Enhanced photoactivity and oxidizing ability simultaneously via internal electric field and valence band position by crystal structure of bismuth oxyiodide

Yan Guo\(^a\), Wexin Shi\(^{a,c,*}\), Yongfa Zhu\(^b,***\), Yongpeng Xu\(^a\), Fuyi Cui\(^c\)

\(^a\) State Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin Institute of Technology, Harbin 150090, China
\(^b\) Department of Chemistry, Tsinghua University, Beijing, 100084, China
\(^c\) School of Environment and Ecology, Chongqing University, Chongqing, 400044, China

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**A B S T R A C T**

Herein, the photoactivity and oxidizing ability of bismuth oxyiodide were enhanced simultaneously via crystal structure regulation. The internal electric field is enhanced via unit cell dipole with various crystal structures. The reduction of I in bismuth oxyiodide crystal increased dipole and crystal internal electric field, as a result promoting the photogenerated charge separation. This is also the intrinsic reason for the different photoactivity of bismuth oxyiodide with various crystal structures (BiOI, Bi\(_4\)O\(_5\)I\(_2\) and Bi\(_5\)O\(_7\)I). Irradiated below 420 nm, the photocatalytic activity of Bi\(_5\)O\(_7\)I is 4.65 times and 6.59 times greater than that of Bi\(_4\)O\(_5\)I\(_2\) and BiOI, respectively. Meanwhile, since the decreasing of valence band position for bismuth oxyiodide with the reduction of I, the oxidizing ability remarkably increase, resulting the mineralization ability significantly strengthened. The crystal structure regulation is a promising candidate for enhancing both photoactivity and oxidizing ability of photocatalysts simultaneously.

1. Introduction

Photocatalysis is a potential route for directly degrading organic pollutants in water into CO\(_2\) without chemical addition [1–3]. The photocatalytic activity depends on the ability of the photogenerated charge to participate in the chemical reaction. Therefore, the recombination of the electron and hole must be prevented as much as possible for a photocatalyzed reaction to be favored [4,5]. In principle, the electric field causes the charge to migrate directionally. Compared with the photoelectrochemical method, the internal electric field (IEF), an effective means to adjust the photoelectric properties of the material without increasing the energy consumption, is caused by the dipole [6–10]. In recent years, Bi-based materials, have been favored since their special layered crystal structure leading to possess an efficient IEF as a separation “accelerator” [9–14]. The IEF of BiOCl contributes to the improvement of hydrogen production efficiency [15]. Photocatalytic activity under visible light is promoted by enhancing the dipole of Bi\(_2\)MoO\(_6\) unit cell [16]. Not only the difference in the exposed crystal plane of Bi\(_2\)O\(_4\)Cl photocatalyst would affect the strength of its IEF [17], doping also affects the IEF by changing its crystal electron effect [12]. These studies provoke us to explore simpler strategies to enhance the IEF for promoting photogenerated charge separation.

In addition to the photoactivity, the mineralization degree of organic pollutants, governed by the band position of the photocatalysts, is another key indicator for evaluating photocatalysts. The reason is that the degradation products produced by the incomplete oxidizing may be more harmful to the environment than the target pollutants, causing secondary pollution [18–20]. Therefore, enhancing simultaneously photoactivity and oxidizing ability is essential particularly for photocatalysis used in environmental remediation. Recently, the organic photocatalyst material has realized the control of band position by flexibly designing molecular structure [7,21]. Inorganic photocatalysts as a comparison, most of studies indirectly control the band position by complicatedly introducing defects and doping intricately at present [5,22–25]. Consequently, designing directly the crystal structure of the inorganic photocatalytic material to adjust its band position for improving the oxidizing ability is of great importance and remains a challenge for the utilization of inorganic photocatalyst.

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\(^*\) Corresponding author: state Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin Institute of Technology, Harbin 150090, China.

\(^***\) Corresponding author.

E-mail addresses: swx@hit.edu.cn (W. Shi), Zhuyf@mail.tsinghua.edu.cn (Y. Zhu).

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Since the IEF is caused by the dipole inside the unit cell, it is anticipated that the change of crystal structure by changing the element content in the unit cell could enhance the dipole further strengthening the IEF, meanwhile, because the band position is affected by its crystal structure, this change could also adjust the band position, so that the separation efficiency of the photogenerated charge and the oxidizing ability of the active species could be simultaneously promoted. On the one hand, considering that bismuth oxyhalide as one of the most promising series of Bi-based photocatalysts is in full swing [6,26–29], and due to the layered structure connected by van der Waals force, it is relatively easy to adjust the halogen content by a simple method. On the other hand, although some literatures have systematically reported differences in photocatalytic activity of bismuth oxyhalide with different halogen contents, unfortunately, these reports do not pay attention to the changes in the IEF and do not give a general theory to disclose the intrinsic origin of the improved separation effect of photo-generated electron-hole pairs [30–33]. Therefore, studying the regulations of the crystal structure of bismuth oxyhalide in photoactivity and oxidizing ability and further revealing the essence of different activity is crucial for realizing efficient solar-driven environmental remediation. Note that the bismuth oxyhalide as far as different kinds of halide has the similar crystal structure [34,35], which makes the regulation law drawing inferences about other cases from one instance.

Herein, bismuth oxyiodide with the highest activity under visible light in bismuth oxyhalide was taken as an example, designing the crystal structure by changing the content of I element, and selected BiOI, Bi$_2$O$_5$I$_2$ and Bi$_2$O$_5$I with obvious structural features as research objects. Combining the density functional theory (DFT) computations and testing results, it is confirmed that the IEF and valance band position could be adjusted successfully by simply changing the crystal structure. This study not only reveals the mechanism of the photocatalytic difference in bismuth oxyiodide with different structures, but also provide an effective way to simultaneously enhance the photogenerated charge separation efficiency and mineralization ability via designing crystal structure.

2. Experimental

2.1. Sample preparation

2.1.1. Synthesis of BiOI

BiOI was prepared using a solvothermal procedure. Bi(NO$_3$)$_3$·5H$_2$O (0.486 g) was mixed with 25 mL water without stirring. Then, glycerol (25 mL) were poured into this mixture and stirred vigorously for 30 min. 1.0 mmol KI was added in 5 mL water, and then poured into the above mixture. Stirring for another 30 min, the mixture solution was sealed into a 100 mL stainless steel autoclave with Teflon in the presence of the above mixture. Stirring for another 30 min, the mixture solution was sealed into a 100 mL stainless steel autoclave with Teflon-lined and maintained at 160 °C for 6 h, and then cooled down to room temperature naturally. Finally, the products were collected by centrifugation, washed with deionized water and anhydrous ethanol, and dried at 50°C.

2.1.2. Synthesis of Bi$_2$O$_5$I$_2$ and Bi$_2$O$_5$I

Bi$_2$O$_5$I$_2$: BiOI prepared by the above method was used as precursor, which calcined at 440°C for 1 h at 3 °C/min heating rate.

Bi$_2$O$_5$I: In addition to calcine at 500°C, the preparation method was the same as that of Bi$_2$O$_5$I$_2$.

2.2. Sample characterization

The crystal phase of the samples was characterized by X-ray diffraction (XRD) (Bruker D8 X-ray) with Cu Ka radiation ($\lambda = 0.15418$ nm). The morphologies of the samples were captured on scanning electron microscopy (SEM, ZEISS Sigma 500), transmission electron microscope operated (TEM, JEM-1400 TEM) at an acceleration voltage of 100 kV and high-resolution transmission electron microscope (HRTEM, Tecnai F20) at an acceleration voltage of 200 kV. The chemical states of the samples were determined by X-ray photoelectron spectroscopy (XPS) in Thermo ESCALAB 250 with Al Ka X-ray ($h\nu = 1486.6$ eV) radiation. The optical properties of the samples were obtained by UV–vis diffuse reflection spectra (DRS) using a UV–vis spectrophotometer (Shimadzu, UV2550) with BaSO$_4$ as reference. The BET surface area were measured on an ASAP2020 instrument. The photoluminescence (PL) spectra was tested by a Perkin L55 fluoroscope spectrophotometer with excitation at 250 nm. The surface photovoltage spectra (SPV) were performed using a self-made device equipped with a lock-in amplifier on SR830 USA synchronized with a light chopper on SR540 USA. The surface potential images were operated at the surface potential mode of atomic force microscopy (AFM) on Bruker, ICON. The water droplets contact angles for the samples were measured using a contact angle analyzer (Data physics OCA20).

Photoelectrochemical measurements were performed on a three-electrode system using a VMP3 Multichannel Electrochemical Workstation with a working electrode (the samples covered FTO glass), a counter electrode (Pt wire), and a reference electrode (a saturated calomel electrode). The working electrode was irradiated with a 300 W Xe lamp equipped with a UVREF cut-off filter and the electrolyte with 0.5 mol/L Na$_2$SO$_4$ aqueous solution was used. Firstly, a sample (5 mg) was initially dispersed in the solvent of Nafion solution (Naphthol: ethanol = 1:9) to obtain a slurry. Then the slurry was coated onto the FTO glass and dried in an oven overnight to volatilize the solvent and then the BiOI, Bi$_2$O$_5$I$_2$ and Bi$_2$O$_5$I electrodes as the working electrodes were obtained. Electrochemical impedance spectroscopy (EIS) spectra was carried out under an AC perturbation signal of 10 mV range from 100 KHz to 0.1 Hz. Mott–Schottky plots were recorded with a scan rate of 5 mV/s at different frequency (1000, 2000, and 3000 Hz).

2.3. Photocatalytic performance evaluation

The degradation of bisphenol A (BPA) was used to evaluate the photocatalytic activity of all samples. A 300 W lamp equipped with a 420 nm cut-off filter is used as a visible light source, and a UVREF cut-off filter is used as a light source below 420 nm. A 30 mg sample was dispersed in 100 mL BPA solution (5 ppm for $\lambda \geq 420$ nm and 10 ppm for $\lambda < 420$ nm). The concentration of BPA was performed using an HPLC system (Waters Baseline 810) with a tunable UV absorption detector at 230 nm and a Supelco LC-18-DB column (250 mm × 4.6 mm). A total organic carbon (TOC) analyzer (Multi N / C 2100s) was used to analyze mineralization degree of the BPA solution.

2.4. Theoretical calculations

The first-principles calculations for bismuth oxyiodide with different crystal structure were performed by the plane-wave pseudopotential method implemented in the CASTEP package. The generalized gradient approximation (GGA) within the Perdew–Burke–Emzerhof (PBE) was used to calculate the exchange-correlation functional implemented. Ion-electron interactions were simulated by optimizing the ultrasoft pseudo-potentials of the elements in the compound. The cut-off energy was 420 eV for plane-wave function. Geometry optimizations were performed at a self-consistent convergence accuracy of $1 \times 10^{-5}$ eV atom$^{-1}$, a force of 0.03 eV Å$^{-1}$, a maximum displacement of $1 \times 10^{-3}$ Å, and a stress of less than 0.05 GPa.

3. Results and discussion

3.1. Crystal structure enhances dipole and IEF of unit cell

Aim to design different crystal structure of bismuth oxyiodide, calculation method was used to change the content of iodine (Fig. S1), and chose BiOI, Bi$_2$O$_5$I$_2$ and Bi$_2$O$_5$I with obvious structural characteristics among them as research objects (Fig. S2). The X-ray diffraction spectra
displays samples prepared successfully (Fig. S3), and the X-ray photoelectron spectroscopy further prove they are pure phases (Fig. S4). The scanning electron microscopy reveals that samples are all flower-like microsheets assembled by nanosheets with about 6 microns in diameter (Fig. S5 a–c). The square nanosheets that make up the flower ball are illustrated by transmission electron microscope (Fig. S5 d–f). As can be seen in Fig. 1, clear and ordered lattice fringes and Fourier transform images indicate high crystallinity characteristics of all samples. A clear be seen in Fig. 1, clear and ordered lattice fringes and Fourier transform – are illustrated by transmission electron microscope (Fig. S5 d).

Electrodeposition experiments not only prove that bismuth oxyiodide with different crystal structure were designed successfully, but also eliminated other interfering factors (crystallinity, morphology, scale and hydrophilicity) that may be triggered by different crystal structures [36], further exploring that the improvement of photocatalytic activity solely originated from IEF regulated by crystal structure.

In order to obtain the local IEF of BiOI, Bi4O5I2 and Bi5O7I, the DFT computations were carried out. Firstly, the [-Bi-O-], [-Bi-Bi-] and [-I-I-] part are divided along the layered stacking direction of bismuth oxyiodide crystal [35]. The [-I-I-] part in Bi4O5I2 and Bi5O7I are disturbed by O and Bi elements attributable to the decrease of I (Fig. 2a). To quantitatively express the effect of I reduction on the IEF in the crystal cell, the local electrostatic potential was calculated by DFT (Fig. 2b & Table S1). The AU of BiOI, Bi4O5I2 and Bi5O7I is 61.30 eV, 57.56 eV and 66.43 eV at [-Bi-O-], 40.26 eV, 42.72 eV and 47.06 eV at [-Bi-I-], 3.39 eV, 13.64 eV, and 28.22 eV at [-I-I-], respectively. The computational results state that the difference of local electrostatic potential is small in [-O-Bi-] and [-Bi-I-], but large in [-I-I-]. Bi5O7I with the lowest I content shows an electrostatic potential of 28.22 eV, which is 2.1 times and 8.3 times bigger than that of Bi4O5I2 (13.64 eV) and BiOI (3.39 eV), respectively, which attribute to the decrease of I making the IEF of [-I-I-] affected by O to varying degrees. Because of the strong electronegativity and charge-trapping ability of O, Bi5O7I with the lowest I content has the greatest IEF in [-I-I-]. The above DFT computations reveal that the reduction of I induces the enhancement of IEF.

Having identified the IEF by DFT computations, then applying experimental means. The intensity of IEF for the samples was measured using the model developed by Kanata [12,37], which proves that IEF strength is determined by surface potential and surface charge density. Firstly, the surface potential of samples was measured by the surface potential mode of atomic force microscopy [38,39] (Fig. 3a–c). The two-dimensional field of the surface potential distribution exhibits obvious difference among samples but relatively uniform for every sample. The surface potential distribution range of BiOI, Bi4O5I2 and Bi5O7I is -200 ~ -290, -315 ~ -335 and -380 ~ -410 mv, respectively (Fig. 3d). Secondly, Zeta potential is used to measure the potential of samples in 5 mg/L BPA, 10 mg/L BPA and water, the results of which are consistent with the trend of surface potential measured by AFM in air (Figs. 3e & S9). Then, the surface charge density was calculated from Zeta potential tested in water by using Gouy-Chapman model [40] (Fig. 3f, see supporting information for related discussions). Finally, after calculation, it is found that the IEF of Bi5O7I are 1.6 times and 3.4 times stronger than that of Bi4O5I2 and BiOI, respectively (Fig. 3g). Combining the experimental results with the theoretical calculation, the essence for the IEF controlled by the crystal structure of bismuth oxyiodide is that the reduction of I induces it enhanced, and the IEF of Bi5O7I with the lowest I content is the strongest.

3.2. Crystal structure decreases valence band (VB) position

The change in crystal structure of semiconductor materials is often accompanied by the change in the band gap structure. The oxidizing ability of photocatalyst depends on the band gap structure which is due to the occurrence of photocatalysis needs to fulfill the corresponding thermodynamic requirements [41–43]. According to the results of the

Fig. 1. HRTEM images of BiOI (a), Bi4O5I2 (b) and Bi5O7I (c).

Fig. 2. (a) Crystal structure and (b) DFT calculated local internal electric field ΔU for bismuth oxyiodide with different crystal structures. The purple, gray and red shaded parts represent the local electric fields of [-Bi-I-], [-I-I-] and [-Bi-O-], respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).
quenching experiment (Fig. S10), photogenerated hole is main active species towards bismuth oxyiodide photodegradation of BPA, whose oxidizing ability depends on the VB position. Therefore, in what follows the characteristic of VB is mainly focused. Firstly, the band gap structure was calculated by DFT, the electron band diagram shows that BiOI, Bi₄O₅I₂ and Bi₅O₇I have indirect semiconductor characteristics (Fig. S11). Secondly, the density of states reflects that the valence band maximum (VBM) is contributed mainly by O₂p states and I₅p states, whereas the contribution of Bi₆p states and Bi₆s states is insignificant (Fig. 4a). With the decrease of I content, the contribution of I to the VBM is gradually reduced, while the O increased. In addition, the VBM charge distribution of bismuth oxyiodide visually shows the devotion of I and O to VBM. For BiOI, the electrons of VBM are concentrated near I, indicating that electrons are mainly contributed by I. The electrons are mainly concentrated near I for Bi₄O₅I₂, but O also shows a few of electrons. With the further decreasing of I content, it is obvious that the electrons are distributed around the I and O atoms of Bi₅O₇I, indicating that the charge of O₂p gradually becomes the main force of VBM and the VBM of Bi₅O₇I is contributed by I and O together (Fig. 4b). The contribution of O₂p states and I₅p states to VBM obtained by integrating the state density map served to quantify the contribution difference between them (Fig. 4c). The contribution of O₂p states is 5.99 times greater than that of I₅p states, whereas this value is 2.17 and 0.84 for Bi₄O₅I₂ and Bi₅O₇I, respectively, which agrees well with the trend of the VBM electronic distribution map. Since the electronegativity of O is greater than I, the position of VB gradually reduces with the decrease of the I content.

Next, the band position of the samples was tested by characterization methods. Firstly, the Mott-Schottky curve was used to determine the conduction band (CB) position of the bismuth oxyiodide. The positive slope shows that all samples prepared are n-type semiconductors. In general, for n-type semiconductors, the flat band potential is about the conduction band potential [44]. Therefore, the conduction band potentials of BiOI, Bi₄O₅I₂ and Bi₅O₇I are estimated -0.67 eV, -0.33 eV and -0.52 eV (vs. standard hydrogen electrode, SHE), respectively (Fig. 5a). According to the Tauc curve, the forbidden bands of BiOI, Bi₄O₅I₂ and Bi₅O₇I are 1.69 eV, 2.00 eV and 2.75 eV, respectively (Fig. 5b), which is the exactly same order as the DFT computations. Then, the position of VB is found to be 1.02 V, 1.67 V, and 2.23 V, respectively. The band position of the samples derived from the characterization methods are summarized in Fig. 5c, which shows that the position of VB of BiOI with the most I is the highest, followed by Bi₄O₅I₂.
and Bi$_2$O$_3$I. The testing results combined with DFT computations prove that the reduction of the I in the bismuth oxyiodide of different crystal structures regulates the position of VB.

3.3. Crystal structure enhances IEF and photoactivity

Photodegradation of BPA was carried to probe the effect of the IEF regulated by crystal structure on photocatalytic activity. The activity of Bi$_4$O$_5$I$_2$ and Bi$_5$O$_7$I was almost the same under visible light irradiation ($\lambda \geq 420$ nm), which were obviously better than BiOI (Figs. S12 and 13). As shown in Fig. 6a, Bi$_4$O$_5$I$_2$ has the highest apparent rate constant (0.07676 min$^{-1}$) under visible light irradiation, rather than Bi$_5$O$_7$I (0.06802 min$^{-1}$) with the strongest IEF. What should be explained is that the UV–vis reflection spectra suggests that the samples differ greatly in the visible light absorption range (Fig. S8). The absorption band edge of BiOI with the smallest IEF could reach 682 nm, which means generates more photogenerated charge under visible light irradiation. The absorption band edge of Bi$_5$O$_7$I with the strongest IEF is only 421 nm, and Bi$_4$O$_5$I$_2$ is between the two, with an absorption edge of 541 nm. This means that BiOI has the strongest visible light capture capability, Bi$_4$O$_5$I$_2$ is second, and Bi$_5$O$_7$I is the weakest. Even so, the apparent rate constant of Bi$_5$O$_7$I is 20.01 times higher than that of BiOI and only slightly lower than Bi$_4$O$_5$I$_2$ (Fig. 6a). These results not only imply that strong IEF can greatly improve the separation efficiency of photogenerated charges so that improving the photocatalytic activity, but also indicate that the separation efficiency of photogenerated charges is a decisive factor for photoactivity. In order to eliminate the influence of the absorbed light, the photocatalytic degradation driven by the conditions of $\lambda \leq 420$ nm was carried out, where the samples absorbance is nearly consistent. Interestingly, compared with the other two, Bi$_5$O$_7$I has the best activity, whose apparent rate constant (0.64012 min$^{-1}$) is 4.65 and 6.59 times higher than that of Bi$_4$O$_5$I$_2$ (0.13779 min$^{-1}$) and BiOI (0.09714 min$^{-1}$), respectively. After eliminating the influence of absorbed light on photocatalytic activity, it is directly proved that the photocatalytic activity is in tune with the IEF. The larger the IEF, the stronger the photocatalytic activity (Fig. 6b).

To gain deeper insights into the mechanism of IEF on photoactivity, the difference in photogenerated charge separation of samples prepared by characterizing carrier behaviors at the ensemble level have been systematically studied. Under $\lambda \leq 420$ nm irradiation, the signal of surface photovoltage enhances significantly with the decrease of I content (Fig. 6c). The reason is the enhancement of IEF increase the number of holes reaching the surface of photocatalyst. Further, the same results have been observed in photocurrent response test under $\lambda \leq 420$ nm irradiation (Fig. 6d). The surface photovoltage and photocurrent intuitively reflect that IEF produced by the unit cell dipole

![Fig. 5.](image_url) (a) Mott-Schottky plots, (b) Plots of the transformed Kubelka–Munk function vs. the light energy and (c) tested results of the band position for samples prepared.

![Fig. 6.](image_url) (a) Comparison of the apparent rate constants under visible light irradiation ($\lambda \geq 420$ nm) on photodegradation of BPA, (b) variation of the IEF magnitude and apparent reaction rate constants under $\lambda \leq 420$ nm irradiation on photodegradation of BPA (The IEF magnitude value of BiOI is set as “1”), (c) surface photovoltage under $\lambda \leq 420$ nm irradiation, (d) Photocurrent under $\lambda \leq 420$ nm irradiation of samples prepared, (e) photoluminescence spectra and (f) cyclic voltammograms curves (inset: electrochemical impedance spectroscopy) for samples prepared.
plays an extremely important role in the separation efficiency of the photogenerated charge. The maximum PL intensity of B1O1 and the weakest value of Bi2O3·I directly indicate the former has the highest recombination rate of photogenerated electron holes, and the latter has the lowest, simultaneously indicates indirectly that strong IEF contributes to the separation of photogenerated electron-hole pairs (Fig. 6e). In addition, a 0.33 V BPA oxidizing peak is observed in the cyclic voltammetry curve, in which Bi2O3·I exhibits the strongest current signal when BPA was oxidized (Fig. 6f), and Bi2O3·I has the smallest Nyquist plot diameter (illustration in Fig. 6f), further reveals the charge transfer rate of photocatalyst strongly depends on its IEF [45,46]. The above data powerfully prove that the IEF regulation directly affects the separation efficiency of photogenerated electron-hole pairs. The huge IEF could remarkably accelerate the photogenerated charges transport speed.

3.4. Crystal structure decreases VB position to boost photocatalytic oxidizing ability

As argued before, the mineralization degree of bismuth oxyiodide is strongly determined by its position of VB. To assess this influence, the mineralization tests of photodegradation of BPA were explored. Surprisingly, although the degradation rate for Bi2O3·I2 is the same as that for Bi2O3·I (λ ≥ 420 nm, t = 60 min), the latter has an enhanced total organic carbon (TOC) removal rate, which means that Bi2O3·I possesses stronger oxidizing ability. Then aim to rule out the effects of light absorption, the mineralization degree under λ ≤ 420 nm irradiation of samples was tested in 10 min. Encouragingly, the removal rate of TOC in Bi2O3·I, Bi4O5I2 and Bi5O7I increased accordingly, which agrees well with the trend of degradation strengthen (Fig. 7a). For photodegradation where the hole is the main active species, the magnitude of external potentials provided by photogenerated hole directly determines whether the oxidizing reaction can proceed spontaneously. The potential of photogenerated hole for BPA degradation, which is defined as the energy difference between the VBM and the BPA oxidation potential (Uh), was determined to be 0.69 V, 1.34 V and 1.90 V for Bi1O1, Bi4O5I2 and Bi5O7I, respectively (See Table S3 for more details on calculations). As shown in Fig. 7b, a value of positive Uh indicates that all samples prepared able to photodegrade BPA by holes. More importantly, the gradually increasing Uh directly clarifies that the oxidizing ability of the holes is enhanced as the I content decreases. In addition, higher Uh also manifests that the photogenerated hole of bismuth oxyiodide would prefer to be transferred to react with BPA rather than with themselves, resulting in a good resistance to the photoinduced corrosion, which is also in line with the recycle performance test results of Bi5O7I (Fig. S14).

To fully understand the mineralization process of BPA in the Bi5O7I system under λ ≤ 420 nm irradiation, the main degradation intermediates and the possible degradation path were analyzed. Firstly, UPLC was used to test the concentration change of BPA photodegradation. As shown by the UPLC curve in Fig. 8a, the peak area of BPA (retention time = 3.33 min) decreased significantly with the progress of photocatalytic process, but the peak area of some intermediate products (retention time = 0.99, 1.61, 1.82, 2.48 min) increased first and then decreased, which also directly suggests that Bi2O3·I has a great mineralization ability. To identify these intermediates, analysis was then performed using UPLC/MS/MS. A total of 7 intermediate products were detected during Bi3O2·I photodegradation BPA. The molecular structure and MS/MS fragmentation information of the oxidation products are displayed in Fig. S15. Based on these degradation intermediates, the possible degradation pathway of BPA is proposed in Fig. 8b. Since the electron density of each aromatic ring is increased by the electron donating hydroxyl group, the bond connecting the two aromatic rings in BPA is more likely to be broken [47,48]. The β-cleavage of the isopropyl group between the two phenyl groups is generated, yielding phenol (m/z = 93) and 4-isopropylphenol (m/z = 133). Phenol is generally oxidized to hydroquinone, but it has not been detected as hydroquinone is not easily ionized [49]. The active oxygen component further oxidizes them to 1-(4-methyl phenyl) ethanone (m/z = 135). Then, the intermediate products were subsequently attacked to form small organic acids such as 1,5-hexadiene-3-ol (m/z = 97), maleic acid (m/z = 115), glycolic acid (m/z = 75) and acetic acid (m/z = 59) eventually mineralized.

The above data implies that the mineralization ability of Bi2O3·I with the lowest position of valence band is the best in both ultraviolet and visible light region, which strongly reveals that the crystal structure decreases the position of VB as a result enhancing the photocatalytic oxidizing ability. Therefore, as illustrated in Fig. 9, crystal structure adjustment achieves simultaneous enhancement of photoactivity and oxidizing ability.

4. Conclusions

In summary, the regulation of bismuth oxyiodide crystal structure on its unit cell dipole and VB position was elucidated. The reduction of I enhances the dipole and IEF as a result promoting the separation of photogenerated charges. Especially, the VB position of bismuth oxyiodide decreasing with the reduction of I, leading the oxidizing ability of holes strengthened. This work vividly reveals that bismuth oxyiodide crystal structure regulation could be utilized as a highly efficient way for improving simultaneously both photoactivity and oxidizing ability.

Declaration of Competing Interest

None.
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Appendix A. Supplementary data

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