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Research Article

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BiOBr/MoWO₄ p-n heterojunction photoanode for photodegradation of norfloxacin in water

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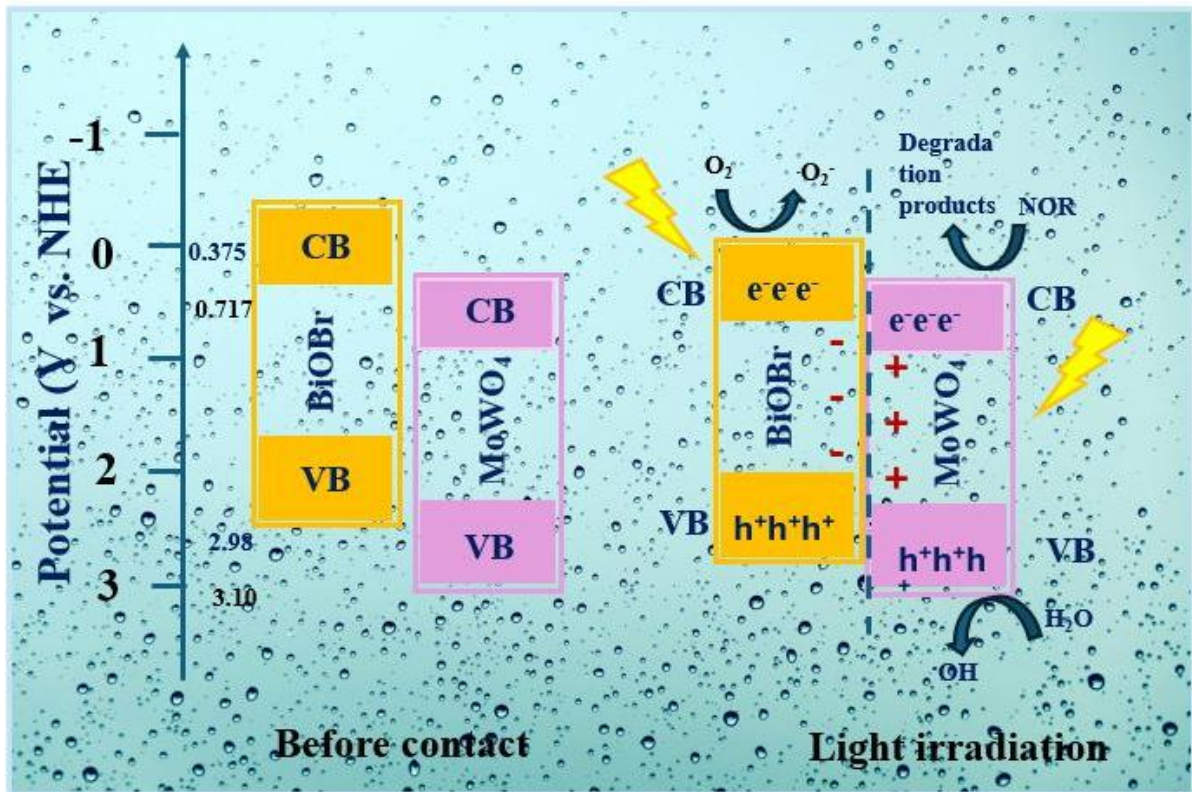
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Abstract

In the quest for alternative, complementary, and sustainable water treatment methods. We report the photoelectrocatalytic degradation of norfloxacin in an aqueous medium using an in situ hydrothermally synthesised bismuthoxybromide-molybdenum tungstate (BiOBr/MoWO₄) p-n heterojunction photoanode. The BiOBr/MoWO₄ heterojunction was strategically used to improve the photoelectrocatalytic performance by lowering photogenerated electron-hole pair recombination, optimising band edge alignment, and elevating the visible light absorption capacity. The BiOBr/MoWO₄ heterojunction was deposited onto a fluorine-doped tin oxide (FTO) substrate to serve as a photoanode for the photoelectrocatalytic breakdown of norfloxacin under visible light irradiation. The structural, morphological, optical, and surface properties of the as-prepared BiOBr/MoWO₄ photoanode were comprehensively characterised using XRD, FTIR, SEM, FE-SEM coupled with EDX, HRTEM, and BET. Under optimized conditions, the BiOBr/MoWO₄ photoanode achieved norfloxacin degradation of 85%, surpassing both pristine BiOBr (71%) and MoWO₄ (56%) photoanodes, thereby confirming the synergistic enhancement conferred by heterojunction formation. Scavenger studies revealed that the photogenerated holes (h^+) and superoxide anion radicals ($\cdot O_2^-$) played a significant role in the degradation of norfloxacin. TOC analysis demonstrated mineralisation efficiency of 41% and 70% in synthetic water and real wastewater matrices, respectively, confirming the effective conversion of norfloxacin into innocuous end products. Reusability studies confirmed the structural stability and sustained catalytic performance of the BiOBr/MoWO₄ photoanode over multiple degradation cycles, underscoring its potential for practical application in the treatment of pharmaceutical-contaminated wastewater.

Graphical Abstract



Keywords: photoelectrocatalytic degradation, BiOBr/MoWO₄ heterojunction, norfloxacin, hydrothermal process, photoanode

Introduction

A plethora of technologies and treatment methods have been developed for water purification processes, particularly for the removal of organics and recalcitrant pharmaceutical pollutants from wastewater [1, 2]. These developments are in pursuit of the United Nations (UN) Sustainable Development Goal (SDG) 6, which aims to ensure the availability and sustainable management of water and sanitation for all. Access to clean and safe water is fundamental to human health, economic development, and environmental sustainability, and remains particularly important for both urban and rural communities in developing countries [3]. Despite considerable progress in improving access to clean drinking water, billions of people still lack access to this essential resource [1]. Conventional wastewater treatment processes, including coagulation, flocculation, sedimentation, filtration, disinfection, ion exchange, air stripping and adsorption, are widely employed for water purification. However, these methods may be ineffective in completely removing biorecalcitrant contaminants, such as norfloxacin

(NOR), from wastewater [4, 5]. The persistence of pharmaceutical residues in aquatic environments is of particular concern because their continued presence may contribute to the development and dissemination of antimicrobial resistance, posing potential risks to human health and the environment. Consequently, there is a growing need for efficient and sustainable treatment technologies capable of degrading these persistent contaminants.

Advanced oxidation processes (AOPs) have emerged as promising technologies for the remediation of contaminated water due to their ability to generate highly reactive oxygen species (ROS), including hydroxyl radicals ($\cdot OH$), superoxide ($\cdot O_2^-$), and sulphate radicals ($SO_4^{\cdot -}$) [6, 7]. These reactive species possess strong oxidising abilities and can promote the degradation and mineralisation of recalcitrant organic pollutants [2, 8]. Among the various AOPs, electrochemical advanced oxidation processes (EAOPs) have attracted considerable attention because of their high oxidation efficiency, operational flexibility, and potential to minimize the formation of secondary pollutants [9]. Therefore, EAOPs represent a promising clean and sustainable approach for the treatment of hazardous and pharmaceutical-contaminated wastewater.

Photoelectrocatalysis (PEC) is an advanced electrochemical oxidation technology that combines the principles of photocatalysis and electrocatalysis. In PEC systems, a semiconductor photoelectrode is activated by light irradiation, while an external electric field is simultaneously applied to enhance the generation, separation and transfer of photogenerated charge carriers. This synergistic combination can improve the oxidation of organic pollutants and enhance the overall degradation efficiency compared with photocatalysis or electrocatalysis alone.

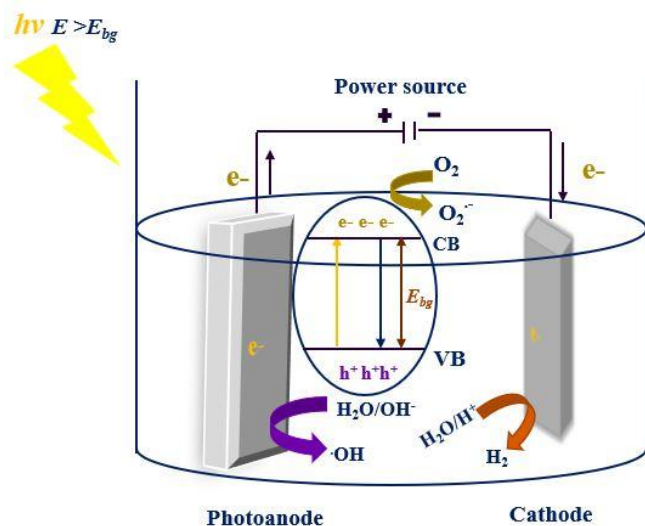
The PEC technique can effectively suppress the recombination of photogenerated electron-hole pairs, thereby prolonging the lifespan of the photogenerated holes and enhancing their availability for oxidation reactions. Scheme 1 illustrates the photoelectrocatalytic system: when light is irradiated, there is the expulsion of an electron (e^-) from the valence band (VB) of a semiconductor to the conduction band (CB), generating a positively charged vacancy or hole (h^+VB), i.e. the photoexcitation of the electron from VB to CB. The light irradiation then allows the generation of electron-hole pairs (e^-CB/h^+VB). The photogenerated holes oxidise the organic pollutant, mineralising it completely to less toxic forms, and also adsorb water to form the hydroxyl radical ($\cdot OH$) that mineralises the organic pollutants. [10, 11].

The photogenerated electrons react with adsorbed oxygen (O_2) to generate superoxide radicals ($\cdot O_2^-$), which can further produce other reactive oxygen species (ROS), including hydrogen peroxide (H_2O_2) and hydroperoxyl radical ($HO_2\cdot$). At the cathode, water undergoes a reduction reaction, (H_2O), to H_2 , contributing to the generation of additional reactive species involved in the degradation process [10, 11]

Various photoelectrocatalytic materials, such as bismuth oxybromide (BiOBr), have been investigated for photoelectrocatalytic degradation. BiOBr is a p-type semiconductor that exhibits good photoelectrocatalytic activity, strong visible - light absorbance, a unique layered crystal structure and an appropriate band gap between 2.0 and 3.0 eV, making it a promising material for photoelectrocatalytic applications [12]. However, the performance of the BiOBr photocatalyst is limited by high photogenerated electron-hole pair recombination efficiency and limited visible light absorption capacity [13-15].

Composites of other tungstates such as Bi_2WO_6 [16, 17], CuWO_4 [18], and SnWO_4 [19] have been extensively investigated as visible-light-responsive photocatalysts. However, molybdenum tungstate (MoWO_4) has only been explored for photoelectrocatalytic degradation applications. MoWO_4 has played a major role in solar energy devices, with zinc oxide and carbon nanotubes forming the composite [20]. It is an n-type semiconductor oxide with a band gap ranging from 2.6 to 3.21 eV, enabling satisfactory absorption of visible-light [21]. Composed of two group 6 transition metals, Mo and W, MoWO_4 exhibits distinctive physicochemical properties arising from the synergistic characteristics of their respective oxides. MoWO_4 has been investigated for various applications, including photoanodes for water splitting, gas sensing, dye-sensitized solar cells, and photocatalytic processes [20]. In addition, MoWO_4 possesses good physical and chemical stability, low toxicity, and oxygen - evolution capability [20], making it a promising material for photoelectrocatalytic applications. Its incorporation into heterojunction systems can also facilitate charge separation and suppress photocorrosion of photoactive materials [22]. In this study, for the first time, MoWO_4 is coupled with the visible-light semiconductor BiOBr to form a heterojunction for the photoelectrocatalytic degradation of norfloxacin.

Therefore, coupling BiOBr with MoWO_4 to form a heterojunction, particularly in the presence of oxygen vacancies in BiOBr, mitigates drawbacks such as low quantum efficiency and poor electron-hole pair separation efficiency [23]. The BiOBr/ MoWO_4 heterojunction facilitates more effective charge separation and suppresses the rapid recombination of photogenerated electron-hole pairs, thereby improving the availability of charge carriers for redox reactions. Consequently, the enhanced charge-transfer and redox capabilities contribute to improved photoelectrocatalytic activity. Thus, this work contributes to the development of effective and durable photoanodes for the degradation of norfloxacin, with potential applications in wastewater treatment.



Scheme 1 Schematic illustration of the proposed photoelectrocatalytic mechanism

Experimental section

Materials

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99%), citric acid, potassium bromide (KBr, 99%), molybdenum oxide (MoO_3 ; 99.97% trace metal basis), sodium tungstate (99.9%), ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$; ACS reagent; $\geq 99.0\%$), and sodium sulphate (Na_2SO_4), Silver nitrate (AgNO_3 , 99.8%), Ethylenediamine Tetra acetic acid disodium salt ($\text{EDTA}-2\text{Na}$), Acrylamide ($\text{CH}_2=\text{CHCONH}_2$), and Tert-Butanol (TBA) were procured from Merck South Africa. All reagents were of analytical grade and were used as received.

Deionised water (resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$) was used in preparing all the solutions. Fluorine-doped SnO_2 (FTO; 15Ω) transparent glass was purchased from Merck South Africa.

Preparation of BiOBr

BiOBr microspheres were synthesised using a facile solvothermal method, following a slightly modified procedure based on the method reported in the literature [24]. Briefly, 5 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 40 mL of ethylene glycol, followed by the dissolution of 5 mmol of KBr and 2 mmol of citric acid with stirring for 60 min. The mixture was then transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 150°C for 12 h and then naturally cooled to room temperature. The precipitate was washed with deionised water and ethanol and then dried in a vacuum oven at 60°C for 12 h [24].

Synthesis of MoWO₄

MoWO₄ was prepared via a hydrothermal process [20]. Initially, 70 mL of deionised water was used to dissolve 3.29 g of MoO₃ and 0.5 g of WO₃, which were vigorously stirred for 1 h. HCl (3 M) was slowly added to the solution until the pH reached approximately 2. An additional 3.30 g of (NH₄)₂SO₄ was added to the resulting solution, which was then constantly stirred for another 30 min and transferred into a Teflon-lined stainless-steel autoclave and kept at 190 °C for 5 h. After cooling to room temperature, the solution was repeatedly cleaned with ethanol and deionized water and allowed to air-dry at 60 °C for 12 h [20].

Preparation of BiOBr/MoWO₄ heterojunction

The BiOBr/MoWO₄ heterojunction was synthesised in situ using the hydrothermal method following a previously reported procedure [20]. Briefly, 0.287 g of MoO₃ and 0.046 g of WO₃ were dissolved in 70 mL of deionised water under vigorous stirring for 1 h. The pH of the resulting mixture was adjusted to 2 using 3 M HCl. Subsequently, 0.5 g of BiOBr was added to the mixture and stirred further for 30 min. Thereafter, 0.290 g of (NH₄)₂SO₄ was added, and the suspension was continuously stirred for an additional 30 min. The resulting mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and hydrothermally treated at 190 °C for 5 h. After naturally cooling to room temperature, the obtained product was repeatedly washed with ethanol and deionised water to remove residual impurities. The washed material was then dried in an oven at 60 °C for 12 h, as illustrated in Fig. 1 [20].

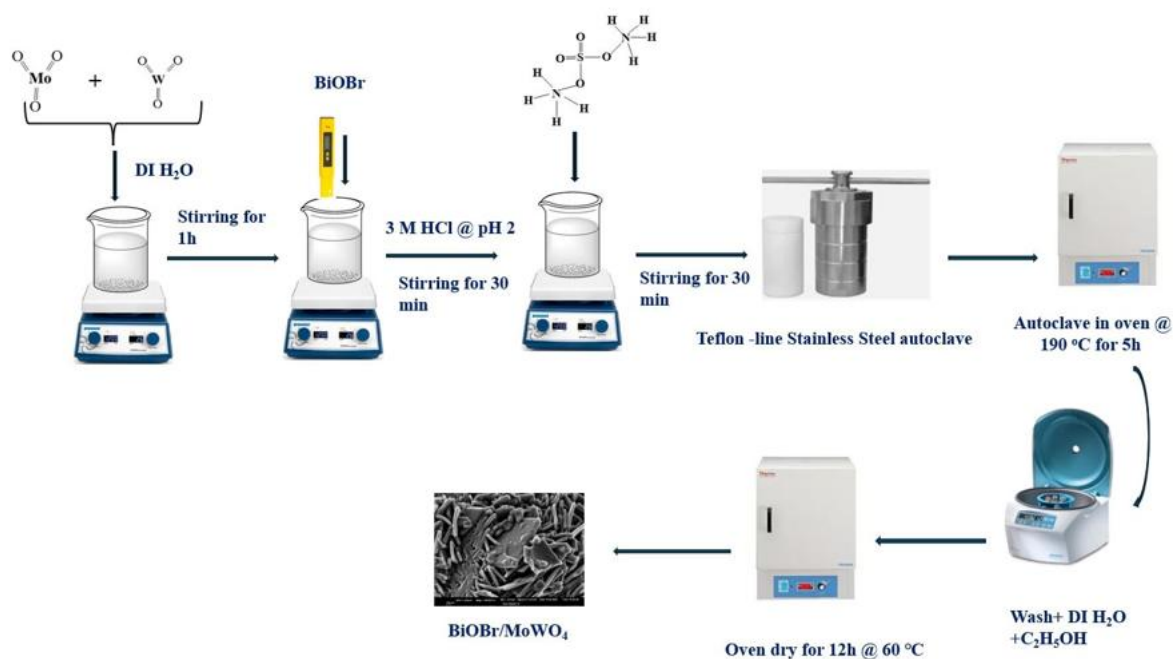


Fig. 1 The preparation of the BiOBr/MoWO₄ heterojunction

Photoelectrochemical degradation studies and electrochemical analysis

Photoelectrochemical degradation studies were conducted using a two-electrode system, with the BiOBr/MoWO₄ photoanode and platinum sheet serving as the working electrode and counter electrode, respectively. The experiments were conducted in a 0.1 M Na₂SO₄ electrolyte solution under light irradiation using a 100 W LED lamp equipped with a 420 nm cutoff filter. The BiOBr/MoWO₄ films were illuminated from the front side of the fluorine-doped tin oxide (FTO)-coated glass substrate, with an effective area of 3.0 cm². All electrochemical potentials were referenced to the Ag/AgCl electrode.

We recorded the UV–Vis diffuse reflectance spectra (DRS) of the samples using an Agilent Carry 60 UV–Vis spectrophotometer (Malaysia). Photoluminescence (PL) spectra were obtained using the Spectrofluorophotometer RF-6000 (Japan).

The electrochemical and photoelectrochemical analyses were performed using the Autolab PGSTAT204 potentiostat/galvanostat (Netherlands) equipped with a three-electrode setup. Electrochemical impedance spectroscopy (EIS) measurements were conducted over a frequency range of 0.1 – 100,000 Hz at open-circuit potential (OCP). Mott-Schottky (MS) analysis, linear sweep voltammetry (LSV) at a sweep rate of 10 mV/s, and transient photocurrent measurements were also carried out using the same electrochemical workstation under controlled potential conditions. The three-electrode configuration comprised a platinum wire as the counter electrode, the photoanode-coated FTO electrode as the working electrode, and an Ag/AgCl electrode as the reference electrode. For the transient photocurrent measurements, a 100 W Xenon lamp was used as the light source, and a bias potential of 1.5 V was applied.

Morphology characterisation and instrumentation

The crystalline structures of the samples were analysed using X-ray diffraction (XRD) with a PANalytical Empyrean equipped with a PIXcell 1D detector at 40 kV and 50 mA. The data were analysed using HighScore Plus software (PANalytical, Almelo, Netherlands). Fourier transform infrared (FTIR) spectra were recorded using a Bruker Alpha FT-IR spectrometer (Germany) to identify the characteristic functional groups present in the samples. The surface morphology of the materials was examined using scanning electron microscopy (SEM) with a TESCAN VEGA3 instrument equipped with an Oxford Instruments X-Max detector, Tescan, Brno, Czech Republic. Field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX) analyses were performed using a Zeiss Crossbeam 540 FEGSEM, a dual-beam system that combines a field-emission gun (FEG) electron microscope with a focused ion beam (FIB) system (Germany). High-resolution transmission electron microscopy (HR–TEM) was conducted using a JEOL JEM-2100TEM (JOEL Ltd., Tokyo,

Japan) equipped with a LaB₆ electron source to further investigate the morphology, microstructure, and elemental composition of the materials. Brunauer Emmett–Teller (BET) surface area and physisorption measurements were carried out using an Anton Paar NOVA 8000 Physisorption analyser (Graz, Austria) to determine the specific surface area and pore characteristics of the samples.

Results and discussion

Characterisation of the morphology

X-ray Diffraction Analysis (XRD)

The XRD patterns of BiOBr, MoWO₄, and BiOBr/MoWO₄ semiconductor samples are displayed in Fig. 2. The diffraction peaks observed for the individual BiOBr and MoWO₄ phases correspond well with the tetragonal phase of BiOBr (JCPDS:04-008-4123) and the monoclinic crystalline phase of MoWO₄ (JCPDS:04-026-9227), respectively. The absence of additional diffraction peaks suggests that the samples were obtained without significant crystalline impurities. The diffraction peaks of BiOBr, at 2θ values of 10.6°(001), 24.9°(101), 31.5°(110), 32.0°(003), 39.2°(112), 46.1°(200), and 56.8°(212), confirming the successful formation of well-crystallised BiOBr [24]. These reflections are consistent with the reported crystal structure of BiOBr. For MoWO₄, the characteristic diffraction peaks are observed at 2θ of 15.5° (020), 22.4° (001), 24.9°(040), 28.5°(021), 29.8° (101), 31.3° (111), 34.7° (200), 39.5° (060), 40.8° (211), 48.7° (220), 50.9° (102), 52.0° (112), 55.5° (310), 57.4° (301), 61.4° (212), and 74.4° (103), which can be indexed to the monoclinic MoWO₄ phase [20]. The well-defined diffraction peaks indicate the formation of a crystalline MoWO₄ structure.

The BiOBr/MoWO₄ heterojunction exhibits the characteristic diffraction features of both BiOBr and MoWO₄; particularly, the (110) and (101) planes, respectively, exhibit slight shifts in their 2θ position compared with those of the individual components. These shifts suggest interaction between BiOBr and MoWO₄ and provide evidence for the successful formation of the BiOBr/MoWO₄ heterojunction [25].

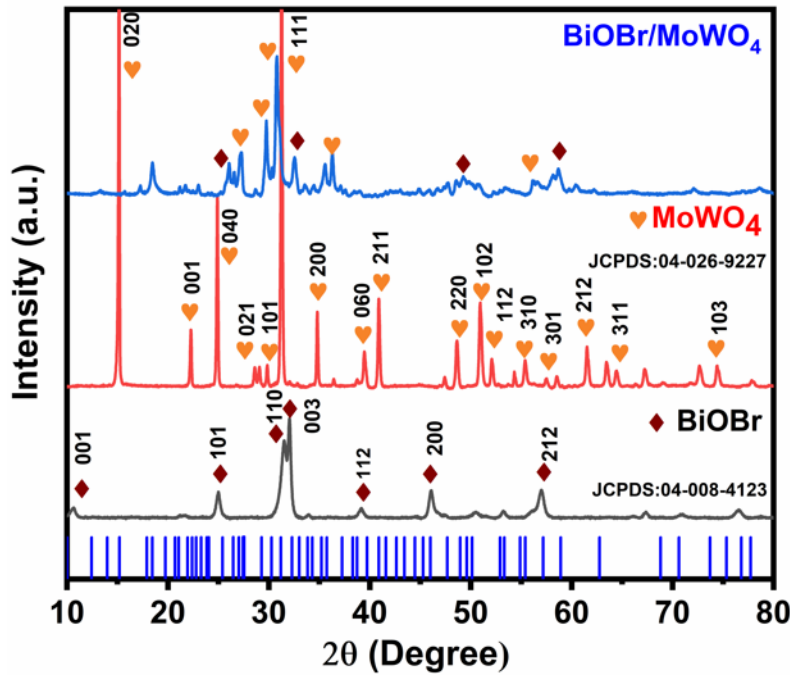


Fig. 2. XRD diffractograms of BiOBr, MoWO₄, BiOBr/MoWO₄

Fourier Transform Infrared (FTIR) Analysis

Figure 3 illustrates the FTIR spectra of BiOBr/MoWO₄ heterojunction, MoWO₄ and BiOBr. The spectra for all the synthesised samples exhibit broad absorption bands at approximately 3471 cm⁻¹, 3461 cm⁻¹, and 3452 cm⁻¹ which are ascribed to the O-H stretching vibrations of surface hydroxyl groups and/or water molecules. The characteristic absorption band observed at around 512 cm⁻¹ is associated with the Bi-O stretching vibration, confirming the presence of BiOBr in the synthesised material [25, 26].

Additional absorption peaks are observed at approximately 1267 cm⁻¹, 1386 cm⁻¹, 1624 cm⁻¹, 2915 cm⁻¹, and 3452 cm⁻¹. These bands can be assigned to the vibrational modes of the C-N, -CH₂, C=O, C-H, and O-H bonds, respectively, which may originate from residual organic species and adsorbed water on the surface of the samples [25, 26]. These characteristic vibrational bands further confirm the chemical composition and surface functional groups of the synthesised BiOBr, MoWO₄, and BiOBr/MoWO₄ materials.

In the FTIR spectrum of MoWO₄, the absorption bands observed at 909 cm⁻¹ and 522 cm⁻¹ can be attributed to the symmetrical vibration of Mo-W-O groups and the stretching vibration of Mo-O bonds, respectively. Moreover, the strong absorption band at 701 cm⁻¹ is assigned to the asymmetrical stretching vibration of W-O bonds within the (W₂O₄)_n chains [20]. The FTIR spectrum of the BiOBr/MoWO₄ heterojunction exhibits the characteristic vibrational bands associated with both MoWO₄ and BiOBr, although slight shifts in the peak

positions are observed. These shifts may be attributed to interfacial interaction between the two semiconductor components and support the successful formation of a BiOBr/MoWO₄ composite.

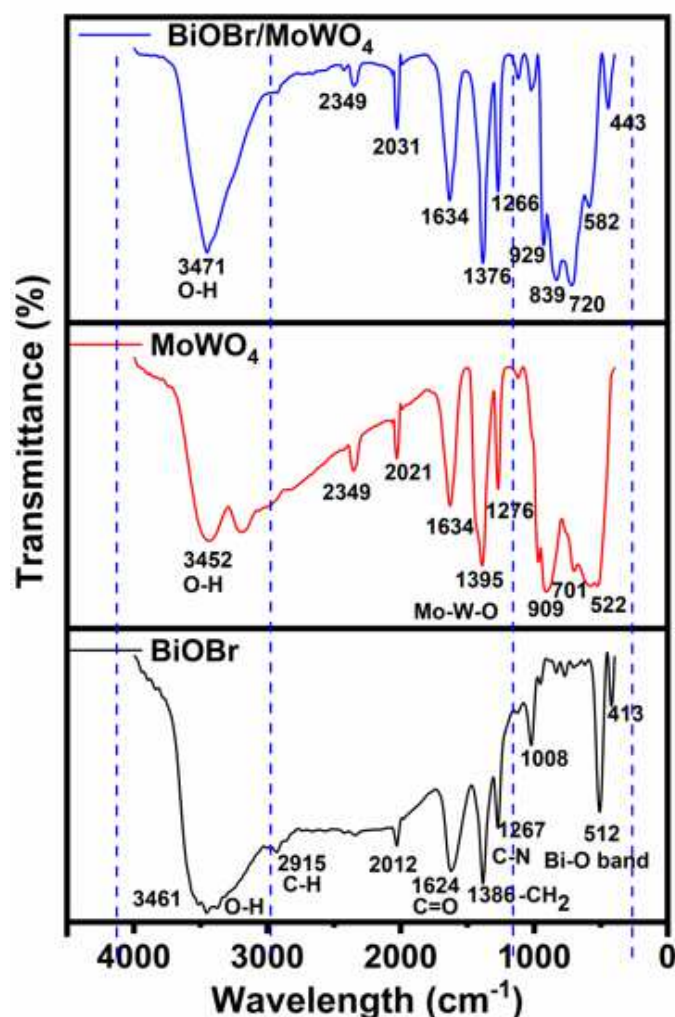


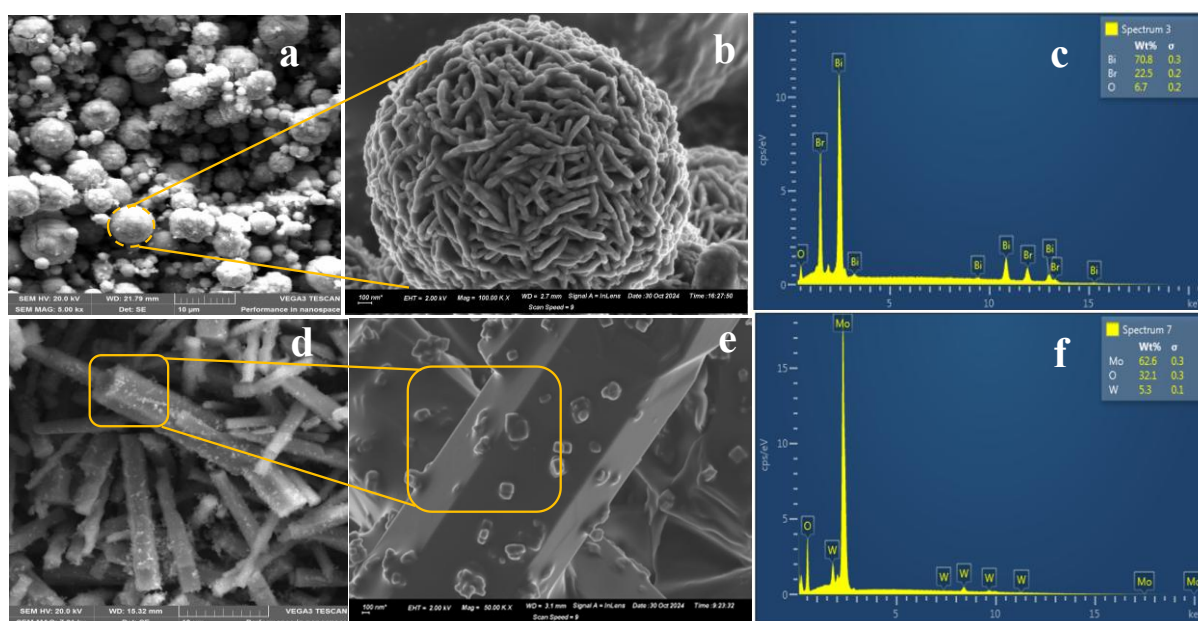
Fig. 3 FTIR spectrum of BiOBr/MoWO₄ heterojunction, MoWO₄, and BiOBr

SEM, FE-SEM, and EDX characterisation

The SEM, FE-SEM, and EDX characterisation of the BiOBr, MoWO₄ and BiOBr/MoWO₄ composite are presented in Fig. 4a-j. The SEM image of BiOBr in Fig. 4a shows a nanoclustered microspherical morphology, which is further supported by the FE-SEM image in Fig. 4b. The BiOBr shows spherical clusters composed of small worm-like nanostructures. The EDX spectrum (Fig. 4c) confirms the presence of Bi, Br, and O, with elemental composition of 70.8%, 22.5%, and 6.7%, respectively [27]. The SEM and FE-SEM images of MoWO₄ (Fig. 4d-f) reveal a predominantly nanorod-like morphology. The corresponding EDX confirms the presence of Mo, O, and W in MoWO₄, with elemental compositions of 62.6%, 32.1%, and 5.3%, respectively [28]. These results confirm the successful incorporation of the constituent elements in the MoWO₄ structure. The FE-SEM

image of the composite BiOBr/MoWO₄ in Fig. 4i reveals the synergistic combination of the microspherical BiOBr and the nanorod-like MoWO₄ structures. The morphological features of both components are retained within the composite, indicating their successful integration and the formation of a heterojunction. The close contact between the two semiconductor phases is expected to facilitate interfacial charge transfer and contribute to the enhanced photocatalytic performance of the BiOBr/MoWO₄.

The EDX analysis and elemental mapping confirmed the presence of the constituent elements Bi, Br, O, Mo and W in the BiOBr/MoWO₄ composite. The elemental mapping presented in Fig. S1 (online Resource 1) demonstrates the uniform distribution of Mo, Bi, Br, O₂, and W throughout the composite, further confirming the successful incorporation of both BiOBr and MoWO₄ components.



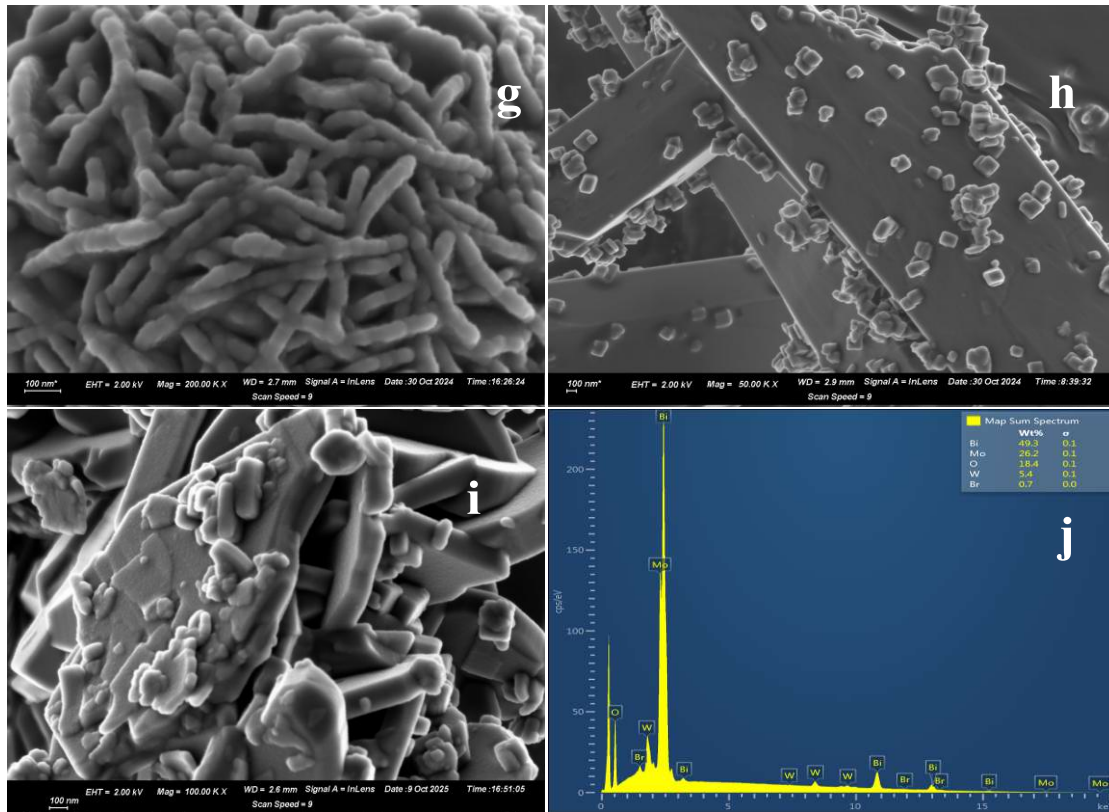


Fig. 4 (a-c) SEM, FE-SEM images & EDX of the as-prepared BiOBr, (d-f) SEM, FE-SEM images & EDX of the as-prepared MoWO₄, (g-j) FE-SEM images of BiOBr, MoWO₄, BiOBr/MoWO₄ and the EDX of BiOBr/MoWO₄

Transmission electron microscopy (TEM)

The TEM images of BiOBr (Fig. 5a) reveal irregular nanosheets with flower-like assembled structures. The corresponding selected area electron diffraction (SAED) analysis displays distinct diffraction rings that can be indexed to (101), (202) and (303), confirming the crystalline nature of BiOBr and its tetragonal crystalline structure. These observations are consistent with the XRD results. The TEM image of MoWO₄ (Fig. 5b) reveals predominantly rectangular or rodlike structures, in agreement with the morphology observed in the SEM and FE-SEM. The corresponding SAED pattern further confirms the crystalline nature of MoWO₄. For the BiOBr/MoWO₄ composite, the SEM and FE-SEM images reveal an integrated morphology in which sheet-like BiOBr structures are closely associated with MoWO₄ nanoparticles or nanorod-like structures. The intimate contact between the two components provides evidence of the formation of the BiOBr/MoWO₄ heterojunction. The distinct lattice fringes observed in the high-resolution TEM images indicate the high crystallinity of the composite. Furthermore, the corresponding SAED pattern exhibits well-defined diffraction features, providing additional evidence of the crystallinity of the composite material. (Fig. 4i and Fig. 5c).

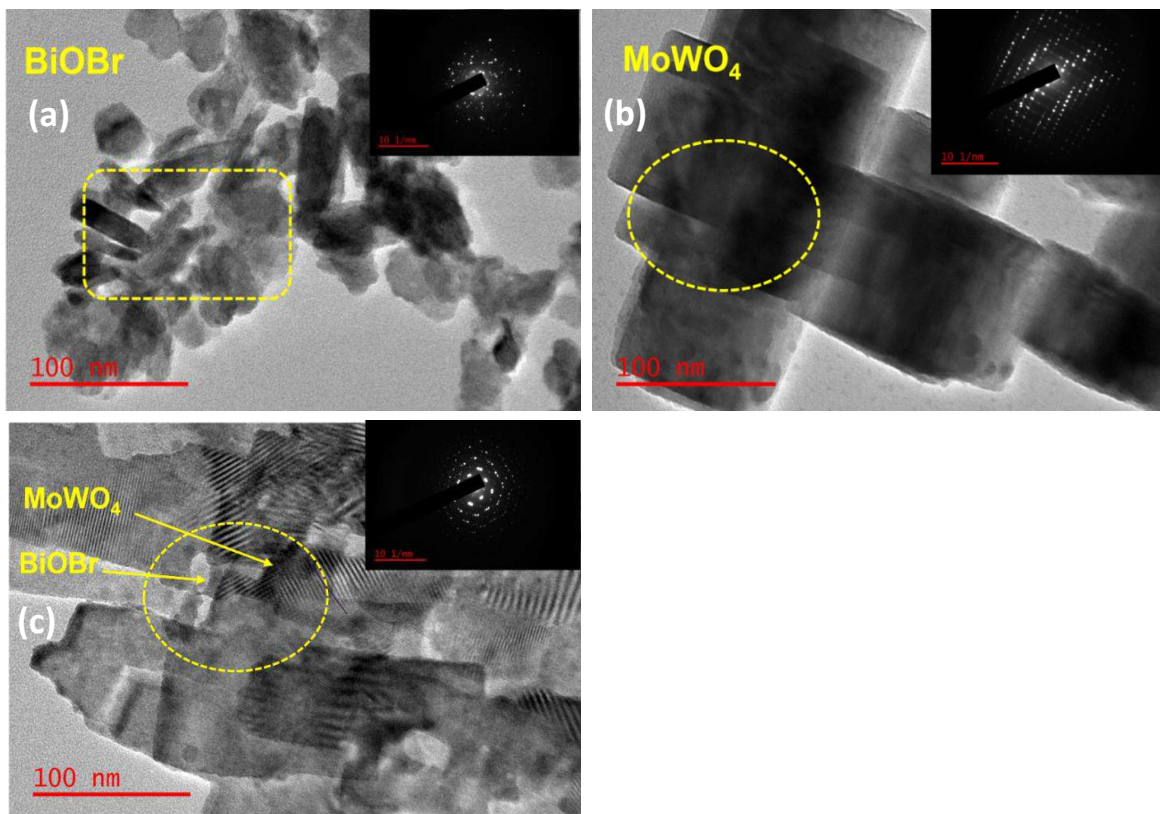


Fig. 5. TEM images of (a) BiOBr, (b) MoWO₄ and (c) BiOBr/MoWO₄ composite and their Selected Area Electron Diffraction (SAED) images

BET analysis of BiOBr, MoWO₄ and BiOBr/MoWO₄ heterojunction

The Brunauer-Emmett-Teller (BET) analysis was conducted to investigate the specific surface areas and textural properties of BiOBr, MoWO₄, and BiOBr/MoWO₄ heterojunction. The BiOBr/MoWO₄ photocatalyst heterojunction exhibited a specific surface area of 25.31 m² g⁻¹, which was higher than those of pristine BiOBr (24.38 m² g⁻¹) and MoWO₄ (22.78 m² g⁻¹).

The increased surface area of the heterojunction indicates surface enrichment, which highlights the successful formation of the BiOBr/MoWO₄ heterojunction and provides a greater number of accessible surface sites for adsorption and subsequent photocatalytic reactions. This enhanced surface area may therefore contribute to the improved photoelectrocatalytic performance of the BiOBr/MoWO₄ heterojunction. The N₂ gas adsorption-desorption behaviour of BiOBr, MoWO₄, and BiOBr/MoWO₄, presented in Fig. S2 (online resource 2), exhibits type IV isotherms, characteristic of mesoporous materials according to the IUPAC classification. The observed hysteresis loops within the relative pressure range (p/p_o) of approximately 0.5-1.0 are indicative of capillary condensation within mesopores. The N₂ sorption results further demonstrate the enhanced textural properties of BiOBr/MoWO₄ heterojunction compared with the individual semiconductor components. The combination of

increased surface area and mesoporosity is expected to facilitate pollutant adsorption and provide more active sites for photoelectrocatalytic degradation.

Optical, photoelectrochemical and electrochemical properties of the photoanodes

The UV–visible diffuse reflectance spectra (UV-Vis-DRS) of BiOBr, MoWO₄, and the BiOBr/MoWO₄ composite, showing their optical absorption properties, are shown in Fig. 6a. All three materials exhibit appreciable absorption in the visible light region, indicating their potential for visible light-driven photoelectrocatalytic applications.

The absorption peak of MoWO₄ is observed near 439 nm, while BiOBr exhibits an absorption at around 465 nm. Notably, the BiOBr/MoWO₄ composite displays a slight red shift in the absorption edge to approximately 469 nm, indicating enhanced visible light absorption following the formation of the heterojunction. This extended absorption response suggests that coupling MoWO₄ and BiOBr improves the utilisation of visible light.

The band-edge alignment of the constituent semiconductors can be estimated from their optical band-gap energies and flat-band potentials [29]. As depicted in Fig. 6b, the band gap energy (E_g) of MoWO₄ and BiOBr was estimated from the corresponding Tauc plot to be 2.39 eV and 2.61 eV, respectively. These values are consistent with previously reported band gap energies for MoWO₄ and BiOBr [13, 20, 30]. The results confirm the successful synthesis of visible light-responsive semiconductor materials and further demonstrate the potential of the BiOBr/MoWO₄ heterojunction for enhanced photoelectrocatalytic activity.

The optical band-gap energies of the MoWO₄ and BiOBr semiconductors were estimated from their UV-Vis-DRS data using the Tauc approach (Eq.1):

$$\alpha h\nu = A(\nu h - E_g)^{\frac{n}{2}} \quad (1)$$

where, α , h , A , E and ν , α is the absorption coefficient, h is Planck's constant, A is the proportionality constant, E_g is the optical band-gap energy, and ν is the incident light frequency. The parameter n is related to the nature of the electronic transition and is selected according to the optical transition characterisation of the semiconductors. Since MoWO₄ and BiOBr are considered direct-transition semiconductors, the appropriate value of n was used for direct electronic transition.

The flat-band potentials (E_{fb}), of MoWO₄ and BiOBr were obtained from the corresponding Mott-Schottky plots presented in Fig. 6c-e. The E_{fb} values were 0.11 eV and -0.20 eV vs. Ag/AgCl, corresponding to 0.304 eV and -0.006 eV vs. NHE for MoWO₄ and BiOBr, respectively. The slope of the Mott-Schottky plots indicates that BiOBr

exhibits p-type semiconductor behaviour based on its negative slope (Fig. 6c), whereas MoWO₄ exhibit n-type semiconductor behaviour as evidenced by its positive slope (Fig. 6d). For an n-type semiconductor, the conduction-band potential (E_{CB}) is generally close to or slightly more negative than the flat-band potential, whereas for a p-type semiconductor, the valence band potential (E_{VB}) is slightly more positive than the flat-band potential [29]. Using the appropriate band-edge relationship, the E_{VB} and E_{CB} values of BiOBr were calculated to be 0.375 eV and 2.985 eV versus NHE, respectively. Similarly, the corresponding E_{VB} and E_{CB} of MoWO₄ were also calculated to be 0.717 eV and 3.107 eV versus NHE, respectively, using equations 2 and 3.

$$E_{CB} = X - E_c - 0.5E_g \quad (2)$$

$$E_{VB} = E_g + E_{CB} \quad (3)$$

where X represents the absolute electronegativity of the semiconductor, and E_c denotes the energy of free electrons on the hydrogen scale. Mott-Schottky analysis was performed to investigate changes in the flat band potential and charge-carrier density associated with the formation of the BiOBr/MoWO₄ heterojunction. The relationship between the semiconductor capacitance and applied potential was evaluated using the Mott-Schottky (Eq. 4). The charge-carrier density with negative values signifies the allocation of electrons in the region, whereas positive values indicate the presence of holes.

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 q A^2 N_D} \left[V - V_{fb} - \frac{K_B T}{q} \right] \quad (4)$$

The charge-carrier density was subsequently determined from the slope of the Mott-Schottky plot using Eq. 5:

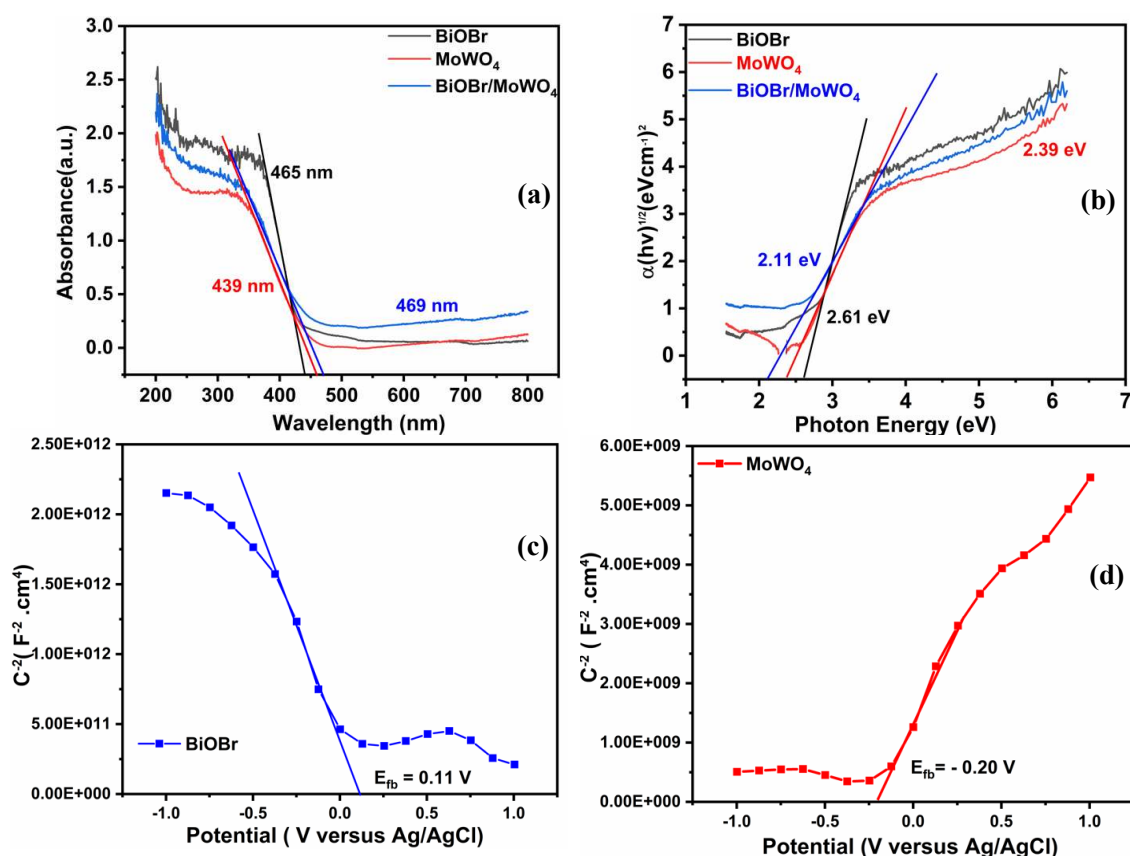
$$N_D = \frac{2}{\epsilon\epsilon_0 q m} \quad (5)$$

where C represents the capacitance, ϵ the dielectric constant of the semiconductor, ϵ_0 the permittivity of free space, q is the charge of the electrons ($-1.69 \times 10^{-19} C$), A the surface area, N_D the concentration of the major charge carrier (donor density), V the applied voltage, V_{fb} is the flat-band potential, K_B is the Boltzmann constant, and T is the absolute temperature, m slope of the linear region of the Mott-Schottky plot [31, 32].

The sign and magnitude of the Mott-Schottky slope provide information about the semiconductor type and charge-carrier characteristics. A positive slope is generally associated with an n-type semiconductor, indicating electrons as the majority charge carriers, whereas a negative slope is characteristic of a p-type semiconductor, in which holes are the majority charge carriers. Changes in the slope and flat-band potential following heterojunction formation provide insight into interfacial charge redistribution and the electronic interaction between BiOBr and MoWO₄. The slope of the Mott-Schottky plot is inversely proportional to the concentration of the majority charge carriers, which is approximately related to the electron density, as described by Eq.5. An increase in electron

density in an n-type semiconductor indicates a shift of the Fermi level closer to the conduction band, reflecting enhanced electronic conductivity and charge carrier availability.

The BiOBr/MoWO₄ heterojunction exhibits a higher transient photocurrent response than the pristine BiOBr and MoWO₄, as shown in Fig. 6f. The enhanced photocurrent indicates more efficient generation, separation and transport of photogenerated electron-hole pairs within the heterojunction. This improved charge-carrier separation reduces electron-hole recombination and increases the availability of charge carriers for surface redox reactions, thereby contributing to the high photoelectrocatalytic activity of the BiOBr/MoWO₄ heterojunction. Transient photocurrent measurements are typically used to investigate interfacial charge-transfer dynamics of semiconductor materials. The subsequently enhanced transient photocurrent density observed for the BiOBr/MoWO₄ heterojunction, compared with pristine MoWO₄ and BiOBr, demonstrates its superior photoelectrochemical charge-transfer characteristics [33, 34].



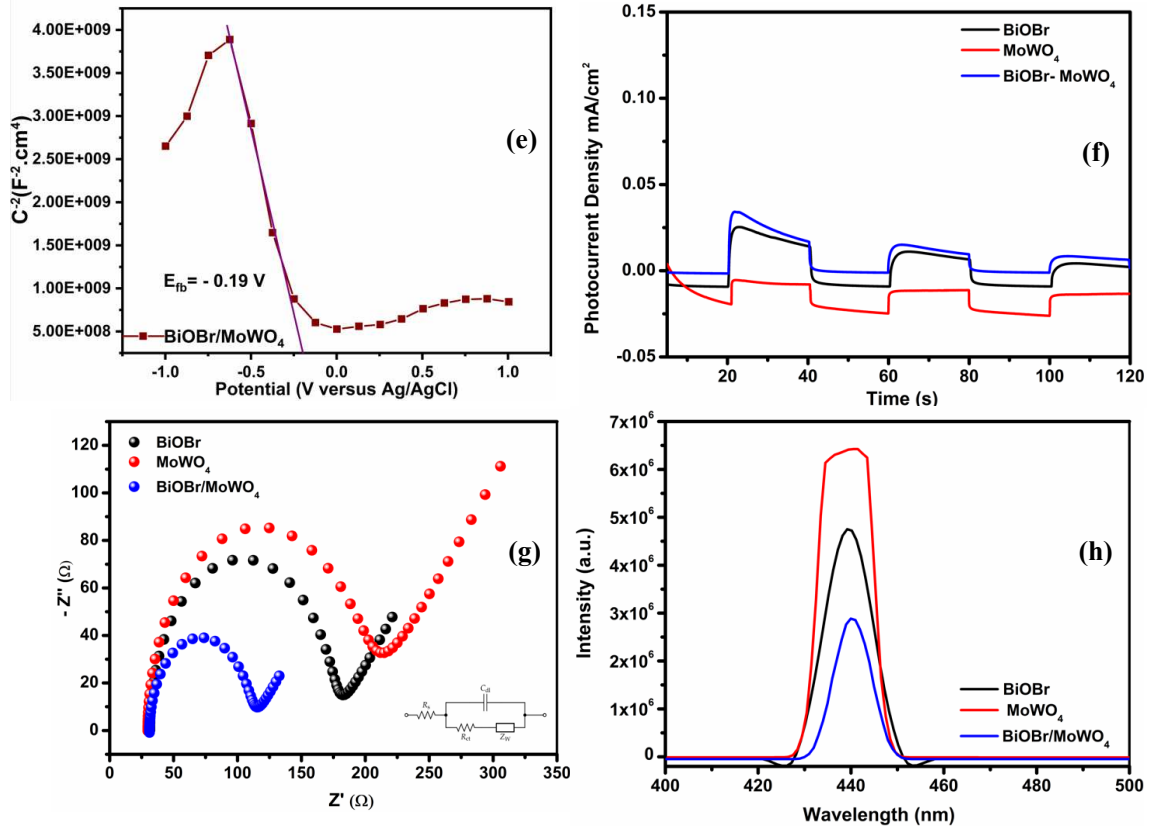


Fig. 6 (a) UV-Visible diffuse reflectance spectra and (b) the energy band gap edges of MoWO₄, BiOBr, BiOBr/MoWO₄ electrode (c-e) Mott Schottky plot for BiOBr, MoWO₄, BiOBr/MoWO₄, photoanodes in 5 mM [Fe(CN)₆]^{3-/4-} in 0.1 M KCl (f) Transient photocurrent response in 0.1 M Na₂SO₄ (g) Nyquist EIS plot for MoWO₄, BiOBr, BiOBr/MoWO₄, photoanodes in 5 mM [Fe(CN)₆]^{3-/4-} in 0.1 M KCl (h) Steady-state Photoluminescence (PL) spectra.

Electrochemical impedance spectroscopy (EIS) was employed to investigate the charge-transfer kinetics and interfacial electrochemical properties of the photoanodes. The Nyquist plots are presented in Fig. 6g. The BiOBr/MoWO₄ photoanode exhibited the smallest charge-transfer resistance (R_{ct}) of 78.3 Ω , compared with 142.4 Ω and 231.8 Ω for pristine BiOBr and MoWO₄, respectively. The lower R_{ct} of the BiOBr/MoWO₄ heterojunction indicates more efficient interfacial charge transfer and reduced resistance to the movement of photogenerated carriers. This enhanced charge-transfer behaviour can promote the effective separation of photogenerated electron-hole pairs and suppress their recombination, thereby contributing to the superior photoelectrocatalytic performance of the heterojunction [31, 35].

The electroactive surface area of the photoanodes was further determined from the slopes of the corresponding calibration curves using the Randles-Sevcik equation (Eq. 6).

$$(I_{pa} = 2.69 \times 10^5 \times A \times \sqrt{D} \times \sqrt[3]{n} \times C) \quad (6)$$

where I_{pa} is the anodic peak current, n is the number of electrons transferred, A is the electroactive surface area, D is the diffusion coefficient of the ferri/ferrocyanide ($7 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$), C is the concentration of the ferri/ferrocyanide electrolyte ($5 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$). 2.69×10^5 represents the proportionality constant. The calculated electroactive surface area provides further insight into the availability of active sites and the electrochemical accessibility of the photoanode surfaces.

The calculated electrochemical surface areas of BiOBr, MoWO₄, and BiOBr/MoWO₄ were 0.5712 cm^2 , 1.2770 cm^2 , and 1.8327 cm^2 respectively. The BiOBr/MoWO₄ heterojunction exhibited the largest electrochemical surface area, indicating a greater number of electrochemically accessible active sites. The increased active surface area can facilitate interfacial electron transfer and provide more reaction sites for pollutant degradation. Consequently, the enhanced electrochemical accessibility of the heterojunction may promote more efficient charge separation and contribute to its superior photoelectrocatalytic performance.

The photoluminescence (PL) spectra of BiOBr, MoWO₄ and the BiOBr/MoWO₄ heterojunction were analysed to evaluate the recombination behaviour and separation efficiency of photogenerated electron-hole pairs. As shown in Fig. 6h, the BiOBr/MoWO₄ heterojunction promotes efficient separation and transfer of photoinduced electrons and holes [12]. This enhanced charge-carrier separation is expected to increase the availability of reactive charge carriers for surface redox reactions, thereby contributing to the improved photoelectrocatalytic activity of the heterojunction.

Photoelectrocatalytic degradation studies of norfloxacin

Figure 7 shows the photoelectrocatalytic activity and degradation kinetics of BiOBr, MoWO₄, and BiOBr/MoWO₄ heterojunction for the degradation of aqueous norfloxacin (NOR) solution under simulated solar irradiation using a LED light source for 180 min. The effect of solution pH on the photoelectrocatalytic degradation of NOR was evaluated at pH 4.5, pH 7.0, and pH 10.0 (Fig 7a). Among the investigated conditions, the highest degradation efficiency was achieved at pH 4.5, indicating that the solution pH plays an important role in the photoelectrocatalytic degradation of NOR.

The effect of applied current density was also evaluated, and the current density of 5 mA cm^{-2} was identified as the optimum condition, resulting in a degradation efficiency of 85% (Fig. 7b).

Under the optimised conditions, the photoelectrocatalytic process displayed substantially higher norfloxacin degradation efficiency (85%) compared with electrocatalysis (77%), photocatalysis (5.8%) and photolysis (5%)

(Fig. 7c). Also, the kinetics for the photoelectrocatalytic process gave the highest rate constant of 0.0105 min^{-1} in (Fig. 7d). The enhanced performance demonstrates the synergistic effect of light irradiation and the applied electric field in promoting charge separation and the generation of reactive species responsible for pollutant degradation.

Among the investigated photoanodes, the BiOBr/MoWO₄ heterojunction displayed enhanced NOR degradation efficiency of 85% compared with 78% for pristine BiOBr and 56% for MoWO₄ (Fig. 7e). The superior performance of the heterojunction can be attributed to the formation of a p-n heterojunction between BiOBr and MoWO₄, which facilitates interfacial charge transfer and improves the separation of photogenerated electron-hole pairs. The formation of the p-n heterojunction, with higher surface area and enhanced photocurrent response, promotes efficient separation of photogenerated electron-hole pairs and lowers their recombination. This improved charge separation facilitates the formation of radicals needed for the PEC process. The BiOBr/MoWO₄ heterojunction also promotes a superior interfacial separation rate and migration of photogenerated electrons, particularly through the conduction band, thereby enhancing the availability of charge carriers for surface redox reactions. The larger valence-band potential of the heterojunction enhances the oxidation capability of photogenerated holes, contributing to the improved photo-oxidation and overall photoelectrocatalytic capability.

The degradation of norfloxacin was found to follow a pseudo-first-order reaction kinetics model (Fig 7f), which is commonly assumed when the initial pollutant concentration is sufficiently low, such that the process can be treated as catalytic. The kinetic behaviour is described by the following expression:

$$\ln \frac{C_0}{C_t} = kt \quad (7)$$

where C_0 and C_t are the concentrations of norfloxacin in solution at *time 0 and time t*, respectively, and k is the apparent first-order rate constant.

Based on Eq. 7, the PEC degradation of norfloxacin using the BiOBr/MoWO₄ photoanode exhibits the highest rate constant of 0.01048 min^{-1} , outperforming both the individual BiOBr and MoWO₄ photoanodes with rate constants of 0.00793 min^{-1} and 0.00636 min^{-1} , respectively, demonstrating the superior catalytic efficiency of the composite material.

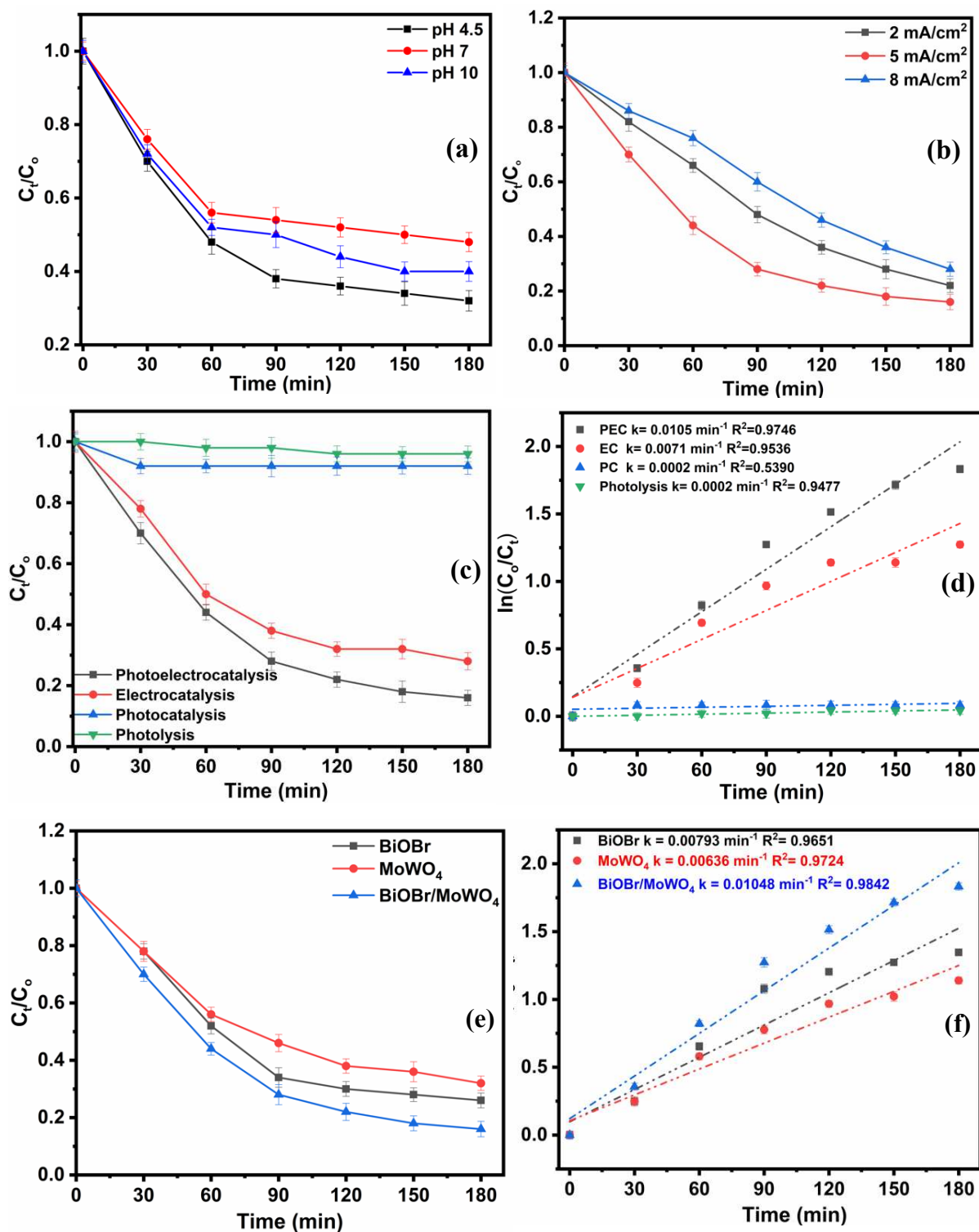
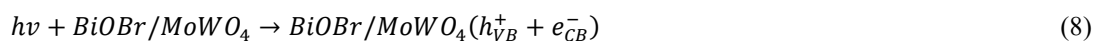


Fig. 7 The PEC degradation of norfloxacin (NOR) under optimal conditions ($C_0 = 5 \text{ mg L}^{-1}$, $0.1 \text{ M Na}_2\text{SO}_4$ current density of 5 mA cm^{-2}) (a) pH studies, (b) current density, (c) PEC degradation of NOR using different degradation methods, (d) Kinetics plot for PEC degradation of NOR using different degradation methods, (e) PEC degradation of NOR using different photoanodes, (f) Kinetics plot for PEC degradation of NOR using BiOBr, MoWO₄ and BiOBr/MoWO₄ photoanodes.

Scavenger studies

In photoelectrocatalytic degradation experiments, hydroxyl radical ($\cdot OH$), superoxide radical ($\cdot O_2^-$), and photogenerated holes (h_{VB}^+) are the primary reactive oxygen species responsible for attacking and oxidising organic pollutant molecules, ultimately leading to their complete mineralisation. The mechanistic pathways governing the formation of these reactive species and their subsequent oxidation reactions with the pharmaceutical molecules are described by equations 8 – 14. To evaluate the individual contribution of each reactive species to the PEC degradation of the norfloxacin molecule, trapping experiments were performed by introducing specific scavengers into the reaction medium. Sodium-ethylenediaminetetraacetate salt (Na-EDTA) was used to quench photogenerated holes (h_{VB}^+), tert-butanol (t-BuOH) was used to scavenge hydroxyl radicals ($\cdot OH$), Acrylamide (C_3H_5NO) was used to trap superoxide radicals ($\cdot O_2^-$), and silver nitrate ($AgNO_3$) served as an electron scavenger.



As shown in Fig. 8a, photogenerated holes were identified as the most dominant reactive species in the degradation of norfloxacin, as evidenced by the drop in removal efficiency to almost 8.0% upon the addition of Na-EDTA as a hole scavenger. Furthermore, hydroxyl radicals were also found to play a significant role in the degradation of the norfloxacin molecules, as the addition of t-butanol reduced the degradation efficiency to 77.0%, confirming their active participation. The hydroxyl radicals in the reaction system were generated through the oxidation of water molecules by photogenerated holes, as represented in Eq. 10. The superoxide radicals also played a

seemingly important role in the oxidative degradation of norfloxacin, as demonstrated by the reduction in removal efficiency to 40.3% upon the addition of acrylamide as a scavenger. Additionally, when AgNO_3 was introduced to trap photogenerated electrons, the degradation efficiency decreased to 71.2%, further confirming the contribution of electrons to the overall PEC degradation process.

In this work, the scavenger study results reveal that photogenerated holes and superoxide radicals are the predominant reactive species governing the breakdown of the pharmaceuticals. This finding is consistent with the formation of the $\text{BiOBr}/\text{MoWO}_4$ heterojunction, which facilitates enhanced charge separation and suppresses the recombination of photogenerated electron-hole pairs. The relative band edge potential of the conduction band and valence band of both semiconductors provides a thermodynamic driving force for the spontaneous mobility of photogenerated charge carriers across the interface of the two semiconductors as described by Eqs. 14 and 15 [12, 30].

The stability and reusability of a photoanode are critical parameters for evaluating its practical applications in real-world water treatment systems. To assess these properties, PEC degradation experiments were carried out over five consecutive cycles under identical conditions using the same $\text{BiOBr}/\text{MoWO}_4$ photoanode. As shown in Fig. 8b, the photodegradation efficiency of norfloxacin exhibited a gradual decrease from an initial removal rate of 85% across successive cycles, indicating progressive degradation of the photoanode over repeated use.

To further assess the structural integrity of the photoanode after repeated use, the $\text{BiOBr}/\text{MoWO}_4$ photoanode was recovered following the fifth consecutive PEC degradation cycle and analysed by XRD. As represented in Fig. 8c, no significant changes were observed in the diffraction peak positions and intensity before and after degradation experiments, confirming that the crystal structure of the $\text{BiOBr}/\text{MoWO}_4$ composite photoanode remained intact and stable. These results demonstrate the excellent structural stability of the $\text{BiOBr}/\text{MoWO}_4$ photoanode under prolonged PEC operation conditions.

To evaluate the broader applicability of the $\text{BiOBr}/\text{MoWO}_4$ photoanode beyond norfloxacin degradation, its PEC performance was further tested against other pharmaceutical pollutants, vis., tetracycline and ciprofloxacin, under the same experimental conditions. As illustrated in Fig. 8d, the $\text{BiOBr}/\text{MoWO}_4$ photoanode displayed good degradation efficiency for both analytes, highlighting its potential as a versatile and effective photoanode material for the remediation of a broader range of pharmaceutical contaminants in aqueous environments.

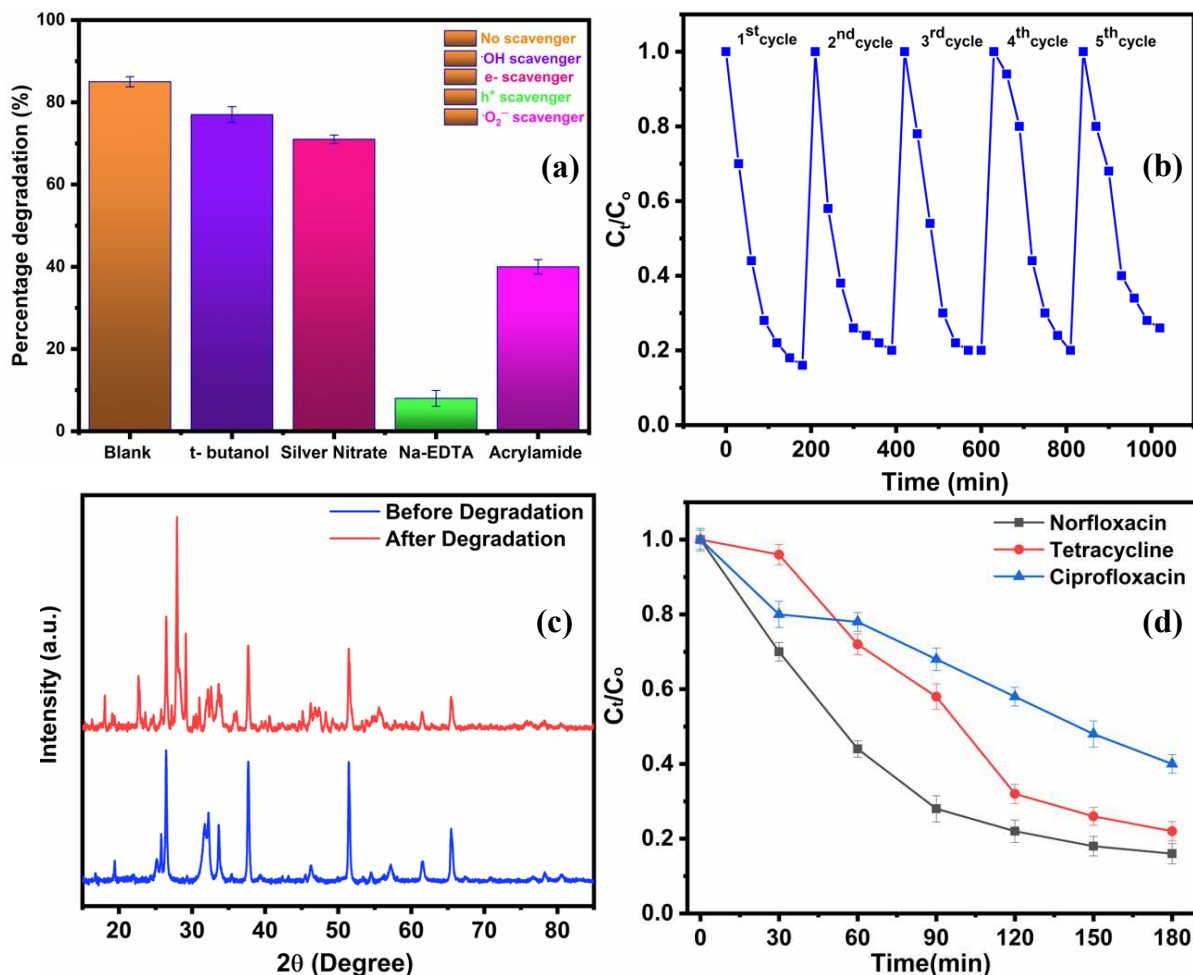


Fig. 8 (a) Scavenger studies of the PEC degradation of norfloxacin on FTO-BiOBr/MoWO₄ (b) Reusability study (c) Diffraction peaks before and after degradation (d) Photoanode used with other analytes

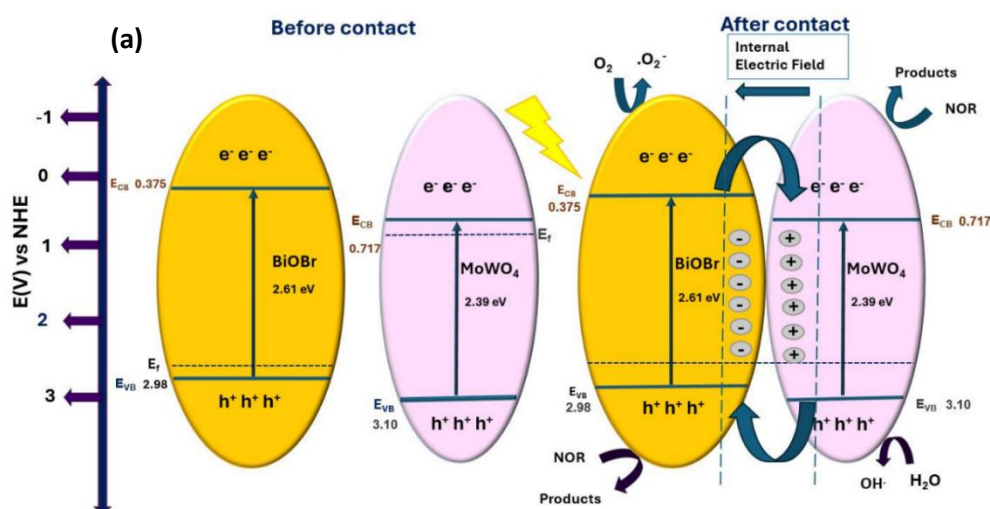
The possible charge transfer mechanism of photogenerated electron (e^-) and hole (h^+) in the BiOBr/MoWO₄ heterojunction is illustrated in Scheme 2. Based on the charge-transfer mechanism, photo-excited electrons generated in the conduction band of MoWO₄ migrate to the valence band of BiOBr, where they recombine with the photogenerated holes. In this way, the BiOBr/MoWO₄ heterojunction not only achieves effective spatial separation of e^-/h^+ pairs but also has a good redox capability, offering a distinct advantage over conventional Type II heterojunctions by broadening the light absorption and response range.

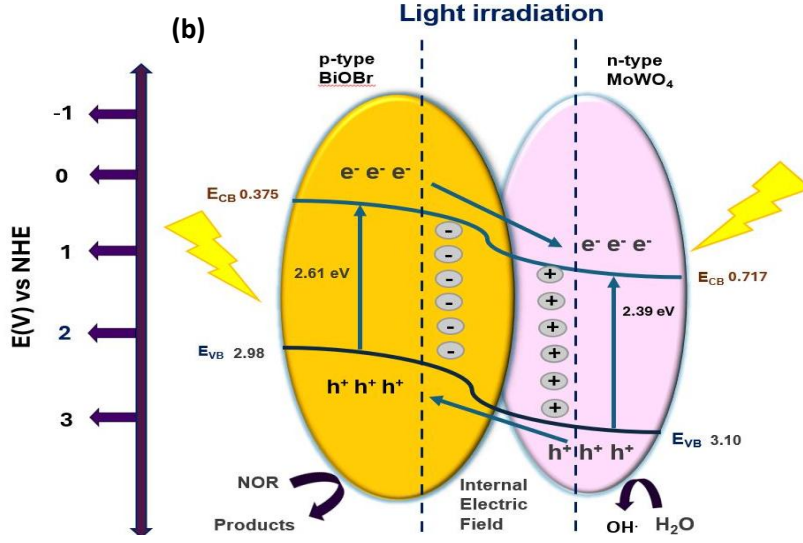
The position of the Fermi energy level is intrinsically related to the semiconductor type. In p-type semiconductors, the Fermi level is close to the valence band, whereas in n-type semiconductors, it is positioned near the conduction band [36, 37]. Accordingly, as a p-type semiconductor, BiOBr possesses a Fermi level located slightly above its valence band, while n-type MoWO₄ has its Fermi level situated slightly below its conduction band, as depicted in Scheme 2(a).

Upon physical contact between BiOBr and MoWO₄, a p–n heterojunction is formed at their interface. Driven by the difference in Fermi levels, electrons spontaneously diffuse from MoWO₄ into BiOBr, resulting in accumulation of negative charges in the BiOBr region near the junction. Simultaneously, holes migrate from BiOBr to MoWO₄, resulting in accumulation of positive charges in the MoWO₄ region adjacent to the junction. This redistribution of charge carriers continues until thermodynamic equilibrium is reached, at which point the Fermi levels of BiOBr and MoWO₄ align to form a unified stable Fermi level, as shown in Scheme 2(a).

As a consequence of charge redistribution at the p–n junction interface, the energy bands of BiOBr shift upward along with its Fermi level, while those of MoWO₄ shift downward, as illustrated in Scheme 2b. This band bending establishes an internal electric field directed from MoWO₄ towards BiOBr, which serves as the primary driving force for the directional separation and transfer of photogenerated charge carriers.

Under visible-light irradiation, BiOBr is photoexcited to generate electron–hole pairs. Because of the internal electric field, the photogenerated electrons in the conduction band (CB) of BiOBr are efficiently transferred to the conduction band of MoWO₄. These accumulated electrons subsequently react with adsorbed oxygen molecules on the surface of the catalyst to generate superoxide radicals, which are highly reactive oxidising species responsible for the degradation of organic pollutants. Consequently, the photogenerated holes retained in the VB of BiOBr directly participate in the oxidative degradation of the norfloxacin molecule adsorbed on the surface of the BiOBr/MoWO₄ heterostructure, yielding intermediate oxidative products, carbon dioxide, and water as the final mineralisation products. The efficient spatial separation of photogenerated charge carriers, facilitated by the well-designed heterojunction interface between BiOBr and MoWO₄, significantly suppresses electron–hole recombination, resulting in the enhancement of photoelectrocatalytic activities of the composite photoanode, as depicted in Scheme 2b.





Scheme 2. (a) and (b) Proposed mechanism for the photoelectrocatalytic degradation of norfloxacin by BiOBr/MoWO₄ nanocomposite.

The extent of mineralisation of norfloxacin following PEC degradation was evaluated through the Total Organic Carbon (TOC) analysis using a Shimadzu TOC analyser. The analysis was conducted on both synthetic (deionised) water and real wastewater samples to assess the performance of the BiOBr/MoWO₄ photoanode under environmentally relevant conditions. The real wastewater samples were collected from the Erwat Wastewater Treatment Plant, South Africa, and subsequently spiked with an accurately weighed amount of norfloxacin to achieve a final concentration of 5.0 mg L⁻¹ in a 100 mL volumetric flask. The percentage mineralisation of norfloxacin in both synthetic and real wastewater matrices was calculated using the following expression in Eq. 15:

$$\text{Percentage mineralisation (\%)} = \frac{TOC_o - TOC_t}{TOC_o} \times 100 \quad (15)$$

where TOC_o represents the initial total organic carbon concentration before treatment, and TOC_t denotes the residual total carbon concentration measured at a given time t after treatment. As presented in Fig. S3 (Online Resource 3), the BiOBr/MoWO₄ photoanode achieved a mineralisation efficiency of 41% for norfloxacin in synthetic wastewater and a notably higher mineralisation efficiency of 70% in real wastewater. The superior mineralisation performance observed in the real wastewater matrix suggests that the additional ionic species and organic constituents naturally present in real wastewater may have contributed positively to the generation of reactive oxygen species, thereby enhancing the overall mineralisation of norfloxacin under photoelectrocatalytic conditions.

Conclusion

A BiOBr/MoWO₄ p-n heterojunction photoanode was successfully prepared through a hydrothermal method. The deliberate construction of the p-n heterojunction effectively addressed the critical challenge of rapid recombination of photogenerated electron-hole pairs by facilitating efficient spatial separation of charge carriers. The enhanced PEC performance of the composite is attributed to the favourable migration of photogenerated electrons from the *CB* of MoWO₄ to the hole-rich *VB* of BiOBr, driven by the electrostatic attraction between oppositely charged carriers across the heterojunction interface. The superior charge separation efficiency of the BiOBr/MoWO₄ heterojunction was further corroborated by photoluminescence (PL) spectroscopy, which revealed a significantly lower emission intensity compared to the pristine BiOBr and MoWO₄ semiconductors, confirming a reduced electron-hole recombination rate in the composite material. When evaluated for the photoelectrocatalytic degradation of norfloxacin, the BiOBr/MoWO₄ photoanode achieved an impressive removal of 85% under optimum conditions. Furthermore, TOC analysis confirmed effective mineralisation of norfloxacin in synthetic wastewater (41%) and real wastewater (70%), demonstrating the capability of the photoanode to convert organic pollutants into benign end products such as CO₂ and H₂O. Overall, the findings of this study established the BiOBr/MoWO₄ p-n heterojunction photoanode as a promising and efficient material for the oxidative degradation of recalcitrant pharmaceutical pollutants in aqueous matrices, including pre-treated real pharmaceutical effluents. These results provide a strong foundation for the further development and scale-up of heterojunction-based photoanodes for practical water and wastewater treatment applications.

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