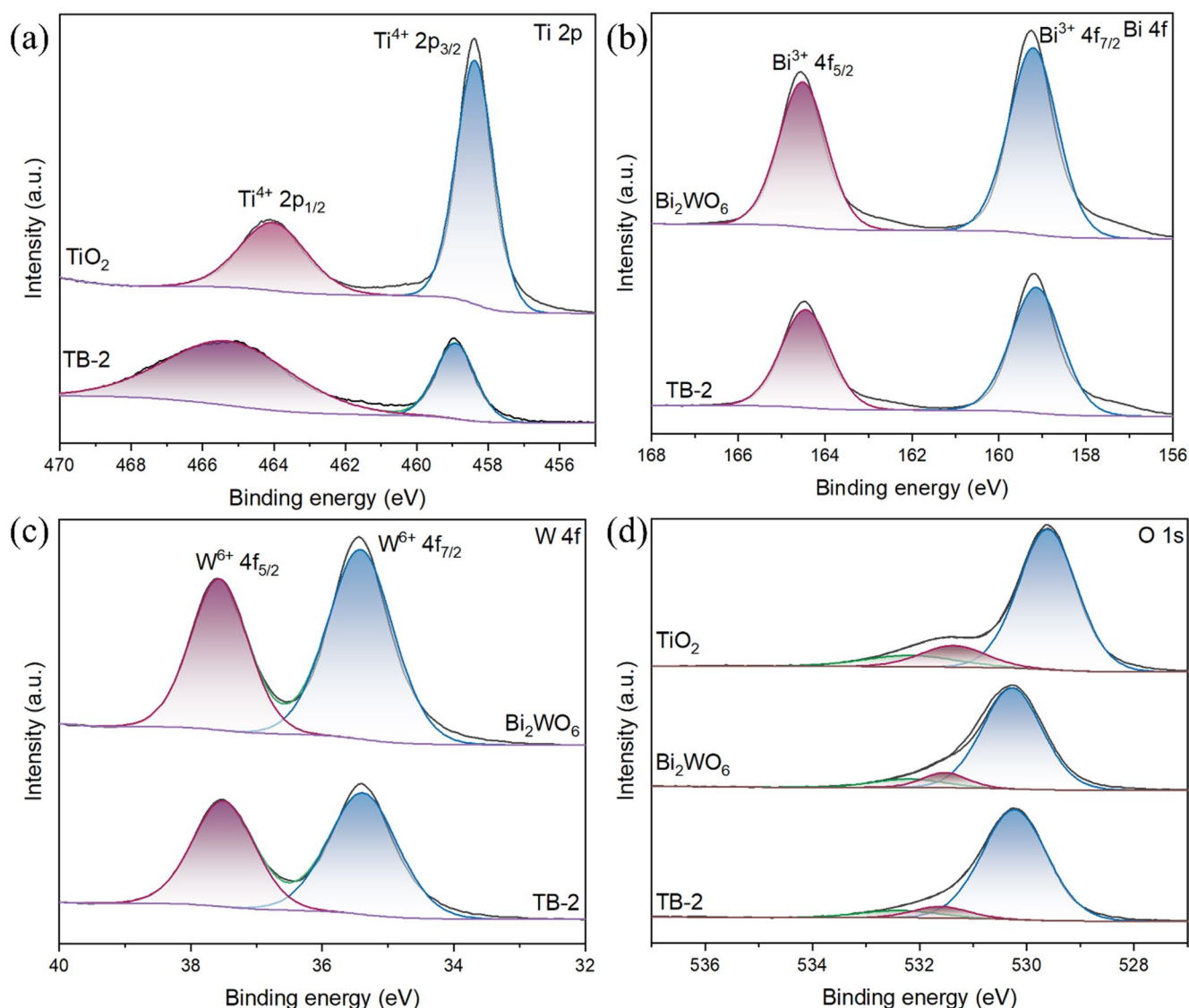


Fig. 3 High-resolution XPS spectra of TB-2 with the reference catalysts (e.g., TiO_2 and Bi_2WO_6): (a) Ti 2p, (b) Bi 4f, (c) W 4f, and (d) O 1s

of reactive oxygen species, thereby enhancing the photocatalytic performance.

Electron paramagnetic resonance (EPR) spectroscopy was employed to probe defect states in the samples. Pristine Bi_2WO_6 exhibits a significantly stronger Lorentzian signal than BWO-H, indicating a higher concentration of unpaired electrons (Fig. S7a). This difference can be attributed to the synthesis of Bi_2WO_6 in ethylene glycol, which, owing to its reducing nature, favors the generation of oxygen vacancies compared with the aqueous synthesis of BWO-H. A similar trend is observed for TB-2 and TBH-2 (Fig. S7b), where TB-2 shows a markedly stronger Lorentzian signal than TBH-2, suggesting a higher density of oxygen vacancies. The enriched oxygen vacancies in TB-2 are beneficial for charge separation and activation of reactants, thereby promoting the photocatalytic degradation of toluene.

The concentration of oxygen vacancies in TBH-2 and TB-2 was further analyzed using PALS (Fig. S8), a technique sensitive to variations in local electron density within the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructure. Both samples display two distinct lifetime components in their PALS spectra. The longer lifetime component ($\tau_2 = 365$ ps) is attributed to positron annihilation at small vacancy clusters (e.g., divacancies or trivacancies), whereas the shorter lifetime component ($\tau_1 = 205$ ps) is characteristic of positron trapping at oxygen vacancy [38]. In PALS analysis, the relative intensity (I) of each lifetime component reflects the relative abundance of the corresponding defect species. A comparison of the intensity ratios reveals that TB-2 exhibits a markedly higher I_1/I_2 value (0.21) than TBH-2 (0.03). This substantial difference indicates that oxygen vacancies are more prevalent in TB-2,

suggesting a higher defect density associated with oxygen vacancies in this sample [39].

3.2 Photocatalytic degradation of toluene

3.2.1 Photocatalytic performance of the TB composites for toluene degradation

Toluene was selected as the target VOC pollutant to evaluate the photocatalytic performance of the prepared TB photocatalyst samples. To distinguish the contribution of adsorption and photocatalysis, the experiments were conducted continuously from dark to light conditions. This approach first allows for adsorption–desorption equilibrium under dark and then for catalytic activity under UV irradiation. Under darkness, the outlet toluene concentration stabilized and matched the inlet concentration from 10 to 40 min,

indicating the establishment of adsorption–desorption equilibrium (Fig. 4a). Upon UV light irradiation, photocatalytic oxidation (PCO) of toluene was confirmed by a pronounced decrease in its outlet concentration. Pristine TiO_2 , BWO-H, and Bi_2WO_6 exhibited limited toluene conversion efficiencies (X_T) of only 28.4%, 35.0%, and 57.3%, respectively, after 1 h of illumination, which are insufficient for practical upscaled applications. Notably, Bi_2WO_6 demonstrated higher photocatalytic activity than BWO-H. This enhancement can be attributed to the ethylene-glycol-assisted synthesis of Bi_2WO_6 , which generates a higher density of oxygen vacancies serving as reactive active sites, along with a more open and loosely packed morphology compared to BWO-H synthesized in water. After coupling TiO_2 with Bi_2WO_6 , the X_T of TBH-2 increased to 79.0%. More importantly, the X_T of TB-2 further rose to 97.22%, which is 3.42 and 1.70 times higher than those of pristine TiO_2 and

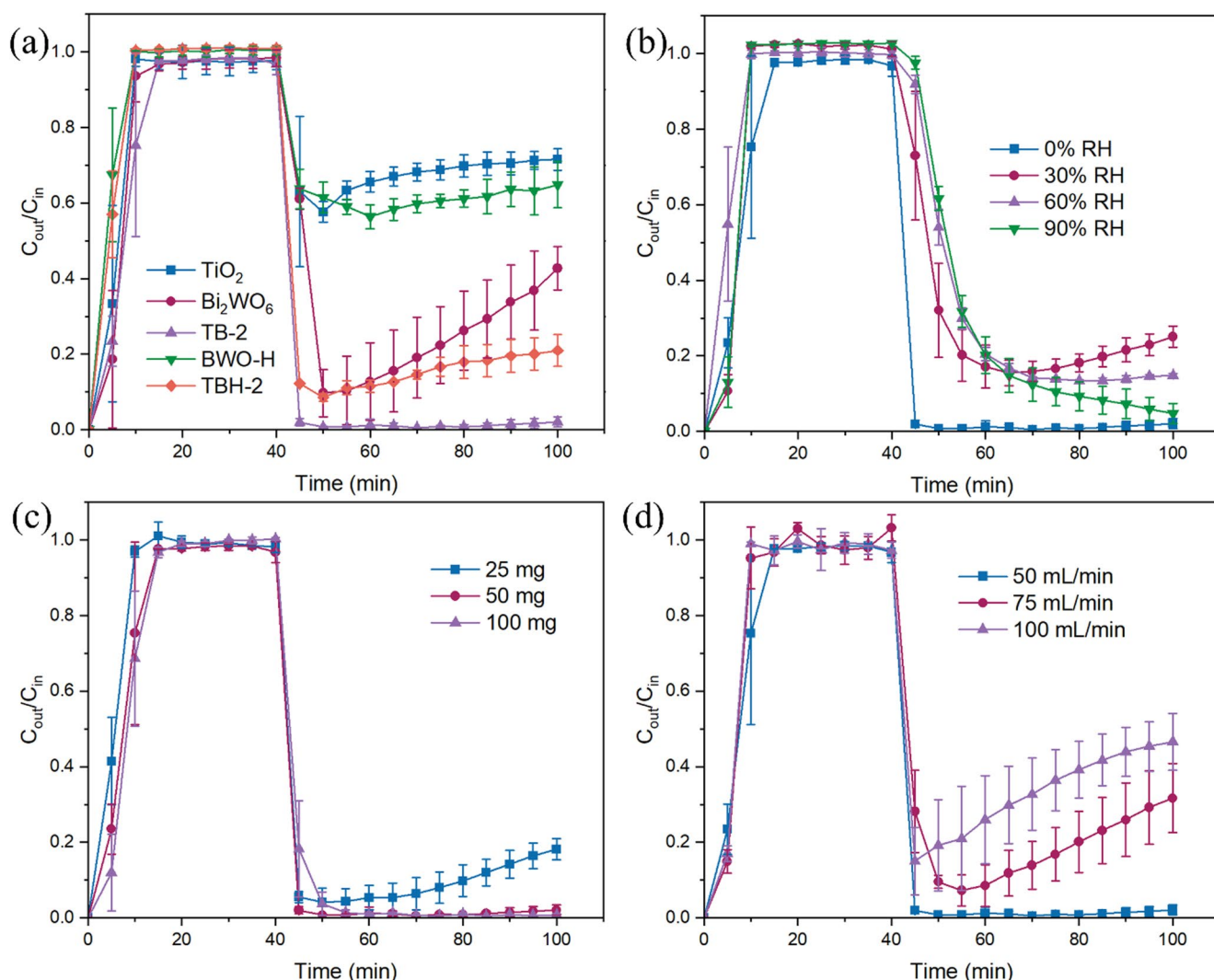


Fig. 4 Dynamic flow photocatalytic removal efficiency of gaseous toluene (5 ppm) by TB-2: (a) comparison with reference catalysts (TiO_2 , Bi_2WO_6 , BWO-H, and TBH-2), (b) effect of relative humidity, (c) effect of catalyst dosage, and (d) effect of flow rate

Bi_2WO_6 , respectively, indicating a strong synergistic effect between TiO_2 and Bi_2WO_6 .

The effects of varying T/B molar ratios were also studied in relation to the PCO performance for toluene. As shown in Fig. S9, the X_T values of TB-0.5, TB-1, TB-2, TB-5, and TB-10 were 63.39%, 81.59%, 97.22%, 83.84%, and 77.84%, respectively. As such, TB-2 exhibits the best toluene photodegradation performance, which may reflect the attainment of optimal interfacial contact at T/B molar ratio of 2. The higher contact area should have facilitated more efficient separation and transfer of photoinduced charge carriers between TiO_2 and Bi_2WO_6 , thereby promoting the PCO efficiency against toluene. Additionally, the sufficient interfacial interaction should have improved the dispersion of TiO_2 nanoparticles, increasing the availability of active sites and further enhancing the PCO performance.

Furthermore, Table 2 summarizes the photocatalytic and adsorption performance of the prepared samples based on key metrics: D-CADR, AQY, and MAQY. The D-CADR values ($\text{L h}^{-1} \text{g}^{-1}$) reveal a clear performance hierarchy, with TB-2 achieving the highest rate at 1940, followed by TB-5 (1673), TB-1 (1627), TB-10 (1553), TB-0.5 (1385), Bi_2WO_6 (1142), and TiO_2 (567). In terms of AQY, TB-2 again outperforms the others with a maximum value of 0.10%, while TB-5 and TB-1 follow closely at 0.090% and 0.087%, respectively. The MAQY further confirms the superior activity of TB-2, which reaches $2.07\text{E-}2$ molecules $\text{photon}^{-1} \text{g}^{-1}$, the highest among all samples. Given the confirmed superior performance of TB-2, the effects of various operational parameters on the PCO efficiency of TB samples were primarily investigated using TB-2, as discussed below.

Table 2 Photocatalytic performance comparison of TB-2 photocatalytic bed with its pristine counterparts for dry gaseous toluene (5 ppm) degradation under dynamic flow conditions and UV illumination

Order	Photocatalyst	X_T (%)	D-CADR ($\text{L h}^{-1} \text{g}^{-1}$)	AQY (%)	MAQY (Molecules $\text{photon}^{-1} \text{g}^{-1}$)
1	TiO_2	28.4	567	0.030	$6.05\text{E-}3$
2	Bi_2WO_6	57.2	1142	0.061	$1.22\text{E-}2$
3	TB-0.5	69.4	1385	0.074	$1.48\text{E-}2$
4	TB-1	81.5	1627	0.087	$1.74\text{E-}2$
5	TB-2	97.2	1940	0.104	$2.07\text{E-}2$
6	TB-5	83.8	1673	0.090	$1.78\text{E-}2$
7	TB-10	77.8	1553	0.083	$1.66\text{E-}2$
8	BWO-H	35.0	699	0.037	$7.46\text{E-}3$
9	TBH-2	79.0	1569	0.083	$1.68\text{E-}2$

The photocatalytic degradation of toluene for all listed data was carried out using 5 ppm toluene at a flow rate of 50 mL min^{-1} with 50 mg of catalyst and under an incident light power of 0.0754 W on the catalyst surface

3.2.2 Effects of process variables on photodegradation of toluene

The impact of different RH levels (0%, 30%, 60%, and 90%) on the toluene degradation efficiency of TB-2 was investigated. As shown in the Fig. 4b, the highest toluene degradation efficiency was obtained at 0% RH with the X_T value of 97.22% over TB-2 in 1 h. Meanwhile, the increase in RH led to a decline in toluene removal efficiency within the first 20 min of illumination, reflecting competitive adsorption between water molecule and toluene molecules [40]. However, under the low RH condition (e.g., 30%), the X_T gradually decreased from 88.5% to 75.3% as the illumination time increased from 20 min to 1 h, likely due to the accumulation of reaction by-products on the catalyst surface (i.e., deactivation of TB-2). In contrast, under the high RH condition (90%), X_T increased with prolonged illumination time. This phenomenon may be accounted for by the active generation of hydroxyl radicals over TB-2 in the presence of sufficient moisture, which in turn promotes the photodegradation of toluene [41].

The effect of TB-2 catalyst mass on the degradation of toluene (5 ppm) was studied by varying its masses (e.g., 25, 50, and 100 mg) under 0% RH condition. As seen in Figs. 4c and 25 mg of TB-2 degraded 82.84% of toluene within 60 min under UV light irradiation. With increasing the mass of TB-2 catalyst, the degradation efficiency of toluene was improved. The maximum degradation of toluene was achieved when 100 mg of TB-2 was loaded, which achieved 98.13% toluene degradation after 60 min of UV light exposure. In general, an increase in the catalyst mass increases the number of active sites and augment the catalytic region on the TB-2 surface, accelerating the degradation process of toluene. However, as the catalyst mass exceeds 50 mg, the enhancement in photocatalytic performance was less pronounced. In particular, increasing the TB-2 mass from 50 mg to 100 mg resulted in a moderate improvement in X_T , from 97.2% to 99.5%. Thus, considering both economic and catalytic performance factors, 50 mg was selected as the optimal catalyst mass for degrading gaseous toluene in the fixed-bed reactor.

To investigate the influence of flow rate, the PCO performance of TB-2 (50 mg) was examined at three toluene flow rates (50, 75, and 100 mL min^{-1}) under UV light irradiation. Accordingly, the toluene removal efficiency of TB-2 was highest in the case of 50 mL min^{-1} flow rate at dry condition (Fig. 4d). Moreover, the X_T declined from 97.2% to 55.4% as the flow rate increased from 50 to 100 mL min^{-1} . This phenomenon might be ascribed to the inadequate contact between toluene and TB-2 under the high flow rate.

Based on the above results, the photostability of the TB-2 photocatalyst under UV irradiation was further examined. As shown in Fig. S10, a rapid decrease in toluene concentration is observed, highlighting the strong PCO capability of TB-2. Importantly, this high activity is well preserved during repeated operation: after five consecutive cycles, the catalyst retains approximately 89% of its initial performance. To elucidate the origin of the observed durability, comprehensive post-reaction characterizations were carried out. As presented in Figs. S11–13, no discernible changes are observed in the morphology, crystalline structure, or surface chemical states of the catalyst after reaction. These results collectively demonstrate that the sustained PCO performance arises from the robust structural stability of the TB-2 photocatalyst.

3.3 Optical and electrochemical properties

Electrochemical impedance spectroscopy and photocurrent measurements were to study the photoinduced charge transfer capabilities of TB-2 along with its reference samples (e.g., TiO_2 and Bi_2WO_6). As shown in Fig. 5a, TB-2 exhibited a smaller semicircular radius in the Nyquist plot than those of TiO_2 and Bi_2WO_6 , indicating lower charge transfer resistance and more efficient electron mobility. This confirms that the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunction facilitates the separation and transfer of photoinduced charge carriers. A consistent trend was observed in photocurrent transient response (Fig. 5b), where TB-2 generated a significantly higher photocurrent than TiO_2 and Bi_2WO_6 . This enhancement suggests that charge carrier recombination is substantially suppressed in the TB-2 composite, consistent with its superior photocatalytic activity.

To elucidate the real-time charge carrier dynamics in the TB-2 heterostructures, femtosecond transient absorption (fs-TA) spectroscopy was performed, and the corresponding spectra are presented in Fig. 6. As shown in Fig. 6a–c, all samples display a broad excited-state absorption (ESA) band with a peak centered around 640 nm, which can be attributed to photoinduced charge carrier transitions. Kinetic analysis of the ESA signal at 640 nm reveals distinct carrier decay behaviors for each sample. For pristine TiO_2 , the decay can be fitted with two components of 3.6 ps (82%) and 71.5 ps (18%), giving an average lifetime of 15.8 ps (Fig. 6d). In the case of Bi_2WO_6 , the decay process is notably faster, with time constants of 0.9 ps (85%) and 33.8 ps (15%), corresponding to an average lifetime of 5.18 ps (Fig. 6e), indicating a high recombination rate of photo-generated carriers.

In contrast, the TB-2 heterostructure exhibits remarkably prolonged carrier lifetimes, characterized by two decay components of 4.2 ps (81%) and 93.3 ps (19%), resulting in an average lifetime of 21.1 ps (Fig. 6f). The prolonged average carrier lifetime of 21.1 ps in TB-2 provides direct evidence of highly effective charge separation. This extended lifetime provides the photogenerated electrons and holes with a much greater opportunity to migrate to the catalyst surface and participate in redox reactions before they can recombine, which is the fundamental reason for the dramatically enhanced photocatalytic activity. The extended carrier lifetime in TB-2 suggests the formation of a more efficient charge transfer pathway at the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ interface, which promotes spatial separation of electrons and holes and retards their recombination. Such efficient interfacial charge separation effectively suppresses exciton–exciton annihilation, enabling a higher population of long-lived free

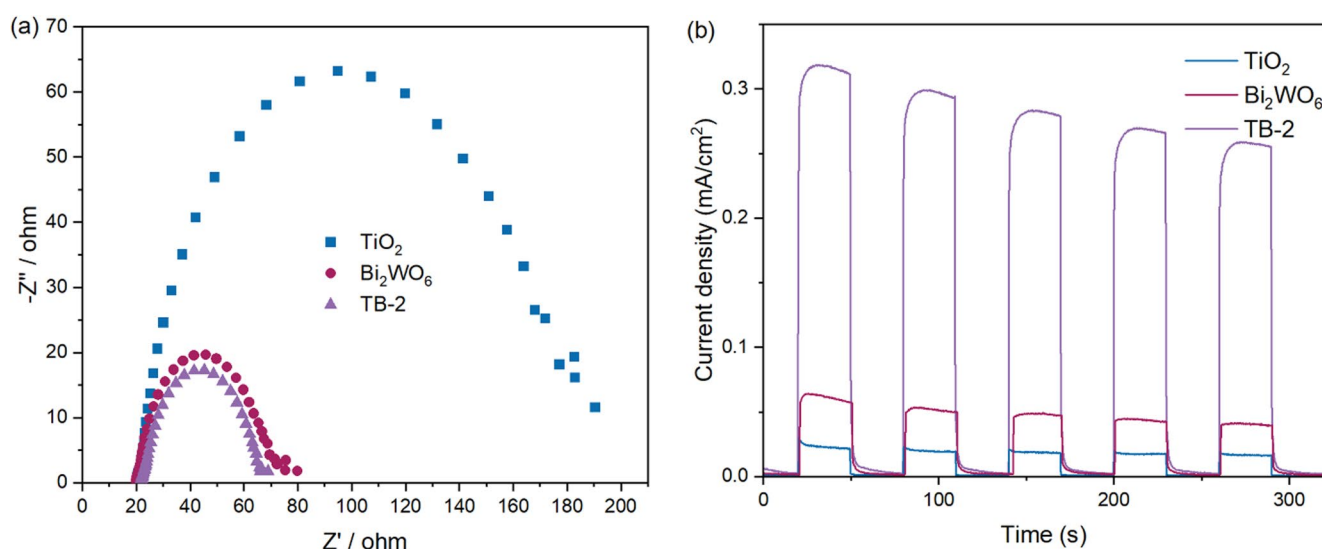


Fig. 5 Photoelectronic properties of TB-2 with the reference catalysts (e.g., TiO_2 and Bi_2WO_6): (a) EIS spectra and (b) Transient photocurrent spectra

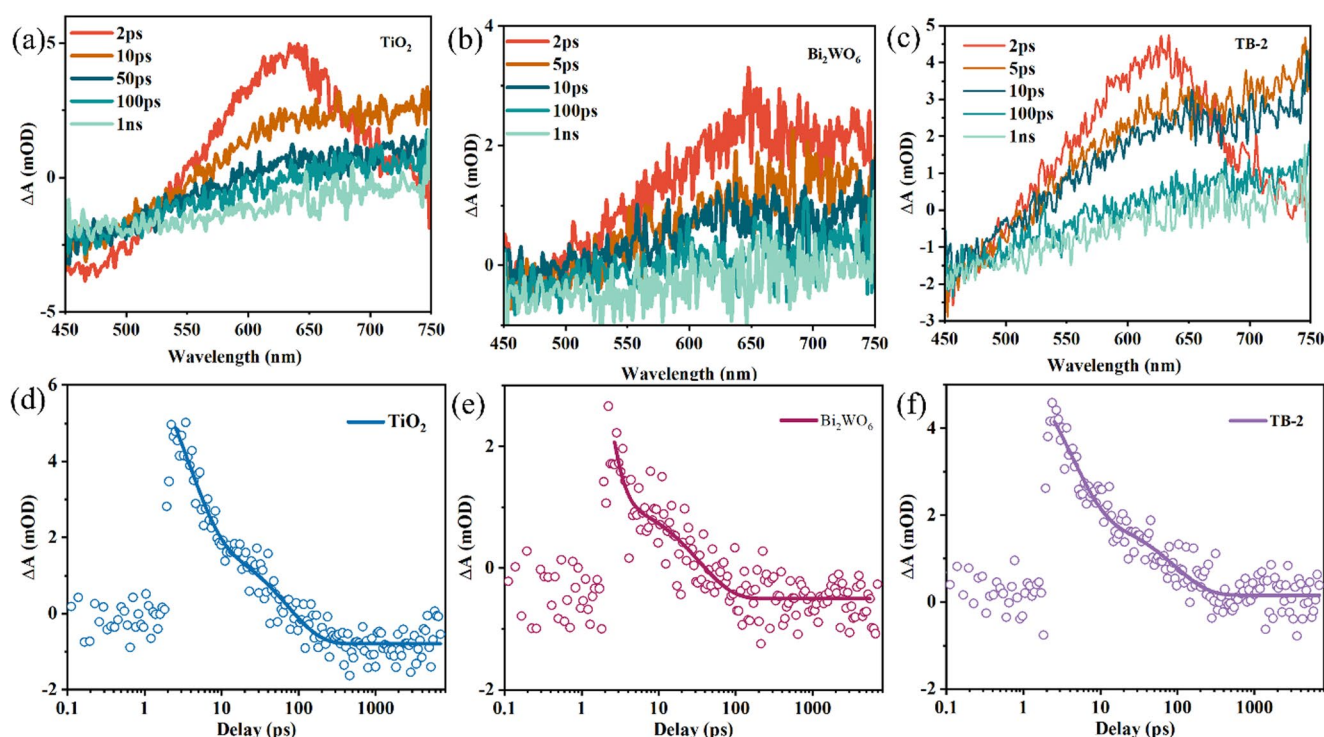


Fig. 6 Dynamics behavior of charge carriers in TB-2 with the reference catalysts (e.g., TiO_2 and Bi_2WO_6): fs-TAS spectroscopy of (a) TiO_2 , (b) Bi_2WO_6 , and (c) TB-2, charge carrier kinetic fitting curve at 640 nm of (d) TiO_2 , (e) Bi_2WO_6 , and (f) TB-2

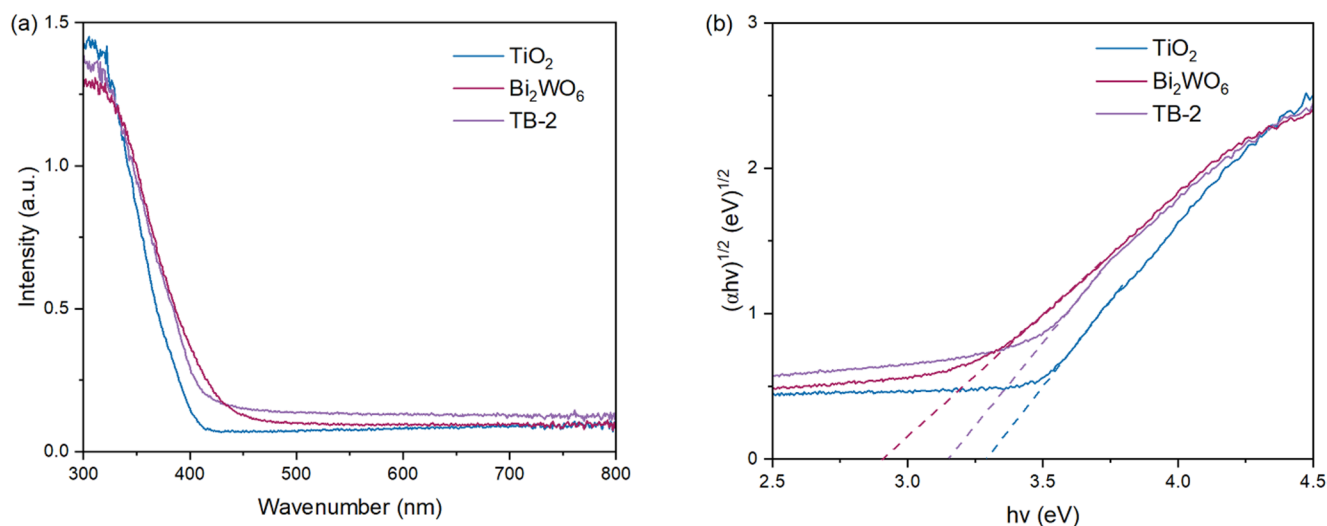


Fig. 7 Optical properties of TB-2 with the reference catalysts (e.g., TiO_2 and Bi_2WO_6): (a) UV/Vis DRS Spectra and (b) Tauc plots

charge carriers to participate in surface redox reactions [42]. Thus, the retarded carrier recombination and generation of long-lived charge carriers in TB-2 are attributed to synergistic of interfacial electronic coupling and the built-in electric field across the heterojunction interface. These factors collectively enhance charge transfer efficiency and photo-generated carrier utilization, ultimately leading to superior photocatalytic performance compared with the individual components.

The electronic band structure of the TB-2, along with its reference samples (e.g., TiO_2 and Bi_2WO_6) was investigated using UV-Vis DRS. As displayed in (Fig. 7a), the absorption edges of TiO_2 , Bi_2WO_6 , and TB-2 were about 408 nm, 438 nm, and 450 nm, respectively. In comparison with TiO_2 , TB-2 exhibited a red shift in its absorption edge, indicating enhanced visible-light absorption. The optical bandgap energies were calculated by the Kubelka-Munk function based on the Tauc plots, as shown in Fig. 7b; the bandgaps

of TiO_2 and Bi_2WO_6 , and TB-2 were calculated as 3.28 eV, 2.91 eV, and 3.18 eV, respectively. While the calculated bandgap of TB-2 (3.18 eV) is only slightly smaller than that of TiO_2 (3.28 eV), the UV-Vis DRS spectrum shows a distinct red-shift in the absorption edge to ~ 450 nm, indicating an improved light absorption capability that contributes to its enhanced photocatalytic performance compared to pure TiO_2 [43].

The Mott-Schottky analysis were carried out to investigate the band structure of TiO_2 and Bi_2WO_6 photocatalysts (Fig. S14a and b). The positive slopes observed in both curves indicate that TiO_2 and Bi_2WO_6 are n-type semiconductors. Based on the intercepts of the linear regions, the flat-band potentials of TiO_2 and Bi_2WO_6 relative to Ag/AgCl reference electrode were determined to be -0.79 eV and -0.22 eV, respectively. When converted to the normal hydrogen electrode (NHE) scale, these values correspond to -0.593 eV for TiO_2 and -0.023 eV for Bi_2WO_6 . For n-type semiconductors, the conduction band (CB) potential is typically ~ 0.2 eV more negative than the flat-band potential. Therefore, the CB potentials of TiO_2 and Bi_2WO_6 were -0.793 eV and -0.223 eV vs. NHE, respectively.

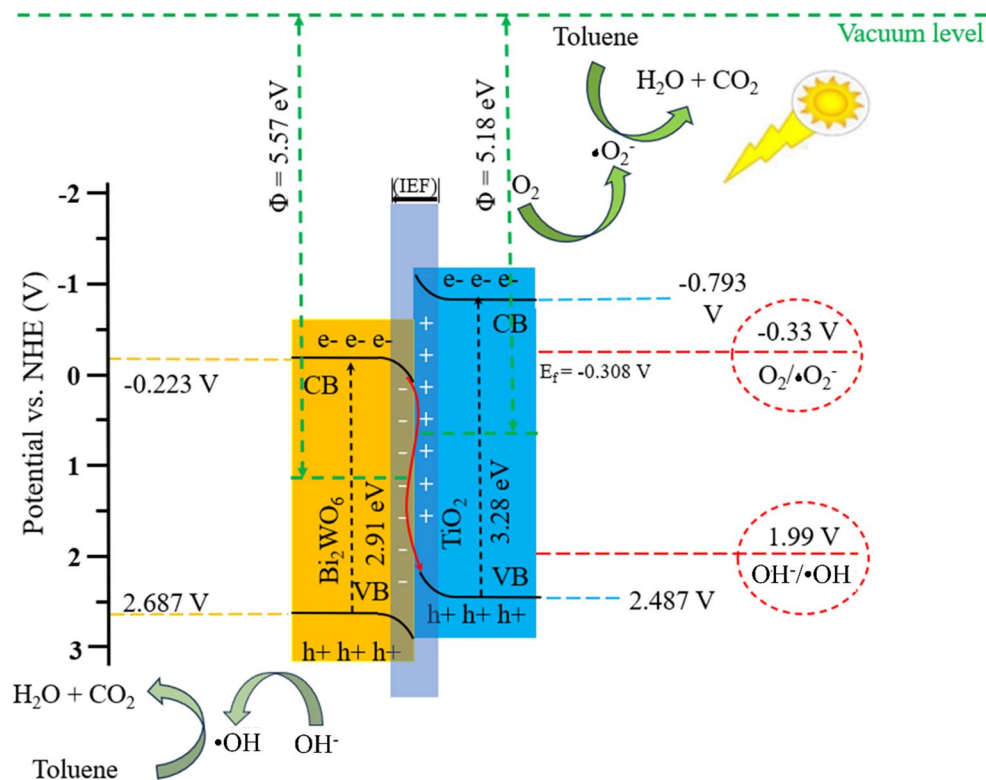
Using the equation $E_g = E_{\text{VB}} - E_{\text{CB}}$, the VB potentials (E_{VB}) of TiO_2 and Bi_2WO_6 photocatalysts was determined to be 2.487 eV and 2.687 eV, respectively. Besides, ultraviolet photoelectron spectroscopy (UPS) was employed to determine their work functions, which were calculated as 5.18 eV and 5.57 eV, respectively (Fig. S15). The

corresponding band structures of TiO_2 and Bi_2WO_6 are depicted in Fig. S16.

As illustrated in Fig. 8, upon contact between TiO_2 and Bi_2WO_6 , electrons spontaneously transfer from TiO_2 to Bi_2WO_6 owing to the higher Fermi level of TiO_2 . This interfacial charge redistribution establishes an internal electric field, resulting in upward band bending in TiO_2 and downward band bending in Bi_2WO_6 . Under light irradiation, photogenerated electrons in the conduction band of Bi_2WO_6 recombine with holes in the valence band of TiO_2 at the interface, which is characteristic of an S-scheme heterojunction. In contrast to a conventional type-II mechanism, where electrons and holes would migrate to lower redox-potential bands, the S-scheme configuration preserves the highly oxidative holes in the valence band of Bi_2WO_6 and the strongly reductive electrons in the conduction band of TiO_2 . Consequently, TB-2 retains strong redox capability, enabling efficient generation of reactive oxygen species, including hydroxyl radicals ($\cdot\text{OH}$) from OH^- and superoxide radicals ($\cdot\text{O}_2^-$) from dissolved oxygen. These reactive species synergistically drive the efficient oxidation and complete mineralization of toluene.

The charge-transfer mechanisms at the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ interface has been debated, with type-II, Z-scheme, and S-scheme models proposed in previous studies [21–23]. The present work provides clear evidence identifying an S-scheme pathway. The simultaneous generation of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, together with the preserved strong redox potentials,

Fig. 8 Energy band diagram of TB-2 and charge transfer pathway for toluene PCD



is inconsistent with a conventional type-II mechanism that would weaken the redox ability. Meanwhile, unlike traditional Z-scheme systems that rely on external mediators or solid electron conductors, the charge transfer in this system is driven by an intrinsic interfacial electric field and band bending. Consequently, a direct S-scheme $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunction is realized, enabling efficient charge separation while preserving strong redox ability, which accounts for its superior photocatalytic performance.

3.4 PCO reaction pathway of toluene over TB photocatalysts

To investigate the reaction pathway for toluene degradation, electron paramagnetic resonance (EPR) spectroscopy was performed using DMPO as a spin-trapping agent (Fig. S17). Under light irradiation, TB-2 exhibited a distinct six-line EPR signal characteristic of $\bullet\text{O}_2^-$, indicating that the conduction band potential of TB-2 is sufficiently negative to reduce molecular oxygen to $\bullet\text{O}_2^-$. In addition, a clear signal corresponding to $\bullet\text{OH}$ was also observed, demonstrating that TB-2 is capable of generating $\bullet\text{OH}$ species during the photocatalytic process.

In-situ DRIFTS analysis was employed under dry and humid conditions to investigate the adsorption and photocatalytic reaction mechanisms of toluene over the TB-2 catalyst and to identify key reaction intermediates (Fig. 9). A summary of the identified intermediates is provided in Table S1. Generally, the peak intensities increased significantly upon UV illumination, indicating that photocatalytic oxidation plays a dominant role in toluene removal.

Under dark conditions (Fig. 9a), a small peak around 1495 cm^{-1} appeared, which can be assigned to the C–H

stretching vibration from aromatic rings, indicating the adsorption of toluene molecules on the TB-2 surface [44]. Additionally, a peak at 1245 cm^{-1} corresponds to the C–O stretching vibration of benzyl alcohol while that at around 1723 cm^{-1} is associated with C=O stretching vibration of benzaldehyde [45, 46]. These findings indicate that adsorbed toluene can undergo partial oxidation to form benzyl alcohol, which may then be further oxidized to benzaldehyde. When light was switched on (Fig. 9b), more peaks with stronger intensity were observed. Apart from the peaks (1467 cm^{-1} , 2901 cm^{-1} , and 2968 cm^{-1}) corresponding to absorbed toluene (Table 2) [47, 48], two additional peaks at 1158 cm^{-1} and 1200 cm^{-1} appeared in association with the C–O stretching vibration of benzyl alcohol [49]. A distinct peak at 1658 cm^{-1} was indicative of C=O stretching in benzoic acid [50]. In addition, the peaks around 1415 cm^{-1} and 1450 cm^{-1} were associated with the O–H banding of carboxylic acid and C–H bending of alkane, respectively [51, 52]. Thus, more reaction intermediates (benzyl alcohol, benzaldehyde, and benzoic acid) were produced over TB-2 photocatalyst. These intermediates are subsequently broken down through ring-opening reaction to yield harmless products such as alkanes, carbon dioxide, and water [43].

The effect of moisture on the toluene PCO was also investigated. Under dark conditions (Fig. S18a), more IR peaks were found under humid condition than under dry condition. The peaks at 1363 cm^{-1} and 1466 cm^{-1} were ascribed to symmetric and asymmetric stretching vibration of CH_3 group, while the peak at 1158 cm^{-1} corresponded to the C–O stretching vibration of benzyl alcohol [53]. Additionally, the C–H stretching vibrations of toluene exhibited shifts to 2853 cm^{-1} and 2915 cm^{-1} under humid conditions, suggesting that the adsorption of toluene gas on

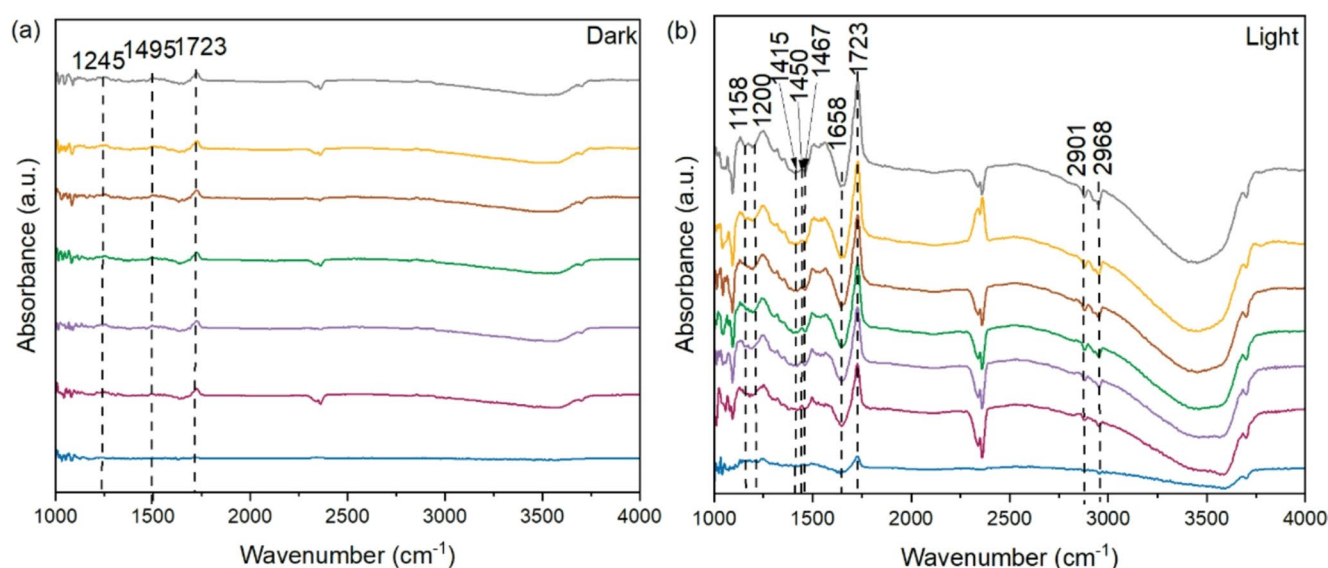


Fig. 9 In situ DRIFTS spectra for the removal of toluene onto TB-2 under (a) dark and (b) UV light illumination

TB-2 catalyst was affected by the presence of H_2O molecules [54]. When the light was turned on (Fig. S18b), peaks at 1363 cm^{-1} and 1495 cm^{-1} were observed again to reflect the adsorption of toluene. A peak at 1330 cm^{-1} further confirmed the formation of benzyl alcohol. A new peak at 1450 cm^{-1} indicated the formation of alkanes. These results suggest that under humid, illuminated conditions, toluene is initially converted into phenyl-containing intermediates, which are subsequently transformed into alkanes and non-toxic final products over the TB-2 catalyst.

The overall intensities of the peaks associated with adsorbed toluene and reaction intermediates are markedly lower under humid conditions than under dry atmospheres, indicating that the presence of H_2O adversely affects both the adsorption and subsequent photocatalytic degradation of toluene on the TB-2 catalyst. This activity suppression can be attributed to competitive adsorption between water molecules and toluene, as well as possible blockage of active surface sites by adsorbed H_2O species [55]. Despite this inhibitory effect, the formation of an S-scheme heterojunction remains highly advantageous. By promoting efficient charge-carrier separation while preserving strong redox potentials, highly reductive electrons in the conduction band of TiO_2 and strongly oxidative holes in the valence band of Bi_2WO_6 are retained. This provides sufficient thermodynamic driving force to generate reactive oxygen species and ultimately enabling efficient oxidation and complete mineralization of toluene.

Density functional theory (DFT) calculations were carried out to gain deeper insight into the structure–function relationship of the investigated photocatalysts. The total and partial density of states (DOS) of the different systems are presented in Fig. 10a–e. As shown in Fig. 10a, the valence band maximum (VBM) of BWO-H is mainly composed of O 2p orbitals, indicating that the valence-band electronic structure is dominated by oxygen states. A similar electronic feature is also observed for pristine Bi_2WO_6 (Fig. 10b), where the VBM is likewise governed by O 2p states. In addition, an intermediate electronic state appears within the band gap of Bi_2WO_6 , which can be attributed to the presence of oxygen vacancies, consistent with defect-induced electronic modulation. For pristine TiO_2 (Fig. 10c), the conduction band minimum (CBM) is primarily contributed by Ti 3d orbitals, while the VBM is dominated by O 2p orbitals, in good agreement with previous theoretical reports. Upon constructing the heterojunction, the electronic structure shows distinct but systematic evolution. For TBH-2 (Fig. 10d), the CBM and VBM are still mainly composed of Ti 3d and O 2p states, respectively, suggesting that the band-edge characteristics are largely inherited from the TiO_2 component. A similar DOS distribution is also observed for TB-2 (Fig. 10e), confirming the dominant role of TiO_2 in defining the band-edge electronic structure of the $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterojunctions. Notably, the calculated electronic structure reveals that the conduction band of TB-2 is shifted closer to the Fermi level compared with the pristine

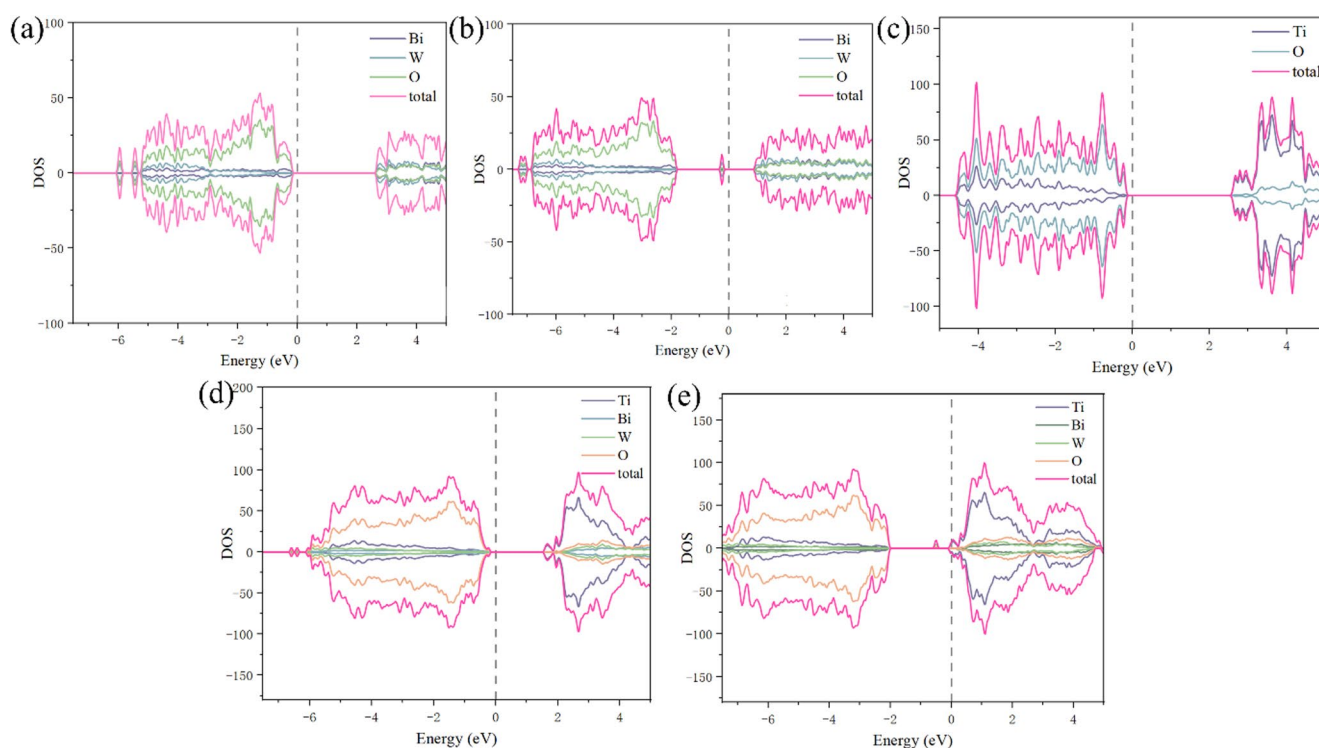


Fig. 10 Calculated DOS curves: (a) BWO-H, (b) Bi_2WO_6 , (c) TiO_2 , (d) TBH-2, and (f) TB-2

components. This upward shift implies a reduced effective band gap and enhanced electronic delocalization near the CB edge, which is expected to facilitate photoexcited electron migration and interfacial charge transfer. Such favorable band alignment is highly beneficial for suppressing charge recombination and improving the photocatalytic performance of the TB-2 heterojunction.

Furthermore, DFT-derived charge-density-difference maps (Fig. 11a, b) clearly reveal pronounced interfacial electron redistribution, with electron accumulation on Bi_2WO_6 (yellow) and electron depletion on TiO_2 (cyan). This spatial charge separation signifies the formation of a built-in electric field within the TB-2 heterojunction, which drives the migration of photogenerated electrons toward the conduction band of Bi_2WO_6 while retaining holes in the valence band of TiO_2 , thereby providing direct evidence for an S-scheme charge transfer pathway. To establish a direct correlation between electronic structure modulation and catalytic activity, the adsorption and activation behavior of H_2O were systematically investigated (Fig. 11c–f). Upon H_2O adsorption, TB-2 exhibits pronounced charge redistribution at the adsorption interface, indicative of strong electronic coupling between the adsorbate and the defect-engineered surface. In contrast, TBH-2 displays only weak charge polarization, reflecting limited adsorbate and substrate interaction. Collectively, these results demonstrate that defect-induced electronic states effectively regulate intermediate adsorption and activation, thereby promoting enhanced catalytic reactivity.

3.5 Performance comparison

To facilitate real-world implementation of photocatalytic air purification technologies, it is essential to assess not only the intrinsic activity of the catalysts but also their practical performance under conditions relevant to industrial and indoor applications. Such evaluations help determine whether a material possesses the necessary balance of efficiency, scalability, and energy utilization to be considered commercially viable. In particular, metrics that reflect catalytic productivity per unit of energy or mass, as well as pollutant removal capacity, are critical for benchmarking against existing technologies.

In order to evaluate the practical feasibility of the prepared TB-2 photocatalyst, its photodegradation performance was compared with those of similar catalysts reported to date (Table 3). This comparison was made in terms of X_T (%), D-CADR ($\text{L h}^{-1} \text{g}^{-1}$), AQY (%), and MAQY ($\text{molecules photon}^{-1} \text{mg}^{-1}$). These metrics collectively enable a quantitative assessment of the photocatalytic activity level of the hybrid system, providing insight into both its intrinsic reactivity and practical applicability.

Our TB-2 photocatalyst demonstrates superior performance in toluene removal, achieving a near-complete conversion ($X_T = 97.2\%$). This high single-pass efficiency is critical for practical applications where minimizing contaminant breakthrough is paramount. This value significantly surpasses those reported for other advanced photocatalysts, such as $\text{TiO}_2/\text{HKUST-1}/\text{RGO}$ (90.1%) and $\text{TiO}_2\text{-CeO}_2$ NCs (90%), highlighting its potential for efficient degradation.

Fig. 11 Charge density difference calculation results of TB-2 and its comparative sample (TBH-2): (a, b) charge density difference of TB-2 with an isosurface of 0.002 e/Bohr^3 , (c, d) H_2O charge difference TBH-2, and (e, f) H_2O charge difference TB-2

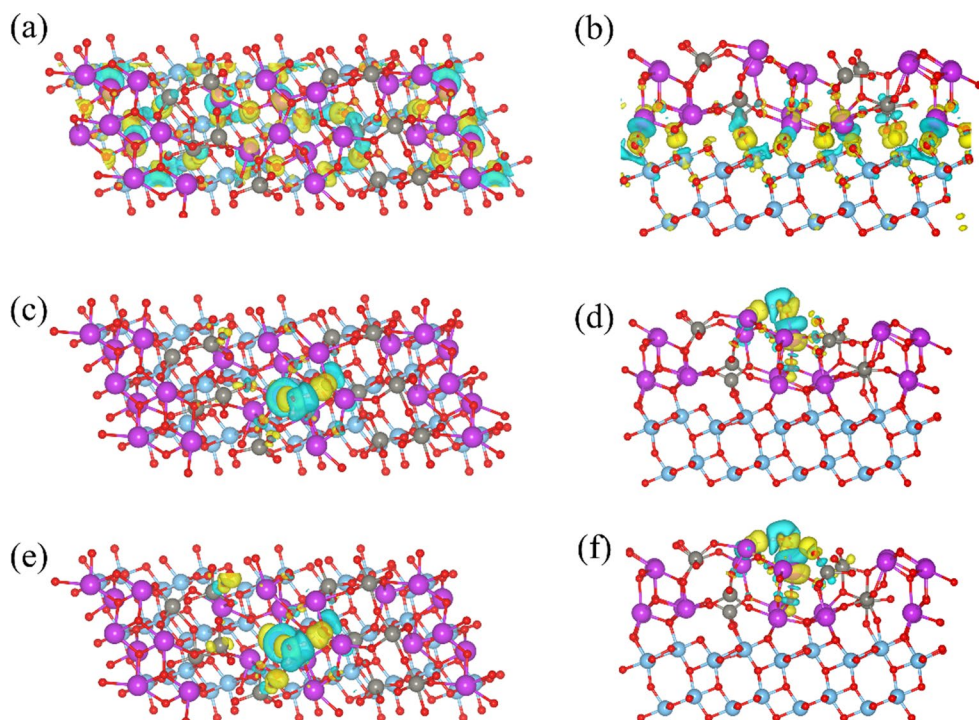


Table 3 PCD performance comparison of TB-2 (in this study) with other published photocatalysts toward gaseous toluene removal

Order	Photocatalyst	Light source (W)	Reactor	Catalyst mass (mg)	Concentration (ppm)	Reaction duration (min)	Conversion (%)	Flow rate (mL min ⁻¹)	D-CADR (L h ⁻¹ g ⁻¹)	AQY (%)	MAQY (molecular photon ⁻¹ g ⁻¹)	Reference
1	TiO ₂ /HKUST-1/RGO	UV (15)	Batch	375	50	150	90.1	-	-	8.91E-7	2.38E-8	[57]
2	TiO ₂ -CeO ₂ NCs	UV (6)	Batch	500	10	150	90	-	-	1.40E-5	2.80E-7	[58]
3	CuS-CdS/TiO ₂	Xenon (35)	fixed-bed tube	-	4215	100	88.1	-	-	-	-	[59]
4	TiO ₂ -350°C	Xenon (300)	fixed-bed tube	40	200	120	82.0	50	1025	2.21E-4	5.44E-7	[60]
5	TiO ₂ /BaTiO ₃	UV (300)	fixed-bed tube	400	50	60	85.9	60	128.9	2.78E-5	6.901E-7	[61]
6	TiO ₂ /MgAl-LDHs	UV (300)	fixed-bed tube	400	50	30	74.3	100	185.75	4.01E-5	9.80E-7	[62]
7	TiO ₂ -UiO-66-NH ₂	UV (125)	fixed-bed tube	100	25	240	72.7	25	181.75	2.35E-4	2.35E-6	[63]
8	Bi ₂ SiO ₅ /TiO ₂	UV (300)	fixed-bed tube	1000	50	30	80.8	1000	808	4.31E-4	4.31E-6	[56]
9	TB-2	UV (32)	fixed-bed tube	50	5	100	97.2	50	1940	2.45E-4	4.88E-5	This work

Because of the general absence of the actual incident power data in many studies, the AQY and MAQY values are computed based on the total output power of the light source. However, for TB-2, an AQY value of 0.104% was computed using the actual light power on the surface (0.0754 W) while 2.45E-4 is derived using the total light power of 32 W

From the perspective of photocatalytic activity level, TB-2 can be classified among the top-performing hybrid photocatalysts reported for gas-phase toluene degradation to date. While a high X_T is essential, the D-CADR metric provides a more practical measure of the air volume that can be purified per unit time and catalyst mass. With a D-CADR of 1940 L h⁻¹ g⁻¹, TB-2 is nearly twice as effective as the next best performer, TiO₂-350 °C (1025), demonstrating its superior kinetic performance under continuous flow conditions. It is important to note that direct comparison of AQY values across different studies is challenging due to variations in light source reporting (see Note, Table 3). Nevertheless, the performance of TB-2 remains superior even when considering these potential discrepancies. Importantly, its AQY (1.04E-3) places it within the upper tier of reported photocatalysts, indicating efficient photon-to-charge conversion capability. In terms of AQY, the top three catalysts were identified as Bi₂SiO₅/TiO₂ (1.83E-3) > TB-2 (1.04E-3) > TiO₂/MgAl-LDHs (1.70E-4). The high AQY of Bi₂SiO₅/TiO₂ can be attributed to the formation of a Bi/Si-O-Ti interfacial structure, which enhances charge separation and accelerates interfacial electron transfer [56]. This structure improved the generation of reactive species and facilitated the photocatalytic degradation of toluene. Furthermore, when normalized for catalyst mass, the MAQY of TB-2 (2.07E-2) is an order of magnitude higher than its closest competitors like Bi₂SiO₅/TiO₂ (1.83E-6). The high MAQY of TB-2 clearly demonstrates that this hybrid system possesses a superior intrinsic photocatalytic activity at the molecular level, reflecting highly efficient photon utilization. This indicates that the intrinsic photon utilization efficiency per gram of our TB-2 catalyst is exceptionally high, a key factor for designing cost-effective and scalable air purification systems. Overall, considering multiple performance indicators, the photocatalytic activity of the TB-2 hybrid can be regarded as being at an advanced level among currently reported photocatalytic systems.

4 Conclusion

In summary, the S-scheme TiO₂/Bi₂WO₆ heterojunction exhibits outstanding toluene degradation performance, delivering a high D-CADR (1940 L h⁻¹ g⁻¹), AQY (0.104%), and MAQY (2.07×10^{-2} molecular photon⁻¹ g⁻¹). This performance originates from the synergistic effect between oxygen vacancies in Bi₂WO₆ and the TiO₂/Bi₂WO₆ heterojunction, which establishes an efficient S-scheme charge-transfer pathway. As a result, the carrier lifetime is prolonged (21.1 ps), and strong redox capability is maintained, and good structural stability is achieved. Stable operation under dynamic flow and varying humidity

highlights the practical applicability of TB-2. Combined in situ spectroscopy and theoretical analysis further elucidate a multistep toluene mineralization mechanism. Overall, this work provides a rational framework for designing high-performance heterojunction photocatalysts with both mechanistic clarity and real-world relevance for air purification.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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