

Efficient Removal of Endocrine Disrupting Chemicals by BiOBr/Bi₂O₂CO₃ Heterojunctions with the Presence of Chlorite: Photocatalytic and Chlorite Activation Mechanisms

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Research Article

Keywords: S-scheme heterojunctions, (001) planes, ClO₂-photocatalysis reaction system, OV-mediated chlorite activation, Facet engineering

Posted Date: August 25th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10649571/v1>

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Additional Declarations: No competing interests reported.

Abstract

The visible light-driven chlorite activation process has demonstrated remarkable potential for wastewater treatment applications. In this study, a series of flower-like S-scheme heterojunction photocatalysts (composed of BiOBr and $\text{Bi}_2\text{O}_2\text{CO}_3$, denoted as xyDBi) were successfully synthesized, with the (001) facet serving as the predominantly exposed crystal plane. An integrated ClO_2^- photocatalytic system was established using xyDBi to enhance the degradation of bisphenol A (BPA) in aqueous solutions. Comprehensive characterization and theoretical calculations revealed the formation of a robust internal electric field at the heterojunction interface, enabling efficient spatial separation of photogenerated charges through an S-scheme charge transfer mechanism. Density functional theory (DFT) calculations and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analyses indicated that oxygen vacancies (OVs) functioned as Brønsted acid sites, facilitating the adsorption of chlorite ions (ClO_2^-). Chlorine dioxide (ClO_2) was identified as the primary reactive species, generated through two distinct pathways involving OVs and hydroxyl radicals ($\bullet\text{OH}$). Under visible light irradiation, the addition of chlorite to the 11DBi-based photocatalytic system achieved 92.7% removal of BPA within 25 minutes. The 11DBi catalyst demonstrated exceptional stability across a broad spectrum of reaction conditions, encompassing initial pH variations, coexisting anions and cations, catalyst recyclability, and diverse water matrices. Additionally, the degradation mechanism of BPA was deduced to be demethylation, hydroxylation, and cleavage of the isopropylidene bridge. This study elucidated the synergistic interaction between oxygen vacancy-rich S-scheme heterojunctions and chlorite activation, providing a novel approach for advanced oxidation processes in wastewater treatment.

1. Introduction

- Endocrine disrupting chemicals (EDCs) are widely recognized as persistent and hazardous pollutants present in industrial wastewater, posing significant risks to both ecosystems and human health [1, 2]. Among these contaminants, bisphenol A (BPA) is extensively used in a variety of consumer products, including personal care items, tableware, and medical devices. The release of BPA into aquatic environments has been associated with adverse effects on the human reproductive, nervous, and immune systems [3]. Visible light-driven photocatalysis has garnered considerable attention due to its high efficiency in mitigating water pollution [4]. Compared to conventional treatment technologies such as adsorption [5], flocculation [6], biodegradation [7], and membrane filtration [8], photocatalytic processes enable the rapid degradation of organic pollutants into less toxic compounds or complete mineralization products [9]. During photocatalysis, reactive oxygen species (ROS) such as hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$) are generated and exhibit non-selective reactivity toward a broad range of organic contaminants. Nevertheless, the practical application of photocatalysis in water treatment faces inherent limitations, primarily attributable to the scavenging effects of background water matrix components on ROS [10].
- The integration of photocatalysis with chemical oxidants, such as hydrogen peroxide [11], peroxymonosulfate [12], or persulfate [13], has emerged as a highly effective strategy for enhancing

photocatalytic efficiency. Compared to conventional reactive oxygen species (ROS), chlorine dioxide (ClO_2) exhibits superior selectivity in oxidizing specific functional groups and demonstrates greater resistance to environmental interference [14]. As a promising alternative to chlorine, ClO_2 generated from chlorite (ClO_2^-) produces fewer halogenated disinfection byproducts (DBPs), primarily due to electron transfer oxidation rather than chlorine substitution [15]. Moreover, ClO_2 -based oxidation processes show significant potential for degrading phenolic compounds, which are widely present in aquatic environments [16]. Wajon et al. proposed that the reaction between ClO_2 and phenolic moieties proceeds via a two-step mechanism: an initial electron transfer step followed by oxygen transfer to the carbon-centered radical [17]. However, the synergistic mechanism underlying the degradation of BPA through heterogeneous visible-light photocatalysis coupled with chlorite remains insufficiently explored.

- For heterogeneous systems, the development of photocatalysts capable of efficiently utilizing visible light is of paramount importance for chlorite activation. Two-dimensional (2D) materials have been extensively investigated due to their distinctive properties, including abundant active sites, high specific surface area, and enhanced charge carrier separation efficiency [18, 19]. Among these, 2D Bi^{3+} -based semiconductors have garnered significant attention in photocatalysis applications owing to their favorable energy band structures and unique layered architectures [20]. Compared to bulk Bi-based counterparts, 2D nanostructures exhibit shorter charge transfer pathways and improved light absorption capabilities, thereby demonstrating greater potential for practical applications [21]. However, the photocatalytic performance of these materials remains suboptimal due to the rapid recombination of photogenerated charge carriers.
- To mitigate the aforementioned limitation, facet engineering—a strategic approach aimed at maximizing the exposure of highly reactive crystal facets—has emerged as a promising solution and has garnered increasing attention in the scientific community [22, 23]. In 2D Bi^{3+} -based semiconductors, the exposed (001) facet can induce an internal electric field within the layer, thereby facilitating electron transfer. This phenomenon originates from the weak van der Waals interactions between adjacent stacked layers [24–26]. Previous studies have demonstrated that a higher concentration of oxygen defects tend to form along the z-axis, attributable to the high density of terminal oxygen atoms on the (001) facets and the square antiprismatic coordination of Bi-O bonds [27]. Surface OVs not only serve as active sites for adsorption and surface reactions but also function as electron traps, effectively suppressing the recombination of photogenerated carriers [28, 29].
- Furthermore, the integration of facet engineering with other modification strategies can significantly enhance photocatalytic efficiency. For instance, Liu et al. developed a Ti_3C_2 MXene/exfoliated montmorillonite-decorated $\text{Bi}_2\text{MoO}_6/\text{BiOBr}$ S-scheme heterojunction with dominant (001) facets of BiOBr , achieving over 90% degradation efficiency for multiple fluoroquinolone antibiotics [30]. Similarly, Xi et al. successfully constructed a $\text{ZnIn}_2\text{S}_4/\text{BiOBr}$ -(001) composite, which enabled the formation of a strong built-in electric field and pronounced band bending in the space charge region near the interface [31]. However, the construction of heterojunctions between the (001) facets of

both Bi-based components, as well as the interaction between such heterojunctions and chlorite ions, remains an area requiring further systematic investigation.

- In this study, a series of flower-like S-scheme photocatalysts comprising BiOBr and $\text{Bi}_2\text{O}_2\text{CO}_3$ (xyDBi) were successfully fabricated through a facile one-step hydrothermal method. By decorating the catalysts with cetyltrimethyl ammonium bromide (CTAB), the internal electric field was systematically constructed by matching the work functions of the dominant exposed (001) planes. The photocatalytic performance of these materials was evaluated through the degradation of BPA under visible light illumination in the presence of chlorite. The S-scheme heterojunction structure was rigorously verified through a combination of experimental characterizations and theoretical calculations. The generation of active oxygen species was directly detected, and the chlorite activation mechanism was systematically deduced and calculated by considering various possible reaction sites. The degradation mechanism of BPA was elucidated by analyzing the intermediate products and reactive sites. This study provides a novel approach for constructing heterojunctions through facet engineering and offers a new pathway for chlorite activation in photocatalytic systems.

2. Experimental section

2.1 Chemicals and characterizations

- All chemicals were used without further purification. The characterizations and theoretical calculations used in this paper are presented in the Supporting Information.

2.2 Synthesis of xyDBi catalysts

- The xyDBi photocatalysts were synthesized through a one-step hydrothermal method. In a standard synthesis procedure, 1.455 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, together with a specified amount of KBr and urea, was added to a beaker containing 50.0 mL of solvent (comprising 25.0 mL of distilled water and 25.0 mL of ethylene glycol) to form solution A. Simultaneously, 0.12 g of CTAB was dissolved in 10.0 mL of distilled water to prepare solution B. Solution B was subsequently added dropwise to solution A under continuous stirring (500 RPM) for a duration of 15 minutes. The resulting suspension was transferred into a high-pressure reactor and heated at 160°C for 24 hours. The obtained xyDBi (where x and y represent the relative molar ratios of BiOBr and $\text{Bi}_2\text{O}_2\text{CO}_3$) were isolated via centrifugation, washed with ethanol and distilled water, and dried at 60°C in a vacuum oven. For comparative analysis, single BiOBr, $\text{Bi}_2\text{O}_2\text{CO}_3$, and their respective components synthesized without CTAB (designated as BOB1 and BOC1) were also prepared through a similar process. Unless otherwise noted, the single components discussed in this paper refer to 2D materials.

2.3 Photocatalytic experiments

- The photocatalytic performance of the fabricated catalysts for bisphenol A (BPA) degradation was evaluated under visible light illumination. Batch experiments were conducted in a photocatalytic reaction apparatus (CEL-PE300L-3A, China Education Au-light Co., Ltd.). A 300 W xenon lamp equipped with an optical filter served as the light source, with a measured radiation flux of 30 mW/cm². In a typical experiment, 50 mg of the catalyst was dispersed in 100 mL of BPA solution (25 mg/L), and the suspension was stirred in the dark for 10 minutes to achieve adsorption-desorption equilibrium. Subsequently, sodium chlorite solution was added to the reaction system under irradiation. After the reaction, the samples were centrifuged, and the residual BPA concentration was measured by high-performance liquid chromatography (HPLC, LC-20A, SHIMADZU). The mineralization efficiency was quantitatively assessed using a total organic carbon (TOC, TOC-L) analyzer. Additionally, the degradation intermediates and products were analyzed by liquid chromatography-mass spectrometry (LC-MS, 1290II-6460, Agilent).

3. Results and discussion

3.1 Structure and morphology

The XRD patterns of the prepared catalysts are shown in Fig. 1a and Fig. S1. For pure Bi₂O₂CO₃, the diffraction peaks at $2\theta = 12.9^\circ, 23.9^\circ, 25.9^\circ, 30.3^\circ, 32.7^\circ$, and 39.3° are consistent with the (002), (011), (004), (013), (110), (006) planes, matching well with tetragonal Bi₂O₂CO₃ (PDF No. 41–1488). The BiOBr diffraction peaks at $2\theta = 10.9^\circ, 21.9^\circ, 25.2^\circ, 31.8^\circ, 32.2^\circ, 39.3^\circ, 44.7^\circ$ are ascribed to the (001), (002), (011), (012), (110), (112) and (004) planes, respectively. These peaks match those of tetragonal BiOBr (PDF No. 52–0084). The BiOBr peaks exhibit higher intensity in the 11DBi spectrum, confirming BiOBr as the dominant phase. The presence of peaks corresponding to both components in the xyDBi composites verifies successful hybrid fabrication.

In Fig. 1b, the optical absorption properties of BiOBr, Bi₂O₂CO₃, and xyDBi were measured using UV–vis DRS. BiOBr exhibited an absorption edge at approximately 435 nm, while Bi₂O₂CO₃ displayed a slightly weaker absorption strength in the visible light region. In contrast, xyDBi demonstrated a significantly enhanced light absorption capability, with hybrid samples showing a broad absorption range in the visible light region. The band gap values of BiOBr and Bi₂O₂CO₃ were calculated using the Kubelka–Munk function formula (Eq. (1)).

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

where a , h , ν , E_g and A are absorption coefficient, Planck constant, optical frequency, band gap energy and constant, respectively. Both BiOBr and Bi₂O₂CO₃ were deemed to be indirect band gap semiconductors ($n = 4$), and the E_g values of BiOBr and Bi₂O₂CO₃ are calculated to be 2.80 and 3.15 eV, respectively[32, 33]. The band gap values shows that both components are able to make use of visible light.

Figure 1e shows the XPS survey spectra of BiOBr, Bi₂O₂CO₃, and 11DBi. In Fig. 1f, the Bi 4f spectrum of 11DBi has two strong peaks at 159.4 eV and 164.7 eV, corresponding to Bi 4f^{7/2} and Bi 4f^{5/2} transitions of Bi³⁺ in Bi-based semiconductors [34]. Figure 1g displays the Br 3d spectrum fitted into two peaks: 68.9 eV (Br 3d^{5/2}) and 69.7 eV (Br 3d^{3/2}) of BiOBr [35]. Figure 1h shows peaks at 529.7 eV, 530.1 eV, and 531.8 eV from Bi-O bonds, CO₃²⁻, and surface H₂O [36]. Figure 1i indicates that the peaks at 284.4 eV and 285.0 eV are due to exogenous carbon, while the peak at 288.7 eV is from the carbonate ion in Bi₂O₂CO₃ [37].

For the single components (Fig. S3), the peak positions of Bi 4f, Br 3d, and C 1s in the spectra of BiOBr and Bi₂O₂CO₃ are higher than that of BOB1 and BOC1. The binding energy shifts suggest chemical environment changes due to charge redistribution from surface electron density alterations, attributed to high (001) crystal facet exposure [38, 39]. The low-temperature ESR spectra (Fig. S4) show 11DBi with the highest peak intensity, with ESR signals identified as paramagnetic species from oxygen vacancies trapping single electrons, indicating more oxygen vacancies in 11DBi structures [40, 41].

In contrast to the XPS spectra of pure BiOBr, the Bi 4f (159.4 eV and 164.7 eV) and Br 3d (68.9 eV and 69.7 eV) peaks of 11DBi display shifts to higher binding energies, demonstrating that BiOBr loses electrons when fabricated with Bi₂O₂CO₃. On the other hand, the Bi 4f and C 1s (288.7 eV) spectra of 11DBi show negative shifts to lower binding energies than those of Bi₂O₂CO₃. These binding energy changes between 11DBi and the single-component materials are caused by the "electron screening effect," highlighting the strong interaction between the two components. The electron loss from BiOBr and the electron influx into Bi₂O₂CO₃ lead to a depletion layer of BiOBr and an accumulation layer of Bi₂O₂CO₃ at the interface, thereby establishing an internal electric field in the heterojunction. Moreover, the in-situ XPS measurement in Fig. 1j illustrates an increased binding energy of C 1s in the irradiated 11DBi compared to the non-illuminated sample, indirectly indicating the loss of electrons from Bi₂O₂CO₃ to BiOBr under the internal electric field [42]. Additionally, the calculated work functions of BiOBr (6.81 eV for the (001) plane) and Bi₂O₂CO₃ (8.35 eV for the (001) plane) clearly confirm the migration of charge carriers from BiOBr into Bi₂O₂CO₃ (Fig. 1k and Fig. 1l). The DFT calculations are in good agreement with the XPS analysis, further supporting the formation of strong electronic interactions between the two components.

The morphology and microstructure of the as-prepared 11DBi composite and its components were investigated using SEM and TEM. In Fig. S5, 2D stacked sheet-like structures are evident for both BiOBr and Bi₂O₂CO₃. The SEM image of the 11DBi hybrid in Fig. 2a shows flower-like structures, which may provide a tighter bond between components and a larger specific surface area (Fig. S6). This nanosheet structure is beneficial for shortening charge transfer distance and prolonging recombination time. The TEM image in Fig. 2b further illustrates the intimate relationship between BiOBr and Bi₂O₂CO₃. HRTEM images (Fig. 2c and Fig. 2d) demonstrate a lattice spacing of 0.28 nm, corresponding to the (110) plane of BiOBr [43]. Additionally, the SAED pattern reveals diffraction planes of (020) and (110) at a 45° crossing angle (Fig. 2e and Fig. 2f), with all planes perpendicular to the (001) plane [44]. For Bi₂O₂CO₃, the HRTEM images display clear lattice fringes with 0.27 nm spacing, indexed to the (110) crystal planes

[45]. The 90° angle between (110) and (1-10) indicates that the exposed surfaces belong to the (001) facet [46].

- The photoelectrochemical properties of the synthesized catalysts were characterized via photoluminescence (PL) spectroscopy. As shown in Fig. S8, the PL intensity of the 11DBi composite is significantly lower than that of either BiOBr or $\text{Bi}_2\text{O}_2\text{CO}_3$, indicating enhanced separation efficiency of photogenerated electron-hole pairs. Transient photocurrent responses and electrochemical impedance spectroscopy (EIS) Nyquist plots were further employed to evaluate charge transfer dynamics. As depicted in Fig. S9a, the 11DBi heterojunction exhibits a substantially higher and more stable photocurrent density over time compared to the individual monocomponents. Moreover, the EIS Nyquist plot in Fig. S9b reveals a markedly smaller semicircular arc for 11DBi, signifying reduced interfacial charge transfer resistance. These improved charge transport characteristics are attributed to the establishment of a built-in electric field at the BiOBr/ $\text{Bi}_2\text{O}_2\text{CO}_3$ interface, which facilitates directional migration of photogenerated carriers and suppresses recombination losses, as previously corroborated by XPS and work function analyses.

3.2 Photocatalytic performances

- Figure 3a demonstrates the elimination of BPA in the combined ClO_2^- -photocatalysis system under visible light irradiation. The degradation efficiencies of BPA by BiOBr and $\text{Bi}_2\text{O}_2\text{CO}_3$ reached 55.4% and 47.9%, respectively. Although these materials achieved ClO_2^- activation, their charge transfer capabilities remained constrained by limited active sites and carrier recombination. In contrast, 11DBi exhibited maximum degradation and mineralization efficiencies of 92.7% and 67.5%, respectively. Figure 3b presents experimental results under varying reaction conditions, revealing that neither pure visible light nor 11DBi alone could effectively activate ClO_2^- . However, the 11DBi/light/ ClO_2^- system achieved the highest degradation efficiency (92.7%), outperforming the photocatalytic system without ClO_2^- (52.5%). This enhanced removal efficiency is attributed to effective ClO_2^- activation, which stems from the efficient generation and conversion of diverse active species. In repetitive degradation experiments (Fig. 3c), 11DBi maintained a removal efficiency of 89.5%, confirming its excellent operational stability. Furthermore, all optimal parameters for BPA degradation were selected to evaluate 11DBi's performance in real/natural water bodies. As shown in Figure S10, the total removal of BPA reached 93.5% in secondary effluents and 92% in river water, respectively.
- The effect of interference factors were investigated to verify the stability of catalytic performance of 11DBi. As for the inorganic anions, HCO_3^- , SO_4^{2-} , and Cl^- were selected. In Fig. 3d, only trivial decline of the removal efficiency was observed with the increase of HCO_3^- , and the degradation percentage can still reach 88.5%. The reason can be explained from two reasons: (i) the ClO_2^- competitively reacted with photo-induced $\bullet\text{OH}$, which offset the negative effects of HCO_3^- ; and (ii) the photoconverted $\bullet\text{CO}_3^-$ reacted with ClO_2^- to produce ClO_2 ($k = 3.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), resulting in the

increase of ClO_2 yield (Eq. 2)[47]. Similarly, SO_4^{2-} exhibited nearly no inhibition effect on the BPA degradation (Fig. 3e), which was attributed to the offset of the negative effect from SO_4^{2-} by the efficient reaction between $\bullet\text{OH}$ and ClO_2^- (Eq. 3). Different from the former two anions, stimulation effect was obtained with the presence of Cl^- , which was caused by the formation of $\bullet\text{Cl}_2^-$ (Fig. 3f). It has been reported that $\bullet\text{Cl}_2^-$ can achieve the degradation of surrounding pollutants by electron transfer and H-abstraction reactions[48].

- Cation species and natural organic matter were also selected to study their effects on BPA removal. In Fig. 3g, the BPA removal rate increased at low Cu^{2+} concentrations (0.1 mmol and 0.5 mmol), primarily due to the electron shuttle effect of Cu^{2+} [49]. Cu^{2+} gained an electron to form Cu^+ , which then reacted with O_2 to produce $\bullet\text{O}_2^-$ (Eq. 4–5). In contrast, high Cu^{2+} concentrations and the addition of Zn^{2+} (Fig. 3h) exhibited varying degrees of inhibition in the combined ClO_2^- -photocatalysis process, likely caused by active site occupation or active species quenching. Furthermore, humic acid (HA) was selected to test its influence on BPA removal (Fig. 3i). This phenomenon can be explained by two mechanisms: (i) HA competed with BPA for photoinduced ROS and ClO_2^- consumption, and (ii) HA hinders ROS conduction[50, 51]. Regarding pH influence (Fig. S11), BPA degradation was only inhibited under alkaline conditions (pH = 9), which can be attributed to $\bullet\text{OH}$ radical quenching and subsequent hindrance of ClO_2^- activation[52].

- $\bullet\text{CO}_3^- + \text{ClO}_2^- \rightarrow \text{CO}_3^{2-} + \text{ClO}_2$ (2)
- $\bullet\text{OH} + \text{ClO}_2^- \rightarrow \text{ClO}_2 + \text{OH}^-$ (3)
- $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$ (4)
- $\text{Cu}^+ + \text{O}_2 \rightarrow \text{Cu}^{2+} + \bullet\text{O}_2^-$ (5)
- 3.3 Degradation pathways and toxicity evaluation

Table 1
Condensed Fukui function and dual descriptor of BPA.

No.	Atom	q(N)	q(N + 1)	q(N-1)	f ⁻	f ⁺	f ⁰	CDD
1	O	-0.1233	-0.1503	-0.0836	0.0397	0.0271	0.0334	-0.0126
2	O	-0.1233	-0.1503	-0.0836	0.0397	0.0271	0.0334	-0.0126
3	C	0.0056	-0.0334	0.057	0.0513	0.039	0.0452	-0.0123
4	C	0.0369	0.004	0.0642	0.0273	0.0329	0.0301	0.0056
5	C	0.0369	0.004	0.0642	0.0273	0.0329	0.0301	0.0056
6	C	-0.1487	-0.2137	-0.0598	0.0889	0.065	0.077	-0.0239
7	C	-0.1487	-0.2137	-0.0598	0.0889	0.065	0.077	-0.0239
8	C	-0.0354	-0.0738	-0.0029	0.0325	0.0385	0.0355	0.006
9	C	-0.0354	-0.0738	-0.0029	0.0325	0.0385	0.0355	0.006
10	C	-0.0323	-0.0702	-0.0001	0.0322	0.0379	0.0351	0.0056
11	C	-0.0323	-0.0702	-0.0001	0.0322	0.0379	0.0351	0.0056
12	C	-0.0635	-0.0971	-0.0293	0.0342	0.0336	0.0339	-0.0006
13	C	-0.0635	-0.0971	-0.0293	0.0342	0.0336	0.0339	-0.0006
14	C	-0.066	-0.0994	-0.031	0.0351	0.0333	0.0342	-0.0017
15	C	-0.066	-0.0994	-0.031	0.0351	0.0333	0.0342	-0.0017
16	C	0.0759	0.0527	0.1083	0.0324	0.0232	0.0278	-0.0092
17	C	0.0759	0.0527	0.1083	0.0324	0.0232	0.0278	-0.0092

- To better explore the mechanism of BPA degradation, the reactive sites of BPA were predicted via DFT theoretical calculation and the intermediate products were corroborated on account of the LC-MS analysis. The optimized molecular structure, the HOMO and LUMO orbital distribution of BPA were exhibited in Fig. S13 and Fig. S14, respectively. In Fig. 4, the results of Fukui function mapped electron density isosurface and dual descriptor map were presented to analyze the reactive sites of BPA. In Table 1, C6, C7, and C3 show larger f⁻ values, which are correspondingly susceptible to attack by the electrophile ($\cdot\text{OH}$, $\cdot\text{O}_2^-$)[53]. The sites of O1, O2, C14, and C15 are also vulnerable to be attacked to initiate the electrophilic reaction. In addition, the isosurface map of f⁰ reveals that C6, C7, and C3 are more vulnerable to be attacked by free radicals (ClO_2 , $\cdot\text{OH}$, and $\cdot\text{O}_2^-$), suggesting the reaction was more likely to occur at these sites. It can be obtained from the condensed dual descriptors (CDD) values (Fig. 4d and Table 1) that C6, C7, C3, O1, O2, C14, and C15 demonstrate negative values, suggesting that these regions have electrophilic reactivity, which is consistent with

the conclusion of Fukui function[54]. In contrast, the C4, C5, C8, and C9 with positive CDD values also demonstrate the high nucleophilic activity. Furthermore, the Wiberg bond order was calculated to analyze the bond cleavage and bond strength. As described in Fig. S15, the Wiberg bond orders in the skeleton of BPA molecule shows that the C3-C6, C3-C7 and C3-C5 (C3-C4) bonds have smaller bond orders, indicating that the breakage is most likely to occur at these bonds.

- Based on the MS spectra (Fig. S16) and DFT calculation results, the degradation pathway of BPA in the vis/11DBi/ ClO_2^- system was proposed, as summarized in Fig. 4e. The BPA degradation can be initiated mainly via three pathways: (i) demethylation, (ii) hydroxylation, (iii) isopropylidene bridge cleavage. Judging from the DFT calculation (pathway i), C6 and C7 atoms within the methyl groups are proved to be highly vulnerable due to the high f^- (0.0889) and f^0 (0.077), respectively. Therefore, the intermediate of P1 (Bis(4-hydroxyphenyl)methane, $m/z = 199$) can be obtained through the attack of ClO_2 and radicals on the C-C bonds, which is consistent with the results of Wiberg bond orders. Then, the intermediate P2 (4-Hydroxyacetophenone, $m/z = 135$) generated by opening ring reaction on the reactive site on the aromatic ring, in which C5 with higher CDD value (0.0056) is susceptible to be attacked by ClO_2 . As for pathway ii, the degradation is initiated mainly by electrophilic attack in the ortho position (C14 or C15) to form P3 (5-Hydroxybisphenol, $m/z = 243$), deriving from the large f^- value (0.0351)[55]. The intermediate P4 (4-(prop-1-en-2-yl)benzene-1,2-diol, $m/z = 149$) can be generated by the breaking of C3-C4 (or C3-C5) bond, followed by the dehydrogenation reaction. Similarly, pathway iii can be initiated by direct isopropylidene bridge cleavage (with a lower Wiberg bond value of 0.84) to generate P5 (4-Isopropylphenol, $m/z = 136$), which is followed by dehydrogenation to form P6 (α -Methylstyrene, $m/z = 118$). All the byproducts above can be further oxidized to smaller products (P7, P8, P9, and P10) and eventually converted to CO_2 and H_2O .
- The Toxicity Estimation Software Tool (T.E.S.T.) was employed to assess the potential risks of degradation products using the quantitative structure-activity relationship (QSAR) method. As shown in Fig. S17, except for P7, which exhibits slightly higher developmental toxicity than original BPA, the developmental toxicity of other intermediates has been reduced. Notably, P2 and P8 products are classified as "developmental non-toxicants." Regarding the bioconcentration factor, only P6 displays a value higher than that of BPA, likely due to its lipophilic structure. These results indicate that the total actual toxicity in the reaction system has decreased. However, some intermediates warrant closer attention due to their potential ecotoxicity.
- 3.4 Photocatalytic and ClO_2^- activation mechanisms
- Scavenging experiments were carried out to determine the active species involved in BPA degradation in the presence of 11DBi in the vis/ ClO_2^- system. According to the rate constants of the scavengers and corresponding active species, TBA (100.0 mM), BQ (1.0 mM), L-histidine (10.0 mM), FA (10.0 mM), and $\text{Na}_2\text{S}_2\text{O}_4$ (1.0 mM) were selected as scavengers for $\cdot\text{OH}$, $\cdot\text{O}_2^-$, $^1\text{O}_2$, h^+ , and ClO_2 , respectively[14, 56]. As shown in Fig. S18, BPA degradation is obviously inhibited in the presence of TBA, $\text{Na}_2\text{S}_2\text{O}_4$, and FA, which indicates that $\cdot\text{OH}$, ClO_2 , and h^+ are the primary reactive species. It can

be seen that the inhibiting effects of these three scavengers are close, which indirectly proved the activation of chlorite by $\cdot\text{OH}$.

- ESR was further conducted to clarify the reactive species existing in the vis/11DBi/ ClO_2^- reaction systems. In Fig. 5a, four peaks with a peak intensity ratio of 1:2:2:1 are detected for $\cdot\text{OH}$ in the single photocatalysis and vis/ ClO_2^- processes. Similarly, $\cdot\text{O}_2^-$ with an peak intensity ratio of 1:1:1:1, and h^+ with an intensity ratio of 1:1:1, can also be observed (Fig. 5b and Fig. 5c). With the addition of ClO_2^- , the signal strength of $\cdot\text{OH}$ decreases, demonstrating the consumption of $\cdot\text{OH}$ by ClO_2^- . However, the generation of $\cdot\text{O}_2^-$ and h^+ was not significantly influenced by ClO_2^- , ruling out the reaction of ClO_2^- with $\cdot\text{O}_2^-$ and h^+ . In addition to the species above, four characteristic peaks of ClO_2 , which has an unpaired electron can be considered as a radical, can also be detected (Fig. 5d)[57]. ClO_2 can be generated by the reaction of $\cdot\text{OH}$ and chlorite (scavenging effect on $\cdot\text{OH}$), which played a crucial role in BPA degradation[58].
- The generation of corresponding active species are closely related to the energy band positions. Hence, the valence band (VB) positions of the semiconductors in 11DBi were measured to explore the catalytic mechanism. As shown in Fig. 5e and Fig. 5f, the VB values of BiOBr and $\text{Bi}_2\text{O}_2\text{CO}_3$ are 2.09 eV and 2.86 eV, respectively. The Mott-Schottky plots of BiOBr and $\text{Bi}_2\text{O}_2\text{CO}_3$ in Fig. 5g and Fig. 5h exhibit positive slopes, which demonstrates that both the components are n-type semiconductors[59]. The flat band potentials (E_{fb}) were calculated by linear fitting of the curves, and the values for BiOBr and $\text{Bi}_2\text{O}_2\text{CO}_3$ were obtained to be -0.57 eV and -0.12 eV vs Normal Hydrogen Electrode (NHE), respectively. For n-type semiconductor, the conduction bands (CB) always possess more negative potential (~ 0.2 eV) over the flat band potential[42, 60]. Hence, the CB potentials corresponding to BiOBr and $\text{Bi}_2\text{O}_2\text{CO}_3$ are -0.77 eV and -0.32 eV, respectively. Combined with the band gap values, the VB potentials can be deduced to be 2.03 eV and 2.83 eV, which coincide well with those values directly obtained from the XPS-VB test. Furthermore, the Mott-Schottky plots of 11DBi (Fig. 5i) exhibits a moderate value (-0.30 eV) towards single BiOBr and $\text{Bi}_2\text{O}_2\text{CO}_3$. According to the comparative values, the downward E_{fb} shift of BiOBr (0.27 eV) and upward E_{fb} shift of $\text{Bi}_2\text{O}_2\text{CO}_3$ (-0.18 eV) demonstrates the existence of electron transfer from BiOBr to $\text{Bi}_2\text{O}_2\text{CO}_3$ to form the n-n heterojunctions.
- To probe the relationship between OV and chlorite activation, DFT calculations for OV-mediated chlorite activation were conducted. Considering the crucial role of $\cdot\text{OH}$ in chlorite activation, investigation of surface -OH generation is crucial to explain why chlorite activation occurs at the solid-liquid interface. The adsorption energy (ΔE_{ads}) of H_2O at two possible sites on the (001) plane of BiOBr and $\text{Bi}_2\text{O}_2\text{CO}_3$, including the OV sites (Site 1 and Site 3) and the Bi sites (Site 2 and Site 4) were calculated (Fig. 6a and Fig. 6b). In Fig. 6c-f, H_2O adsorption at Site 1 and Site 3 ($\Delta E_{\text{ads}} = -1.28$ and -3.00 eV) are more thermodynamically favorable than at Site 2 and Site 4 ($\Delta E_{\text{ads}} = 0.11$ and -1.80 eV). H_2O molecules can be stabilized at the OVs by hydrogen bonds, and the stabilization of H_2O elongates the O - H bonds, leading to the H_2O dissociation. Thus, OVs favor the adsorption

and dissociation of H_2O molecules, and the formed surface $-\text{OH}$ can be regarded as Brønsted acid sites for the activation of chlorite. On this basis, chlorite adsorption on the surface hydroxyls were calculated to be exothermic ($\Delta E_{\text{ads}} = -0.62$ eV for BiOBr and -0.85 eV for $\text{Bi}_2\text{O}_2\text{CO}_3$) (Fig. 6g and Fig. 6h). The adsorption of chlorite on the surface hydroxyl leads to elongation of the $\text{O}-\text{H}$ bond, which is followed by the capture and transfer of photogenerated h^+ to the chlorite, causing further cleavage of the $\text{O}-\text{H}$ bond. Subsequently, chlorite accepts the dissociated H atom to form HClO_2 , which releases to solution and further decomposes to ClO_2 .

- In situ DRIFTS was further conducted to investigate the evolution of chlorite (Fig. S19). The characteristic vibrational band at 1024.2 cm^{-1} can be ascribed to the symmetric vibration of ClO_2 , which is strengthened all the time[61]. Two absorption bands at 1628.1 and 3226.7 cm^{-1} are assigned to $-\text{OH}$ stretching $\nu(\text{H}_2\text{O})$ and bending vibrations $\delta(\text{H}_2\text{O})$, which is due to the consumption of adsorbed water molecules[62, 63]. In addition to the absorption bands of adsorbed H_2O , one weaker peak of surface hydroxyl at 3757.2 cm^{-1} is corresponding to the $\nu(\text{OH})$ vibration of the bridging hydroxyls.[64, 65].
- Based on the results above, the mechanism of the ClO_2 -photocatalysis process is proposed in Fig. S20 and Fig. 7. In Fig. S20a, the higher Fermi level drives the majority electrons in BiOBr migrating to $\text{Bi}_2\text{O}_2\text{CO}_3$, resulting in a bending up/down band structure. Meanwhile, a built-in electric field can be formed from BiOBr to $\text{Bi}_2\text{O}_2\text{CO}_3$ until the two Fermi levels coming equally (Fig. S20b). When being irradiated, the internal electric field of BiOBr is able to inhibit the photogenerated electrons continuous migrating to $\text{Bi}_2\text{O}_2\text{CO}_3$, as well as the holes transferring from $\text{Bi}_2\text{O}_2\text{CO}_3$ to BiOBr . Therefore, the original strong reduction ability of BiOBr and the oxidation power of $\text{Bi}_2\text{O}_2\text{CO}_3$ in the hybrid can be well maintained. Concurrently, the weak reductive electrons at the conduction band of $\text{Bi}_2\text{O}_2\text{CO}_3$ and weak oxidizing holes at the valence band of BiOBr suffer a recombination via the built-in electric field, better suggesting the S-scheme characteristic in xyDBi heterojunctions (Fig. S20c).
- The production of ClO_2 can be proposed by two pathways, including the radical-induced (pathway 1) and OV-mediated (pathway 2) pathways. In pathway 1 (Fig. 7a), the photogenerated electrons in the CB of BiOBr react with dissolved O_2 to generate $\cdot\text{O}_2^-$ (Eq. 6). Subsequently, H_2O molecules can be oxidized by the produced $\cdot\text{O}_2^-$ to create $\cdot\text{OH}$ (Eq. 7 – 9). In addition, H_2O molecules can also be oxidized by h^+ to generate $\cdot\text{OH}$ (Eq. 10), followed by the reaction with ClO_2^- to generate ClO_2 (Eq. 11). In pathway 2 (Fig. 7b), H_2O molecules are adsorbed on surface OVs and dissociated into hydroxyl group, which can be regarded as a bridge for chlorite adsorption via hydrogen bond for Brønsted acid–base pairs. Then, the surface $-\text{OH}$ could act as channels for h^+ transfer and cleaved under visible light irradiation, donating protons to chlorite to form HClO_2 . The metastable HClO_2 is released to the aqueous solution and disproportionated to ClO_2 . Finally, all these oxidative species worked together on the degradation of BPA, which can be oxidized to smaller molecules and mineralized into inorganic species (Eq. 12).

- $e^- + O_2 \rightarrow \cdot O_2^-$ (6)
- $\cdot O_2^- + H^+ \rightarrow HO_2\cdot$ (7)
- $HO_2\cdot + H^+ + e^- \rightarrow H_2O_2$ (8)
- $H_2O_2 + e^- \rightarrow \cdot OH + OH^-$ (9)
- $h^+ + H_2O \rightarrow \cdot OH + H^+$ (10)
- $ClO_2^- + \cdot OH \rightarrow ClO_2 + OH^-$ (11)
- $ClO_2 + \cdot O_2^- + \cdot OH + h^+ + BPA \rightarrow \text{degradation products}$ (12)

4. Conclusion

- In summary, the combined ClO_2 -photocatalysis process generates ClO_2 through photocatalytic activation by $BiOBr/Bi_2O_2CO_3$ heterojunctions (xyDBi), which combines the advantages of a single photocatalytic system and ClO_2 oxidation. The conducted reaction system exhibited excellent degradation effect on BPA, showing great advantages in curbing the production of toxic byproducts. Compared to the single ClO_2 oxidation or photocatalytic process, the combined ClO_2 -photocatalysis process displayed superior resistance to various influencing factors, which were attributed to the involvement of various reactive species. The construction of the S-scheme heterojunctions enhanced the charge transfer efficiency, and the production of ClO_2 was confirmed to be derived from the radical-induced and OV-mediated pathways. The results of this study enrich the intrinsic relationship between photocatalyst defects and chlorite activation, substantiating the necessity for OV-abundant catalyst design. In addition, the clarity of mechanism of visible-light photocatalytic chlorite activation by heterojunctions further allows the vis/chlorite technique to be more competitive in water and wastewater treatment.

Declarations

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contribution

All the authors wrote the main manuscript text. Yuhan Wang: Project Administration, Formal Analysis, Funding acquisition Guocong Liu: Software, Formal Analysis, Funding acquisition Jinyu Yang: Project Administration, Software, Funding acquisition Yuanhao Wang: Project Administration, Formal Analysis Ming Lu: Formal Analysis, Software Zhu Liu: Investigation, Data Curation, Funding

Acknowledgments

The authors genuinely appreciate the financial support of this work from the National Natural Science Foundation of China (51909119), Guangdong Basic and Applied Basic Research Foundation (Grant No. 2024A1515110218), The Key Project of Guangdong Provincial Basic and Applied Basic Research Joint Fund (2024B1515120020), Key Scientific Research Projects of Regular Higher Education Institutions under the Guangdong Provincial Department of Education (2025ZDZX1037), "Hundred Thousand Project" Rural Science and Technology Commissioner Project (KTP20240327), Guangdong Basic and Applied Basic Research Foundation (No. 2025A1515140114), 2025 Guangdong Province Youth Innovative Talents Project (2025KQNCX091), Independent Innovation Foundation of Huizhou University (No. HZU202507).

Data availability

Data will be made available on request.

Acknowledgments

The authors genuinely appreciate the financial support of this work from the National Natural Science Foundation of China (51909119), Guangdong Basic and Applied Basic Research Foundation (Grant No. 2024A1515110218), The Key Project of Guangdong Provincial Basic and Applied Basic Research Joint Fund (2024B1515120020), Key Scientific Research Projects of Regular Higher Education Institutions under the Guangdong Provincial Department of Education (2025ZDZX1037), "Hundred Thousand Project" Rural Science and Technology Commissioner Project (KTP20240327), Guangdong Basic and Applied Basic Research Foundation (No. 2025A1515140114), 2025 Guangdong Province Youth Innovative Talents Project (2025KQNCX091), Independent Innovation Foundation of Huizhou University (No. HZU202507).

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Figures

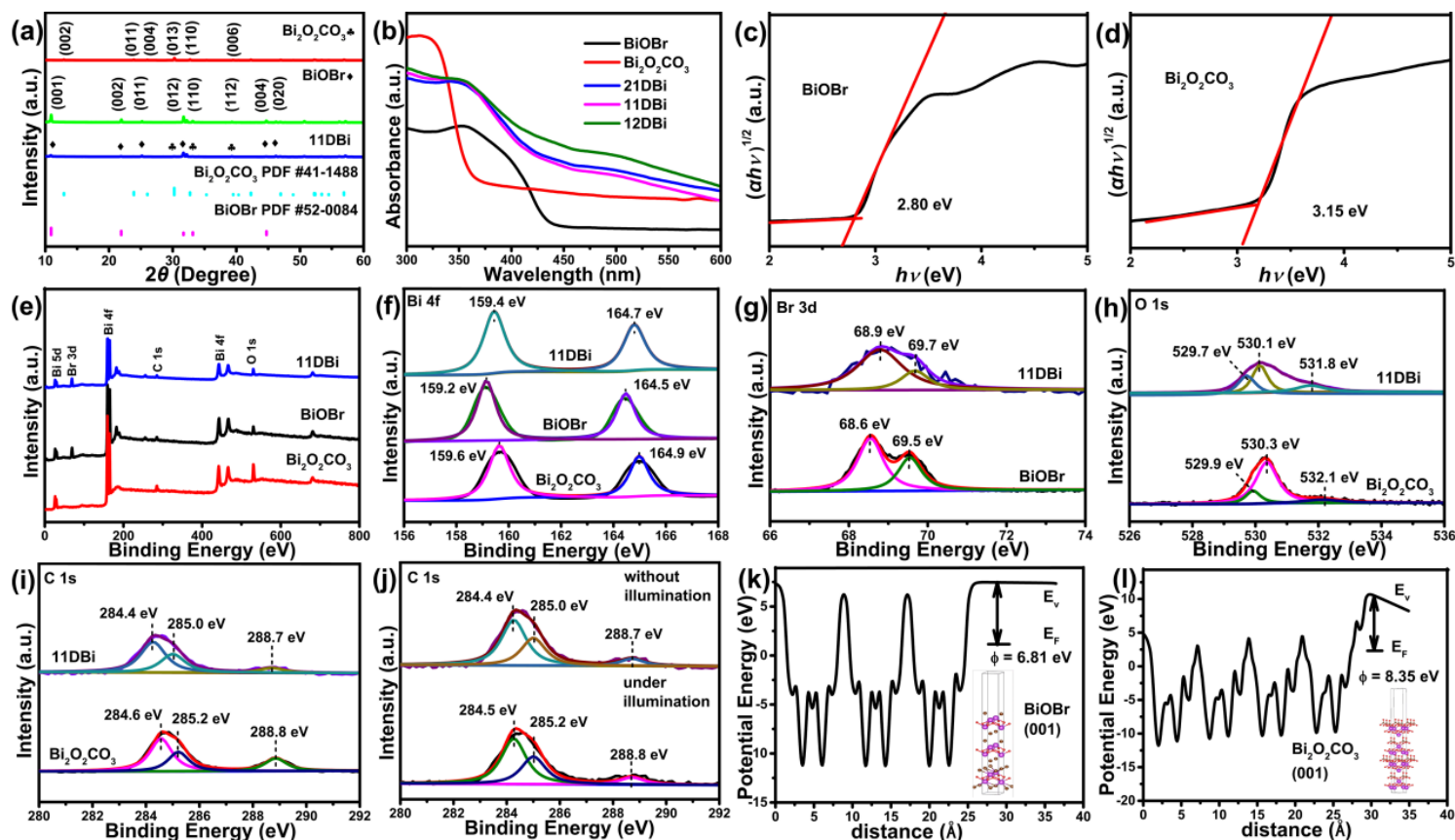


Figure 1

(a) XRD patterns, (b) UV-vis DRS of BiOBr, $\text{Bi}_2\text{O}_2\text{CO}_3$, and xyDBi, and band gap values of (c) BiOBr, (d) $\text{Bi}_2\text{O}_2\text{CO}_3$, XPS spectra of BiOBr, $\text{Bi}_2\text{O}_2\text{CO}_3$, and 11DBi: (e) full spectra, (f) Bi 4f, (g) Br 3d, (h) O 1s, (i) C 1s, (j) C 1s of 11DBi with or without illumination, and calculated work functions of (k) (001) plane of BiOBr, and (l) (001) plane of $\text{Bi}_2\text{O}_2\text{CO}_3$.

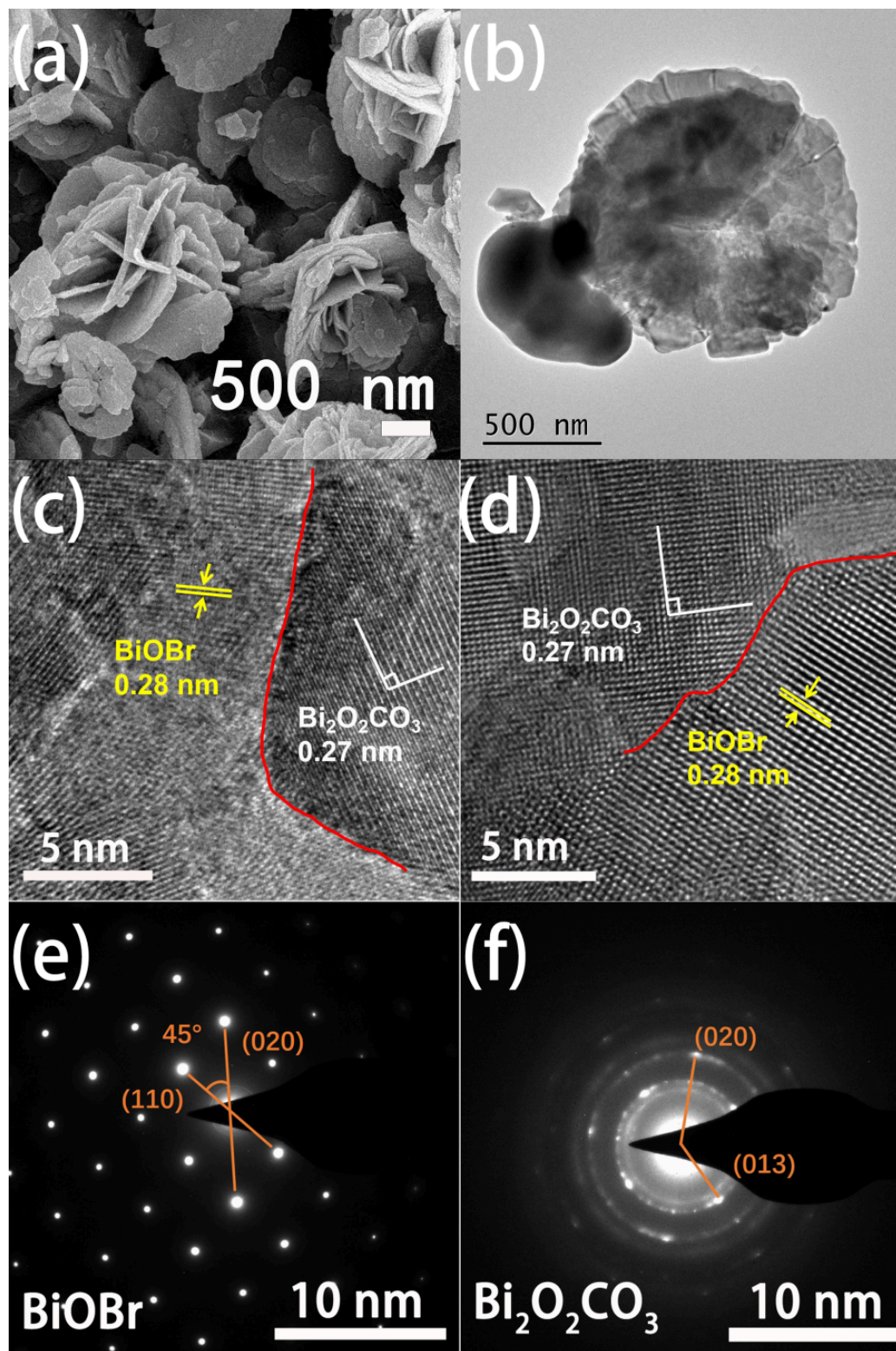


Figure 2

(a) SEM image, and (b-d) TEM images and high-resolution TEM images of 11DBi, Fourier transform maps of (e) BiOBr, and (f) Bi₂O₂CO₃.

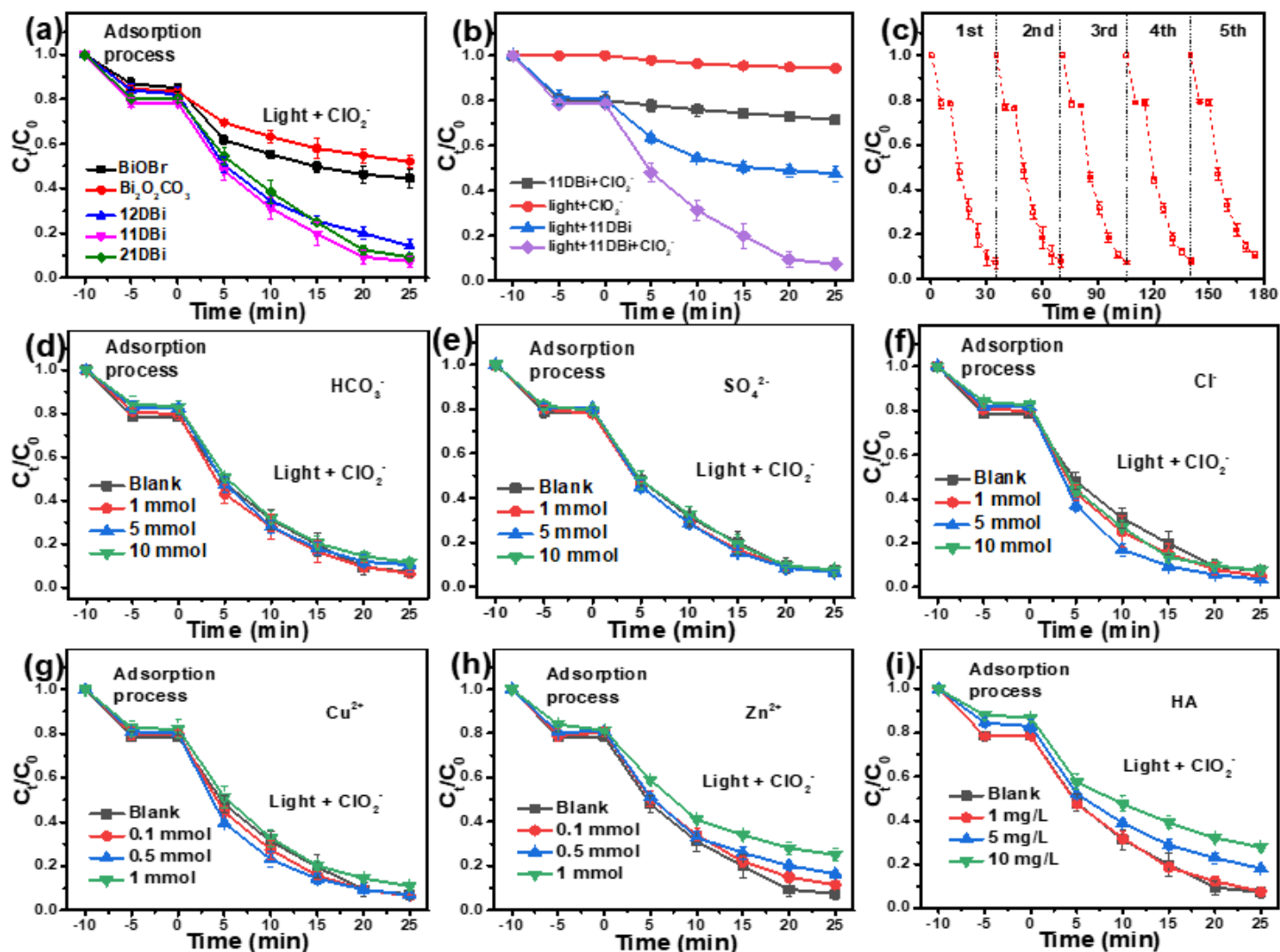


Figure 3

BPA degradation experiments: (a) different catalysts in the light/ ClO_2^- system, (b) different reaction systems, (c) successive recycling experiments, BPA removal with different interference factors: (d) HCO_3^- , (e) SO_4^{2-} , (f) Cl^- , (g) Cu^{2+} , (h) Zn^{2+} , (i) HA ($[\text{BPA}]_0 = 25 \text{ mg/L}$, 50 mg of photocatalyst, $[\text{NaClO}_2]_0 = 0.1 \text{ mM}$, light intensity: 30 mW/cm^2).

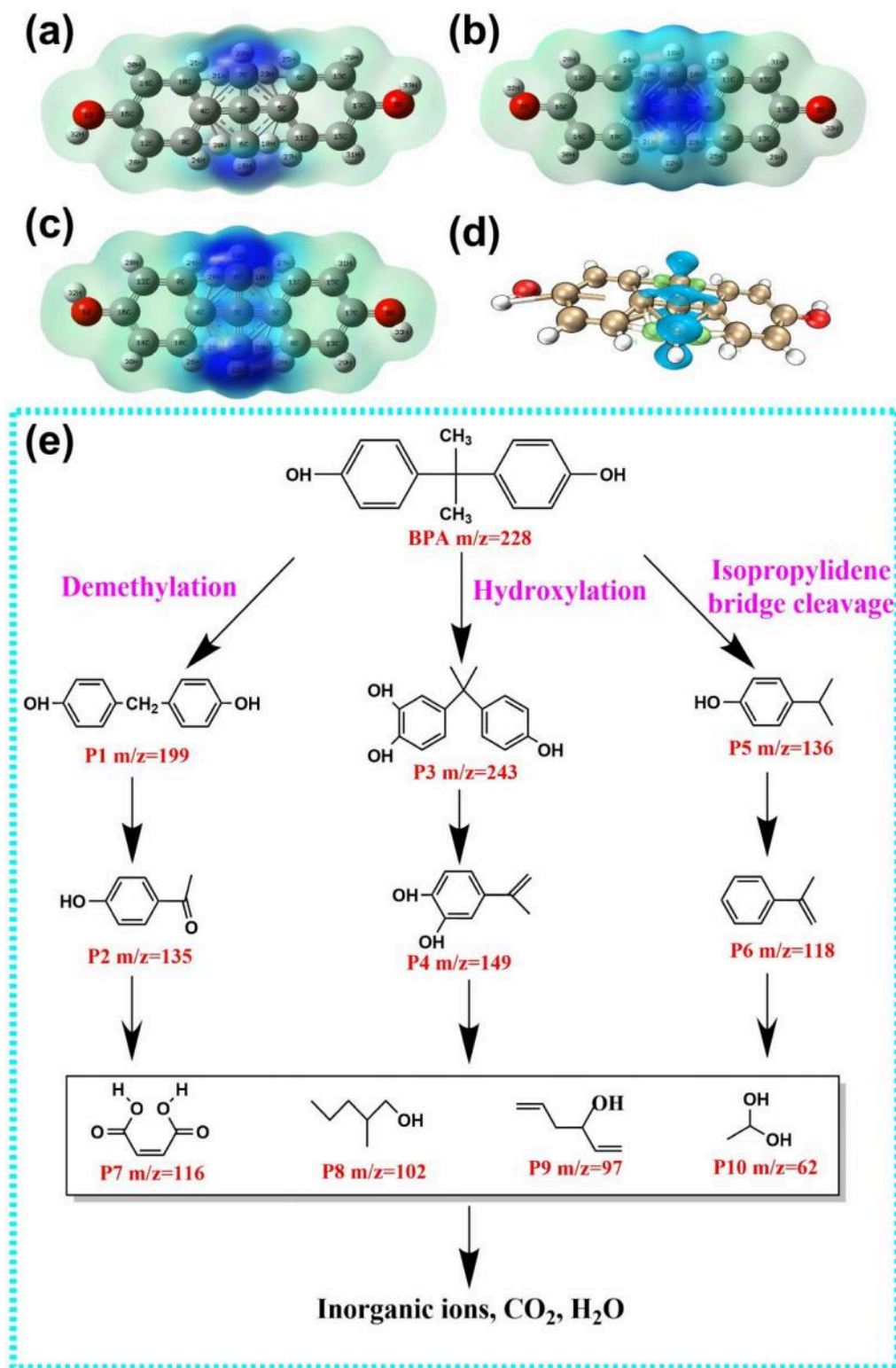


Figure 4

The Fukui function mapped electron density isosurface ($\rho = 0.01$ a.u.): (a) f^- , (b) f^+ , (c) f^0 , and (d) dual descriptor map (The isovalue is 0.002. Green and blue surfaces correspond to positive and negative regions, respectively), (e) the possible degradation pathways of BPA in the vis/11DBi/ ClO_2^- system.

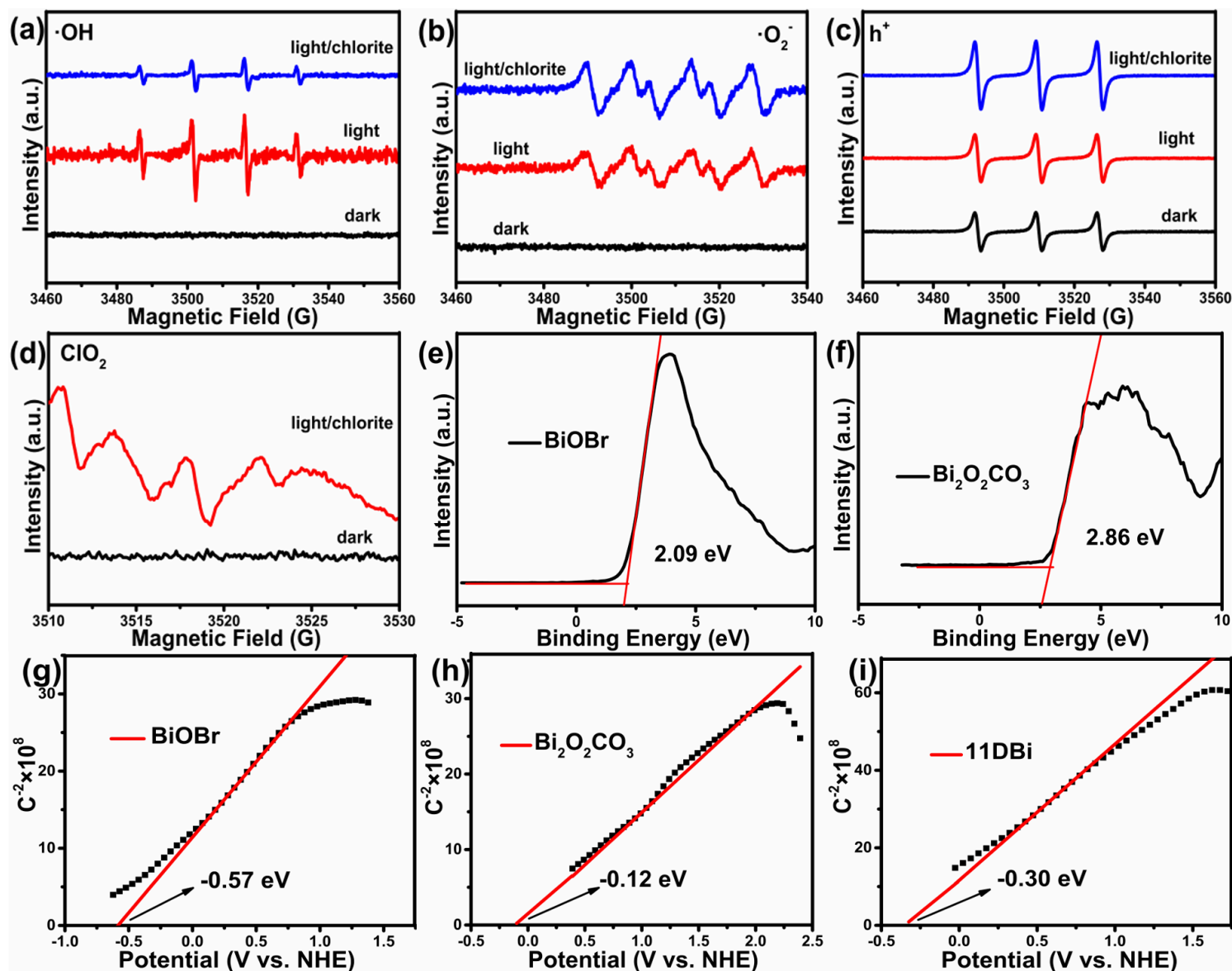


Figure 5

ROS generation in different reaction systems containing 11DBi: (a) $\cdot\text{OH}$ -DMPO, (b) $\cdot\text{O}_2^-$ -DMPO, (c) h^+ -TEMPO, (d) ClO_2 , XPS valence band spectra of (e) BiOBr, (f) $\text{Bi}_2\text{O}_2\text{CO}_3$, and Mott-Schottky plots of (g) BiOBr, (h) $\text{Bi}_2\text{O}_2\text{CO}_3$, (i) 11DBi.

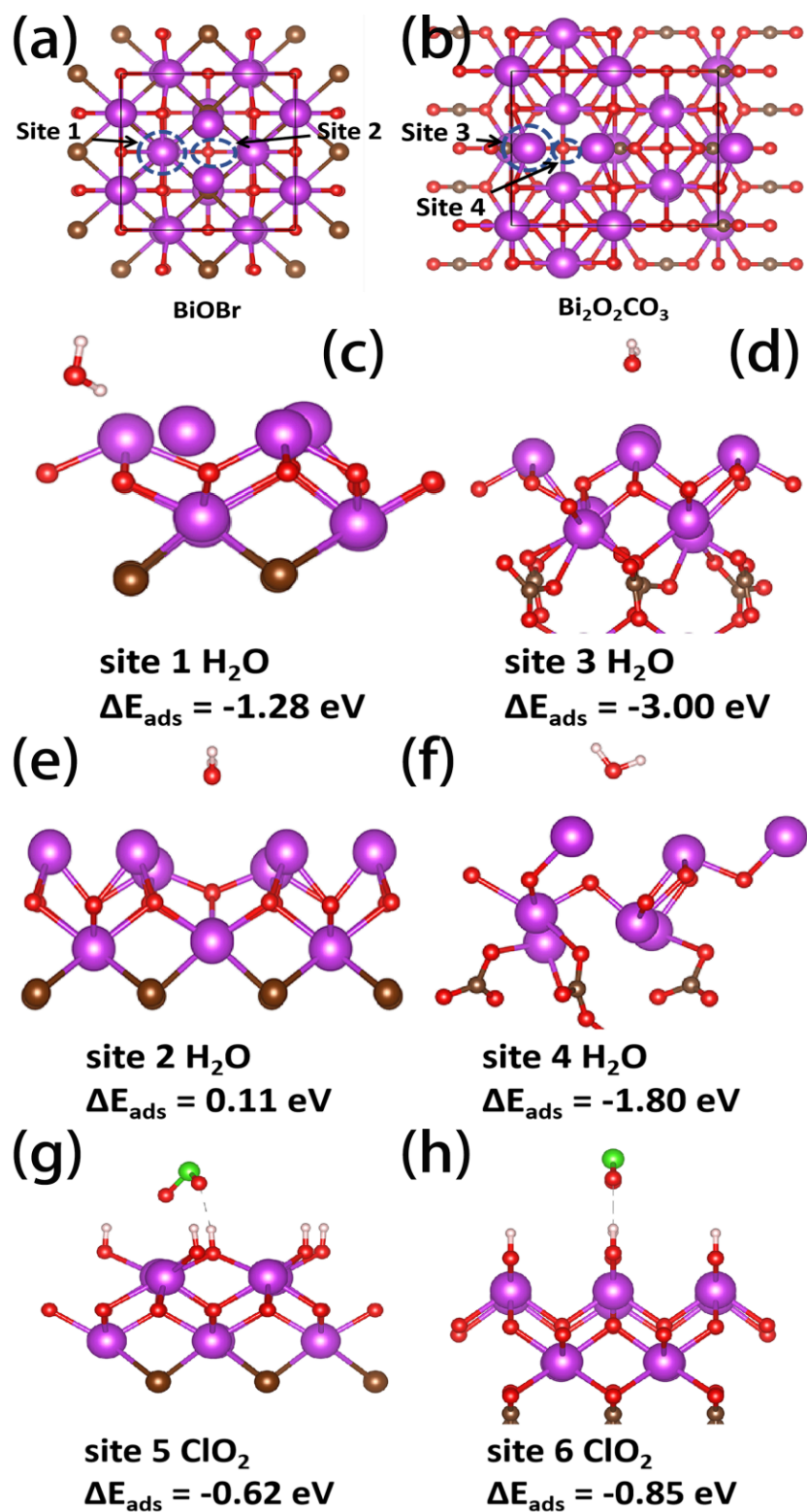


Figure 6

(a, b) Possible adsorption positions (Site 1 and Site 3: OV sites; Site 2 and Site 4: Bi sites) for H_2O adsorption; (c-f) relative adsorption energy of H_2O , (g, h) relative adsorption energy of ClO_2 .

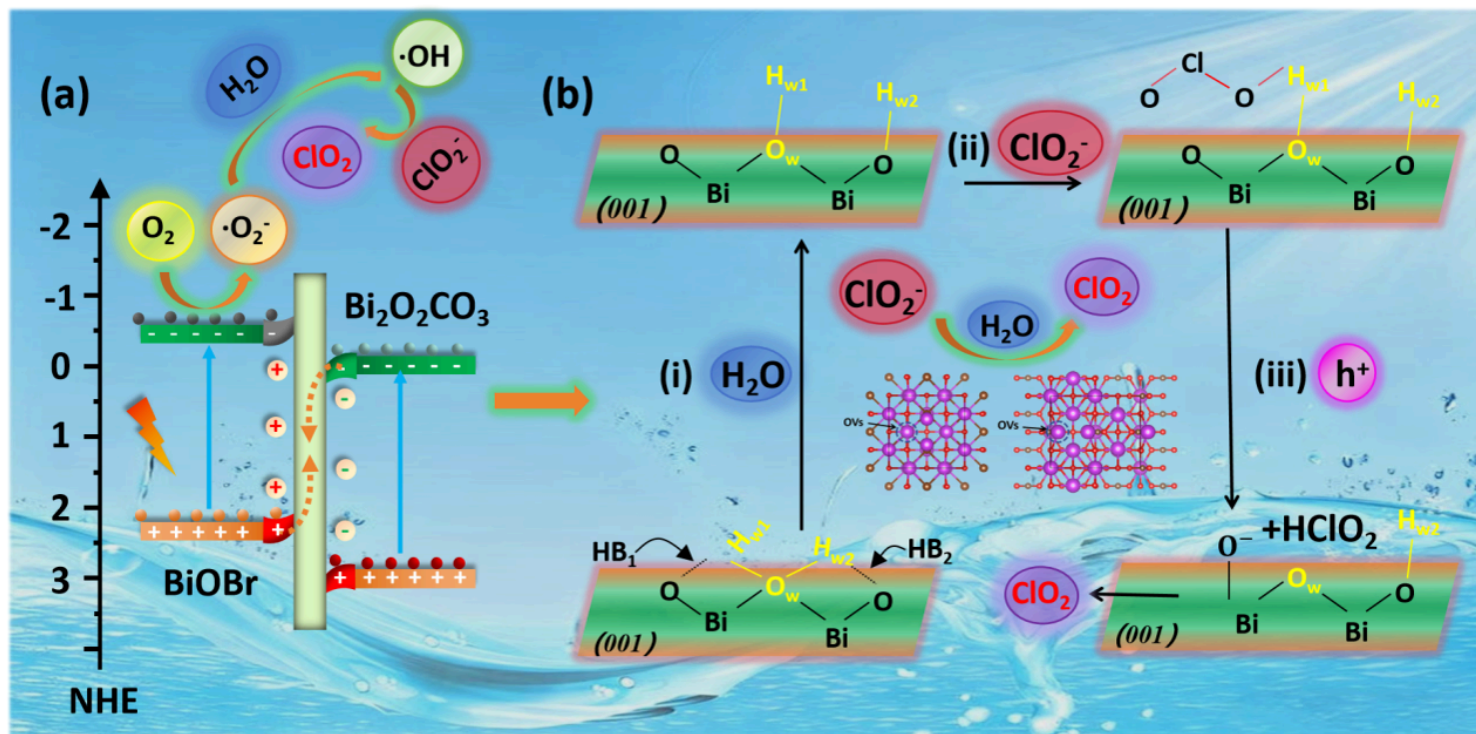


Figure 7

The BPA degradation mechanism in the in the vis/11DBi/ClO₂⁻ system.

Supplementary Files

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