


 Cite this: *RSC Adv.*, 2026, 16, 27621

Bi₃O₄Br nanosheets immobilized in chitosan microspheres as efficient and recyclable hybrid catalysts for water treatment

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Access to clean water is a critical global priority. Thus, photocatalysis using semiconducting materials has emerged as a promising technology for wastewater treatment. Herein, a novel Bi₃O₄Br@Chitosan hybrid composite was successfully prepared by immobilizing Bi₃O₄Br in chitosan (CS) beads. First, Bi₃O₄Br was prepared *via* a solvothermal process, followed by its physical embedding in the CS matrix *via* a simple coprecipitation method. The surface morphology, elemental composition, crystal structure, and optical properties of the Bi₃O₄Br@CS material were comprehensively investigated using SEM, EDS, FTIR, XRD, TGA, zeta potential, Raman, and UV-vis spectroscopy, indicating excellent compatibility, multifunctional structure, and high structural robustness. Consequently, the Bi₃O₄Br@CS catalyst exhibits high efficiency in the UV-light-driven photodegradation of Rhodamine B (RhB), achieving 88% RhB degradation within 150 minutes and total reduction of 4-nitrophenol (4-NP) in the presence of NaBH₄ within 5 min at room temperature. Additionally, the catalyst shows good stability and can be reused over seven successive cycles without significant loss of activity. Therefore, the combination of adsorption capacity and photocatalytic activity within this hybrid catalyst provides an efficient and practical approach for wastewater treatment applications.

 Received 29th March 2026
 Accepted 4th May 2026

DOI: 10.1039/d6ra02619b

rsc.li/rsc-advances

Introduction

Water pollution and the escalating scarcity of safe drinking water are among the most critical environmental and public health challenges of the modern era.^{1–3} Driven by rapid demographic expansion and ongoing industrialization, severe over-exploitation of water resources has significantly increased the concentration of recalcitrant organic contaminants, such as industrial dyes, pharmaceutical phenols, and agricultural

pesticides, in global aquatic ecosystems.^{4,5} While conventional remediation strategies, including chlorination, ozonation, and advanced membrane filtration, are widely employed, their large-scale application is frequently hindered by prohibitive operational costs, stringent technical requirements, and the generation of hazardous secondary byproducts.⁶ Consequently, semiconductor inorganic–organic photocatalysis, such as 6,13-pentacenequinone/TiO₂ (PQ/Ti)⁷ has emerged as a highly efficient, cost-effective, and environmentally benign alternative that thoroughly mineralizes pollutants rather than merely transferring them between phases.^{8,9}

Thus, extensive research has focused on developing novel photocatalytic architectures for wastewater treatment, *e.g.*, metal oxides,¹⁰ metal sulfides,¹¹ metal phosphides,¹² metal nitride,¹³ metal carbide,¹⁴ perovskite-based materials,¹⁵ graphene-based materials,¹⁶ graphitic carbon nitride (g-C₃N₄),¹⁷ and metal–organic framework.¹⁸ Among these, metal oxides, particularly bismuth oxyhalides (BiOX),^{1,2} are particularly attractive due to their low toxicity, low cost, and important photoredox properties.^{19–24} Importantly, bismuth oxybromide (BiOBr) has particularly attracted immense attention as a superior photocatalytic material.^{22,24} This prominence is attributed to their unique layered structure, enhanced visible-light absorption, low toxicity, and exceptional charge-separation

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efficiency, which collectively enable robust environmental remediation applications.

To further optimize the intrinsic photocatalytic efficacy of BiOBr, researchers have actively engineered their morphological and electronic profiles.^{23,25,26} For instance, precisely modulating the pH during synthesis yields distinct morphologies that significantly affect and improve the degradation rates of organic dyes and phenolic compounds. Beyond morphological tuning, constructing heterojunctions is a primary strategy to suppress the rapid recombination of photogenerated electron-hole pairs.^{27–29} Coupling BiOBr with specialized conductive modifiers, such as carbon quantum dots, two-dimensional MXenes, and BiVO₄, has been shown to significantly accelerate the degradation kinetics of persistent organic pollutants.^{27,30} Recently, Niu *et al.* developed a Z-scheme Bi₃O₄Br/BiVO₄ nanocomposite *via* microwave hydrothermal methods to optimize organic pollutant degradation. This heterojunction architecture suppresses carrier recombination, generating reactive radicals that completely degrade methyl orange in 80 minutes under sunlight. The material also removes 85% of norfloxacin in 75 minutes while maintaining high structural stability across multiple cycles. Its efficiency and eco-friendly nature suggest significant potential for sustainable, industrial-scale wastewater purification.³⁰ These advanced materials demonstrate remarkable efficiency in the degradation of toxic organic dyes under visible light. By utilizing a richer bismuth content, they facilitate more effective charge separation and enhanced light absorption compared to standard alternatives.^{1,23,25,26,31,32}

Despite these catalytic advantages, the practical, industrial-scale deployment of powdered BiOBr is constrained by significant logistical challenges in post-treatment catalyst recovery and physical recyclability. To resolve this limitation, immobilizing the active photocatalytic powder onto stable macroscopic support structures has proven highly effective and challenging.^{30,33} For instance, natural biopolymers, especially polysaccharides, represent ideal candidates to meet this requirement due to their multi-functional structure, biocompatibility, and diverse availability, which increase their affinity to several organic pollutants.^{34–38} Among them, chitosan (CS), provides more flexibility in catalysis due to the presence of functional groups such as amino (–NH₂) and hydroxyl (–OH) functionalities that exhibit a strong inherent chemical affinity for both the catalytic species and the target aqueous pollutants, thereby establishing a highly stable, reusable, and sustainable platform for advanced water purification.^{2,19,39–41} Consequently, integrating the distinct photocatalytic proficiency of BiOBr with the exceptional adsorption capacity and structural flexibility of CS presents a highly promising research frontier. This synergistic combination is anticipated to yield novel hybrid composites characterized by unique catalytic properties and enhanced operational robustness, providing a strong motivation for continued innovation in sustainable wastewater remediation.^{2,3,27}

Despite these important advances, current BiOX–chitosan and Bi₃O₄Br-based systems still face several limitations, including limited structural integration, difficulties in catalyst

recovery, and the lack of multifunctional systems combining different catalytic processes. In many cases, the materials remain in powder form, which restricts their practical use in real water treatment conditions. Although Bi₃O₄Br offers improved light absorption and charge separation compared to BiOBr, its integration into a stable, recoverable, and multifunctional architecture remains insufficiently explored. Herein, we bridge this gap by immobilizing Bi₃O₄Br nanosheets within chitosan beads *via* a facile synthetic strategy, creating a robust platform that prevents nanoparticle leaching and ensures seamless catalyst recovery. This approach allows us to combine the advantages of nanoscale catalytic activity with a macroscopic structure that facilitates recovery and reuse. In addition, the system exhibits a dual functionality, enabling both RhB photodegradation and 4-nitrophenol reduction within the same material, which represents a clear improvement over previously reported system.

Experimental section

Starting materials and reagents

Chitosan (CS) with a molecular weight of 600 000 kD was obtained from Sigma-Aldrich. Its deacetylation degree was calculated using pH metric titration of about (~95%). All other starting materials, solvents, and reagents, including bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), sodium bromide (NaBr), sodium hydroxide (NaOH), acetic acid (CH₃COOH), and RhB, are commercially available and used as received.

Characterization methods

The composition and crystal phase structure of the prepared hybrid materials were investigated by XRD measurement using a Rigaku X-ray diffractometer equipped with a Cu-K α X-ray source with a wavelength of ($\lambda = 1.5418 \text{ \AA}$). The XRD patterns were recorded in a 2θ range of 5–90° at step size of 0.02°/step and a scanning speed of 2–5° min^{–1}. The surface morphology and microstructure of the prepared hybrid materials were observed using SEM. SEM observations were performed using “Tescan Vega3” microscope, equipped with an energy dispersive X-ray spectrometry (EDS) analyser, allowing the determination of chemical compositions. The preparation of the samples consists in depositing the materials as powder or pellets on an aluminum sample holder with a double-sided carbon adhesive. TGA was used to investigate the thermal behavior and stability of the obtained material. TGA was carried out using a 0650-0580 (192.168.1.2) TGA analyzer in a temperature range of 10–700 °C with a heating rate of 10 °C min^{–1}. The chemical structure of the prepared materials was further analyzed by FTIR spectroscopy analysis. The FTIR spectra were recorded on a PerkinElmer spectrum 100 FTIR spectrophotometer. The samples were grinded with KBr powder as a reference matrix (standard) and then pressed to form transparent pellets in IR radiation. The optical properties and the light absorption ability of Bi₃O₄Br sheets were studied by UV-visible diffuse reflectance spectroscopy recorded on a Shimadzu (UV-2600) spectrophotometer equipped with an integrating sphere in a wavelength range of



200–1200 nm. The measurements were carried out in a transparent quartz cuvette with an optical path of 1 cm. For this, the sample was prepared by the dispersion of $\text{Bi}_3\text{O}_4\text{Br}$ sheets in water with concentration of 1 mg mL^{-1} . The chemical structure of the $\text{Bi}_3\text{O}_4\text{Br}$ sheets were also investigated by Raman spectroscopy analysis using a NanoSp confotec-MR520. The samples were analyzed using a “LCM-S-111” laser with a wavelength of 532 nm in a 1200 line per mm network. Particle size distribution and zeta potential were measured in triplicate at $25 \text{ }^\circ\text{C}$ using a Malvern ZetaSizer instrument to determine the particle size distribution and zeta potential of the materials. For this, the sample was prepared by dispersing $\text{Bi}_3\text{O}_4\text{Br}$ in water with a concentration of 2.5 mg mL^{-1} , and charged in the measurement cell, which was a “disposable folded capillary cell (DTS1070)”.

Catalysts preparation and utilization

Synthesis of $\text{Bi}_3\text{O}_4\text{Br}$ sheets. $\text{Bi}_3\text{O}_4\text{Br}$ sheets were prepared through a solvothermal synthesis in a water/ethylene glycol mixture using $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NaBr as starting materials, followed by thermal treatment at $500 \text{ }^\circ\text{C}$. To achieve this, 3 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ($\sim 6.18 \text{ mmol}$) were mixed with 80 mL of a mixture of water/ethylene glycol (1 : 1, v/v), and sonicated for about 10 min. Then, 0.5 equiv. of NaBr (317.9 mg, 3.09 mmol) was added to the above mixture under magnetic stirring. After about 15 min, the mixture was transferred to a 100 mL Autoclave and heated at $180 \text{ }^\circ\text{C}$ for 17.5 h. Next, the precipitates were collected by centrifugation, washed several times with distilled water and methanol, and oven-dried in air at $\sim 75 \text{ }^\circ\text{C}$. Finally, the resulting product was calcined at $500 \text{ }^\circ\text{C}$ for 2 hours with a heating rate of about $5 \text{ }^\circ\text{C min}^{-1}$ (Fig. S1, SI).

Preparation of $\text{Bi}_3\text{O}_4\text{Br}@CS$ beads. $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid beads were obtained through a co-precipitation method. Briefly, 400 mg of CS and 150 mg of $\text{Bi}_3\text{O}_4\text{Br}$ were sonically dispersed in 20 mL of H_2O for 1 h. Then, 200 μL of acetic acid (1% v/v) was added to the above solution under magnetic stirring to dissolve the CS (pH ~ 3). The formation of CS beads was achieved by instantaneous precipitation *via* dropping the obtained solution into 200 mL of NaOH (2 M). After 1 hour in the alkaline solution, the $\text{Bi}_3\text{O}_4\text{Br}@CS$ beads were filtered and washed with distilled water several times until a neutral pH solution (Fig. S2, SI). The choice of a chitosan content of 25 wt% was guided by both practical and functional considerations. During preliminary tests, lower chitosan contents resulted in fragile beads that were difficult to handle, while higher contents tended to partially block the active sites of $\text{Bi}_3\text{O}_4\text{Br}$, limiting catalytic accessibility. Therefore, this composition was selected as a reasonable balance between mechanical stability, porosity, and catalytic efficiency, in agreement with previous studies on chitosan-based hybrid systems.

Adsorption/desorption study. Adsorption/desorption ability is a crucial parameter in the heterogeneous catalytic process. This feature is highly beneficial for photodegradation and reduction reactions; thus, in control experiments, the adsorption/desorption of 6 mL of aqueous RhB (5 mg L^{-1}) and 4-NP (10 mg L^{-1}) solution over pure CS beads and $\text{Bi}_3\text{O}_4\text{Br}@CS$

composites were investigated in the dark, under UV light irradiation, and under ambient conditions. At a regular time interval, aliquots of both RhB and 4-NP were collected from the reaction media and analyzed using UV-vis.

Photodegradation of RhB. The photocatalytic behavior of the $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid materials was investigated in the photodegradation of organic dyes under UV light irradiation. For this, RhB was chosen as a model organic dye. The photodegradation experiments of RhB over $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid materials were carried out in a quartz cuvette (25 mL) covered with a Teflon cover. In a typically, the quartz cuvette was charged with a certain amount of $\text{Bi}_3\text{O}_4\text{Br}@CS$ and 6 mL of RhB (5 mg L^{-1}) aqueous solution with pH ~ 6.6 . The reaction was stirred under simulated UV light using a Philips HPL-N 125 W lamp with a wavelength of 365 nm as a light source. The progress of the photocatalytic reaction was performed by withdrawing a aliquot of RhB solution at regular intervals and monitoring the absorbance *vs.* wavelength spectra using the UV-vis.

Reduction of 4-NP to 4-aminophenol. The catalytic performance of $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid beads in the reduction of 4-NP was performed in an aqueous solution using NaBH_4 as a reducing agent. In a typical reduction process, a mixture of 6 mL of 4-NP aqueous solution (10 mg L^{-1}), $\text{Bi}_3\text{O}_4\text{Br}@CS$ and 2 mL NaBH_4 (0.5, 1 or 2 M) was stirred at room temperature at selected period of time. The progress of the reduction process was determined by monitoring the absorbance band of 4-NP at $\lambda_{\text{max}} = 402 \text{ nm}$ using UV-vis spectrophotometer.

Results and discussion

Catalysts characterization

Highly crystalline $\text{Bi}_3\text{O}_4\text{Br}$ nanosheets were successfully obtained through a solvothermal route followed by calcination. As observed in SEM and TEM images (Fig. 3), the material exhibits a lamellar morphology, which can enhance surface exposure and facilitate charge separation. This structural feature is consistent with the good photocatalytic performance observed in our system. To overcome the inherent recovery challenges of powdered suspensions, these nanosheets were successfully immobilized within macroscopic CS microspheres using a rapid alkaline co-precipitation strategy. The resulting $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid composite directly integrates the robust physical adsorption capacity of the biopolymer network with the potent photo-oxidation capabilities of the semiconductor. This synergistic coupling provides a stable, easily recoverable, and highly efficient dual-functional platform for advanced wastewater remediation. XRD analysis indicates that $\text{Bi}_3\text{O}_4\text{Br}$ diffractogram, show the presence of peaks at 10.56° , 18.52° , 24° , 29.39° , 31.80° , 35.70° , 38.10° , 43.13° , 45.23° , 50.44° and 54.53° were respectively indexed to (002), (004), (112), (114), (020), (211), (008), (206), (220), (208)/(033), (110) and (134) diffraction planes confirm the successful preparation of pure and crystalline orthorhombic $\text{Bi}_3\text{O}_4\text{Br}$ (Fig. 1), exhibiting high thermal stability as confirmed by TGA and crystal size of about 345.5 \AA as calculated using the Debye Scherrer formula (Fig. S3, SI).^{23,25,27,42–44} For pure CS patterns, the peaks at 2θ values of about 12.56° and 20.16° are well indexed to the (020) and (101)



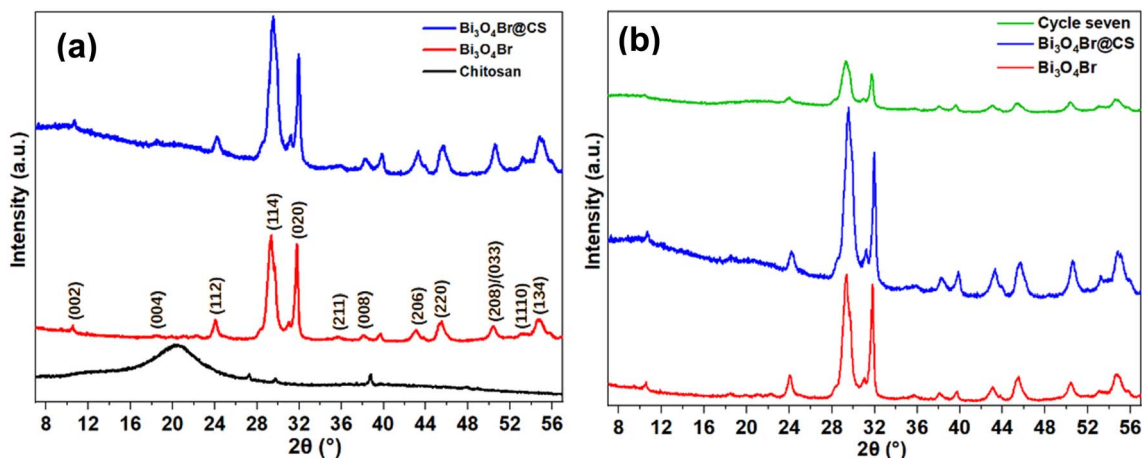


Fig. 1 XRD patterns (a) of pure CS, $\text{Bi}_3\text{O}_4\text{Br}$ sheets, and (b) $\text{Bi}_3\text{O}_4\text{Br}@CS$ before and after 7 photocatalytic cycles.

reflection planes of the amorphous phase of CS, respectively.⁴⁵ After the combination, the $\text{Bi}_3\text{O}_4\text{Br}@CS$ composite shows a relatively similar profile to $\text{Bi}_3\text{O}_4\text{Br}$, this observation is consistent with the TGA observation (Fig. S3, SI), which confirms the successful process. Nevertheless, after incorporating the $\text{Bi}_3\text{O}_4\text{Br}$ into the CS structure, the diffraction peaks characteristic of the amorphous phase of CS were clearly decreased, indicating the high crystallinity of the obtained materials. Moreover, XRD patterns of the reused materials clearly confirmed that no noticeable changes were observed even after 7 photocatalytic runs (Fig. 1).

While FTIR analysis of pure CS reveals a strong and broad absorbent band between $3000\text{--}3700\text{ cm}^{-1}$ ascribed to the stretching vibration of $-\text{OH}$ and $-\text{NH}_2$ groups. Similarly, the absorption band at $2800\text{--}3000\text{ cm}^{-1}$ is attributed to C-H (sp^3) groups. The absorption band at 1650 cm^{-1} is assigned as C=O groups (amide I) vibrations. The absorption band at 1427 cm^{-1} is due to C-H wagging. The absorption bands at 1375 cm^{-1} and 1079 cm^{-1} are assigned to the stretching vibration of C-N and C-O groups, respectively. Finally, the absorption band at

598 cm^{-1} is due to N-H stretching vibration. For the $\text{Bi}_3\text{O}_4\text{Br}$ sheets, the absorption bands at 1638 and 3440 cm^{-1} could be attributed to the bending vibrations of O-H bond related to the adsorbed water molecules.³¹ The absorption band at 535 cm^{-1} could be ascribed to the stretching mode of the Bi-O bond of $\text{Bi}_3\text{O}_4\text{Br}$ ³¹ as further confirmed by Raman analysis. Additionally, the FTIR spectra of $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid materials showed much similar absorbent bands of pure CS, the major differences are the shift of the broad band observed between $535\text{--}640\text{ cm}^{-1}$ to the lower wavenumber, which could be due to the strong interaction between the amino groups $-\text{NH}_2$ and $\text{Bi}_3\text{O}_4\text{Br}$ sheets (Fig. 2a). Moreover, Raman analysis is consistent with FTIR observation, displays various vibration modes for $\text{Bi}_3\text{O}_4\text{Br}$ sheets, shifts at 60.82 , 99.35 , and 162.3 cm^{-1} could respectively be assigned to the A_{1g} external, A_{1g} internal, and E_g internal of Bi-Br stretching modes.²⁵ The band at 73.68 cm^{-1} corresponds to the F_{1u} stretching mode of the O-Bi-O bond.²⁵ The A_{1g} and E_g modes of Bi-O covalent bonds are situated at 206.8 and 621.94 cm^{-1} , respectively.²⁵ The two modes at 145.5 and

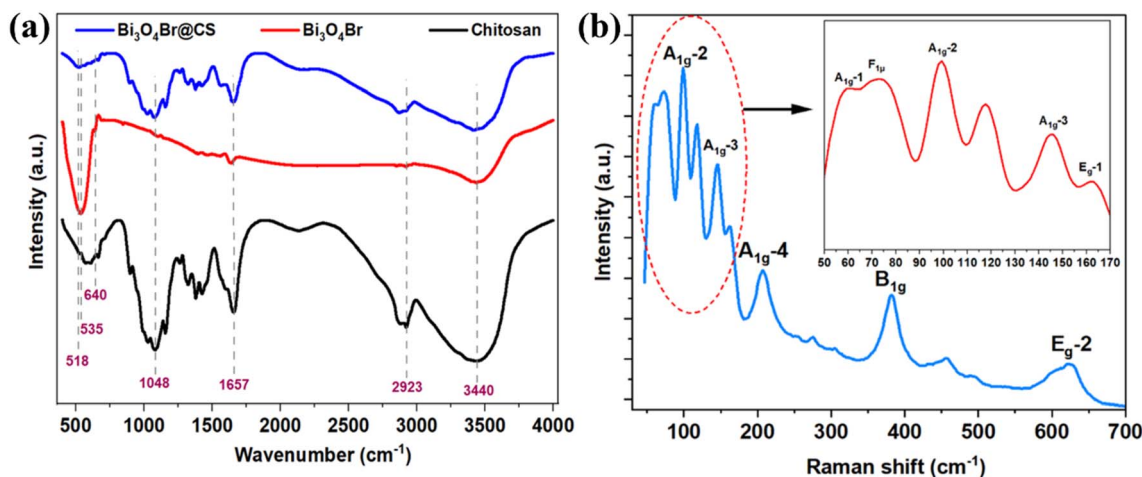


Fig. 2 (a) FTIR spectra of pure chitosan, $\text{Bi}_3\text{O}_4\text{Br}$ sheets, and $\text{Bi}_3\text{O}_4\text{Br}@CS$, (b) Raman spectra of $\text{Bi}_3\text{O}_4\text{Br}$ sheets.



382.56 cm^{-1} belong to the A_{1g} -3 of B-O vibration mode and B_{1g} mode caused by the movement of oxygen atoms (Fig. 2b).²⁵

Additionally, SEM was used to study the morphology of the prepared samples. The SEM, FE-SEM, and TEM images of $\text{Bi}_3\text{O}_4\text{Br}$ sheets and $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid materials are shown in Fig. 3. SEM/FE-SEM images (Fig. 3a–f) show that the prepared $\text{Bi}_3\text{O}_4\text{Br}$ particles are ultrathin sheets, uniform in shape, and exhibit a porous network, which was further confirmed by TEM

as shown in the images (Fig. 3g–i). Furthermore, SEM images (Fig. 3j–l) revealed that $\text{Bi}_3\text{O}_4\text{Br}@CS$ beads were spherical in shape with a uniform dispersion of $\text{Bi}_3\text{O}_4\text{Br}$ particles on their surface. In addition, EDS has been used to give further information about the elemental composition and chemical structure of the prepared materials (Fig. 4). Likewise, the EDS spectra of $\text{Bi}_3\text{O}_4\text{Br}$ sheets (Fig. 4a) revealed the presence of elemental bismuth (Bi), oxygen (O), and bromine (Br) in this material.

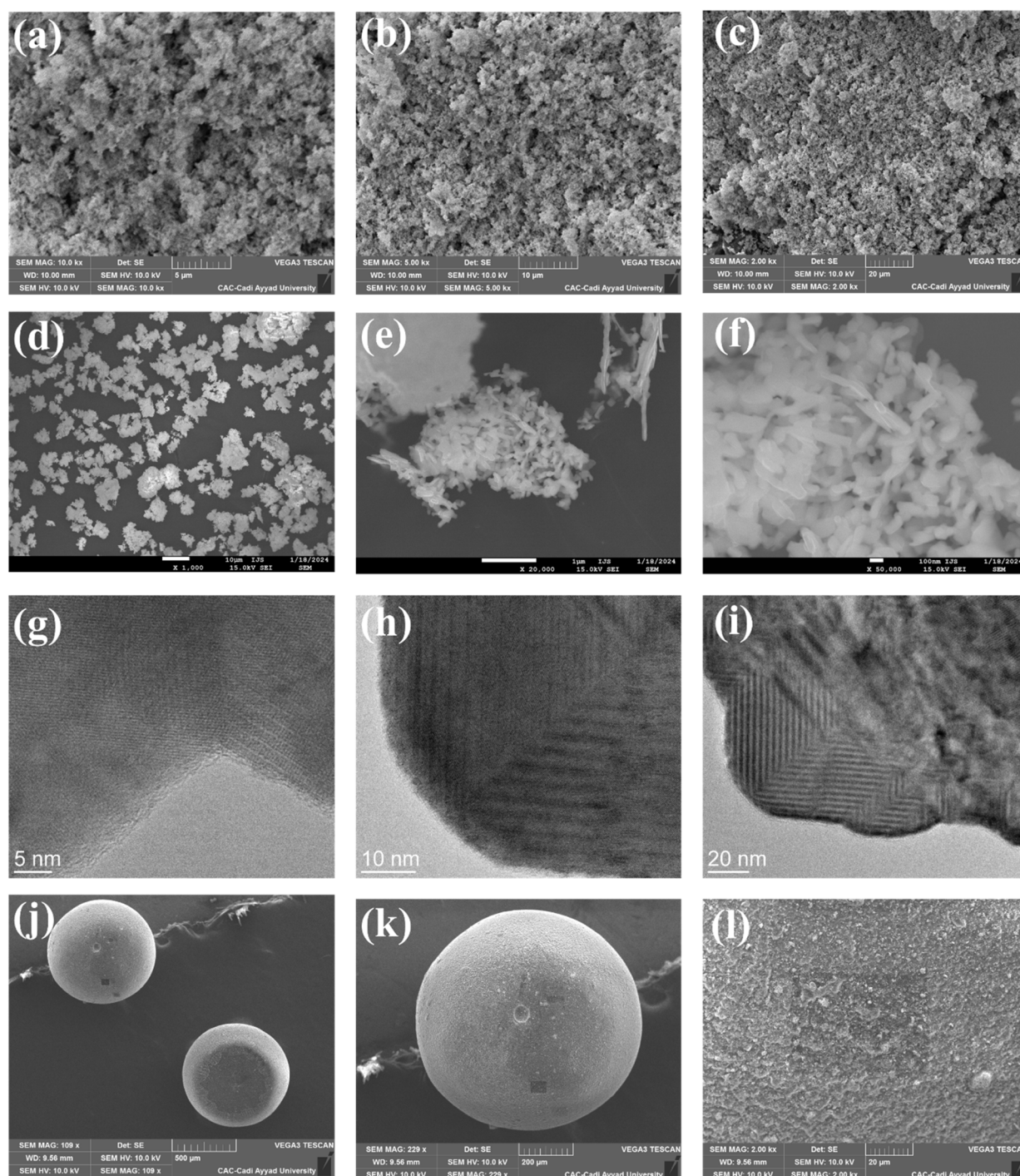


Fig. 3 (a–c) SEM, (d–f) FE-SEM, and (g–i) TEM images of $\text{Bi}_3\text{O}_4\text{Br}$ sheets; (j–l) SEM images of $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid materials.



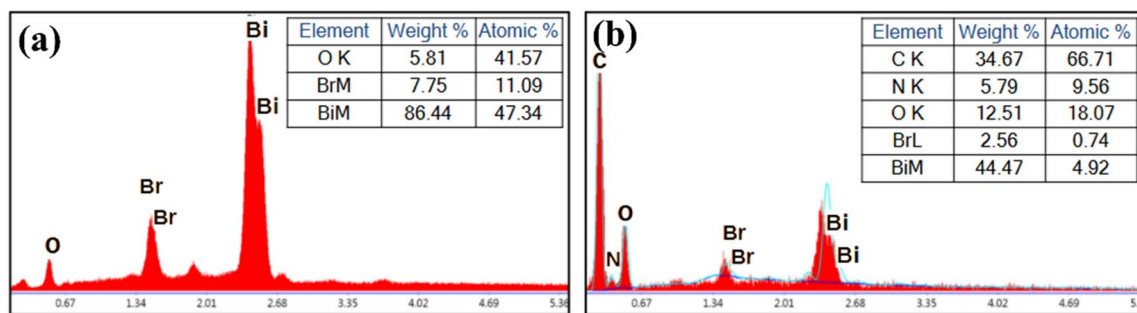


Fig. 4 EDS spectra: (a) $\text{Bi}_3\text{O}_4\text{Br}$, (b) $\text{Bi}_3\text{O}_4\text{Br}@CS$.

After the combination, the EDS spectra of $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid materials (Fig. 4b) show the presence of Bi, Br, C, O, and N in the materials, which remain slightly similar even after three catalytic uses. These results give a clear indication of the successful incorporation and effective immobilization of $\text{Bi}_3\text{O}_4\text{Br}$ in the CS structure.

Importantly, the light absorption capabilities of $\text{Bi}_3\text{O}_4\text{Br}$ sheets were studied using UV-visible diffuse reflectance spectroscopy (UV-DRS). It is clearly observed that $\text{Bi}_3\text{O}_4\text{Br}$ sheets display strong absorption in the UV light region (Fig. 5a). From the UV-DRS spectrum and by applying the Kubelka–Munk function (eqn (1)), the band gap value of the $\text{Bi}_3\text{O}_4\text{Br}$ sheets can be estimated. This is achieved using Tauc plot of the transformed Kubelka–Munk function $[(F(R)/hv)^n = A/(hv - E_g)]$ plotted against the incident photon energy ($h\nu$), which is calculated from the reflectance *versus* wavelength spectra (Fig. 5b).^{46–48} As a result, the estimated band gap is approximately 2.38 eV. Furthermore, the conduction band edge potential (E_{cb}) and valence band edge potential (E_{vb}) of $\text{Bi}_3\text{O}_4\text{Br}$ sheets can be calculated using Mulliken electronegativity theory (eqn (2) and (3)). Here, E_g is the bandgap energy of $\text{Bi}_3\text{O}_4\text{Br}$, E_c is the energy of the free electron on the hydrogen scale ($E_c = 4.5$ eV), and χ is the absolute electronegativity of $\text{Bi}_3\text{O}_4\text{Br}$. The absolute electronegativity (χ) of $\text{Bi}_3\text{O}_4\text{Br}$ can be simply calculated according to Mulliken's definition (eqn (4)), using the constituent atoms (Bi = 4.69 eV, O = 7.54 eV, and Br = 5.64 eV), resulting in $\chi = 6.1$ eV.^{49,50} Therefore, the calculated E_{cb} and E_{vb} are 0.41 eV and 2.79 eV, respectively.

$$F(R) = K/S = [(1 - R)^2]/2R \quad (1)$$

$$E_{cb} = \chi - E_c - 0.5 E_g \quad (2)$$

$$E_{vb} = E_{cb} + E_g \quad (3)$$

$$\chi_{\text{Bi}_3\text{O}_4\text{Br}} = (\chi_{\text{Bi}}^3 \times \chi_{\text{O}}^4 \times \chi_{\text{Br}})^{1/8} \quad (4)$$

In photodegradation processes, the particle size and surface charge distribution are two important factors that may determine the overall performance of any photocatalytic material. Fig. 5 illustrates the size distribution and zeta-potential spectra of the prepared $\text{Bi}_3\text{O}_4\text{Br}$ sheets. The spectrum of size distribution revealed that the obtained $\text{Bi}_3\text{O}_4\text{Br}$ sheets have one population

with an average size value of 253.4 nm, which is consistent with TEM observation. In addition, the zeta-potential of the particles was found to be approximately -2.917 mV. These results indicate that the $\text{Bi}_3\text{O}_4\text{Br}$ sheets exhibit a negative surface charge that may enhance the repulsion between the particles and prevent their agglomeration and increase the interaction with polycationic CS and RhB. Thus, contributing to the high dispersion of $\text{Bi}_3\text{O}_4\text{Br}$ sheets and their stabilization within CS matrix.

Catalytic study

It is widely recognized that the adsorption–desorption behavior of photocatalytic materials plays a critical role in the photodegradation of organic dyes. Consequently, the adsorption of RhB onto the $\text{Bi}_3\text{O}_4\text{Br}@CS$ composite was investigated through a control experiment conducted in the dark. As illustrated in the UV-vis spectra (Fig. 6C), the $\text{Bi}_3\text{O}_4\text{Br}@CS$ catalyst exhibits relatively limited adsorption capacity. This behavior is attributed to the functional groups present in both $\text{Bi}_3\text{O}_4\text{Br}$ and CS; notably, the adsorption profile of the composite closely resembles that of native CS (Fig. 6B), confirming a similar interaction mechanism. To evaluate the photostability of the dye, RhB was irradiated under UV-vis light in the absence of a catalyst. No significant degradation was observed even after 150 minutes (Fig. 6A), confirming that the catalyst is essential for the degradation process. In contrast, the introduction of the $\text{Bi}_3\text{O}_4\text{Br}@CS$ catalyst resulted in approximately 88% degradation of RhB within 150 minutes (Fig. 6D). These results demonstrate that the prepared catalyst exhibits high photocatalytic activity, which can be attributed to the combined effect of adsorption and photocatalysis within the hybrid system.

Similarly, the adsorption of 4-NP onto pure CS beads and the $\text{Bi}_3\text{O}_4\text{Br}@CS$ composite showed no measurable change in the characteristic absorption band of 4-NP. This indicates that the 4-NP concentration remained constant, suggesting the absence of a significant adsorption–desorption process on the catalyst surface (Fig. 9). In control experiments, no reduction of 4-NP was observed when using native CS beads, even in the presence of a large excess of NaBH_4 . This confirms that the $\text{Bi}_3\text{O}_4\text{Br}$ component is essential for catalytic reaction. Furthermore, no reaction occurred when using the $\text{Bi}_3\text{O}_4\text{Br}@CS$ composite without NaBH_4 , nor did it occur with NaBH_4 in the absence of the catalyst. These observations confirm that both the $\text{Bi}_3\text{O}_4\text{Br}@CS$ catalyst and the NaBH_4 reducing agent are indispensable for the process.



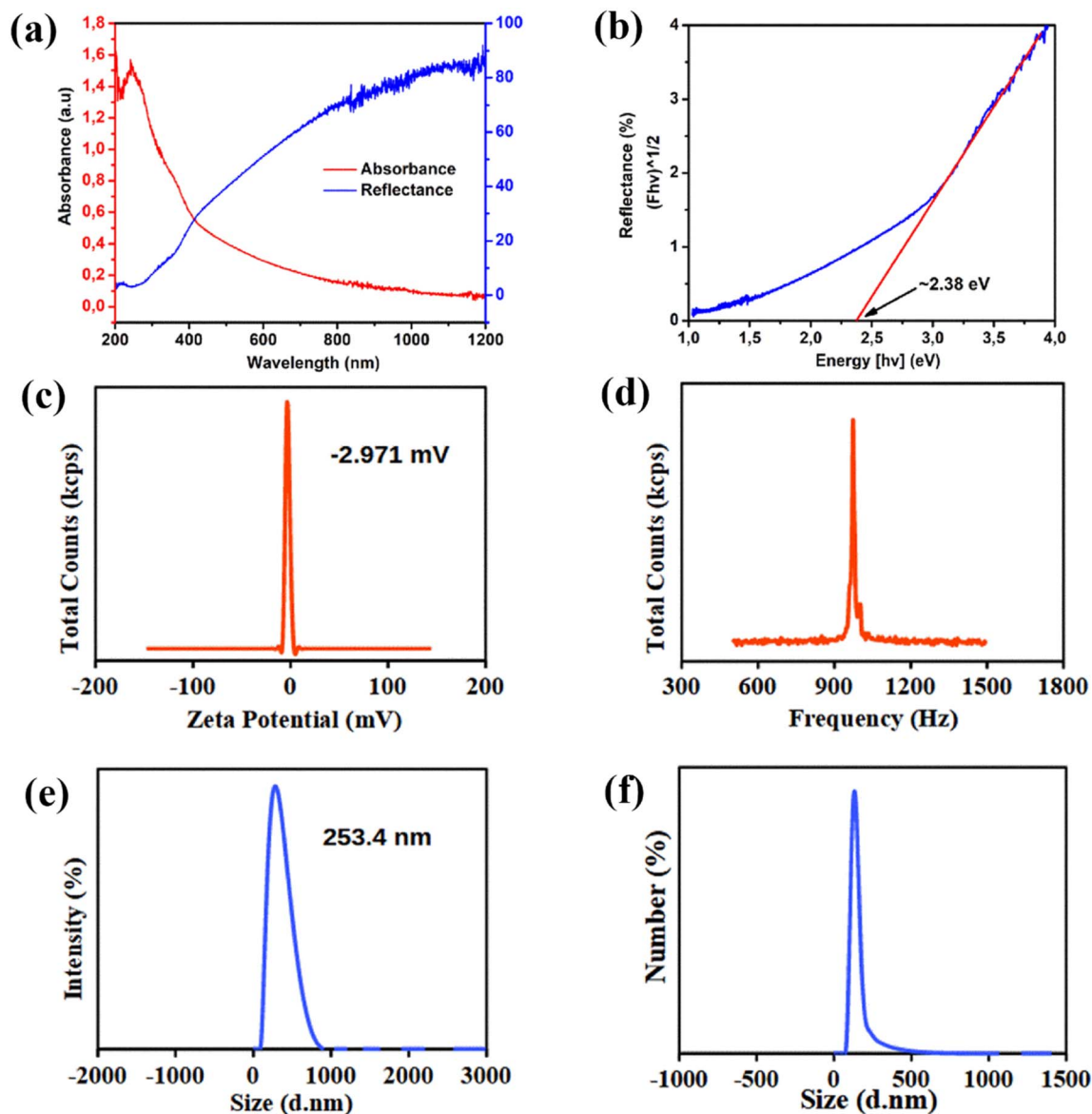


Fig. 5 (a) UV-vis spectra (b) Tauc plot of the transformed Kubelka–Munk function $[F(R)hv]^{1/2}$ against photon energy ($h\nu$), plots of (c) zeta potentials distribution and (d) frequency distribution, (e) size distribution by intensity and (f) size distribution by number of $\text{Bi}_3\text{O}_4\text{Br}$ sheets.

Increasing the NaBH_4 concentration was found to slightly enhance the reaction rate, indicating its influence on the kinetics of the reduction (Fig. 7a–c). Additionally, the $\text{Bi}_3\text{O}_4\text{Br}@CS$ catalyst exhibited high efficiency and excellent reusability, maintaining stable performance over 10 consecutive cycles without significant loss of activity (Fig. 7d).

Kinetic studies

The photocatalytic activity of the prepared $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid materials was evaluated in the photodegradation of RhB under UV irradiation. Control experiments were performed in the absence of a catalyst and with pure CS beads to account for potential self-photolysis and the individual contribution of the CS support. The degradation process was monitored using UV-vis spectroscopy. The time-dependent UV-vis absorption spectra for the degradation of RhB over the $\text{Bi}_3\text{O}_4\text{Br}@CS$ composite are

presented in Fig. 6d. As illustrated, approximately 88% of the RhB was removed within 150 minutes of UV exposure. Analysis of the kinetic curves at the 40 minute mark revealed that the degradation rate increased proportionally with the photocatalyst loading (Fig. 8b). This enhancement in performance is attributed to the increased density of active sites available within the reaction medium, which facilitates more efficient interaction between the catalyst and the organic dye molecules. Additionally, the prepared material demonstrates good recyclability in the photodegradation of RhB over 7 consecutive cycles with minimal decrease in the catalytic performance (Fig. 8b).

In the same way, the UV spectra of 4-NP reduction in the presence of NaBH_4 as a reducing agent are described in Fig. 9. It is obviously observed that in the presence of pure CS beads without $\text{Bi}_3\text{O}_4\text{Br}@CS$, the concentration of 4-NP remains constant during the reduction process. In contrast, when



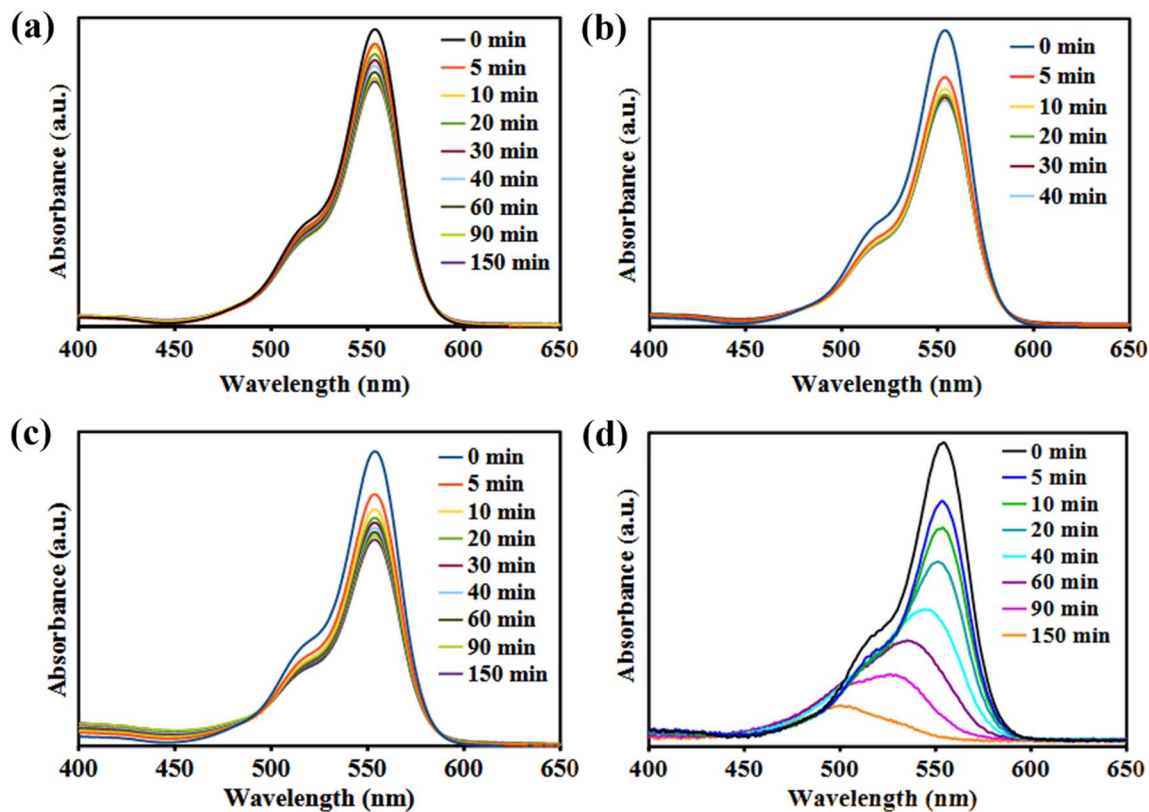


Fig. 6 UV spectra of (a) RhB aqueous solution under UV light (b) in the presence of pure CS beads under UV light (c) in the presence of $\text{Bi}_3\text{O}_4\text{Br@CS}$ in dark, and (d) in the presence of $\text{Bi}_3\text{O}_4\text{Br@CS}$ under UV light.

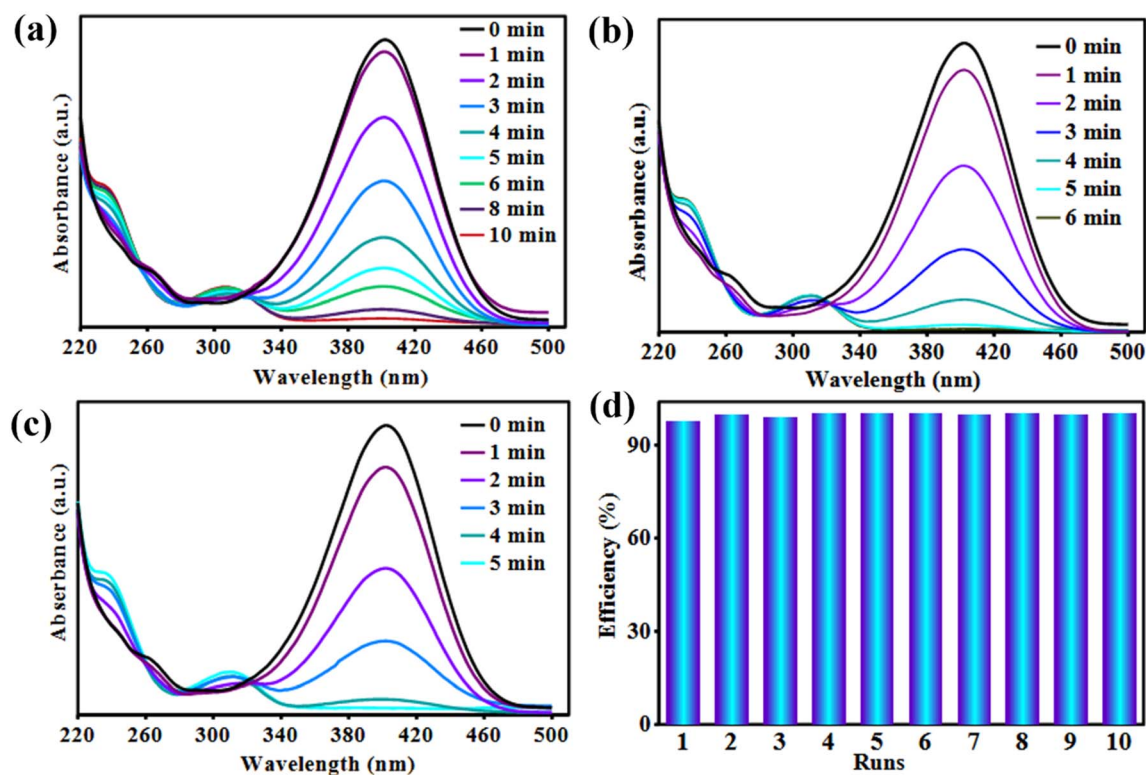


Fig. 7 UV spectra of 4-NP aqueous aliquot withdrawn from reaction in the presence of $\text{Bi}_3\text{O}_4\text{Br@CS}$ (0.4 g L^{-1}) and (a) NaBH_4 (0.5 M), (b) NaBH_4 (1 M), (c) NaBH_4 (2 M). (d) Recyclability graph of $\text{Bi}_3\text{O}_4\text{Br@CS}$ in the reduction of 4-NP.



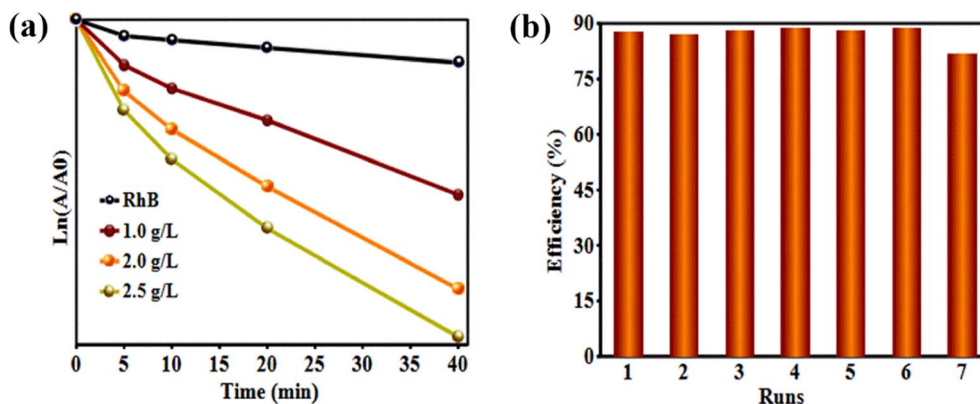


Fig. 8 Kinetic study plots of A_0/A and $\ln(A/A_0)$ versus photodegradation time of RhB (a). Recyclability graph of $\text{Bi}_3\text{O}_4\text{Br@CS}$ in the degradation of RhB (b).

$\text{Bi}_3\text{O}_4\text{Br@CS}$ was used as a catalyst instead of pure CS beads, the concentration of 4-NP decreased progressively with reaction time. In addition, the presence of a large excess of NaBH_4 without a catalyst, no reduction was observed. These results indicated that the reduction process could not be achieved without $\text{Bi}_3\text{O}_4\text{Br@CS}$ hybrid materials and NaBH_4 as a hydrogen source. Moreover, it was also observed that the reduction rate increases linearly with increasing the $\text{Bi}_3\text{O}_4\text{Br@CS}$ loading (Fig. 9b and c). Additionally, the effect of NaBH_4 concentration on the 4-NP reduction was also studied in the range of (0.5, 1, and 2 M) with a fixed catalyst amount. As shown in Fig. 9a and d, it can be clearly observed that the NaBH_4 concentration has a significant effect on the reduction rate of 4-NP. These results demonstrated that there is a linear relationship between the reduction rate and the NaBH_4 concentration.

Recycling experiments were performed to comprehend the behavior and the stability of $\text{Bi}_3\text{O}_4\text{Br@CS}$ hybrid materials in the reduction and photodegradation process. At the end of each reaction, the $\text{Bi}_3\text{O}_4\text{Br@CS}$ catalyst was recovered by simple filtration, washed three times with distilled water, and then reused in another catalytic cycle. Fig. 7d and 8b show the graph obtained for both 4-NP reduction and RhB photodegradation process. It is clearly observed that the $\text{Bi}_3\text{O}_4\text{Br@CS}$ hybrid materials have excellent recyclability in the reduction of 4-NP and RhB photodegradation. These materials could be reused about 7 times in the photodegradation process and 10 times in the reduction reaction with no significant loss in their catalytic performances. Consistently, our system exhibits excellent activity and good robustness, making it an ideal catalyst for water treatment.

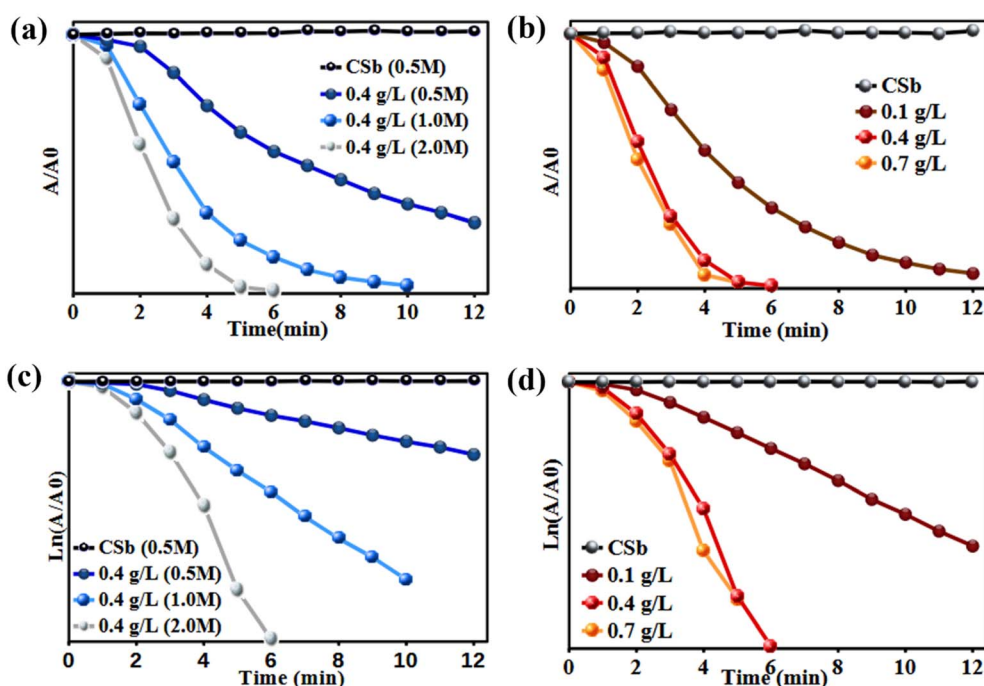


Fig. 9 Kinetic study plots of A/A_0 and $\ln(A/A_0)$ versus reduction time of 4-NP: effect of NaBH_4 concentration (a and c) and $\text{Bi}_3\text{O}_4\text{Br@CS}$ catalyst loading (b and d).



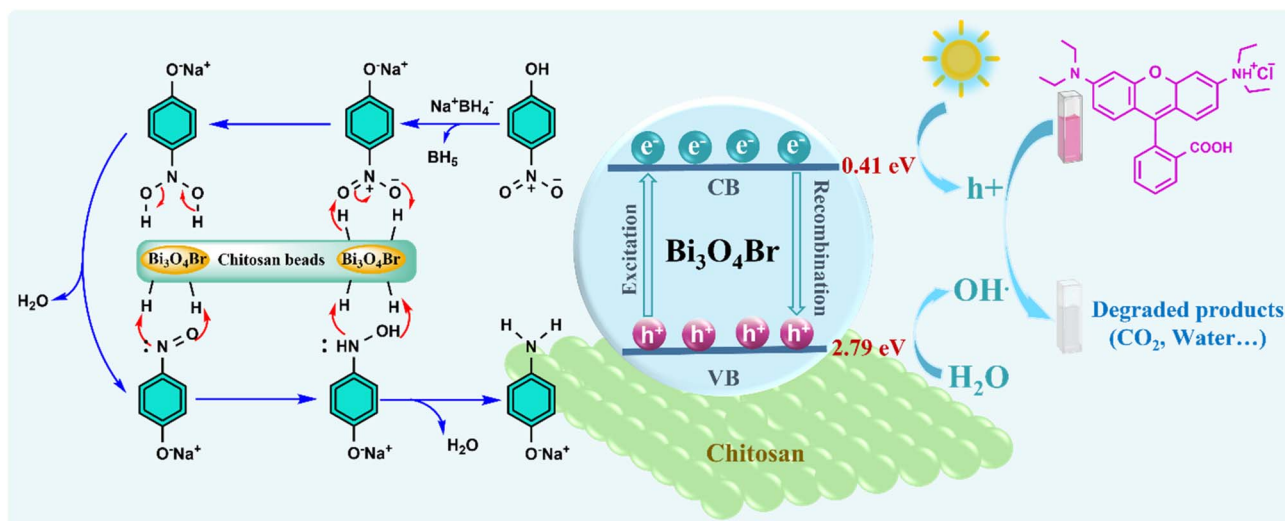
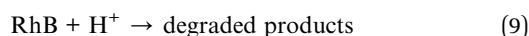
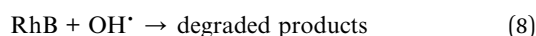
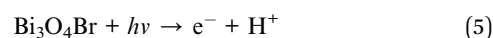


Fig. 10 Schematic illustration of the proposed RhB photodegradation and 4-NP reduction mechanism over $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid materials.

Proposed photodegradation and reduction mechanisms

The photodegradation reaction usually starts with the photoexcitation of $\text{Bi}_3\text{O}_4\text{Br}$ by light irradiation. This process leads to the creation of electrons and holes (charge carriers) at the valence band (VB) and conduction band (CB) of the photocatalyst, respectively (eqn (5)). Then, the generated electrons and holes can participate in several photoreduction and photooxidation reactions at the surface of $\text{Bi}_3\text{O}_4\text{Br}$, respectively.^{51,52} Based on the calculated valence band position (2.79 eV), which is more positive than the oxidation potential of $\text{H}_2\text{O}/\cdot\text{OH}$ (+2.27 eV), the formation of hydroxyl radicals ($\cdot\text{OH}$) is thermodynamically feasible. In parallel, the conduction band position (0.41 eV) allows the reduction of dissolved oxygen into superoxide species ($\cdot\text{O}_2^-$), which are known to play a key role in dye degradation processes. In addition, the photogenerated electrons may react with dissolved oxygen to form superoxide radicals ($\cdot\text{O}_2^-$), which can also contribute to the degradation process (eqn (7)–(9)). Furthermore, the catalytic reduction of 4-NP was scrutinized using NaBH_4 as a reducing agent in the presence of the $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid catalyst. The process follows a Langmuir–Hinshelwood (LH) mechanism, wherein the CS matrix plays a pivotal role by serving as a high-capacity adsorbent that concentrates 4-NP and NaBH_4 in proximity through its abundant functional groups. This biopolymer framework ensures the uniform dispersion of $\text{Bi}_3\text{O}_4\text{Br}$ active sites and prevents their aggregation, which is essential for facilitating efficient electron transfer from the NaBH_4 donor to the 4-NP acceptor. Following the initial deprotonation of 4-NP to 4-nitrophenolate under the alkaline conditions provided by the reductant, the process proceeds *via* sequential hydrogen transfers. This pathway generates critical intermediates, including 4-nitrosophenolate and 4-hydroxylaminophenol, before reaching the final product, 4-aminophenolate. Beyond its kinetic contributions, the integration of the CS matrix enhances the structural stability of the hybrid system, enabling

facile catalyst recovery and sustained catalytic activity over multiple operational cycles (Fig. 10).



Conclusion

In conclusion, a high-performance $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid photocatalyst was successfully prepared through a simple steps strategy. The composite integrates the photocatalytic properties of $\text{Bi}_3\text{O}_4\text{Br}$ with the biodegradable and mechanically robust characteristics of CS, leading to a structured material in which $\text{Bi}_3\text{O}_4\text{Br}$ nanosheets are uniformly embedded within chitosan microspheres. This design facilitates catalyst handling and recovery compared to conventional powder systems.

The hybrid material demonstrated effective performance in both the photodegradation of RhB under UV irradiation and the reduction of 4-NP in the presence of NaBH_4 . The catalytic activity was influenced by operational parameters such as catalyst amount and reducing agent concentration, confirming good accessibility of active sites. In addition, the composite maintained consistent performance over repeated cycles, indicating satisfactory stability and reusability.

Overall, the results show that integrating $\text{Bi}_3\text{O}_4\text{Br}$ nanosheets within a chitosan matrix is an effective strategy to improve catalyst usability, particularly in terms of recovery, stability, and multifunctional performance. This approach provides a practical and sustainable pathway for designing



recoverable catalytic systems with potential application in wastewater treatment.

Conflicts of interest

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the contents of the manuscript, and there is no financial interest to report. We certify that the submission is original work and is not under review at any other publication.

Data availability

All data supporting this study are included in the article and its supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6ra02619b>.

Acknowledgements

The authors would like to express their sincere gratitude to the PRIMA program (Partnership for Research and Innovation in the Mediterranean Area, project BIOMEDPACK). This work was also carried out with the support of the Ministry of Science, Innovation and Universities of the Government of Spain for funding the research stay of senior teaching and/or research staff at foreign institutions.

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