

THE HIGHLY EFFICIENT BiOCl/KBiO₃ p-n HETEROJUNCTION PHOTO-CATALYSTS UNDER VISIBLE LIGHT IRRADIATION

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Received: 05/16/2024; accepted: 07/29/2024; published online: 09/17/2024

BiOCl/KBiO₃ p-n heterostructures with hierarchical mesoporous architectures were successfully synthesized via a facile *in situ* method. The X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM) results indicate the formation of heterojunctions between BiOCl and KBiO₃. The photocatalytic performance of the as-prepared samples was investigated by the degradation of dye Rhodamine B (RhB) under visible light irradiation. BiOCl/KBiO₃ composite has never been used to photodegrade the RhB which is a common dye and very difficult to degrade. The results demonstrated that KBiO₃ combined with proper amount of BiOCl nanosheets exhibited high efficiency in the photocatalytic process, and BiOCl/KBiO₃ with the molar ratio of 70/30 demonstrated the highest photocatalytic activity due to its large surface area, excellent charge separation characteristics and the suppressed recombination of electron-hole pairs. The results of active species detection reveal that the superoxide radical anions (O₂⁻), hydroxyl free radicals (·OH), photogenerated holes (h⁺) and photogenerated electrons (e⁻) reactive species work together for the photocatalytic degradation of RhB. A possible and new mechanism of photocatalysis that differs from other teams was also explored and proposed. The present study will benefit the development of the new p-n heterojunction photocatalysts and would be of great importance to meet ever-increasing environmental demands in the future.

Keywords: BiOCl/KBiO₃; p-n heterojunction; photocatalytic activity; visible light; photocatalytic mechanism.

INTRODUCTION

Photocatalytic technology has attracted much attention recently because of the shortage of clean water sources and demand for environmental protection.¹⁻³ At present, although TiO₂ has been extensively investigated and widely employed, its use limited due to its low separation efficiency of photo-induced electron-hole pairs and wide bandgap.⁴⁻⁶ In order to improve the efficiency of solar energy, numerous efforts have been devoted to exploiting visible-light driven photocatalysts with high catalytic activity and high stability.⁷

With increasing environmental concern, bismuth containing semiconductors have drawn the attention of many researchers during last decade. Recently, many bismuth containing photocatalysts with high activity for environmental application or water splitting, such as BiVO₄,⁸⁻¹² Bi₂WO₆,¹³⁻¹⁹ CaBi₂O₄, Bi₂O₃,²⁰ BiFeO₃,²¹⁻²³ and Bi₁₂TiO₂₀²⁴⁻³⁰ have been reported. Most bismuthates are trivalent and the Bi³⁺ cation has two 6s electrons and a d¹⁰ closed shell. The Bi 6s and O 2p hybrid orbital is broad and the resulting band gap becomes narrow.³¹⁻³⁶ Therefore, it exhibits exciting activity under the visible light irradiation. While Bi⁵⁺ has an empty 6s orbital but still has a d¹⁰ closed shell. Therefore, pentavalent bismuthates must have different electronic structure compared with trivalent bismuthates.³⁷

In recent years, pentavalent alkali bismuthates have been investigated as new photocatalysts. Among them, KBiO₃ is characterized and tested in many ways. It shows cubic structure with the tunnel segments which is similar to NaBiO₃ with ilmenite structure, as both are formed by edge-sharing octahedral.³⁸ Zheng *et al.*³⁹ have reported that KBiO₃ has efficient photocatalytic activities for many kinds of dyes under the visible light irradiation. Nevertheless, there are some restrictions for practical applications of pure KBiO₃ due to the fast recombination rate of photogenerated electron-hole pairs. The p-n

heterojunction, which can be an efficient and promising method for enhancing the photocatalytic activity of semiconductor photocatalyst can extend the probability of photo-induced electron-hole separation via an additional internal electric field. The p-type semiconductor BiOCl, can be an outstanding candidate⁴⁰ for the heterojunction with KBiO₃ due to its interesting photocatalytic activity. BiOCl has special layered structure with [Bi₂O₂]²⁺ slabs interleaved with two slabs of Cl atoms.^{41,42} This special structure creates static electric fields that enable the effective separation of photo-induced electron-hole pairs, especially along the [001] direction.⁴³

In this work, a facile *in situ* method for the preparation of p-n type heterojunction, BiOCl/KBiO₃ nanocomposite, is illustrated. The phase structures, morphologies and optical properties of as obtained catalysts will be given. The improved photocatalytic property of BiOCl/KBiO₃ composites for Rhodamine B (RhB) degradation through the synergistic effect between BiOCl and KBiO₃ is also examined. It is never tried to use BiOCl/KBiO₃ nanocomposite to photodegrade the RhB which is a common dye and very difficult to degrade. The possible and new mechanism of enhanced photocatalytic activity for the p-BiOCl/n-KBiO₃ heterojunction is discussed in detail.

EXPERIMENTAL

Materials and methods

Chemicals used in the experimental procedure were of analytical grade and were used without further treatment. These include NaBiO₃ (≥ 80.0%, Aldrich, India), KOH (≥ 95.0%, Samchun, Pyeongtaek, Korea), HCl (35-37%, Samchun, Yeosu, Korea), RhB (99.99%, Samchun, Pyeongtaek, Korea), ethanol absolut (99.8%, Haen AG, Hannover, Germany) and ethanol (95%, Samchun, Yeosu, Korea) which were purchased from Sigma-Aldrich. RhB is a common dye in the triphenylmethane family, which contains four *N*-ethyl groups at either side of the xanthene ring. The photolysis of RhB in visible

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Associate Editor handled this article: Cassiana C. Montagner

light is very weak and basically negligible. In this study, it was chosen as the target organic pollutant to investigate its degradation behavior over the p-BiOCl/n-KBiO₃ heterojunction under visible light irradiation. The molecular formula of RhB is C₂₈H₃₁C₁N₂O₃, and its chemical structure is shown in Figure 1S (Supplementary Material).

Synthesis of KBiO₃ nanoparticles

KBiO₃ was synthesized using a solid state reaction method with KOH and NaBiO₃.³⁸ KOH and NaBiO₃ were mixed sufficiently with the K/Bi molar ratio of 2, and then the mixture was heated at 250 °C for 2 h. After the reaction, the resultant powder was washed five times with water to remove alkaline components. Finally, brown powder was obtained after drying the washed powder in an oven at 75 °C.

Synthesis of BiOCl/KBiO₃ p-n heterojunction composites

The BiOCl/KBiO₃ heterostructures were synthesized via a facile *in situ* method.⁴⁴ First, 0.4 g of KBiO₃ powder was dissolved in the solution made of 20 mL of absolute ethanol and 10 mL of deionized water, with ultrasonication for 30 min. Then the mixture was stirred for 30 min at room temperature. Second, 0.4 mL of HCl aqueous solution (7.2 wt.%) was slowly added into the above mixed solution under vigorous stirring and then it was kept for another 4 h at room temperature with continuous stirring. Subsequently, the precipitates were collected and washed using distilled water and absolute alcohol for three times respectively. Finally, the sample was dried overnight in an oven at 75 °C. Thus, BiOCl/KBiO₃ samples with the molar ratio of 15/85 was successfully prepared. Using the same technique with different amount of HCl, BiOCl/KBiO₃ samples with different molar ratio of 30/70, 50/50, 70/30, 85/15, 100/0, respectively, were obtained.

Characterization of samples

Crystallographic information was recorded by using a powder X-ray diffractometer (Rigaku, Tokyo, Japan). The morphology and particle size were determined by a scanning electron microscopy (SEM, Hitachi, S-4800, Ibaraki, Japan). The oxidation states of elements of the sample were analyzed by X-ray photoelectron spectroscopy (XPS, Thermoscientific K-alpha, USA). The Brunauer-Emmett-Teller (BET) surface area of the catalysts was analyzed by nitrogen adsorption apparatus (Miniflex600, belsorp, Japan). UV-Vis absorption spectra were recorded on a spectrophotometer (UV-2450, Shimadzu, Kyoto, Japan) from 300 to 800 nm. The chemical composition was examined using energy dispersive spectroscopy.

Photocatalytic activity test

A 300 W Xe lamp (Excelitas Tech., Fremont, USA) was used as the light source with a 400 nm cutoff filter to provide visible-light irradiation. In each experiment, 0.100 g of photocatalyst was added into 500 mL of RhB solution (10 mg L⁻¹). Every 10 min of the irradiation time, 5 mL of the suspension was collected, then centrifuged (5500 rpm, 10 min) to remove the photocatalyst particles. The concentration of RhB was measured from its maximum absorption peak at a wavelength of 553 nm.

RESULTS AND DISCUSSION

X-ray powder diffraction (XRD) analysis

For pure KBiO₃, it crystallizes in cubic KSbO₃ type structure and the XRD patterns match well with the reported patterns for KBiO₃

(PDF card No. 47-0879). For the pure BiOCl, all peaks can be indexed to the tetragonal system of BiOCl (PDF card No. 85-0861). For BiOCl/KBiO₃ composites with the molar ratio of 15/85, all the diffraction peaks of KBiO₃ can be found, and the intensity of the peaks become weaker due to the addition of BiOCl. The characteristic peak of BiOCl (110) can also be observed, but the intensity of the peak is very low because of the low content of BiOCl. Other characteristic peaks of BiOCl are not observed for the same reason. This result shows a coexistence of BiOCl and KBiO₃ and suggests that BiOCl and KBiO₃ are coupled together successfully.

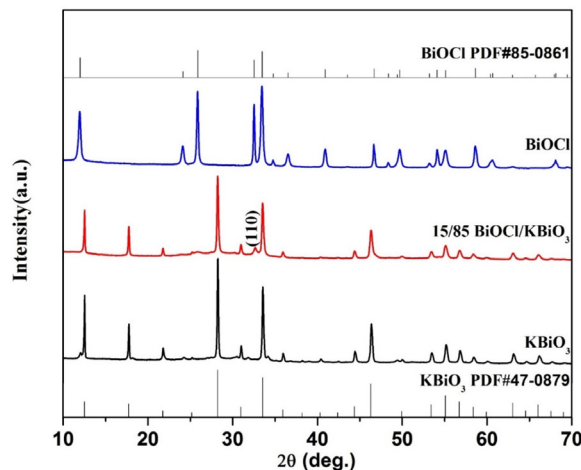


Figure 1. XRD pattern of the KBiO₃, BiOCl and BiOCl/KBiO₃ with the molar ratio of 15/85

X-ray photoelectron spectroscopy (XPS) analysis

The XPS spectrum of BiOCl/KBiO₃ with the molar ratio of 70/30 is shown in Figure 2a. The special peaks in the figure demonstrate that the compound is composed of Bi, O, Cl and K elements. Figure 2b shows the characteristic peaks of Bi. The Bi 4f peak shows asymmetrical forms, and the Bi 4f 5/2 and Bi 4f 7/2 peaks are deconvoluted into two bimodal peaks at binding energies of 164.64 and 162.25 eV, and at 159.33 and 160.72 eV, respectively. This result indicates that both Bi³⁺ and Bi⁵⁺ exist in the BiOCl/KBiO₃ with the molar ratio of 70/30. Both of the two bimodal peaks show very different intensities. This result can be explained by the very different contents of BiOCl and KBiO₃ in the compound. Based on the results of XPS and XRD, it is believed that BiOCl/KBiO₃ heterojunction composites are successfully synthesized.

Scanning electron microscope (SEM) analysis

The typical SEM images of KBiO₃, BiOCl and BiOCl/KBiO₃ with the molar ratio of 70/30 are shown in Figures 3a-3c. For pure KBiO₃, it is composed of irregularly shaped particles with diameters of 50-100 nm (Figure 3a). The pure BiOCl comprises many hierarchical mesoporous architectures⁴⁵ (Figure 3b). BiOCl/KBiO₃ with the molar ratio of 70/30 shows hierarchical mesoporous architectures which is similar to the pure BiOCl because of the larger content of BiOCl (Figure 3c). The structure provides a high surface area for BiOCl/KBiO₃ composites, suggesting its strong adsorption ability, and it is beneficial to the separation of photo generated electron-hole pairs. To further investigate elemental composition and distribution uniformity, the elemental maps of the selected area on BiOCl/KBiO₃ with the molar ratio of 70/30 are displayed in Figures 3d-3g, which indicates that homogeneous distribution of Bi, Cl, O and K constituting elements in the sample. These analyses indicate

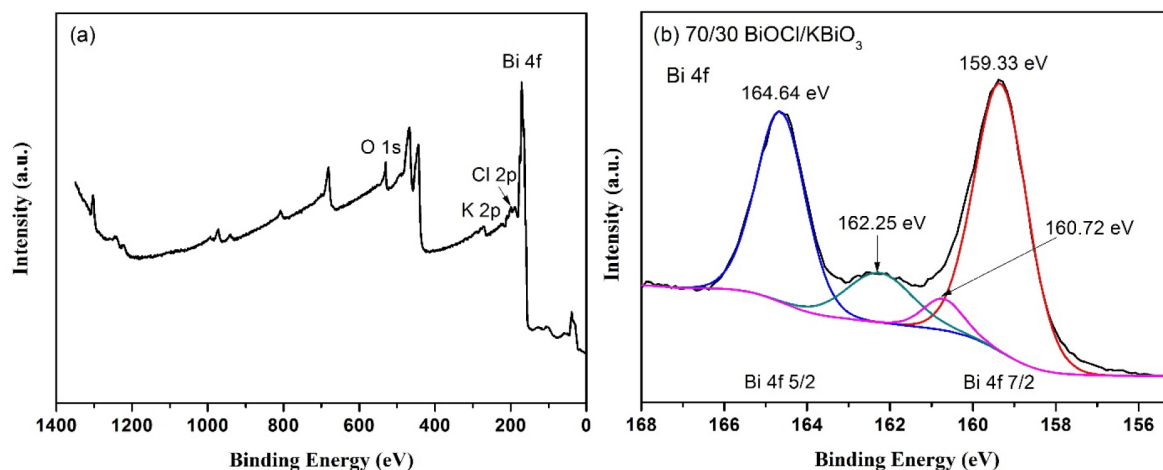


Figure 2. (a) XPS spectrum of BiOCl/KBiO₃ with the molar ratio of 70/30 and (b) high-resolution XPS spectra of Bi 4f

that BiOCl nanoplates are deposited on the surface of KBiO₃ particles firmly. All these results further indicate the formation of heterojunctions between BiOCl and KBiO₃. In addition, Figure 3h shows the chemical composition of BiOCl/KBiO₃ with the molar ratio of 70/30 selected and examined by energy dispersive X-ray spectroscopy (EDS) analysis. The characteristic peaks prove the presence of Bi, Cl, O and K elements, which are also indicative of the BiOCl and KBiO₃ components present in the system. No other impurity appears in the system. The Bi content is 79.74 wt.%, close to the theoretical weight (77.07 wt.%). In order to determine the element content more accurately, elemental analysis of the as-prepared samples was performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Table 1 presents the actual

percentage of K and Bi loaded in the structure of BiOCl/KBiO₃ with the molar ratio of 70/30 and shows the Bi content is 76.4155 wt.%, closer to the theoretical weight (77.07 wt.%).

N₂ adsorption-desorption analysis

The N₂ adsorption-desorption isotherms are measured for determining the surface area and porosity of the as-prepared samples. It is well known that the high specific surface area and mesoporous structure can improve the contact of organic pollutants to catalysts resulting in increased photocatalytic activity.^{46,47} Figure 4 shows N₂ adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) pore size distribution of the KBiO₃, BiOCl and BiOCl/KBiO₃ with

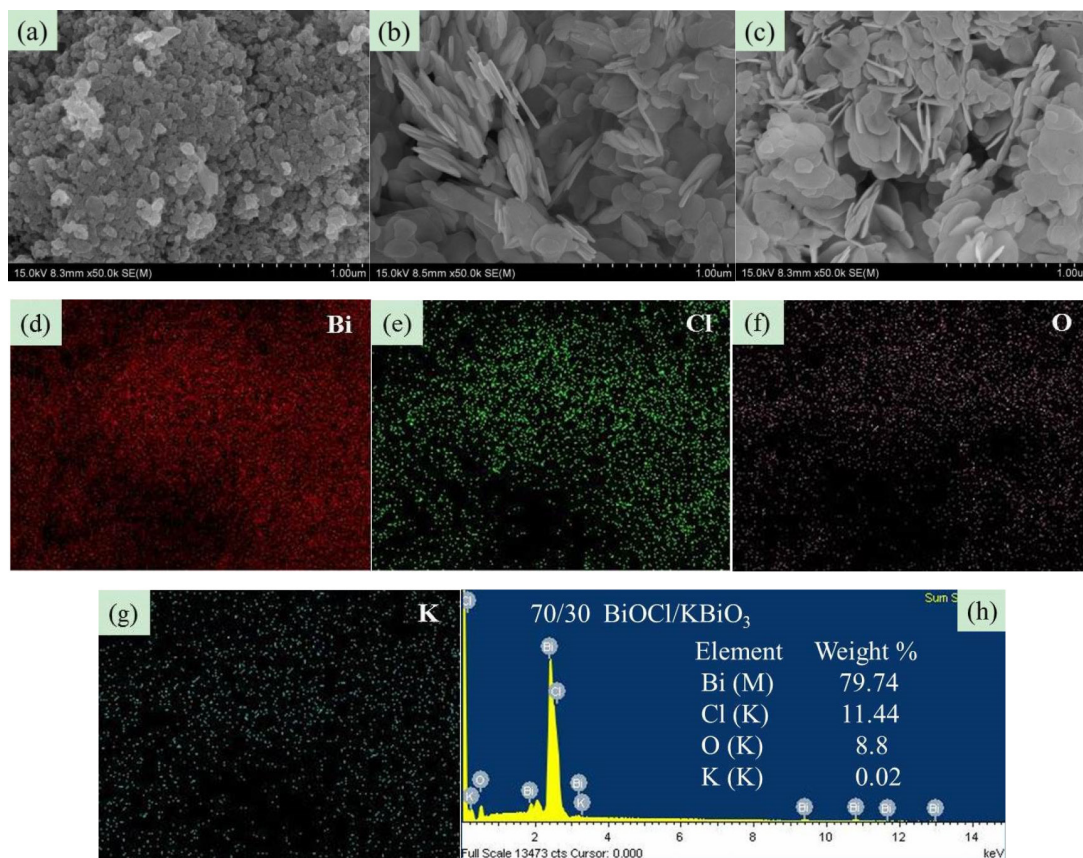


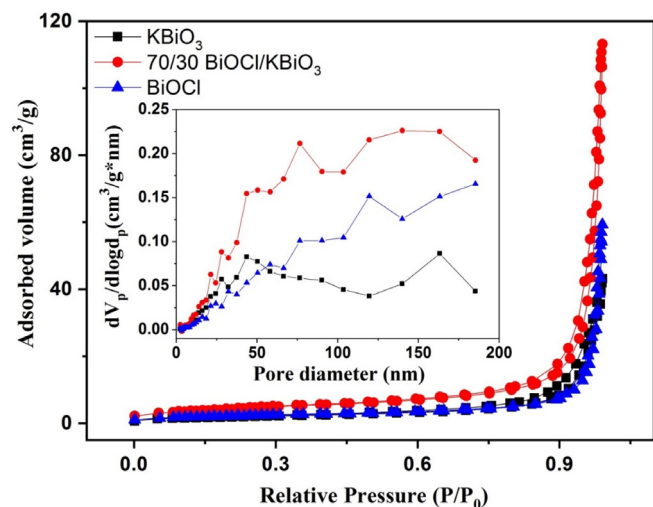
Figure 3. (a-c) SEM images of KBiO₃, BiOCl and BiOCl/KBiO₃ with the molar ratio of 70/30, respectively; (d-g) the corresponding elemental mapping images for Bi, Cl, O and K of BiOCl/KBiO₃ with the molar ratio of 70/30; (h) EDS image of BiOCl/KBiO₃ with the molar ratio of 70/30

Table 1. ICP-AES result of BiOCl/KBiO₃ with the molar ratio of 70/30

Sample	Measured element	Element content / (mg kg ⁻¹)	Mass fraction / %
70/30 BiOCl/KBiO ₃	K	228.9	0.0229
	Bi	764154.5	76.4155

ICP-AES: inductively coupled plasma atomic emission spectroscopy.

the molar ratio of 70/30. According to Brunauer-Deming-Deeming-Teller (BDDT) classification, the N₂ adsorption-desorption isotherms of the KBiO₃, BiOCl and BiOCl/KBiO₃ with the molar ratio of 70/30 show the type IV curves and have the H3 hysteresis loops at the relative pressure of P/P₀ between 0.6-1.0, especially for BiOCl and BiOCl/KBiO₃. This originates from the textural porosity of the samples which could be caused by the stacking of the plates-like structure of the composite photocatalysts.⁴⁵ This result is consistent with the SEM images. The specific surface area and porosity of the KBiO₃, BiOCl and BiOCl/KBiO₃ with the molar ratio of 70/30 are shown in Table 2. The BET surface area of BiOCl/KBiO₃ is much higher than that of KBiO₃ and BiOCl, indicating that the high specific surface area leads to the improvement of photocatalytic properties.

**Figure 4.** N₂ adsorption-desorption isotherms and BJH pore size distribution of pure KBiO₃, pure BiOCl and BiOCl/KBiO₃ with 70/30 molar ratio**Table 2.** BET surface areas and pore volumes of different samples

Sample	BET surface area / (m ² g ⁻¹)	Pore volume / (cm ³ g ⁻¹)	Mean pore diameter / nm
KBiO ₃	6.4017	0.064154	40.086
BiOCl	7.4167	0.087644	47.269
70/30 BiOCl/KBiO ₃	14.581	0.1645	45.132

BET: Brunauer-Emmett-Teller.

UV-Vis DRS analysis

The optical properties of different samples were investigated by a UV-Vis diffuse reflectance spectrum (DRS), and the results obtained are shown in Figure 5a. The absorption edge of BiOCl occurs at about 370 nm. For KBiO₃, a strong absorption is detected at wavelength shorter than around 550 nm and sharply declines from approximately 550 nm. The absorption spectra are consistent with the colors of the samples (Figure 6). As BiOCl builds up in the samples, the color becomes lighter. The phenomenon is ascribed to the interaction of heterojunction between BiOCl and KBiO₃. The heterojunction can effectively improve the separation of

photo-generated electron-hole pairs due to the band gap transition. The band gap (E_g) of semiconductors can be determined from DRS plots as follows:⁴⁸

$$(\alpha h\nu)^n = k(h\nu - E_g) \quad (1)$$

where α is the absorption coefficient, h is Planck constant, ν is light frequency, k is proportionality constant, E_g is the band gap energy. Among them, n is determined by the type of optical transition of a semiconductor ($n = 2$ for direct transition and $n = 1/2$ for indirect transition). According to the previous report,⁴⁰ the ν value of BiOCl and KBiO₃ were all 1/2. From the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ in Figure 5b, the estimated band gap energies of the KBiO₃ and BiOCl are 1.86 and 3.50 eV, respectively, which are consistent with previous reports.^{38,43} The band gap energies of the BiOCl/KBiO₃ composites with different molar ratios are between those of KBiO₃ and BiOCl. On the one hand, the higher band gap energy can inhibit the recombination of the photo-generated electron-hole pairs more effectively than KBiO₃ with small band gap energy. On the other hand, it also can enhance the photocatalytic property theoretically. In addition, in Bi-oxides the chemical nature of spectator cation (Li⁺, Na⁺, K⁺, etc.) plays an important role in tailoring the band structure⁴⁹ as also in stabilizing different oxidation states (+3 to +5) for Bi.³⁹

Photocatalytic activity evaluation

The photocatalytic activities of as-prepared samples are evaluated by the degradation of RhB under visible light ($\lambda \geq 400$ nm). Figure 7a displays the photodegradation of RhB as a function of irradiation time over different photocatalysts. A blank experiment without catalysts demonstrates that the concentration of RhB have no noticeable change after irradiation for 90 min. For KBiO₃, only 55.3% of the RhB was decomposed in 90 min. This suggests that the rapid recombination between conduction band (CB) electrons and valence band (VB) holes occurs mainly because of the narrow bandgap (1.86 eV) of KBiO₃. The photodegradation of RhB with BiOCl is 45.9% after 90 min of irradiation with visible light although it cannot be activated by visible light due to the wide band gap. When comparing these BiOCl/KBiO₃ samples, it is noteworthy that the photocatalytic activity of BiOCl/KBiO₃ composites showed very different trends with the increasing amount of BiOCl. The BiOCl/KBiO₃ sample with the molar ratio of 70/30 shows the highest photocatalytic activity of 91.6% RhB degradation in 90 min. The results indicate that until the suitable BiOCl content in BiOCl/KBiO₃ composites, the photocatalytic activity is significantly enhanced, while it is decreased with excess BiOCl content. This may be attributed to the fact that the introduction of a large amount of BiOCl may lead to shielding of the active sites on the photocatalyst surface and weaken the intensity of light arrived to the reaction solution.⁵⁰ Therefore, it is important to achieve a balance between the active trapping sites, which favoring the inhibition of the recombination of electron-hole pairs, and fewer trapped parts, which leading to a lower capacity for the separation of interfacial charge transfer.⁵¹

The temporal evolution of the absorption spectra during the RhB physisorption and photodegradation over the BiOCl/KBiO₃ with the molar ratio of 70/30 in the dark and under visible light irradiation are shown in Figures 7b and 7c. It is well-known that RhB shows major absorption peak at 553 nm and the intensity of the peak in the spectrum decreases as the concentration of RhB decreases. About 16.9% of RhB decoloration is observed in the dark, which may be due to its plates-like mesoporous structure and large BET special surface. It indicates that the only dark adsorption of RhB with BiOCl/KBiO₃ with the molar ratio of 70/30 is negligible. However,

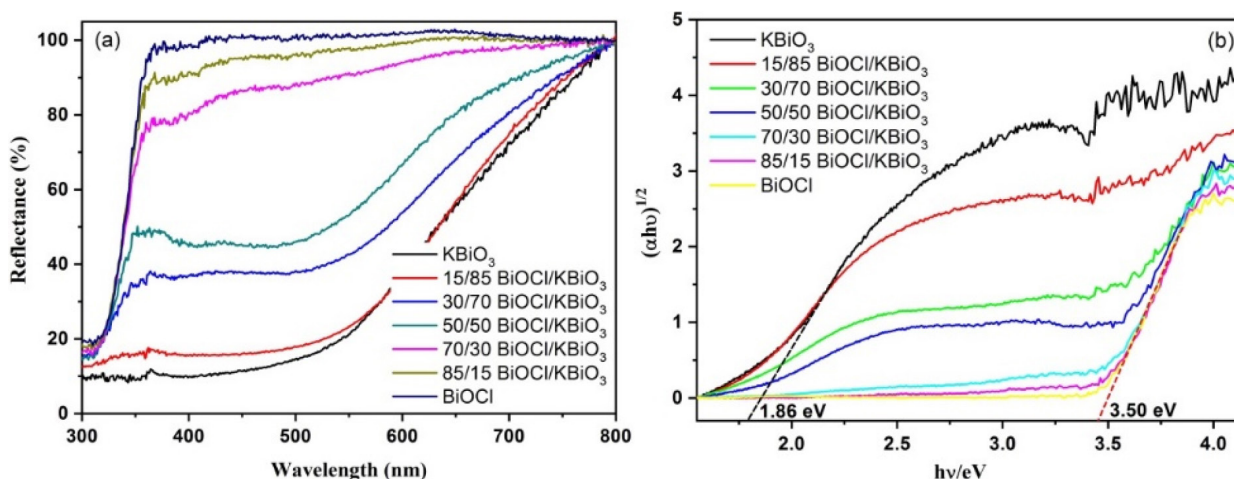


Figure 5. (a) UV-Vis spectra and (b) energy gap calculated by plotting $(\alpha h\nu)^{1/2}$ versus $h\nu$ of the KBiO₃, BiOCl and BiOCl/KBiO₃ composites with different molar ratios



Figure 6. The color of each sample; from left to right KBiO₃, BiOCl/KBiO₃ with the molar ratio of 15/85, 30/70, 50/50, 70/30, 85/15 and BiOCl

in the process of photodegradation within 90 min, it shows an apparently fast decrease in absorption with a concomitant wavelength shift of the band to shorter wavelengths. Under visible illumination, the dye is de-ethylated in a stepwise manner with the color of the dispersion changing from an initial red color to a light green-yellow. The fully de-ethylated RhB molecule has a major absorption band at $\lambda_{\max} = 506$ nm, in accordance with the standard spectra of RhB. The color of the dispersion disappeared after 90 min of irradiation, indicating that at least the chromophoric structure of the dye was destroyed.⁵² And no peak shift of RhB was detected indicating that no other intermediate was formed.

To quantitatively investigate the reaction kinetics of RhB degradation in our experiment, the experimental data were fitted by applying a first-order model as expressed by Equation 2,⁵³ which is well established for the photocatalytic experiments when the pollutant is in the millimolar concentration range.

$$\ln(C_0/C_t) = kt \quad (2)$$

where C_0 and C_t are the concentrations of RhB in solution at times 0 and t , respectively, and k is the apparent first-order rate constant. The influence of the amount of BiOCl on the photodegradation rate of RhB over the KBiO₃, BiOCl and BiOCl/KBiO₃ composites with different molar ratios is shown in Figure 7d. From this figure, there is a linear relationship between $\ln(C_0/C_t)$ and irradiation time, demonstrating that the photocatalytic reaction can depend quantitatively on the pseudo-first-order model.⁷ The reaction rate constants k of KBiO₃, BiOCl/KBiO₃ with the molar ratio of 15/85, 30/70, 50/50, 70/30, 85/15 and BiOCl are 0.00914, 0.00691, 0.00389, 0.00545, 0.02621, 0.01358, 0.00660 min⁻¹, respectively. As shown in Figure 7d, when the molar ratio of BiOCl/KBiO₃ composites is more than 50/50, the kinetic constants of BiOCl/KBiO₃ composites for RhB degradation are higher than that of pure KBiO₃ and BiOCl, and the BiOCl/KBiO₃ composites with the molar ratio of 70/30 shows the highest value of k (0.02621 min⁻¹), which is about 2.9 and 4.0 times higher than

that of pure KBiO₃ (0.00914 min⁻¹) and pure BiOCl (0.00660 min⁻¹), respectively. The result reveals that the optimum amount of BiOCl on KBiO₃ could extremely facilitate the enhancement of photocatalytic activity of single KBiO₃.

Mechanism of enhanced photocatalytic activity

In order to make sure the prime reactive species which are generated during photocatalytic oxidation process, *p*-benzoquinone (BQ, $\cdot\text{O}_2^-$ scavenger), isopropyl alcohol (IPA, $\cdot\text{OH}$ scavenger), ammonium oxalate monohydrate (AO, h^+ scavenger) and AgNO₃ (e^- scavenger) with the amount of 1 mmol L⁻¹ were added into the reaction system. The effects of four scavengers on the degradation of RhB in the presence of BiOCl/KBiO₃ composites with the molar ratio of 70/30 under visible light irradiation are shown in Figure 8. Obviously, the percent of photocatalytic degradation of RhB decreased to nearly zero when AO was added and the similar phenomenon could be found when the BQ, IPA and AgNO₃ were added. It indicates that h^+ , $\cdot\text{O}_2^-$, $\cdot\text{OH}$ and e^- reactive species work together in combination for the photocatalytic degradation of RhB. This result is different from that described by Zhang *et al.*⁵⁴

Based on the above results and discussions, in order to further research the separation process of photo-induced carriers, according to the results of DRS, the band edge positions of the valence band (VB) and conduction band (CB) of BiOCl/KBiO₃ photo-catalysts can be estimated based on the following empirical equations:⁴⁹

$$E_{\text{VB}} = X - E_c + 1/2E_g \quad (3)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g \quad (4)$$

where E_{VB} is the band edge positions of VB, E_{CB} is the band edge positions of CB, X is the electronegativity of the semiconductor (which is the geometric mean of the electronegativity of the constituent atoms), E_c is the energy of free electrons on the hydrogen

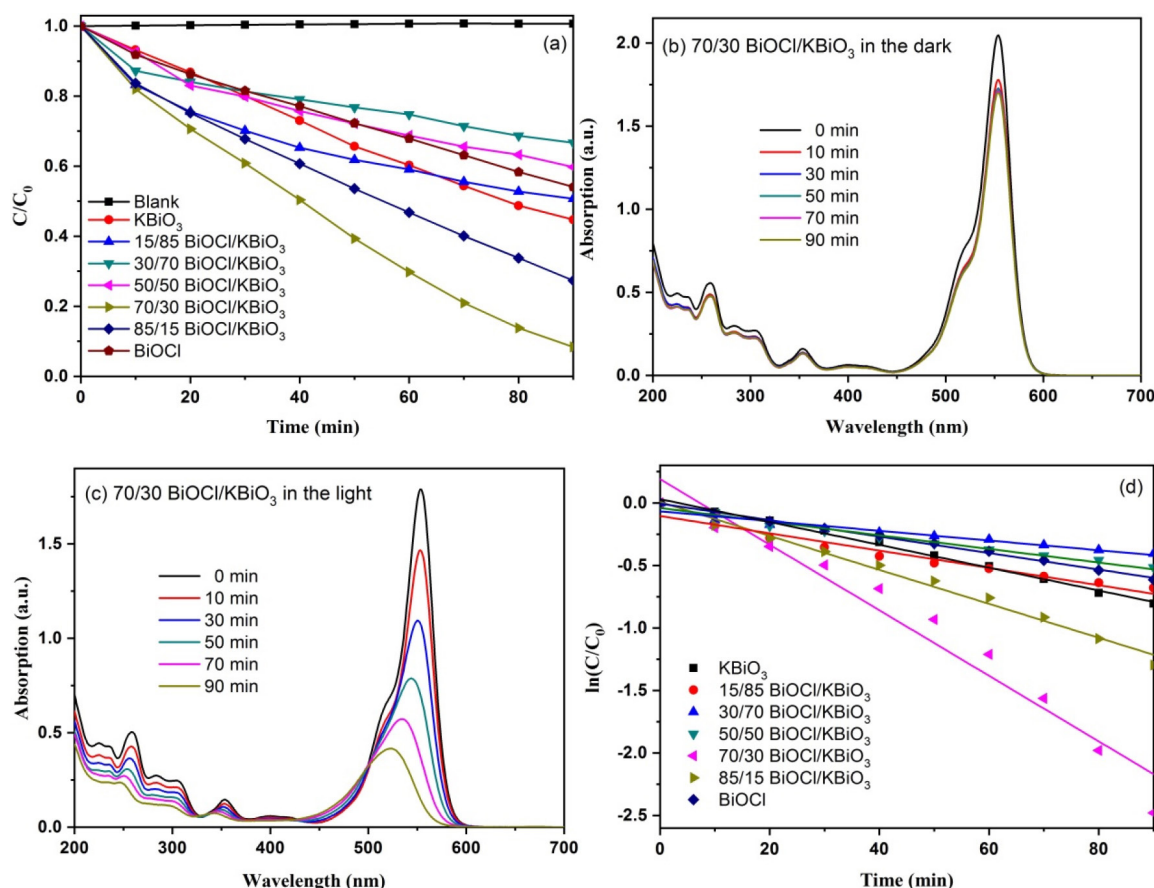


Figure 7. (a) Photocatalytic degradation of RhB with the KBiO₃, BiOCl and BiOCl/KBiO₃ composites with different molar ratios under visible light irradiation; (b,c) UV-Vis spectral changes of RhB aqueous solutions by using BiOCl/KBiO₃ composites with the molar ratio of 70/30 in the dark and under visible light irradiation; (d) the kinetic curves of RhB over the KBiO₃, BiOCl and BiOCl/KBiO₃ composites with different molar ratios under visible light irradiation

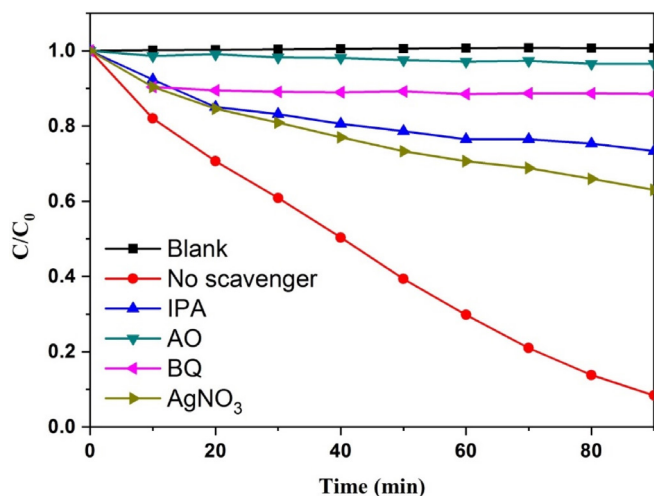


Figure 8. Effect of scavengers on the photocatalytic degradation of RhB by BiOCl/KBiO₃ composites with the molar ratio of 70/30 under visible light irradiation

scale (4.5 eV) and E_g is the band gap energy of the semiconductor. As mentioned above, the band gap of KBiO₃ and BiOCl is 1.86 and 3.50 eV, respectively. From the above empirical formula, the E_{VB} of KBiO₃ and BiOCl is estimated to be 1.89 and 3.90 eV, respectively and the corresponding E_{CB} of KBiO₃ and BiOCl is calculated to be 0.03 and 0.40 eV, respectively, as shown in Table 3.

The band edge positions of KBiO₃ and BiOCl show band alignment as schematically illustrated in Figure 9. As displayed

in Figure 9a, the Fermi level and CB of BiOCl are little lower than that of KBiO₃ before they are in contact. The Fermi levels of p-type BiOCl is near below, while the Fermi levels of n-type KBiO₃ is near above, which seems to be hard to conduct the photocatalytic reaction. However, according to the general p-n heterojunction formation process reported in literatures,^{55,56} when the p-n heterojunction is formed between KBiO₃ and BiOCl, the Fermi levels of KBiO₃ and BiOCl tend to descend and rise up to achieve an equilibrium state, and an inner electric field will be formed in the interface of p-n heterojunction. The inner electric field makes the region of BiOCl have negative charges, while the region of KBiO₃ has positive charges. In comparison, the conduction band and valence band position of BiOCl are all more negative than that of KBiO₃. Under visible light irradiation, only KBiO₃ can be activated to generate electron-hole pairs. The inner electric field at p-n heterojunction interface will push the photogenerated holes on the VB of KBiO₃ toward that of BiOCl, while the electrons still remain on the CB of KBiO₃. In such a way, the photo-induced electrons and holes are efficiently separated and the recombination of electron-hole pairs is hindered.⁴⁹

In addition, the valence band edge potential of BiOCl is more negative than $E_0(-OH/H_2O)$ (2.27 V_{NHE}) or $E_0(OH/HO^-)$ (2.38 V_{NHE}),⁵⁶ suggesting that the photo-induced holes (h^+) on the V_B of BiOCl cannot react with H₂O or OH⁻ to form $\cdot OH$. Thus, the photo-induced holes h^+ on the V_B of BiOCl are consumed to oxidize RhB molecules directly. However, the conduction band edge of KBiO₃ is less negative than $E_0(O_2/\cdot O_2^-)$ (-0.33 V_{NHE}) and $E_0(O_2/HO_2\cdot)$ (-0.05 V_{NHE}).⁵⁷ Therefore, it cannot provide a sufficient potential to reduce O₂ through the one-electron reduction process and further form $\cdot OH$. Therefore,

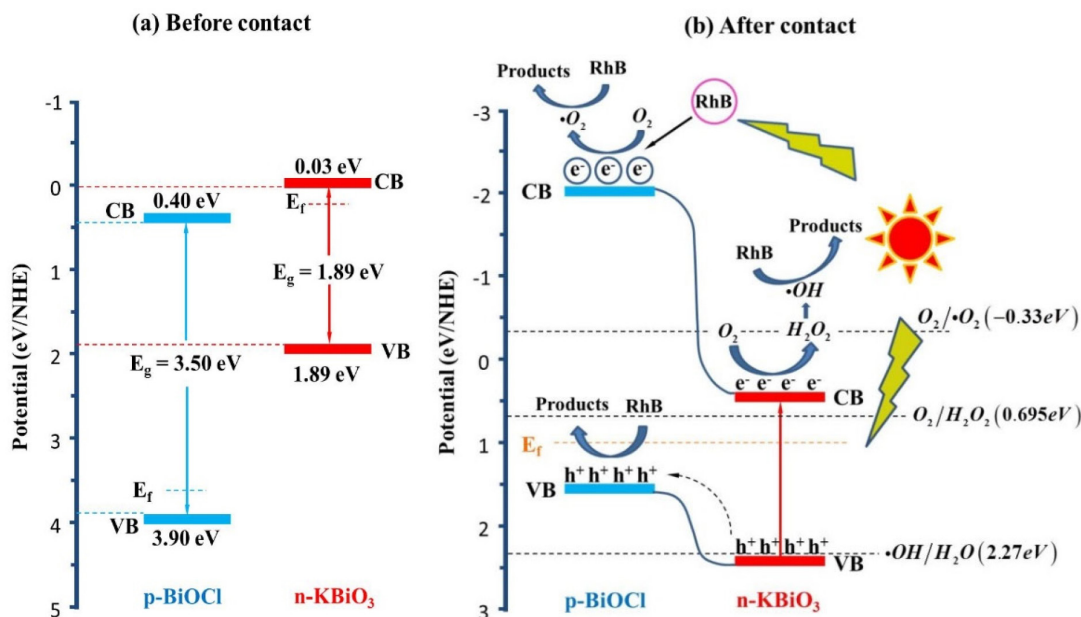
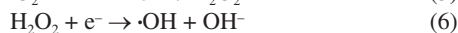


Figure 9. Scheme of band gap match and electron-hole pairs separation of the BiOCl/KBiO₃ composites

Table 3. Electronegativity (X), band gap energy (E_g), conduction band energy (E_{VB}) and valance band energy (E_{CB}) of KBiO₃ and BiOCl

Sample	X	Band gap / eV	E_{VB} / eV	E_{CB} / eV
KBiO ₃	5.46	1.86	1.89	0.03
BiOCl	6.65	3.50	3.90	0.40

it is reasonable for O₂ to react with electrons on the CB of KBiO₃ to generate H₂O₂ (Equation 5) via a two-electron reduction reaction process⁵⁸⁻⁶² ($E_0(\text{O}_2/\text{H}_2\text{O}_2) = +0.695 \text{ V}_{\text{NHE}}$).⁶¹ Then the formed H₂O₂ quickly reacts with an electron to finally form ·OH (Equation 6),⁶³ which are highly oxidative active species to many organic pollutants. At the same time, under visible light irradiation RhB molecules can be photosensitized⁵⁵ and electrons immediately transfer from the excited states of the adsorbed dyes to the conduction band of BiOCl with more negative potential than $E_0(\text{O}_2/\text{O}_2^-)$. Thus, the photosensitized electrons also participate in the oxidation process through the reduction of the adsorbed O₂ on the surface of the catalyst to the superoxide radical ·O₂⁻ (Equation 7). In conclusion the photo-induced holes (h⁺), hydroxyl radicals (·OH) and superoxide radical (·O₂⁻) which all have strong oxidizing ability for organics work together to break down the chromophores of RhB dye into small molecules, e.g., H₂O and CO₂.⁶⁴⁻⁷⁰ The process is in good agreement with the results of trapping experiment. This result is also different from that described by Zhang *et al.*⁵⁴ The specific reasons need to be further studied in subsequent experiments.



CONCLUSIONS

In summary, BiOCl/KBiO₃ p-n heterostructures were successfully synthesized via a facile *in situ* method. The photocatalytic performance of the as-prepared BiOCl/KBiO₃ composites showed very different trends with the increasing amount of BiOCl. BiOCl/KBiO₃ composites with the molar ratio of 70/30 exhibited the highest photocatalytic activity for the degradation of RhB under visible light irradiation due to its large surface area, excellent charge

separation characteristics and the suppressed recombination of electron-hole pairs. In addition, a possible and new mechanism of the degradation over BiOCl/KBiO₃ p-n heterojunction photocatalyst was proposed in detail.

SUPPLEMENTARY MATERIAL

Complementary material for this work is available at <http://quimicanova.sbq.org.br/>, as a PDF file, with free access.

ACKNOWLEDGMENTS

This research was supported by Scientific Research Foundation for the Returned Overseas Chinese Scholars, Hebei Province (C20210101), the Foundation of Hebei Minzu Normal University (DR2022007), the Introduces Foreign Intelligence Projects of Hebei Province (No. 130800), S & T Program of Chengde (No. 202205B090) and China Scholarship Council (CSC) grant #202108130124.

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