



2D/1D Z-scheme heterojunction of Bi₃O₄Br and TiO₂ nanobelt for photocatalytic degradation of pharmaceuticals[☆]

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ABSTRACT

The pharmaceuticals present in wastewater treatment effluents cause significant environmental concern due to their persistence and potential toxicity. In the present work, a novel 2D/1D Z-scheme Bi₃O₄Br and TiO₂ nanobelt (Bi₃O₄Br/TiO₂ NB) photocatalyst was synthesized for the degradation of pharmaceuticals. Photocatalytic activity of this heterojunction catalyst was evaluated in the degradation of paracetamol and the effects of pH, photocatalyst dosage, pollutant concentration, and temperature were investigated. The Bi₃O₄Br/TiO₂ NB with a ratio of 2:1 enabled the highest 89 % degradation of paracetamol. Total organic carbon (TOC) analysis showed 54 % and 70 % TOC removal with 0.2 g and 0.4 g of the composite, respectively. Active species trapping experiments and electron paramagnetic resonance (EPR) analysis confirmed a Z-scheme charge transfer mechanism, improving charge carrier separation and increased generation of reactive oxygen species. Minimal structural degradation over four experimental cycles reflects the good stability of the composite. The degradation of diluted pharmaceutical wastewater using Bi₃O₄Br/TiO₂ NB decreased TOC by 21 % demonstrating the potential of the catalyst in the practical applications.

1. Introduction

The presence of pharmaceuticals in wastewater treatment effluents has become increasingly problematic due to their poor degradability in municipal wastewater facilities [1,2]. During the COVID-19 pandemic, paracetamol consumption increased by 198 %, leading to an increased concentration in wastewater treatment plants [3]. Paracetamol is a commonly used painkiller and is prescribed worldwide [4]. It has been found at a concentration of 6 µg L⁻¹ in European wastewater treatment plant effluents and 10 µg L⁻¹ concentrations in natural waterways in the USA [4]. The discharge of untreated or partially treated wastewater containing paracetamol can have significant harmful impacts on aquatic life and they are potentially carcinogenic and mutagenic for humans [5,6].

Several methods have been noted as effective in removing

paracetamol from water, including adsorption, electrochemical techniques, and advanced oxidation processes (AOPs) [3]. AOPs, such as photocatalysis, electrocatalysis, and sonocatalysis, have garnered considerable interest for the degradation of pollutants [2]. Photocatalysis is a reaction that is initiated by the absorption of light by a photocatalytic semiconductor [7]. Irradiation of the semiconductor with photons having energy greater than its bandgap causes excitation of electrons from the valence band (VB) to the conduction band (CB), generating electron-hole pairs that enable redox reactions [8]. However, many electron-hole pairs can recombine as they move towards the surface, with only a few of them participating in the photocatalytic reaction [9]. Therefore, preventing electron-hole recombination is an effective strategy to enhance photocatalytic reactions. The Z-scheme heterojunction can effectively regulate directional charge migration and enhance the separation of photogenerated charge carriers while

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Table 1

XRF results of the prepared materials.

Sample	Weight %				Atomic %				Compound %	
	Ti	Bi	O	Br	Ti	Bi	O	Br	TiO ₂	Bi ₃ O ₄ Br
TiO ₂ NB	59.43	–	40.11	–	33.11	–	66.88	–	99.14	–
Bi ₃ O ₄ Br	–	80.66	8.61	10.3	–	36.64	51.11	12.24	–	99.84
1:1	16.77	56.79	19.08	5.38	18.61	14.4	63.36	3.58	27.64	69.05
1:2	27.06	42.36	24.83	3.18	23.90	8.58	65.70	1.68	44.34	51.21
1:4	34.28	33.86	27.92	2.37	26.90	6.10	65.70	1.10	56.30	41
2:1	11.73	63.84	16.53	5.98	14.70	18.4	62.28	4.50	19.29	77.48
4:1	6.51	68.93	14.85	6.03	9.20	22.40	63.10	5.10	10.64	83.13

Table 2

BET results of the prepared materials.

Sample	S _{BET} (m ² g ^{−1})	Average pore volume (cm ³ g ^{−1})	Average Pore diameter (nm)
P25	51	0.160	17
TiO ₂	–	–	–
TiO ₂ NB	22	0.104	17
Bi ₃ O ₄ Br	16	0.127	26
2:1	23	0.117	19

retaining the redox potentials [10–14]. In a Z-scheme heterojunction, the CB and VB of the combined photocatalysts need to be well aligned to enable efficient charge carrier transfer. At least one of the photocatalysts should have a negative CB potential and a narrow bandgap to promote reduction reactions and visible light absorption. In Bi₃O₄Br/TiO₂ NB heterojunction, the electrons in the CB of TiO₂ NB recombine with holes in the VB of Bi₃O₄Br leading to efficient separation of the remaining electrons with stronger reducibility in the CB of Bi₃O₄Br and holes with stronger oxidation capability in the VB of TiO₂ NB.

Titanium dioxide (TiO₂) has unique physical and chemical properties, including insolubility in water and organic solvents, as well as stability at high temperatures, which make it a highly effective photocatalyst. TiO₂ exhibits limited light absorption due to its large band gap (3.2 eV), which allows it to absorb only ultraviolet light [15]. Various morphologies of TiO₂, such as nanoparticles, nanobelts, and microspheres, have been developed for different applications ranging from air and water purification to self-cleaning surfaces and renewable energy generation. One-dimensional (1D) TiO₂ nanobelts (TiO₂ NB) are remarkable because of the great electron mobility and high surface-to-volume ratio, which provide benefits over zero-dimensional (0D) TiO₂ nanoparticles [16,17]. Although 0D TiO₂ nanoparticles have a higher specific surface area compared to 1D TiO₂ nanobelts, the accessible surface area and active sites along 1D TiO₂ can be more effectively utilized for photocatalysis. 1D TiO₂ nanobelts provide effective pathways for electron transport, reducing recombination rates and enhancing charge mobility [18,19]. Although several techniques have been developed for TiO₂ nanobelt production, hydrothermal synthesis is particularly suitable due to its ability to control the morphology of TiO₂. This method involves the use of directing agents, such as NaOH, to promote specific crystal growth. The presence of Na⁺ ion leads to the creation of layered Na₂Ti₃O₇ structures. However, the presence of sodium can have a negative impact on photocatalytic activity, and it needs to be removed using an acid solution, for example HCl [20].

The photocatalytic performance of TiO₂ nanobelts has been further improved using surface modification, noble metal doping, and coupling with low bandgap semiconductors to form heterojunctions [21,22]. Bismuth oxybromides (BiOBr) and bismuth-rich oxybromides (Bi_aO_bBr_c) have narrower bandgaps and therefore exhibit visible light activity. In our previous study [23], BiOBr, Bi₃O₄Br and Bi₂₄O₃₁Br₁₀ were studied for the degradation of paracetamol. Since Bi₃O₄Br (band gap 2.6–2.7 eV) was observed to have the best photocatalytic performance, it was selected to form a heterojunction with TiO₂ NB. In a Z-scheme heterojunction, electrons in the CB of TiO₂ NB are recombined with VB holes of

Bi₃O₄Br, leading to electron accumulation on Bi₃O₄Br for reduction reactions and hole accumulation on TiO₂ NB for oxidation reactions. Bi₃O₄Br has a layered two-dimensional structure, whose thin layers lead to a shorter migration distance for electrons and holes [24].

Although bismuth oxybromides (BiOBr) have been extensively studied, investigations focusing on Bi rich bismuth oxybromides, such as Bi₃O₄Br, remain limited. The number of studies exploring the photocatalytic activity of Bi₃O₄Br is considerably lower compared to those on BiOBr. Moreover, Bi₃O₄Br/TiO₂ nanobelt heterojunction has not yet been synthesized. To date, no reports are available on the photocatalytic performance of this material in the degradation of paracetamol and the treatment of real pharmaceutical wastewater. The novel 2D/1D Bi₃O₄Br/TiO₂ NB heterojunction photocatalysts were synthesized by a hydrothermal method at different ratios. The materials were characterized using X-ray Diffraction (XRD), N₂ physisorption using Brunauer-Emmett-Teller method (BET), Diffuse Reflectance Infrared Fourier Transform (DRIFT), Raman spectroscopy, X-ray Fluorescence (XRF), X-ray Photoelectron Spectroscopy (XPS), valence band XPS, Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX), Transmission Electron Microscopy (TEM), High-Resolution Transmission Electron Microscopy (HRTEM), Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS), Photoluminescence spectroscopy (PL), time-resolved PL (TRPL), Electron Paramagnetic Resonance (EPR), and Electrochemical Impedance Spectroscopy (EIS). In addition, the photocatalytic degradation of paracetamol was studied under visible light irradiation. Then, the pH, photocatalyst dosage, pollutant concentration, and temperature were optimized. Photocatalytic mechanisms were further explored by active species trapping experiments, and the migration mechanism of photoinduced charge carriers was discussed. Furthermore, stability and reusability experiments were performed using four cycles. In addition, the performance of Bi₃O₄Br/TiO₂ NB was evaluated in the photocatalytic degradation of real pharmaceutical wastewater.

2. Materials and methods

2.1. Synthesis of TiO₂ NB

To synthesize TiO₂ nanobelts, 1 g of TiO₂ powder (Aeroxide P25, Acros Organics) was dispersed in 60 mL of a 10 mol L^{−1} NaOH (AnalaR NORMAPUR, VWR Chemicals) aqueous solution while stirring for one hour. The mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave for alkali-hydrothermal treatment at 180 °C for 24 h. Upon cooling naturally to room temperature, the resulting precipitate underwent thorough washing with ample ultra-pure Milli-Q water. The resulting Na₂Ti₃O₇ nanobelts were then agitated in 0.1 mol L^{−1} HCl (Fischer Scientific, 1 M) for 24 h. The obtained H₂Ti₃O₇ nanobelts were filtered and properly washed to neutralize the pH. The sample was then dried overnight at 80 °C. Finally, the products were calcined at 600 °C for 2 h for crystallization of TiO₂ nanobelts.

The formation process of TiO₂ nanobelts involves three primary stages outlined in the following equations. Firstly, the dissolving of the TiO₂ precursor and breaking of the Ti-O-Ti bonds lead to the formation

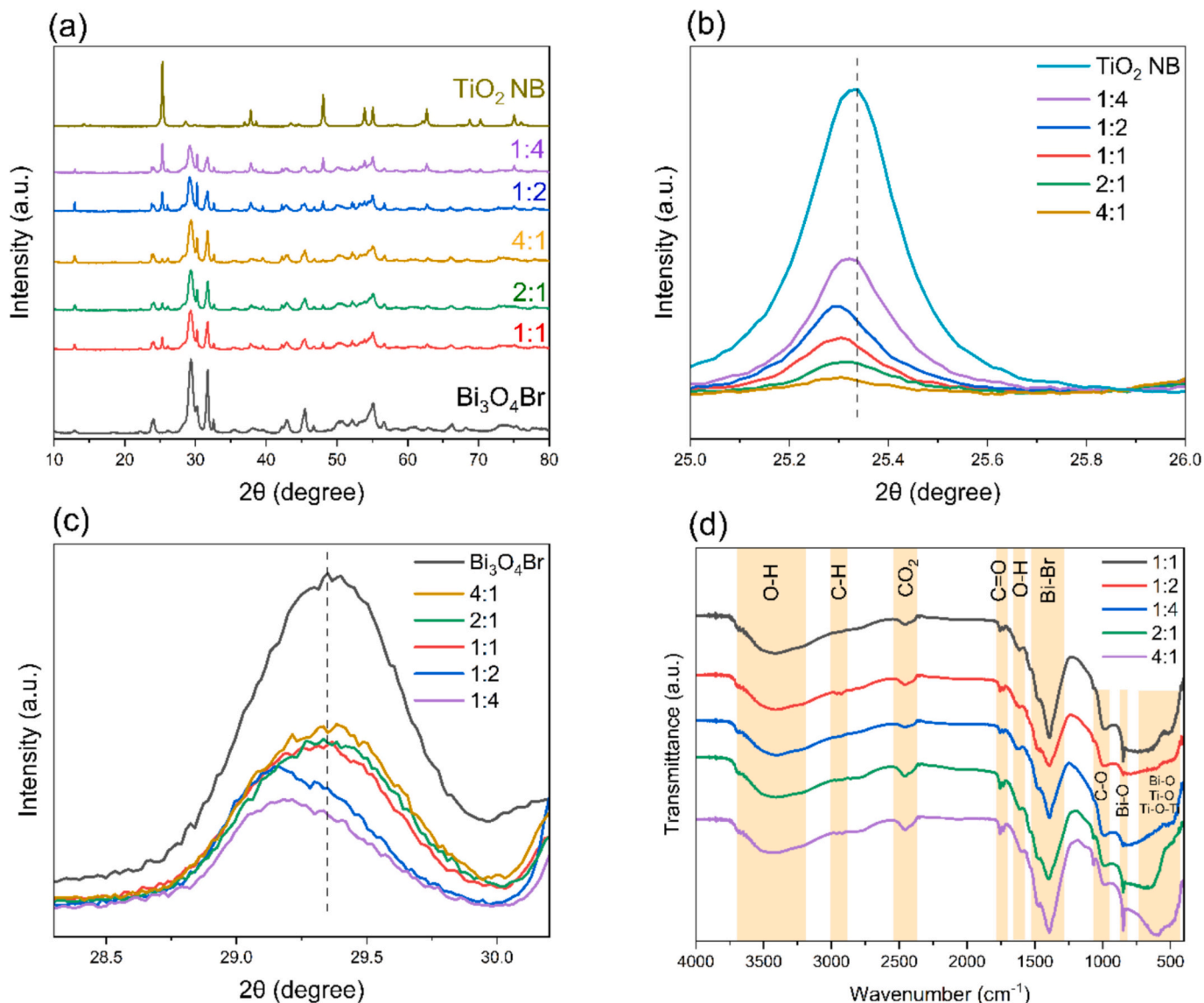


Fig. 1. (a) XRD results of the prepared materials (b) XRD shifts of the composites compared to TiO_2 NB (c) XRD shifts of the composites compared to $\text{Bi}_3\text{O}_4\text{Br}$ and (d) DRIFT results of the composites (in the composite material ratios, the former is $\text{Bi}_3\text{O}_4\text{Br}$, and the latter is TiO_2 NB).

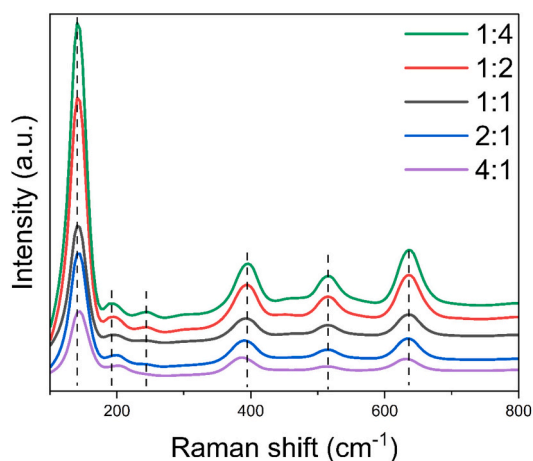
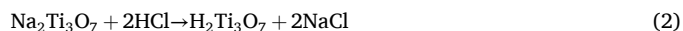
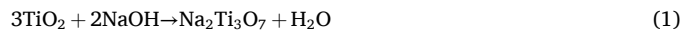


Fig. 2. Raman spectra of composite materials (in the composite material ratios, the former is $\text{Bi}_3\text{O}_4\text{Br}$, and the latter is TiO_2 NB).

of $\text{Na}_2\text{Ti}_3\text{O}_7$ nanobelts. Secondly, the $\text{Na}_2\text{Ti}_3\text{O}_7$ nanobelts are converted to $\text{H}_2\text{Ti}_3\text{O}_7$ nanobelts through an ion-exchange process. Lastly, the $\text{H}_2\text{Ti}_3\text{O}_7$ nanobelts are annealed, resulting in the production of TiO_2 nanobelts via dehydration and crystal-lattice rearrangement [25].



2.2. Synthesis of $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB

$\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ nanobelts were synthesized by hydrothermal method. 2 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (98 % min, ACS, thermo scientific) was dissolved in 10 mL of ethylene glycol (AnalaR NORMAPUR, VWR chemicals) and stirred for 15 min to form a transparent solution. Then, 2 mmol of KBr (99+ % purity, thermo scientific) was added to 10 mL of ultra-pure Milli-Q water with continuous stirring. The above solutions were mixed to form a white suspension, followed by adding the as-prepared TiO_2 NB to the suspension. After 20 min stirring, 5 mL of

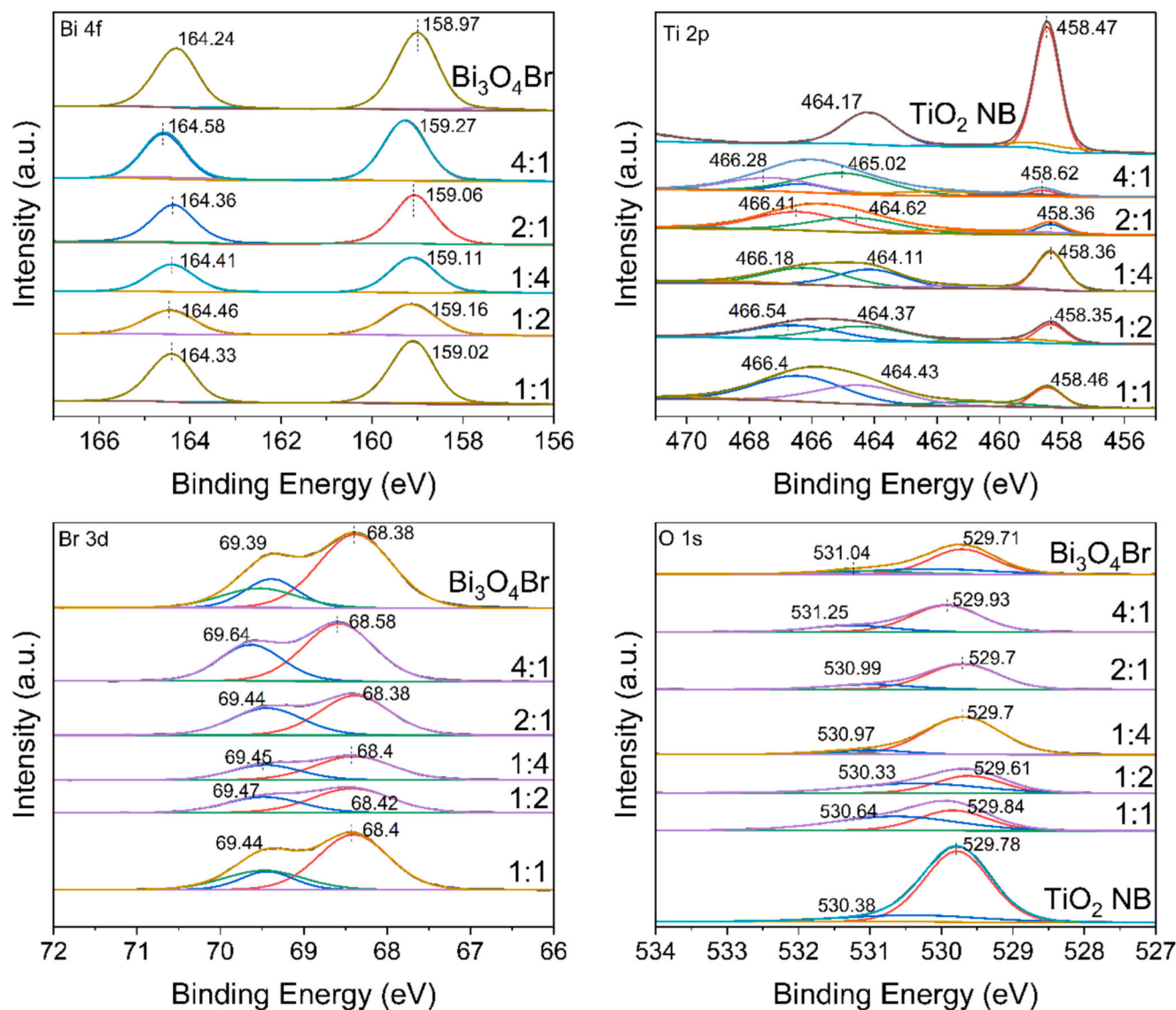


Fig. 3. High resolution XPS spectra of the prepared samples (in the composite material ratios, the former is Bi₃O₄Br, and the latter is TiO₂ NB).

NH₄OH (AnalaR NORMAPUR, 28 %, VWR) was added dropwise into the solution. Next, the obtained mixed solution was transferred into an autoclave and heated at 160 °C for 18 h. Deionized water and ethanol (99.8 % absolute, VWR chemicals) were used to wash the solids multiple times, and the precipitate was dried at 80 °C for 24 h. The Bi₃O₄Br/TiO₂ NB was prepared with different molar ratios of Bi₃O₄Br to TiO₂ NB and denoted as 1:2, 2:1, 1:1, 1:4, and 4:1. For comparison, pure Bi₃O₄Br was prepared under the same conditions as the composite materials, as described in our previous study [23].

2.3. Characterizations

Detailed information on the characterization is provided in the supplementary materials.

2.4. Photocatalytic activity

The photocatalytic activity of the materials was studied using a 250 mL jacketed beaker. A 50 W LED panel was placed above the beaker. Water circulation was used to maintain constant temperature. The light intensity was 111 μW cm⁻² at a distance of 10 cm from the surface of the solution. The schematic of the reactor and spectrum of the lamp can be

found from our previous study [23]. A precise amount of air was fed into the reactor through a flow meter (KOBOLD, USA). The total volume of liquid in each experiment was 200 mL. Before switching on the lamp, dark adsorption was performed for 30 min to achieve adsorption-desorption equilibrium. The photocatalytic experiments were carried out for 210 min. About 2 mL of solution was taken from the reactor at certain time intervals and filtered using a 0.45 μm PTFE syringe filter. A UV-Vis spectrophotometer (UV-2600, SHIMADZU) was used to measure paracetamol concentration (at λ_{max} = 243 nm) and the changes in the spectrum of real pharmaceutical wastewater during the process. Also, a Total Organic Carbon (TOC) meter (TOC-L, SHIMADZU) was used to measure the initial and final TOC.

3. Results and discussion

3.1. Characterization results

XRF can be utilized to quantify the elements present in the sample. The detected elements (Table 1) were Ti, Bi, O, and Br, as expected, and their quantities are in line with the theoretically calculated expected ratios, which are also visible in the table.

The nitrogen adsorption-desorption isotherms and pore size

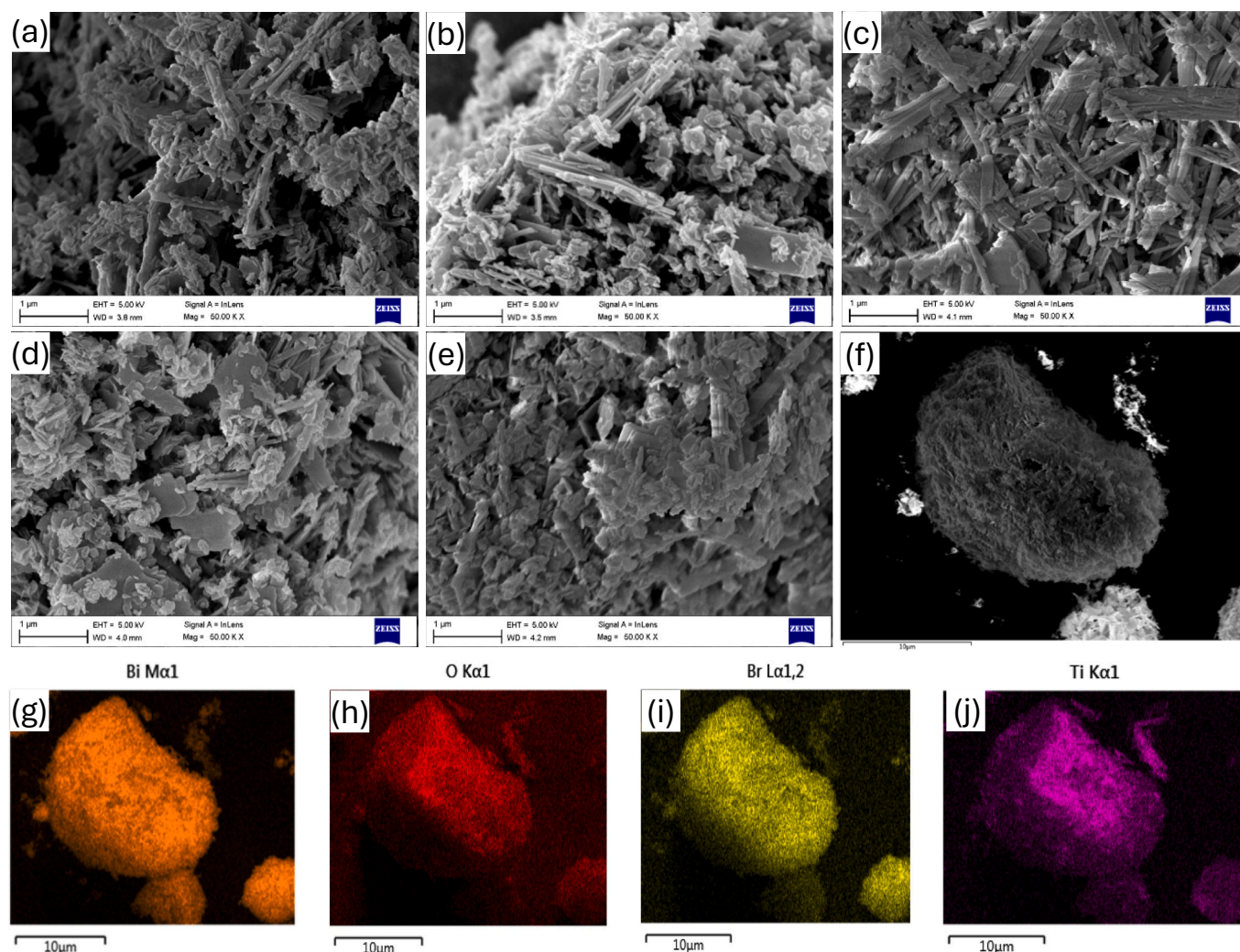


Fig. 4. FESEM images of the composite materials (a) 1:1, (b) 1:2, (c) 1:4, (d) 2:1, (e) 4:1, (f–j) EDX results of the 2:1 sample (in the composite material ratios, the former is $\text{Bi}_3\text{O}_4\text{Br}$, and the latter is TiO_2 NB).

distributions of P25, TiO_2 NB, $\text{Bi}_3\text{O}_4\text{Br}$, and 2:1 material are presented in Fig. S1 and Fig. S2. According to IUPAC classification, all the catalysts display Type IV isotherms with the H_3 type hysteresis loops characteristic of non-rigid aggregates or platelet-like structures with slit-shaped pores. The specific surface area of TiO_2 NB ($22 \text{ m}^2 \text{ g}^{-1}$) was lower than that of P25 TiO_2 ($51 \text{ m}^2 \text{ g}^{-1}$) (Table 2). The specific surface area of the prepared composite (2:1) was $23 \text{ m}^2 \text{ g}^{-1}$.

The XRD diffractograms of TiO_2 NB and P25 TiO_2 are presented in Fig. S3. Tetragonal P25 TiO_2 has anatase (JCPDS card 01–075–2544) and rutile phases (JCPDS card 04–004–4338) with ratios around 81.4 % and 18.6 %, respectively [26,27]. When TiO_2 NB was prepared, the structure changed from tetragonal to monoclinic and the rutile phase disappeared. New peaks in the diffractogram correlated to the TiO_2 -B structure (JCPDS card 04–017–2724) are observed [16,17,28,29]. The TiO_2 -B phase is formed through a series of steps starting with an anatase phase of P25 TiO_2 . Once the nanoparticles come into contact with a highly concentrated NaOH solution (10 mol L^{-1}) under high pressure, they convert into $\text{Na}_2\text{Ti}_3\text{O}_7$ sheets. Through an ion-exchange reaction with HCl, Na^+ ions are replaced by H^+ ions, resulting in a monoclinic $\text{H}_2\text{Ti}_3\text{O}_7$ phase. This is the reason why TiO_2 NB has monoclinic structure. Then, by heating $\text{H}_2\text{Ti}_3\text{O}_7$ at 600°C , the removal of H_2O results in the formation of TiO_2 NB with phases of anatase and TiO_2 -B. The diffraction peaks of $\text{Bi}_3\text{O}_4\text{Br}$ and TiO_2 NB can be seen in all the composite materials (Fig. 1a) without any extra peaks. When the amount of TiO_2 NB is high in

the composite, the peak at around $2\theta = 25.33^\circ$ representing (101) planes of anatase TiO_2 is sharp. For all the composite materials, the diffraction peaks' intensity decreased in comparison with pure $\text{Bi}_3\text{O}_4\text{Br}$ and TiO_2 NB, showing that composite preparation impacted the crystallinity of both the photocatalysts. This indicates that the combination of the two semiconductors creates an interaction at the contact interface and could be related to interfacial strain between $\text{Bi}_3\text{O}_4\text{Br}$ and TiO_2 NB [30–32]. A tiny shift to lower angles in the composite materials is observed. For instance, TiO_2 NB peak at 25.33° shifted negatively around 0.01–0.05 (Fig. 1b). The $\text{Bi}_3\text{O}_4\text{Br}$ peak at 29.35° experienced a negative shift around 0.02–0.15 (Fig. 1c). This negative shift could be indicative of an interaction between $\text{Bi}_3\text{O}_4\text{Br}$ and TiO_2 NB, showing that combining the two photocatalysts can lead to a slight lattice distortion [33,34].

P25 TiO_2 and TiO_2 NB DRIFT results are illustrated in Fig. S4a. The broad band in the range of $3000\text{--}3500 \text{ cm}^{-1}$ is correlated to O–H vibrations of adsorbed water. The band at around 1632 cm^{-1} can be attributed to the molecular water O–H vibration. [35]. The bands are less intense for TiO_2 NB due to calcination. The wide band in the region of $460\text{--}980 \text{ cm}^{-1}$ is ascribed to the stretching vibrations of Ti–O and/or Ti–O–Ti [36,37]. The DRIFT spectrum of $\text{Bi}_3\text{O}_4\text{Br}$ presented in Fig. S4b was thoroughly investigated in our previous study [23]. Regarding the composite materials (Fig. 1d), the bands around $3200\text{--}3650 \text{ cm}^{-1}$ and 1616 cm^{-1} are related to the O–H vibrations of adsorbed water and vibrational mode of O–H in free water molecules [38,39]. The weak

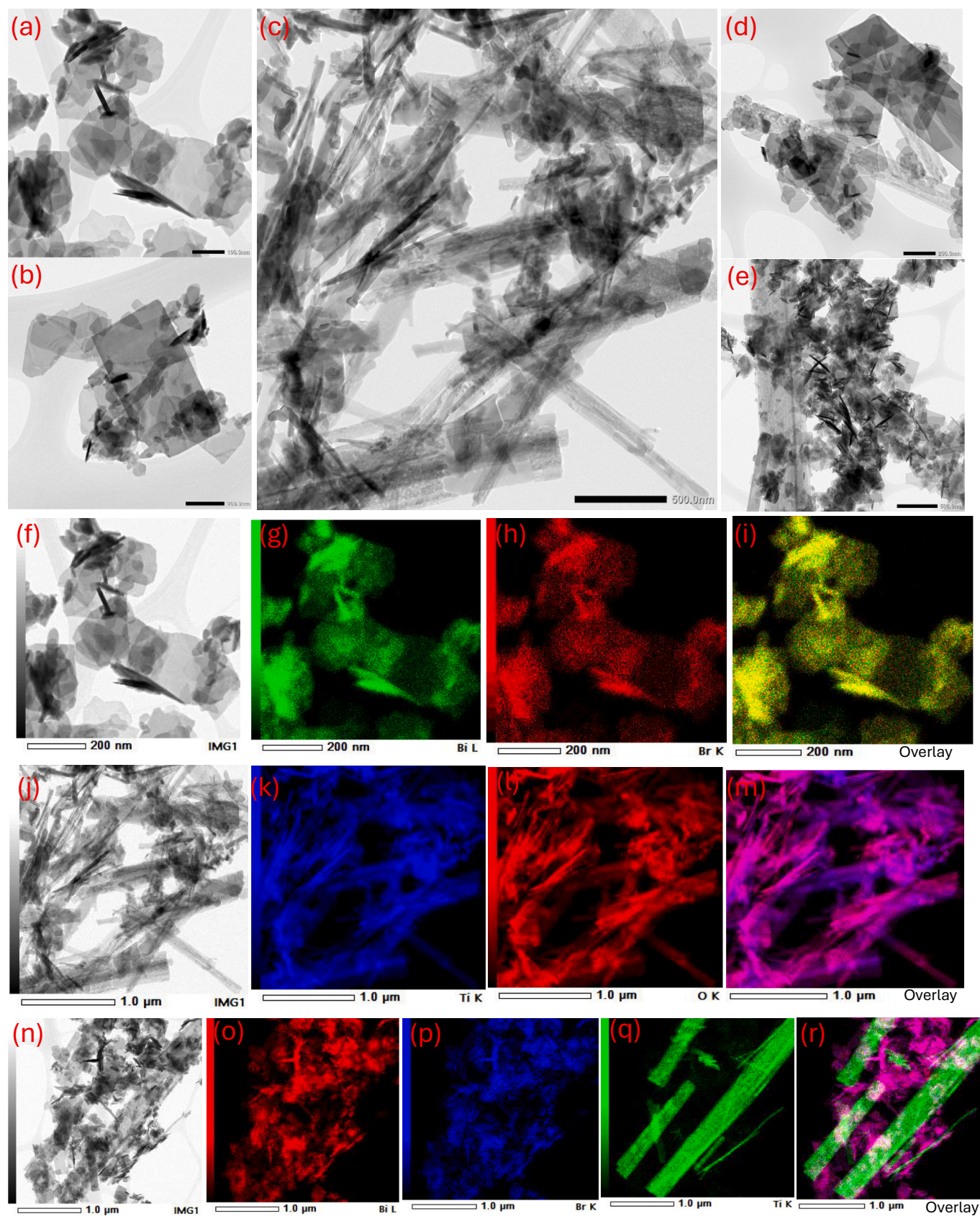


Fig. 5. TEM images of (a-b) $\text{Bi}_3\text{O}_4\text{Br}$, (c) TiO_2 NB, and (d-e) $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB (2:1) and EDS mapping of TEM images of (f-i) $\text{Bi}_3\text{O}_4\text{Br}$, (j-m) TiO_2 NB, and (n-r) $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB (2:1).

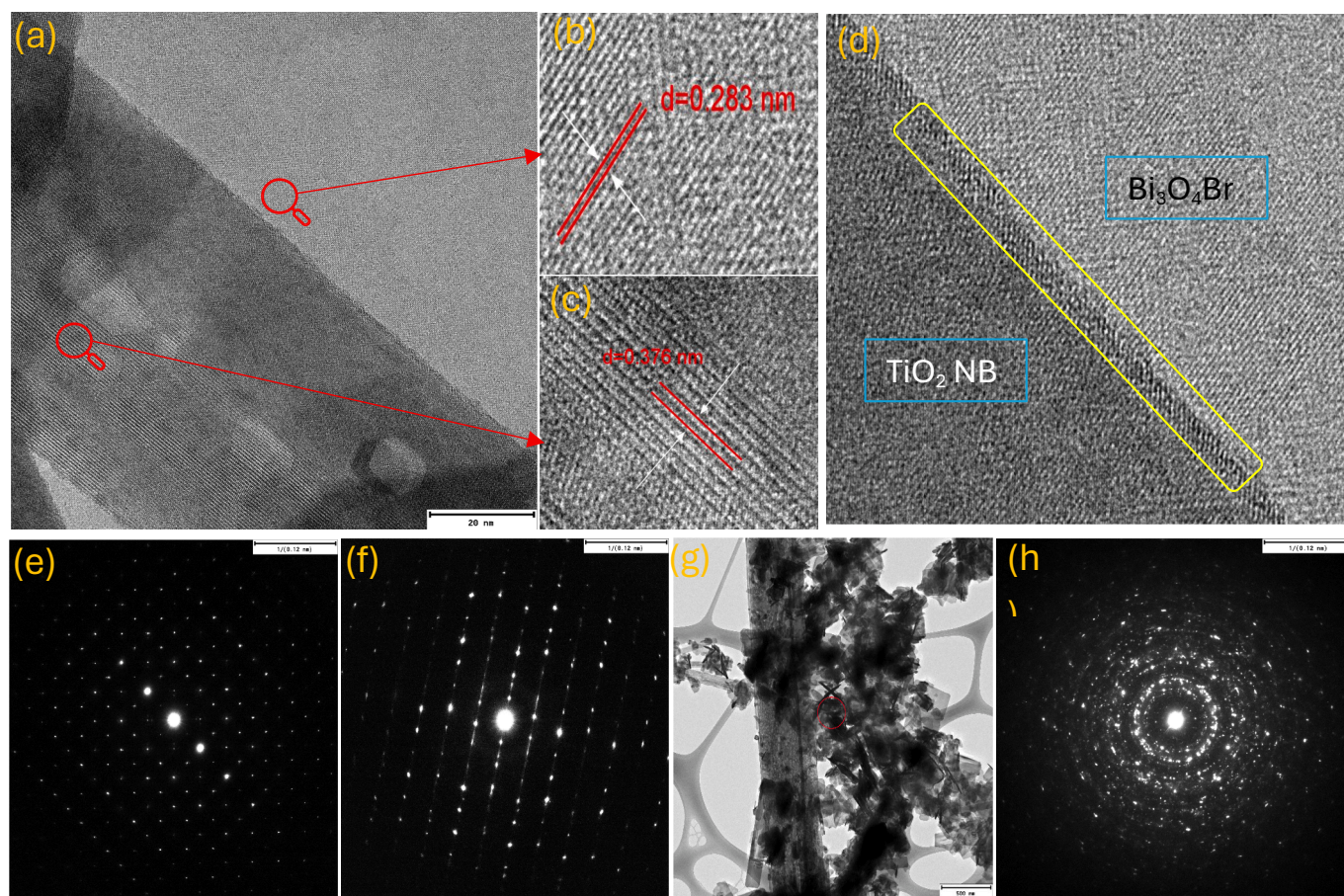


Fig. 6. (a) TEM of $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB (2:1), (b-d) HRTEM of $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB (2:1) with a width of 0.283 nm for $\text{Bi}_3\text{O}_4\text{Br}$ and 0.376 nm for TiO_2 NB, (e) SAED pattern of $\text{Bi}_3\text{O}_4\text{Br}$, (f) SAED pattern of TiO_2 NB, (g-h) TEM image and SAED pattern of anatase TiO_2 NB observed in $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB (2:1).

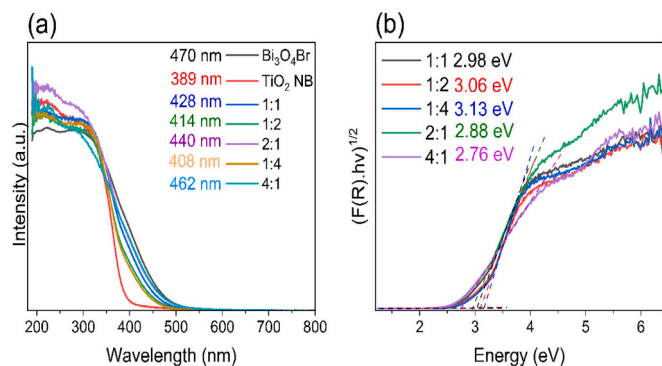


Fig. 7. (a) UV-Vis DRS and (b) band gap energies (in the composite material ratios, the former is $\text{Bi}_3\text{O}_4\text{Br}$, and the latter is TiO_2 NB).

aliphatic C—H vibration at around 2940 cm^{-1} might originate from the ethylene glycol used in the synthesis [23]. Also, the band observed around 1735 cm^{-1} can be attributed to C=O stretching, while the band near 1050 cm^{-1} is associated with C—O stretching, both originating from ethylene glycol or surface CO_2 contamination [23]. The wide band in the region of $1300\text{--}1500\text{ cm}^{-1}$ corresponds to the Bi—Br vibration in $\text{Bi}_3\text{O}_4\text{Br}$ [23]. The Bi—O, Ti—O, and Ti—O—Ti bands fall within the $450\text{--}980\text{ cm}^{-1}$ range. Due to the overlapping of these vibrations, accurate identification of each one is challenging. The Bi—O band at around 848 cm^{-1} is sharp and has more intensity when the amount of $\text{Bi}_3\text{O}_4\text{Br}$ is high in the composite material. For instance, 4:1 sample has the highest intensity of Bi—O band, and the lowest intensity is for 1:4.

Raman spectra of P25 TiO_2 and TiO_2 NB are illustrated in Fig. S5a, showing the peaks centered at 146 , 202 , 399 , 514 , and 637 cm^{-1} for P25 TiO_2 , which can be attributed to the active modes of E_{g1} , E_{g2} , B_{1g} , $A_{1g} + B_{1g}$, and E_g , respectively. The low-frequency E_g modes at 146 cm^{-1} and 637 cm^{-1} are related to vibrations involving O—Ti—O symmetric bending, while the 399 cm^{-1} B_{1g} mode and the 521 cm^{-1} $A_{1g} + B_{1g}$ mode correspond to O—Ti—O counter-bending and symmetric vibrations [40,41]. The peak observed at 202 cm^{-1} (E_{g2}) can be ascribed to anatase phase of P25 TiO_2 [42]. In the case of TiO_2 NB, all the mentioned peaks experienced a negative shift, and a new peak appeared at 242 cm^{-1} suggesting the presence of TiO_2 -B phase. The results are well matched with other studies [43,44]. In Fig. S5b, the Raman peaks of $\text{Bi}_3\text{O}_4\text{Br}$ are observed at 152 , 207 , 380 , 481 , and 614 cm^{-1} . The peak at 152 cm^{-1} could be attributed to E_g mode of Bi—Br stretching. The peaks observed at 207 and 614 cm^{-1} belong to the A_{1g} and E_g modes of Bi—O covalent bonds. Also, the vibration of oxygen atoms leads to a peak at 380 cm^{-1} , assigned as the B_{1g} mode. Regarding the composite materials (Fig. 2), overlapping of $\text{Bi}_3\text{O}_4\text{Br}$ and TiO_2 NB Raman peaks take place, for example, the peaks at 144 cm^{-1} (TiO_2 NB) and 152 cm^{-1} ($\text{Bi}_3\text{O}_4\text{Br}$). The spectrum of the 1:4 composite shows mostly the characteristic peaks of TiO_2 NB, while 4:1 composite shows the characteristic peaks of $\text{Bi}_3\text{O}_4\text{Br}$ as well, as there is a positive shift in the first two peaks, which are closer to the 152 and 207 cm^{-1} peaks of pure $\text{Bi}_3\text{O}_4\text{Br}$. The peak located at 392 cm^{-1} negatively shifted to 384 cm^{-1} , very close to the oxygen atom vibration peak of $\text{Bi}_3\text{O}_4\text{Br}$ (380 cm^{-1}). The results agree with XRD results. Compared to pure $\text{Bi}_3\text{O}_4\text{Br}$ and TiO_2 NB, in all composite materials, a negative shift was observed, which shows interaction between $\text{Bi}_3\text{O}_4\text{Br}$ and TiO_2 NB. This not only results in an increase in interfacial tension and a change in lattice but also indicates the presence of the

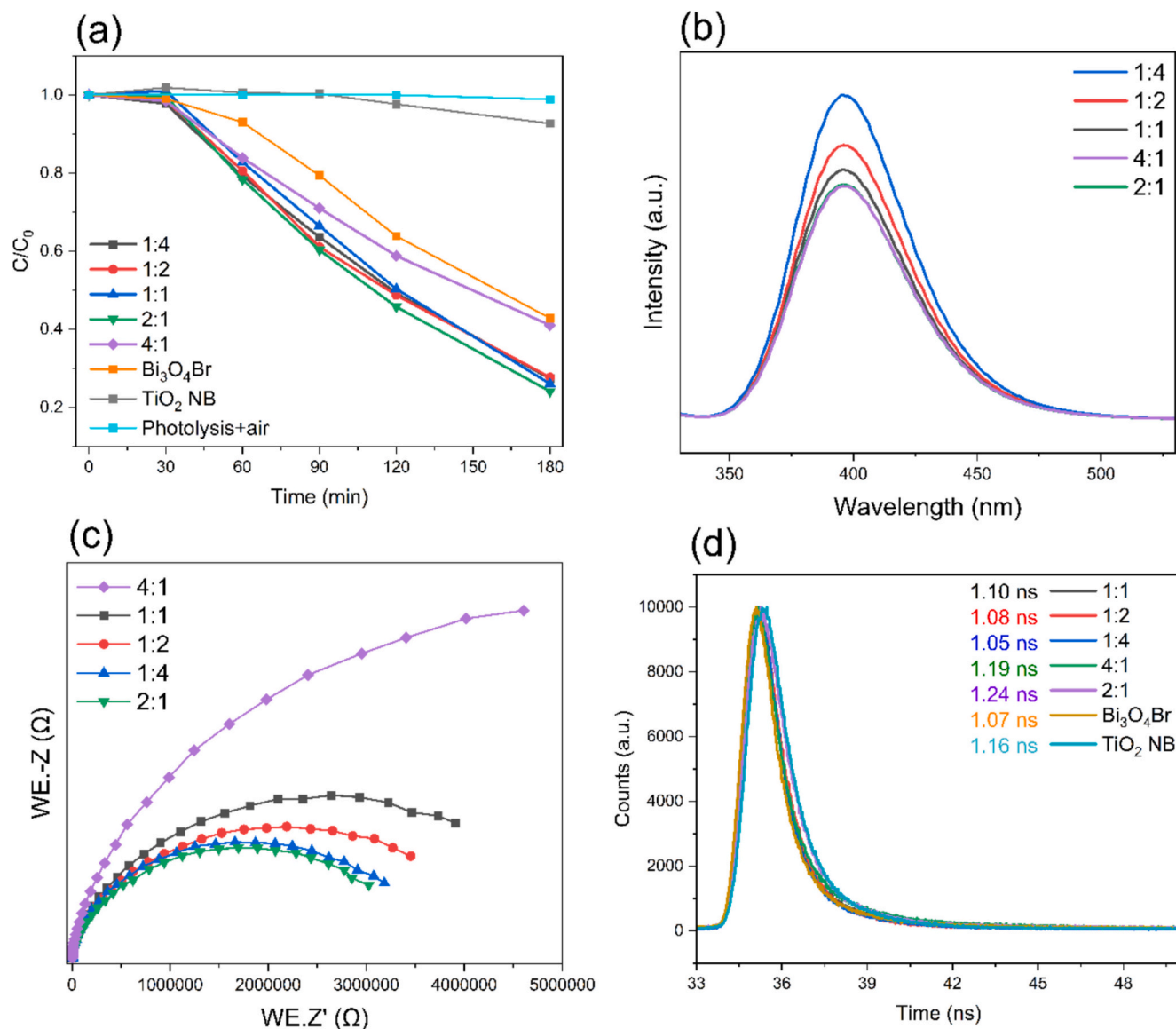


Fig. 8. (a) Photocatalytic degradation of paracetamol under visible light irradiation (0.2 g photocatalyst, 10 mg.L⁻¹ paracetamol, room temperature, and neutral pH of paracetamol), (b) PL spectra, (c) EIS, and (d) time-resolved PL (in the composite material ratios, the former is $\text{Bi}_3\text{O}_4\text{Br}$, and the latter is TiO_2 NB).

Table 3
Kinetic parameters of the emission decay of composites.

Sample	A_1 (1E+16)	τ (ns)
1:1	79	1.10293
1:2	164	1.07949
1:4	368	1.05271
4:1	7.3	1.18959
2:1	2.3	1.24315
$\text{Bi}_3\text{O}_4\text{Br}$	168	1.07436
TiO_2 NB	19.4	1.16125

The single exponential decay curves were fitted using a nonlinear least-squares method with a single component decay law given by $I(t) = Ae^{-t/\tau}$ [68].

heterojunction in composite materials [45,46].

Fig. S6 shows the high-resolution XPS results of P25 TiO_2 and TiO_2 NB. Two peaks located at 458.79 and 464.47 eV for P25 TiO_2 are related to Ti 2p_{3/2} and Ti 2p_{1/2} and represent the existence of Ti^{4+} . These peaks were shifted to lower binding energies of 458.47 and 464.17 eV for TiO_2

NB, indicating that low-valent state of Ti species (Ti^{3+}) might exist in TiO_2 NB or some defects might have been formed by the reduction of Ti^{4+} during the hydrothermal synthesis [47–49]. These defects could be beneficial in photocatalysis because they can boost the interaction between the photocatalyst surface and pollutant molecules [50]. Fig. 3 illustrates the Bi 4f binding energies for $\text{Bi}_3\text{O}_4\text{Br}$ and $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB composites. In the case of $\text{Bi}_3\text{O}_4\text{Br}$, the Bi^{3+} states are represented by Bi 4f_{7/2} at 158.97 eV and Bi 4f_{5/2} at 164.24 eV. For Bi 4f spectrum of $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB composites, these binding energies experience a positive shift, showing an interaction between $\text{Bi}_3\text{O}_4\text{Br}$ and TiO_2 NB [51]. In the Br 3d spectrum of $\text{Bi}_3\text{O}_4\text{Br}$, the main peaks are assigned to Br 3d_{5/2} and Br 3d_{3/2}, with binding energies of 68.38 eV and 69.39 eV, respectively, designated to Br^- . As for the Br 3d of $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB composites, the binding energies are positively shifted. The observed Br 3d shift means that interfacial Br^- species are involved in interactions with TiO_2 NB. In the high-resolution Ti 2p spectra of the composite materials, the binding energies of the Ti 2p_{1/2} and Ti 2p_{3/2} were shifted in comparison with pure TiO_2 NB. A broad bump was also observed due to the partial overlap of Ti 2p_{1/2} and Bi 4d_{3/2} at around 464.5 eV and 466.5 eV, respectively [52]. For Ti 2p, the shift indicates that Ti sites are affected

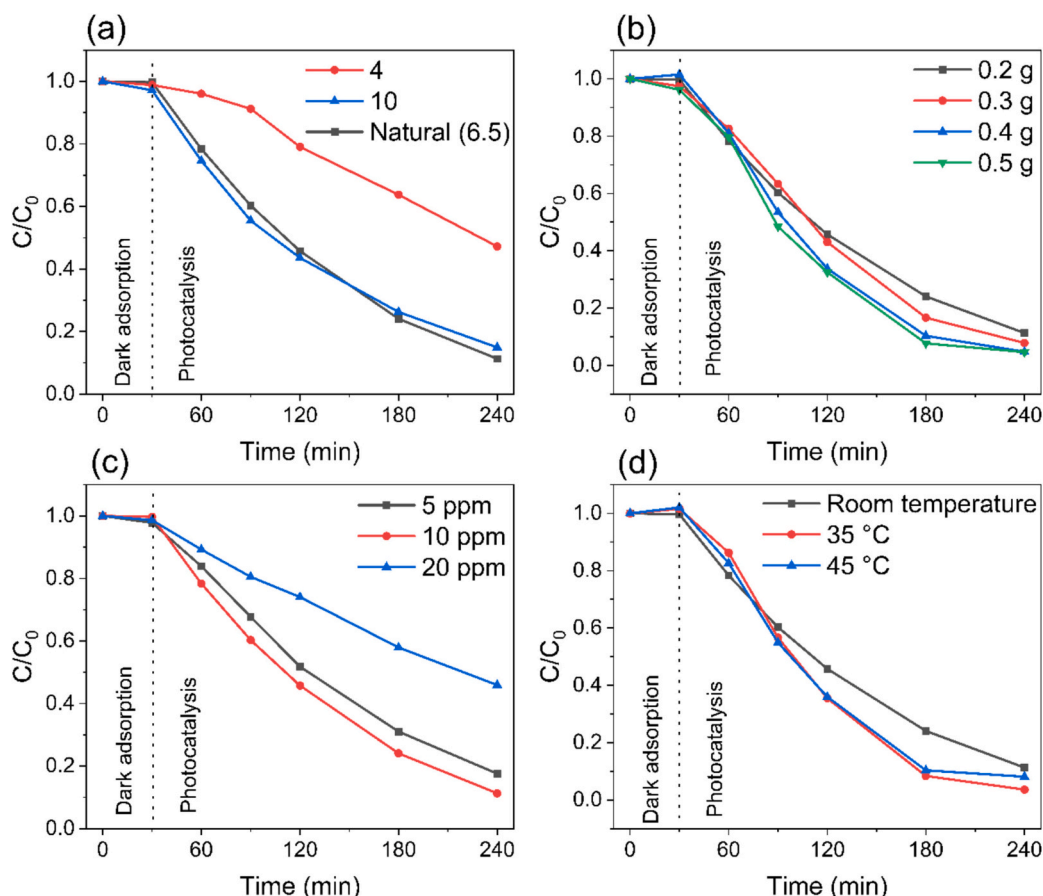


Fig. 9. The effect of (a) pH, (b) photocatalyst dosage, (c) pollutant concentration, and (d) temperature on the removal of paracetamol.

Table 4

Comparison of paracetamol degradation with other studies.

Photocatalyst	Process parameters						Degradation efficiency (%)	Reference
	pH	Dosage (g L ⁻¹)	Initial concentration (mg L ⁻¹)	Reaction time (min)	Light source	Temperature (°C)		
TiO ₂ -orange peel-derived biochar 20 wt%	4	0.8	20	100	300 W Xe lamp	–	94	[75]
TiO ₂ /graphene/g-C ₃ N ₄	9	0.6	50	120	300 W Xe lamp	–	100	[76]
TiO ₂ (5 %)/ZnO	–	0.3	40	50	50 W LED	–	65	[77]
TiO ₂ /Activated carbon 30 %	–	0.5	10	120	18 W UV lamp	–	82	[78]
AgI/Bi ₃ O ₄ Br	–	0.2	10	120	300 W Xe lamp	–	82	[79]
WO ₃ /TiO ₂	–	0.25	1	60	150 W Xe lamp	–	83	[6]
Bi ₃ O ₄ Br/TiO ₂ NB	Natural (6.5)	0.2	10	210	50 W LED	35	97	This study

by interfacial charge transfer during heterojunction formation. The broad bump near Ti 2p_{1/2} overlapping with Bi 4d evidences the mixing of electronic states. Overall, the observed binding energy shifts confirm the formation of the heterojunction and the redistribution of charges at the interface, which contribute to enhanced charge separation and the improved photocatalytic activity. The high resolution XPS spectrum of O 1 s is illustrated in Fig. 3. The XPS survey of all the samples is illustrated in Fig. S7.

Fig. 4a-e shows the morphology of the composite materials, and that the Bi₃O₄Br nanosheets are attached to the TiO₂ nanobelts. When the ratio of Ti is more than Bi, there exists more nanobelts than the nanosheets (Fig. 4c) and vice versa (Fig. 4e). The EDX mapping results of 2:1

sample is illustrated in Fig. 4f-j. The results show the presence and even distribution of all the elements (Bi, Br, O, and Ti) without any extra element.

To further explore the microstructure and interfacial characteristics of the samples, HRTEM investigations were performed. The TEM images (Fig. 5a-b) illustrate that Bi₃O₄Br has a nanoflake or nanoplate morphology, with distribution of thin sheet-like structures. Nanobelts of TiO₂ can be clearly observed as well as the distribution of anatase TiO₂ nanoparticles (Fig. 5c). According to XRD, the TiO₂ NB is composed of both TiO₂-B and anatase phases, which are clearly visible in TEM results (Fig. 5c). After combining the two materials, the Bi₃O₄Br nanoflakes are closely attached onto the surfaces of TiO₂ NB suggesting intimate

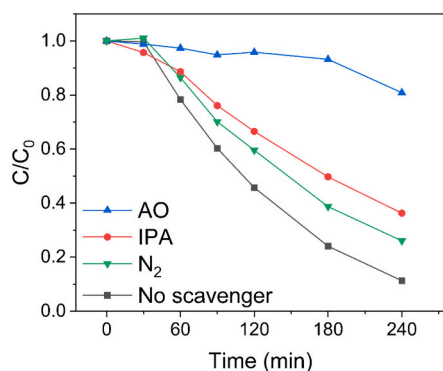


Fig. 10. Trapping experiments of free radicals for paracetamol degradation over $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB (2:1) composite under visible light irradiation (IPA, AO, and N_2 trap $\cdot\text{OH}$, h^+ , and $\text{O}_2^{\cdot-}$, respectively).

contact of the two (Fig. 5d-e). Additionally, EDX elemental mapping of TEM images (Fig. 5f-i) for $\text{Bi}_3\text{O}_4\text{Br}$, (Fig. 5j-m) for TiO_2 NB, and (Fig. 5n-r) for $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB (2:1) reveals a uniform distribution of the elements throughout the sample, suggesting homogeneity of the materials.

The tight contact of $\text{Bi}_3\text{O}_4\text{Br}$ and TiO_2 NB in the composite material can be also seen in Fig. 6a. HRTEM images (Fig. 6b-c) show lattice fringes with interplanar distances of 0.283 nm and 0.376 nm, which correspond to the (020) plane of $\text{Bi}_3\text{O}_4\text{Br}$ (JCPDS 037-0700) and the (201) plane of TiO_2 NB (JCPDS card 04-017-2724), respectively [53–57]. Fig. 6d shows a change in the periodic arrangement of lattice fringes of $\text{Bi}_3\text{O}_4\text{Br}$ and TiO_2 NB at the interface indicating heterojunction

formation. The selected area electron diffraction (SAED) pattern obtained from $\text{Bi}_3\text{O}_4\text{Br}$ nanoplate (Fig. 6e) exhibits well-defined and regularly arranged electron diffraction spots, indicating the high crystallinity and single-crystal nature of the nanoplate. The sharp and symmetric diffraction features confirm that the $\text{Bi}_3\text{O}_4\text{Br}$ possesses a well-ordered crystal structure, which is consistent with the XRD results. The SAED pattern of the TiO_2 nanobelts, shown in Fig. 6f, exhibits a series of sharp and regularly spaced diffraction spots arranged in a well-ordered pattern. The clear periodicity and symmetry of the pattern suggests a uniform and well-aligned atomic arrangement across the nanobelts [58,59]. In some spots of $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB (2:1) (Fig. 6g) anatase nanoparticles were observed, indicating partial formation of this phase. The corresponding SAED pattern (Fig. 6h) displays a series of concentric rings, related to crystalline structure of anatase TiO_2 [60–63]. TEM and HRTEM results indicate formation of $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB heterojunction with interfacial contact, beneficial for enhancing interfacial charge transfer.

Fig. S8 shows the UV–Vis DRS results and bandgaps of P25 TiO_2 and TiO_2 NB. A tiny improvement was observed in the absorption edge of TiO_2 NB (389 nm) in comparison to P25 TiO_2 (385 nm) causing a decrease of bandgap from 3.35 eV (P25 TiO_2) to 3.21 eV (TiO_2 NB). The results are consistent with Makal and Das study, where the band gap narrowing of TiO_2 nanowires was observed [64]. It can be seen from Fig. 7a that when the amount of $\text{Bi}_3\text{O}_4\text{Br}$ is more than TiO_2 NB, the composite can absorb more visible light. The absorption edges of 1:1, 1:2, 1:4, 2:1, and 4:1 are 428, 414, 408, 440, and 462 nm, respectively. The absorption edge of the $\text{Bi}_3\text{O}_4\text{Br}$ is 470 nm and its bandgap was earlier calculated to be 2.73 eV based on Kubelka-Munk equation. The calculated bandgaps of the composites are 2.98, 3.06, 3.13, 2.88, and

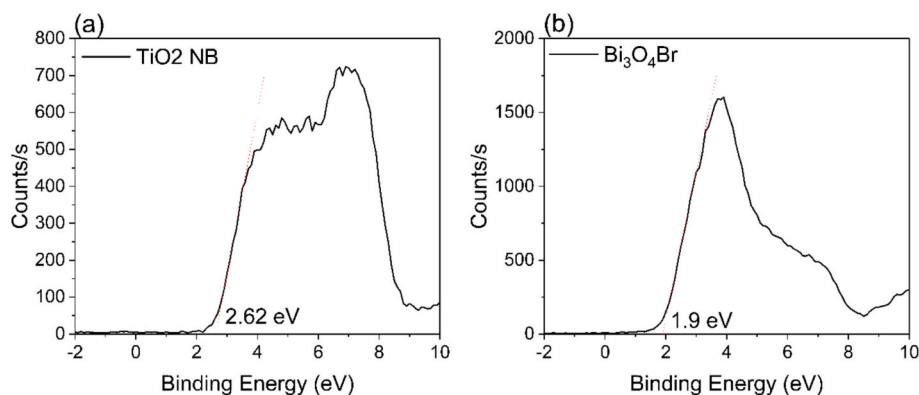


Fig. 11. Valence band XPS of (a) TiO_2 NB and (b) $\text{Bi}_3\text{O}_4\text{Br}$.

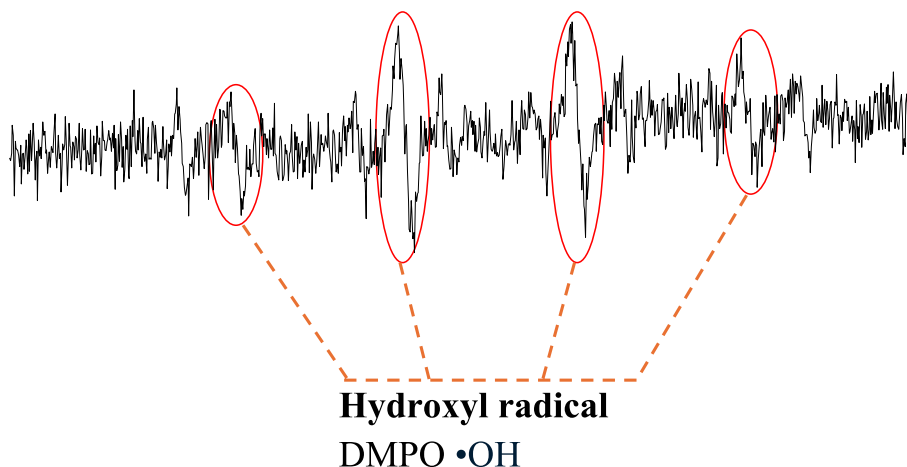


Fig. 12. EPR spectrum of $\text{DMPO}\cdot\text{OH}$ for $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2$ NB (2:1).

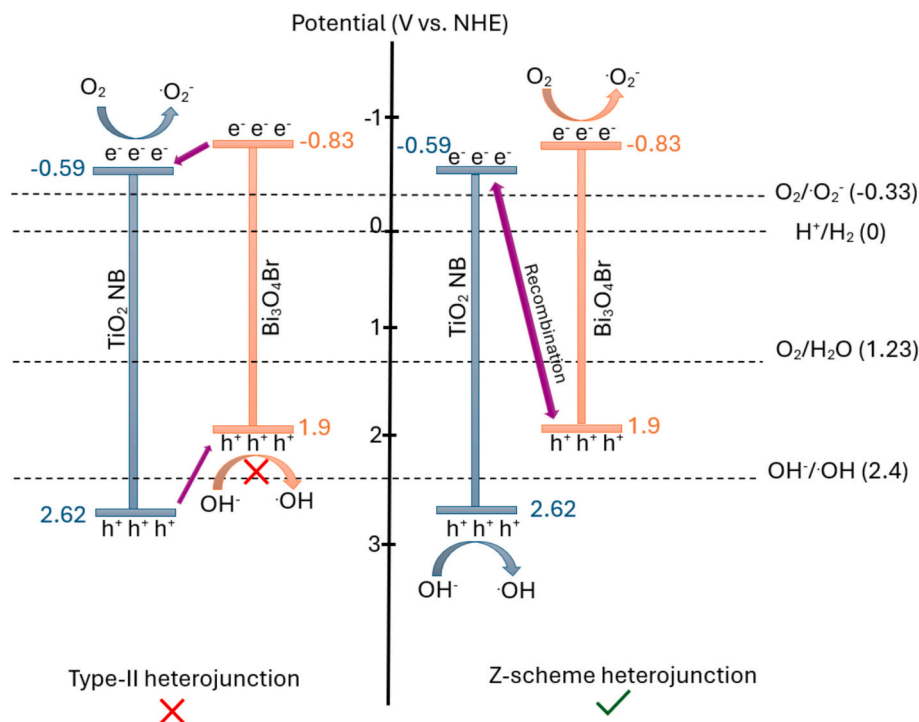


Fig. 13. The proposed photocatalytic mechanism diagram of $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2 \text{ NB}$.

2.76 eV, respectively (Fig. 7b). The higher the amount of $\text{Bi}_3\text{O}_4\text{Br}$ in the composite, the narrower the bandgap. $\text{Bi}_3\text{O}_4\text{Br}$ and $\text{TiO}_2 \text{ NB}$ are indirect band gap photocatalysts [24,65,66] and the Kubelka-Munk function was used to calculate the band gap energies. The method was described in our previous study [23].

3.2. Photocatalytic experiments

The degradation of paracetamol after 180 min was determined to be 2 % in photolysis (without catalyst) under air bubbling, 8 % for $\text{TiO}_2 \text{ NB}$ only, and 58 % for $\text{Bi}_3\text{O}_4\text{Br}$ only. The performance of the composites in the degradation of paracetamol is presented in Fig. 8a. The highest and lowest degradation efficiency was obtained by 2:1 and 4:1 sample with around 76 % for the former and 59 % for the latter after 180 min. The performance of the other samples was quite close to the 2:1 composite. Therefore, in order to find the best composite to continue the work, PL, EIS, and time-resolved PL were carried out. Electron-hole separation efficiency affects the performance of the photocatalysts and can be investigated by photoluminescence spectra [67]. The results presented in Fig. 8b show that the lowest fluorescence emission intensity is achieved for 2:1 composite, resulting in the highest separation efficiency of photogenerated charge carriers. Also, EIS was done to investigate the charge transfer efficiency of the synthesized composites (Fig. 8c). As the arc radius is attributed to the value of electron transfer resistance, the less hindrance to charge transfer can be obtained by smaller radius indicating the best efficiency of 2:1 composite in electron-hole separation. Then, to further investigate the photoelectric properties of the composites, time-resolved PL (PL decays) were measured. The results (Fig. 8d and Table 3) show that the 2:1 composite exhibits an average lifetime of 1.24 ns, longer than that of other composites, resulting in a slower electron-hole recombination in 2:1 composite. The results demonstrated that the photoluminescence lifetimes of $\text{Bi}_3\text{O}_4\text{Br}$ and $\text{TiO}_2 \text{ NB}$ were 1.07 ns and 1.16 ns, respectively. Kinetic parameters of the emission decay of composites are presented in Table 3. The formation of a heterojunction between these two materials was found to enhance the carrier lifetime, enhancing the charge separation efficiency. The above results provide reasonable evidence that the improved photocatalytic

performance of the 2:1 composite stem from the enhanced charge carrier separation, reduced transfer resistance, and slower electron-hole recombination.

The effect of initial pH of the pollutant was investigated at three different pH levels. The pH at the zero-point of charge (pH_{PZC}) of $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2 \text{ NB}$ (2:1) was measured using modified drift method to be 6.5 (Fig. S9) [69,70]. As shown in Fig. 9a, the degradation efficiency of paracetamol was lower at acidic pH ($\text{pH} = 4$). Although the surface charge of the material is positive at $\text{pH} < \text{pH}_{\text{PZC}}$, and paracetamol is nonionic at $\text{pH} < \text{pK}_a$ (pK_a of paracetamol is around 9.5), the removal still decreased. Similar results were obtained by other studies [70–72]. TiO_2 agglomeration can occur in acidic environments, leading to a decrease of surface area and photon absorption, both of which may lower the degradation rate of paracetamol [73]. In contrast, the degradation efficiency at alkaline ($\text{pH} = 10$) and neutral ($\text{pH} = 6.5$) conditions were higher than at acidic pH, with degradation efficiencies of 85 % and 89 % (after 240 min), respectively. This improvement can be attributed to enhanced hydroxyl radical formation at higher pH levels. In alkaline conditions, more hydroxide ions are present on the $\text{Bi}_3\text{O}_4\text{Br}/\text{TiO}_2 \text{ NB}$ surface, which can be oxidized to produce additional hydroxyl radicals [71]. Although pH 10 is above the pK_a of paracetamol (~ 9.5), where the pollutant exists predominantly in its deprotonated (negatively charged) form and the catalyst surface ($\text{pH}_{\text{PZC}} = 6.5$) is also negatively charged, the resulting electrostatic repulsion only slightly reduces the degradation after 240 min. This shows that hydroxyl radical generation plays a more dominant role than adsorption effects in photocatalytic degradation of paracetamol. A drawback of conducting the experiment in an alkaline medium, however, is the increased deprotonation of paracetamol and its precipitation. This precipitation may result in false results related to degradation when only liquid phase concentrations are measured. At $\text{pH} = 6.5$, the catalyst surface is near neutral, and paracetamol remains in its non-ionic molecular form ($\text{pH} < \text{pK}_a$), resulting in minimum water solubility and maximum adsorption onto the photocatalyst surfaces, creating favorable adsorption conditions [70–72]. In addition, the photocatalyst exhibits great stability at the neutral pH of paracetamol (6.5), where no agglomeration occurs. Overall, these results indicate that neutral pH provides optimal operating conditions,

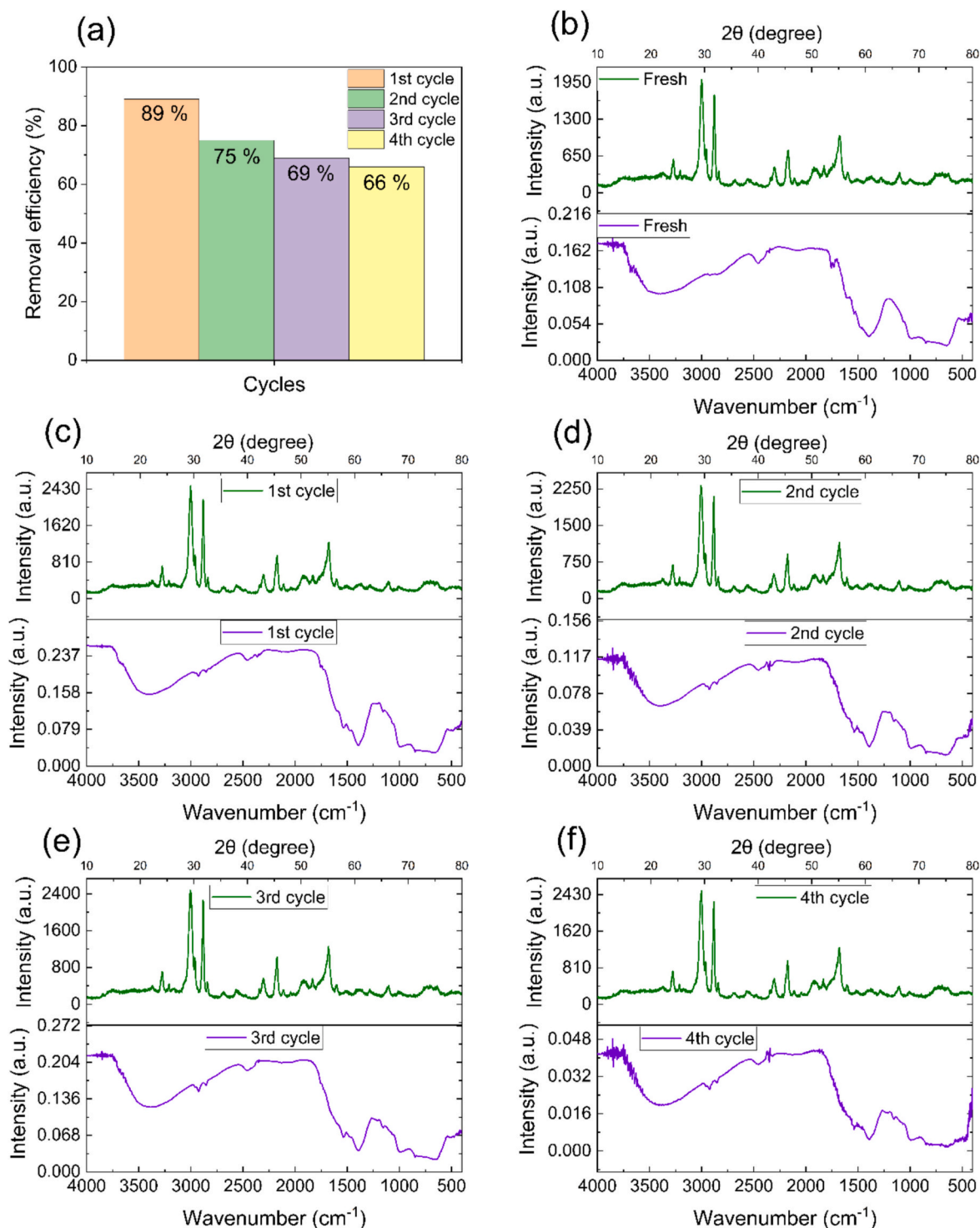


Fig. 14. (a) Reusability of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ NB (2:1) composite for paracetamol degradation, (b) XRD and FTIR results of the fresh sample, and XRD and FTIR results of the used sample after (c) 1st cycle, (d) 2nd cycle, (e) 3rd cycle, and (f) 4th cycle.

combining high degradation efficiency with photocatalyst stability and reliable measurements, while acidic pH significantly lowers the degradation efficiency due to photocatalyst agglomeration and reduced light utilization.

Increasing the photocatalyst dosage from 0.2 g L^{-1} to 0.5 g L^{-1} led to an improvement in the removal from 89 % to 96 % after 240 min (Fig. 9b). The same degradation was obtained when 0.4 g L^{-1} and 0.5 g L^{-1} of catalyst were employed. Some studies [7] have reported that excessive photocatalyst amounts can decrease removal efficiency due to

decreased light penetration in the aqueous medium. However, this effect was not observed in the dosages used in our experiment but may explain why further improvement was not observed between dosages of 0.4 g L^{-1} and 0.5 g L^{-1} .

The results on the effect of initial paracetamol concentrations shown in Fig. 9c, indicate degradation efficiencies of 83 %, 89 %, and 55 % for concentrations of 5, 10, and 20 mg L^{-1} , respectively. While the degradation of 10 mg L^{-1} of paracetamol was slightly higher than at 5 mg L^{-1} , it decreased significantly at 20 mg L^{-1} . At higher concentrations,

Table 5

TOC removal results of real pharmaceutical wastewater.

Pollutant	Photocatalyst dosage (g)	Time (h)	Initial TOC (mg L ⁻¹)	Final TOC (mg L ⁻¹)
Real pharmaceutical wastewater	0.2	24	378	298.6
Real pharmaceutical wastewater	0.4	24	378	322.2
Paracetamol + Real pharmaceutical wastewater	0.4	24	197.4	162

paracetamol could tentatively absorb light, reducing the photons available for activation of charge carriers of Bi₃O₄Br/TiO₂ NB. It is also suggested that high concentrations of paracetamol can cover the catalyst surface by adsorption and block the active sites. Moreover, higher paracetamol concentrations require more reactive species to maintain the high degradation efficiency, while the concentration stays constant in these experiments when catalyst dosage is not changed.

The effect of temperature on paracetamol degradation was also investigated (Fig. 9d). The experiments were carried out at room temperature (23 °C), 35 °C, and 45 °C for 240 min. The degradation efficiency was improved when the temperature increased. The removal efficiency was quite the same until 180 min for 35 °C and 45 °C after which the removal was improved at 35 °C at 240 min. 97 % and 92 % removals for 35 °C and 45 °C were observed, respectively. It is suggested that rising the solution temperature accelerates the photocatalytic degradation due to a higher generation of hydroxyl radicals [74].

Numerous research studies have investigated the photocatalytic degradation of paracetamol using a wide range of photocatalysts. Table 4 provides a detailed comparison of the experimental conditions and degradation efficiencies reported in the present study with those documented in previous investigations. A critical evaluation of these studies clearly demonstrates that the photocatalyst developed in this work exhibits an excellent degradation efficiency of paracetamol.

3.3. Photocatalytic mechanism and TOC removal

Ammonium oxalate (AO), isopropyl alcohol (IPA), and nitrogen

purging were utilized to quench the active species h⁺, •OH, and O₂^{•-} during the photocatalytic degradation of paracetamol. As illustrated in Fig. 10, the degradation efficiency of paracetamol decreased from 89 % to 74 % with N₂ purging, suggesting that O₂^{•-} radicals had a role in the photocatalytic degradation of paracetamol by Bi₃O₄Br/TiO₂ NB. The addition of IPA and AO decreased the removal to 64 % and 20 %, respectively, indicating that •OH and h⁺ play a significant role in the degradation process, with holes being the primary contributor. To propose the type of heterojunction, the band structure of the photocatalysts was calculated through valence band XPS [80]. As illustrated in Fig. 11, the valence band maximum (E_{VB}) of TiO₂ NB was at 2.62 and Bi₃O₄Br at 1.9 eV. The conduction band energy (E_{CB}) was determined using the equation (E_{CB} = E_{VB} - E_g).

Under visible light exposure, the electrons of Bi₃O₄Br/TiO₂ NB are excited forming electron-hole pairs that can follow two distinct pathways: the traditional Type-II mechanism or the Z-scheme mechanism. In the Type-II pathway, photoexcited electrons from the CB of Bi₃O₄Br (-0.83 eV), which has a more negative potential, migrate to the CB of TiO₂ NB (-0.59 eV). Simultaneously, photoinduced holes from the VB of TiO₂ NB (2.62 eV) move to the VB of Bi₃O₄Br (1.9 eV). Consequently, electrons accumulate in the CB of TiO₂ NB, while holes accumulate in the VB of Bi₃O₄Br, favoring the separation of charge carriers. However, under these conditions •OH radicals cannot be formed because the VB potential of Bi₃O₄Br (1.9 eV) is less positive than the redox potential of OH⁻/•OH (2.40 V vs. NHE). However, radical trapping experiments indicate that •OH radicals are present in the photocatalytic degradation of paracetamol by Bi₃O₄Br/TiO₂ NB. This evidence makes the Type-II heterojunction unlikely.

EPR spectroscopy was employed to investigate the generation of active species and to gain deeper insight into the charge transfer mechanisms involved in the photocatalytic process [81]. The spin-trapping agent DMPO (5,5-dimethyl-1-pyrroline N-oxide) was used to detect hydroxyl radicals (•OH), which are typically identified by four characteristic peaks with intensity ratios of 1:2:2:1. Upon visible light irradiation, distinct signals corresponding to DMPO-•OH were observed (Fig. 12), confirming the formation of hydroxyl radicals during photocatalysis with Bi₃O₄Br/TiO₂ NB heterojunction. These findings are consistent with the results of the radical scavenging experiments, further validating the involvement of •OH in the photocatalytic degradation of paracetamol. Consequently, the heterojunction type in Bi₃O₄Br/TiO₂ NB

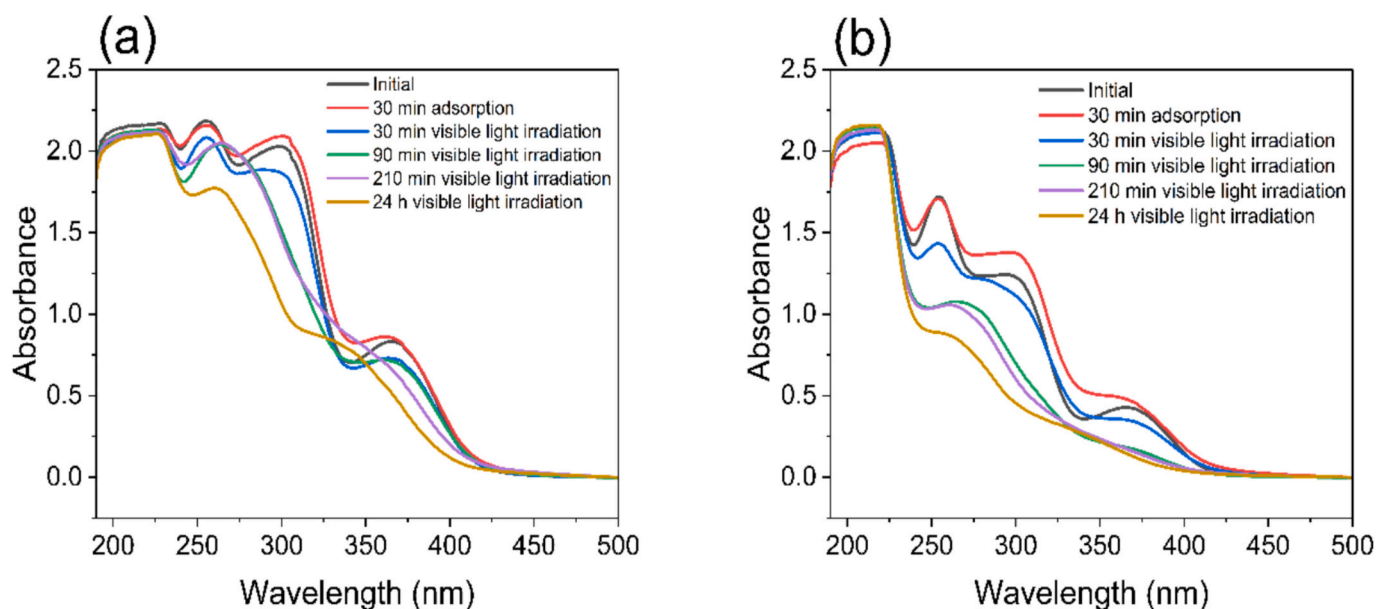


Fig. 15. UV-Vis spectra of (a) real pharmaceutical wastewater degradation in 24 h (0.4 g of Bi₃O₄Br/TiO₂ NB (2:1) and (b) real pharmaceutical wastewater and paracetamol mixture degradation in 24 h (0.4 g of Bi₃O₄Br/TiO₂ NB (2:1).

is not the Type-II.

Alternatively, the Z-scheme heterojunction provides a feasible mechanism. In this case, electrons in the CB of TiO₂ NB recombine with holes in the VB of Bi₃O₄Br, leading to efficient separation of the remaining electrons with stronger reducibility in the CB of Bi₃O₄Br and holes with stronger oxidation capability in the VB of TiO₂ NB. These separated charge carriers are highly reactive, resulting in the formation of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals aligning well with findings from radical trapping experiments and EPR measurement. The described charge transfer mechanisms are illustrated in Fig. 13. By coupling TiO₂ NB and Bi₃O₄Br photocatalysts, a novel heterojunction photocatalyst offers a promising alternative for environmental remediation applications.

The TOC removal of paracetamol was evaluated to be around 54 % with 0.2 g and 70 % with 0.4 g of photocatalyst. The experiments were done at a natural pH of paracetamol, at room temperature, using 10 mg L⁻¹ of paracetamol, and without any scavengers.

3.4. Stability and reusability

One crucial factor in practical application of photocatalysis is the stability and reusability of the photocatalytic materials. Bi₃O₄Br/TiO₂ NB was utilized in photocatalytic degradation experiments for four cycles. The results presented in Fig. 14a show that the removal of paracetamol using Bi₃O₄Br/TiO₂ NB remained at 66 % after four cycles. The decrease of about 23 % can tentatively be explained by the accumulation of intermediate compounds in the pores and on the active sites. The decreased performance will be investigated further in future studies, and information will be used to develop the final form of the catalyst. To assess the stability of the photocatalysts, FTIR and XRD analyses were performed on the used samples. The XRD analysis showed that the photocatalysts maintained their crystalline structure. New aliphatic C–H IR-bands, shown in Fig. 14b–f, were observed at 2854 cm⁻¹, 2925 cm⁻¹, and 2960 cm⁻¹ for all the used samples, stemming with the paracetamol degradation products [23]. Muconic acid and oxalic acid have been recognized as intermediates during the degradation of paracetamol [23,82] and these C–H bands may be linked to these intermediates or paracetamol. The C=O band at around 1735 cm⁻¹ gradually disappeared after each cycle.

3.5. Performance of the composite in diluted wastewater treatment

The activity of Bi₃O₄Br/TiO₂ NB (2:1) was evaluated also in the degradation of real pharmaceutical wastewater over a 24-h period using 0.2 g and 0.4 g of the composite. The results (Table 5) show that TOC removal decreases with an increase in the amount of Bi₃O₄Br/TiO₂ NB. Approximately 21 % TOC removal was achieved within 24 h when 0.2 g of the composite was used. However, this value decreased to around 15 % when composite amount was increased to 0.4 g. Furthermore, the mixture of pharmaceutical wastewater and paracetamol was investigated. The results showed that using 0.4 g of the composite led to about 18 % TOC removal after 24 h of visible light irradiation. The UV–Vis spectra for the removal of real pharmaceutical wastewater and its mixture with paracetamol in 24 h is shown in Fig. 15.

4. Conclusions

In this study, a novel Bi₃O₄Br/TiO₂ NB Z-scheme heterojunction photocatalyst was synthesized and an excellent photocatalytic degradation of paracetamol under visible light irradiation was demonstrated. The 2:1 composition was found the most effective, giving 89 % degradation of paracetamol at optimal reaction conditions. The enhanced photocatalytic activity was explained by improved charge carrier separation, decreased charge transfer resistance, and slower electron-hole recombination. TEM and HRTEM analyses confirm the formation of the Bi₃O₄Br/TiO₂ NB heterojunction with good interfacial contact, which facilitates improved charge transfer across the interface. Studies

confirmed the Z-scheme charge transfer mechanism, facilitating electron-hole separation and the generation of reactive oxygen species. Stability and recyclability experiments indicated reasonable stability of the composite after four cycles of experiments. To approach the real applications, the composite was also used in the treatment of diluted real pharmaceutical wastewater, and 21 % TOC removal was achieved. Overall, the Bi₃O₄Br/TiO₂ NB could be considered as a promising photocatalyst for the degradation of pharmaceutical pollutants. Future research should be directed towards scaling up the synthesis process, optimizing photocatalyst activity under real environmental conditions, improving stability, and exploring its application for the degradation of other emerging contaminants.

CRediT authorship contribution statement

Sajad Ahmadi: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Velma Beri Kimbi Yaah:** Writing – review & editing, Validation, Supervision. **Rafal Sliz:** Writing – review & editing, Investigation. **Sergio Botelho de Oliveira:** Writing – review & editing, Validation, Supervision, Conceptualization. **Antonio Leyva-Pérez:** Writing – review & editing, Investigation. **Anne Heponiemi:** Investigation. **Satu Ojala:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition.

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.cej.2025.167496>.

Data availability

Data will be made available on request.

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