



Enhanced photocatalytic performance of BiOCl benefited from the effective separation of photogenerated carriers and enhanced surface hydroxyl content

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ABSTRACT

Boosting the separation efficiency of photogenerated charge pairs is an effective and robust approach to improve the photocatalytic activity of BiOCl. In this demonstration, thin sheet-like BiOCl photocatalysts were prepared by a facile hydrothermal method using ionic liquids as chlorine source. The enhancement in photocatalytic activity of BiOCl is attributable to enhanced separation efficiency of photoinduced charge pairs and high surface hydroxyl content. Surface photovoltage spectrometer and electrochemical test results confirm that the photocatalysts prepared using ionic liquid as the chlorine source have higher separation efficiency of photogenerated charge pairs and photocurrent signals than the reference BiOCl. X-ray photoelectron spectroscopy results indicate that the hydroxyl content on the surface of the photocatalysts prepared using ionic liquid as the chlorine source was significantly promoted. The photocatalytic activity was assessed by the abatement of rhodamine B under a 500 W Xe lamp (simulated sunlight) irradiation for 45 min. The results show that the photocatalytic activity of BiOCl-H, BiOCl-C and BiOCl-A is 7.72, 4.09 and 3.45 times that of BiOCl, respectively.

Keywords: BiOCl; Ionic liquids; Separation of photogenerated carriers; Surface hydroxyl content

1. Introduction

In the process of industrialization, thousands of organic compounds were used as precursors, solvents or auxiliaries, resulting in a large number of non-degradable organic pollutants with strong toxic effects. Direct discharge of organic pollutants will cause irreversible damage to the living environment. Compared with other methods, photocatalytic technology is more efficient in treating the organic pollutants in light of no secondary pollution, safe and low energy consumption [1–3]. Among the existing photocatalysts, BiOCl has attracted much attention because of its unique layered structure, non-toxic, high stability and high photocatalytic efficiency [4–8]. However, a wide bandgap and

high recombination rate of photogenerated carriers seriously inhibit the catalytic activity of BiOCl [9,10]. In recent years, surface modification, construction of heterojunctions, element doping, crystal plane engineering, morphology control, construction of oxygen vacancies and preparation of solid solutions have been used to promote the photocatalytic activity of BiOCl [11–17].

The application of ionic liquids as reaction solvents and templates in material synthesis has been rapidly developed. Ionic liquids are composed of anions and cations, two special structures of hydrogen-bonded and ion clusters exist in the ionic liquids, which is designable and has high flexibility in the synthesis process [18–20]. Ionic liquids are ideal pollution-free green solvents since their unique

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properties can be tuned by modifying cations or changing anions. The interaction between anions and cations can be used to change the crystallization orientation of BiOCl by adding ionic liquids in the preparation process [21,22]. The studies have well established that ionic liquids can be used as surface modifiers to functionalize the surface of catalysts, inhibiting the recombination of photogenerated electrons and holes, therefore boosting the catalytic activity of photodegradation of organic pollutants [23–25]. The previous studies on the preparation of BiOCl photocatalysts with the assistance of ionic liquids mainly focus on the control of special morphology and construction of heterojunctions [26–29]. However, few studies on the preparation of BiOCl using ionic liquids as chlorine sources have been addressed, the relationship between the photocatalytic performance of BiOCl and the types of chlorine source need to be further revealed.

Herein, BiOCl photocatalysts were prepared by a solvothermal method using imidazolium ionic liquids instead of KCl as a chlorine source. Photocatalytic degradation experiments were carried out to assess the photocatalytic activity of BiOCl using rhodamine B (RhB) as a model pollutant under the simulated sunlight illumination. The results show that BiOCl photocatalysts prepared using ionic liquids as a chlorine source display higher photocatalytic activity than the reference BiOCl.

2. Experimental sections

2.1. Preparation of the samples

All chemicals are analytical grade and used directly without further purification. 5 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 40 mL glacial acetic acid, different ionic liquids and KCl were dissolved in 20 mL deionized water, separately, the molar ratio of Bi^{3+} to Cl^- is 1:1. Under continuous stirring, the solution containing chloride ion was dropwise added into the Bi^{3+} -glacial acetic acid solution and stirred for 1 h, forming a white precipitate. The suspension system was transferred to a Teflon-lined stainless-steel autoclave and maintained at 453 K for 24 h. After the autoclave was naturally cooled to room temperature, the solid was washed with deionized water and ethanol for many times, and then was dried at 333 K for 12 h. The samples prepared with 1-carboxyethyl-3-methylimidazolium chloride ([HOOCEMIm]-Cl), 1-cyanopropyl-3-methylimidazolium chloride ([CPMIm]-Cl), 1-allyl-3-methylimidazolium chloride ([AMIm]-Cl) and KCl as chlorine source were named as BiOCl-H, BiOCl-C, BiOCl-A and BiOCl, respectively.

2.2. Characterization

Crystal structures of the samples were analyzed on a DX-2600 X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation. The morphologies of the samples were observed on a field-emission scanning electron microscopy (SEM) with an accelerating voltage of 3.0 kV. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB MKII X-ray photoelectron spectroscopy. Using BaSO_4 as a reference, the light response ability of the samples was recorded on a TU-1907 UV-Vis spectrophotometer in the range from

250 to 500 nm. The separation efficiency of photogenerated carriers of the samples was measured on a home-build surface photovoltage spectroscopy (SPS) following the recipe as given in Ma et al. [10]. Photoelectrochemical experiments were carried out on an electrochemical workstation (CHI 760E) using a 500 W xenon lamp as a light source.

2.3. Photocatalytic activity evaluation

Photocatalytic activity of the prepared BiOCl was evaluated using RhB as a model organic pollutant and a 500 W xenon lamp was used as a light source (simulated sunlight). The concentration of RhB was 10 mg/L (pH = 7.0) and the dosage of the catalyst was 1 g/L. Nitrotetrazolium blue chloride (NBT) test was performed as the method described in Yang et al. [24].

3. Results and discussion

Brunauer–Emmett–Teller surface areas of the photocatalysts were displayed in Table 1. Compared with BiOCl, the specific surface area of BiOCl-A, BiOCl-C and BiOCl-H slightly increases. It is distinct that the presence of ionic liquids influences the growth of BiOCl-A, BiOCl-C and BiOCl-H. As a surfactant, ionic liquids can effectively disperse the particles, resulting in small particles with a higher specific surface area than BiOCl. The higher specific surface area will provide more active sites in the process of photocatalytic degradation, which is beneficial to the photocatalytic efficiency.

Fig. 1a displays XRD patterns of four as-synthesized samples. The diffraction peaks can be well matched to the tetragonal phase BiOCl with lattice parameters of $a = b = 0.3891$ nm and $c = 0.7369$ nm (JCPDS No.06–0249, space group P4/nmm) [30]. No impurity substances were detected, indicating the high purity of the prepared samples. It is evident that the relative intensities of diffraction peaks of the (001), (002), (101), (110), (102) and (003) crystal planes of BiOCl prepared using ionic liquid as chlorine source have an obvious change, demonstrating that ILs affect the growth of BiOCl. Fig. 1b displays the enlargement of the (001) plane of BiOCl photocatalysts. The diffraction peak intensity of the (001) plane of BiOCl-A, BiOCl-C and BiOCl-H decreases, which indicates that the crystal size of the samples decreases along the [001] crystallization direction [31]. Moreover, the ratio of $I(001)/I(101)$ reduces, which confirms that there exists a strong interaction during the crystallization of BiOCl when ionic liquids were used as chlorine sources.

Table 1
Brunauer–Emmett–Teller (BET) surface areas of the photocatalysts

Photocatalysts	S_{BET} (m^2/g)
BiOCl	6.3
BiOCl-A	8.2
BiOCl-C	8.3
BiOCl-H	9.3

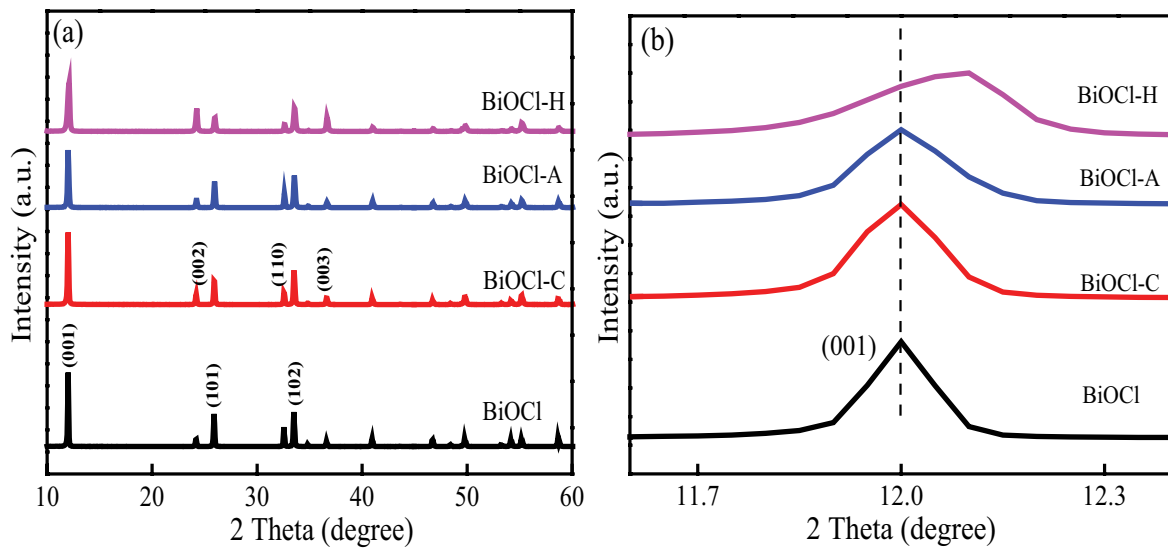


Fig. 1. XRD patterns of the photocatalysts (a) and enlargement of the (001) crystal plane (b).

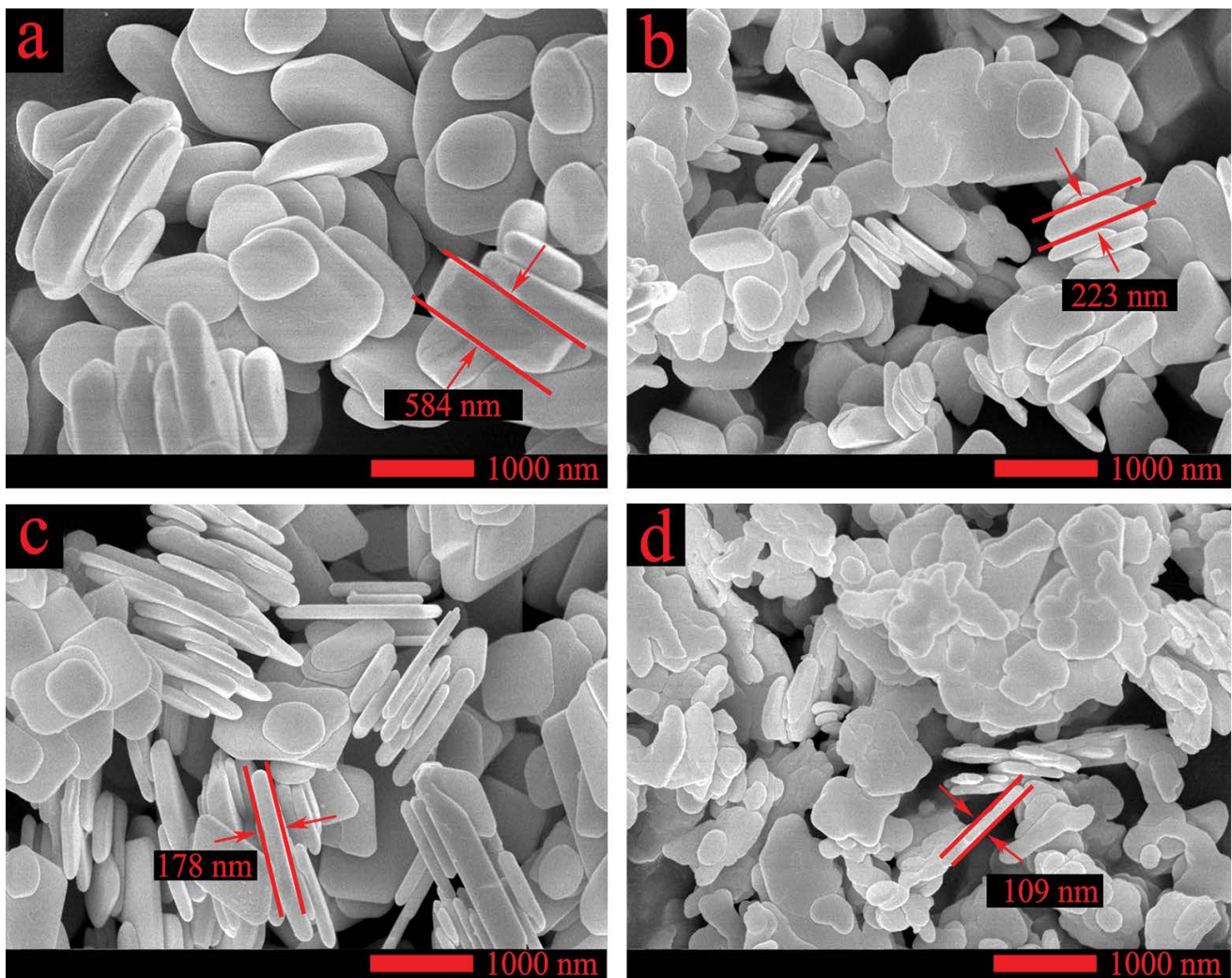


Fig. 2. SEM of the photocatalysts BiOCl (a), BiOCl-A (b), BiOCl-C (c), and BiOCl-H (d).

Fig. 2 shows the morphology of the photocatalysts obtained by SEM. It is evident that the thickness of BiOCl prepared by ionic liquid as the chlorine source becomes thinner. When ionic liquids were used as the chlorine source, the strong interaction between the anion and cation in the BiOCl synthetic system changes the orientation of the microstructure and leads to thin sheets. At the same time, as a kind of surfactant, ionic liquids can obviously promote the dispersion of BiOCl particles and results in thin layered-structure and small particles, resulting in the high specific surface area [32]. The thin sheet significantly reduces the path of photogenerated carrier's transfer to the surface of BiOCl, largely improving the separation efficiency of photogenerated charge, resulting in high photocatalytic activity of the catalyst. The results can be further confirmed by photocatalytic evaluation.

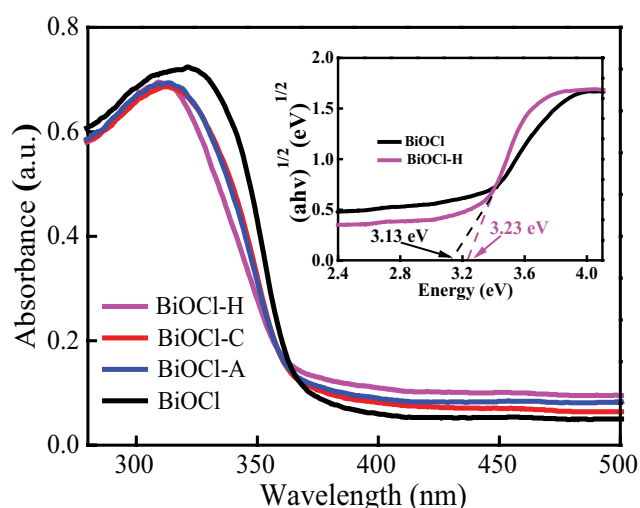


Fig. 3. UV-Vis diffuse reflection spectra of samples, the inset is plots of $(\alpha h\nu)^{1/2}$ vs. $h\nu$.

The optical absorption performance of the catalysts was investigated by UV-Vis spectroscopy. As shown in Fig. 3, compared with the reference BiOCl, the light response ability of BiOCl-A, BiOCl-C and BiOCl-H have a slight red-shift, which indicates narrow bandgap. As shown in the inset of Fig. 3, the bandgap of BiOCl-H increases by 0.1 eV than that of the reference BiOCl. According to the calculation method given in Chen et al. [33] and Di et al. [34], the E_{CB} and E_{VB} of BiOCl are 0.28 and 3.41 eV, the E_{CB} and E_{VB} of BiOCl-H are 0.23 and 3.46 eV. The redox potentials of $\cdot\text{OH}/\text{H}_2\text{O}$ and $\cdot\text{OH}/\text{OH}^-$ are +2.37 and +1.99 eV vs. NHE, respectively [35]. Therefore, photoinduced holes of all the samples have sufficient ability to oxidize hydroxyl groups adsorbed on the surface of photocatalysts to yield $\cdot\text{OH}$.

The separation behaviors of photogenerated carriers of the photocatalysts were revealed by SPS. As shown in

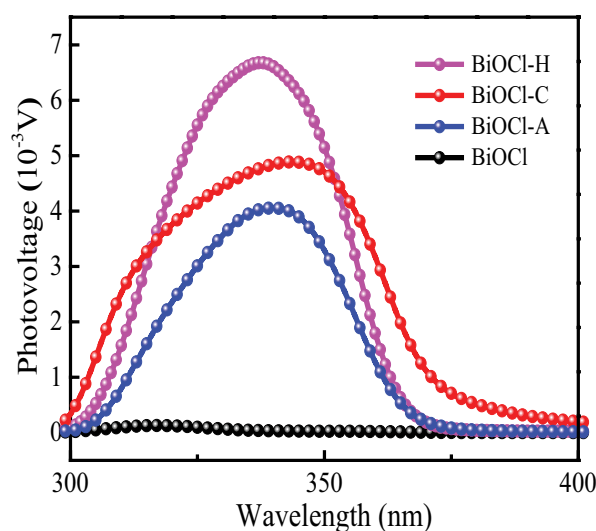


Fig. 4. SPS signals of the photocatalysts.

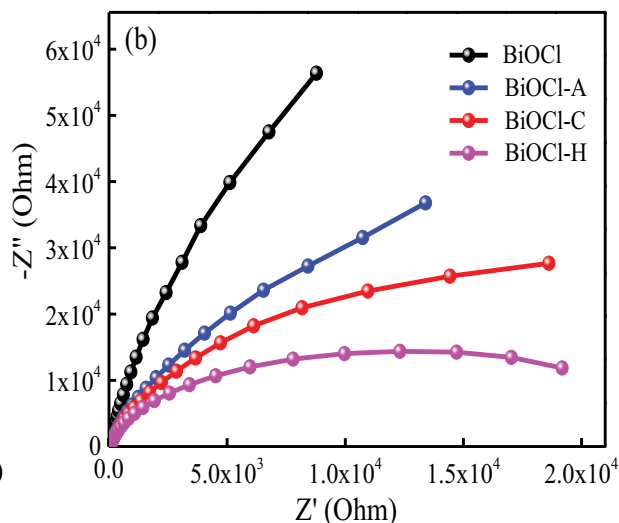
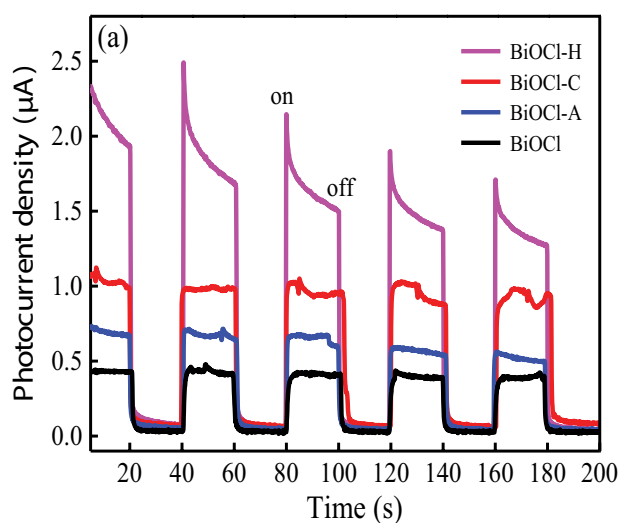


Fig. 5. Photocurrent-time ($I-t$) curve of the BiOCl photocatalysts (a) and EIS Nyquist plots of electrochemical impedance spectrum of the BiOCl photocatalysts (b).

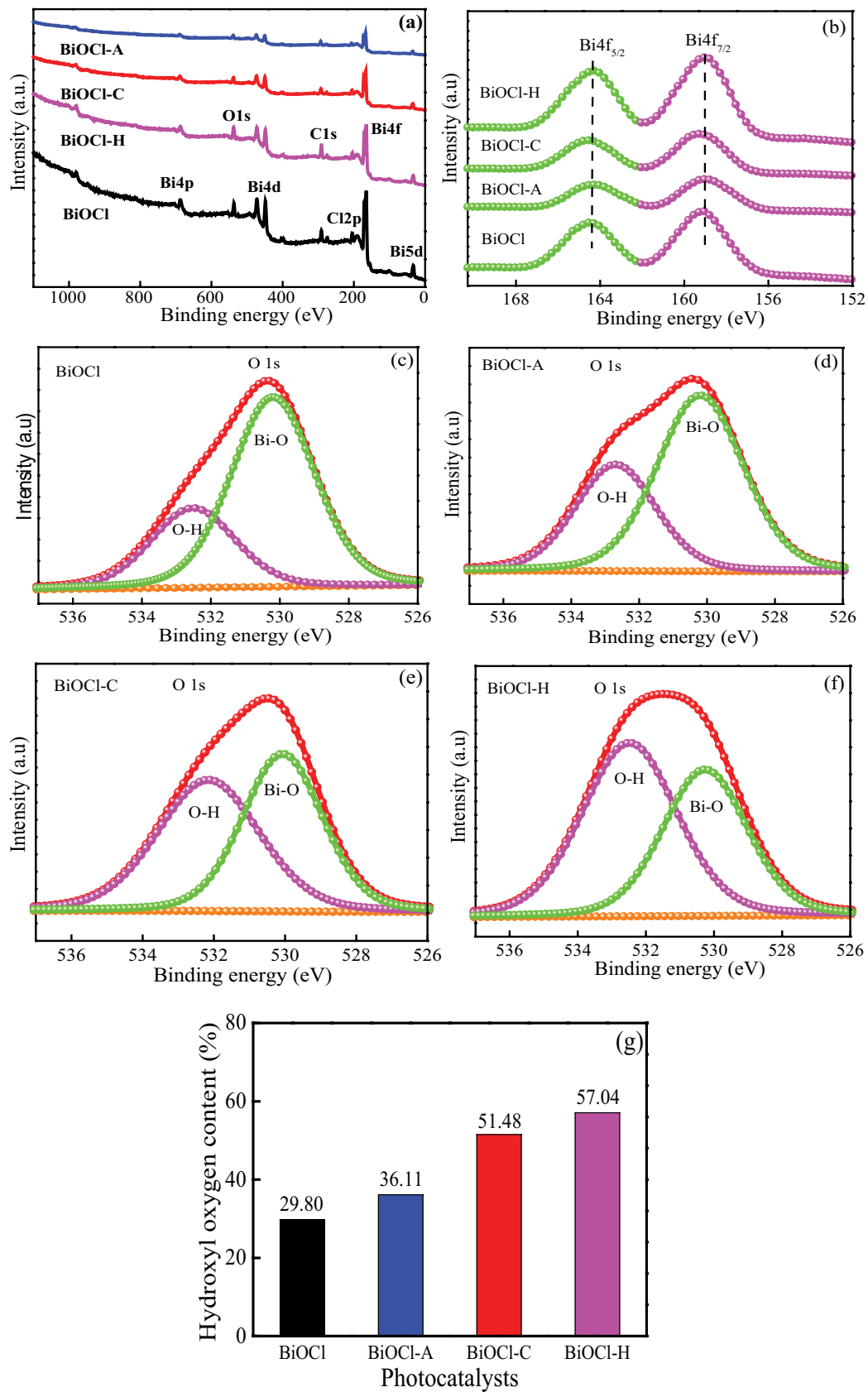


Fig. 6. XPS spectra of the samples (a), Bi 4f (b); high resolution XPS spectra of the O1s on the surface of the photocatalysts: BiOCl (c), BiOCl-A (d), BiOCl-C (e), BiOCl-H and (f); surface hydroxyl content on the photocatalysts (g).

Fig. 4, the separation efficiency of photogenerated charge pairs of BiOCl-H, BiOCl-C and BiOCl-A is higher than that of BiOCl. The high separation efficiency of photogenerated charge suggests that more photoinduced holes and electrons will be produced. The photogenerated holes can oxidize the hydroxyl groups adsorbed on the surface to form hydroxyl radical ($\cdot\text{OH}$) [36]. The enhanced $\cdot\text{OH}$ level will accelerate the photocatalytic degradation of RhB, which is consistent with the test results of catalyst activity.

To further reveal the separation efficiency of BiOCl catalysts, photocurrent and electrochemical impedance (EIS) were performed. In Fig. 5a, BiOCl-H, BiOCl-C and BiOCl-A have higher photocurrent than the reference BiOCl. Results exhibit that BiOCl-H, BiOCl-C and BiOCl-A have a higher separation rate of photogenerated charge than the reference BiOCl, which is consistent with the measurements of SPS. Moreover, after many times of illumination, there was no distinct difference in the photocurrent density of the catalysts, indicating that the catalysts possess excellent stability. As displayed in Fig. 5b, BiOCl has the largest EIS curve radius, which indicates that the recombination rate

of photoinduced carriers of BiOCl is higher than that of BiOCl-A, BiOCl-C and BiOCl-H [37]. Due to higher separation efficiency of photogenerated carriers, it is anticipated that BiOCl-A, BiOCl-C and BiOCl-H will display higher photocatalytic activity than BiOCl, which can be further confirmed by the test of photocatalytic degradation of RhB.

Fig. 6a shows the XPS spectrum of the photocatalysts. Bi, O and Cl were detected and no obvious shift of the peak position for BiOCl-H, BiOCl-C and BiOCl-A was observed. Fig. 6b shows the peaks located at 159.08 and 164.47 eV belong to the binding energies of the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ peaks of BiOCl, respectively [38]. Fig. 6c–f shows the O1s spin orbitals of BiOCl, BiOCl-A, BiOCl-C and BiOCl-H, respectively. Theoretically, 532 eV is the peak of surface hydroxyl ($-\text{OH}$) adsorbed on the surface of the BiOCl, and 530 eV is the peak of Bi–O [16]. Fig. 6g reveals that the surface hydroxyl content on BiOCl-H, BiOCl-C and BiOCl-A is higher than that on BiOCl. During the preparation process of BiOCl, the organic cations dissociated by ionic liquids will inevitably affect the surface energy of BiOCl and adsorption ability, resulting in more hydroxyl groups adsorbed on the surface

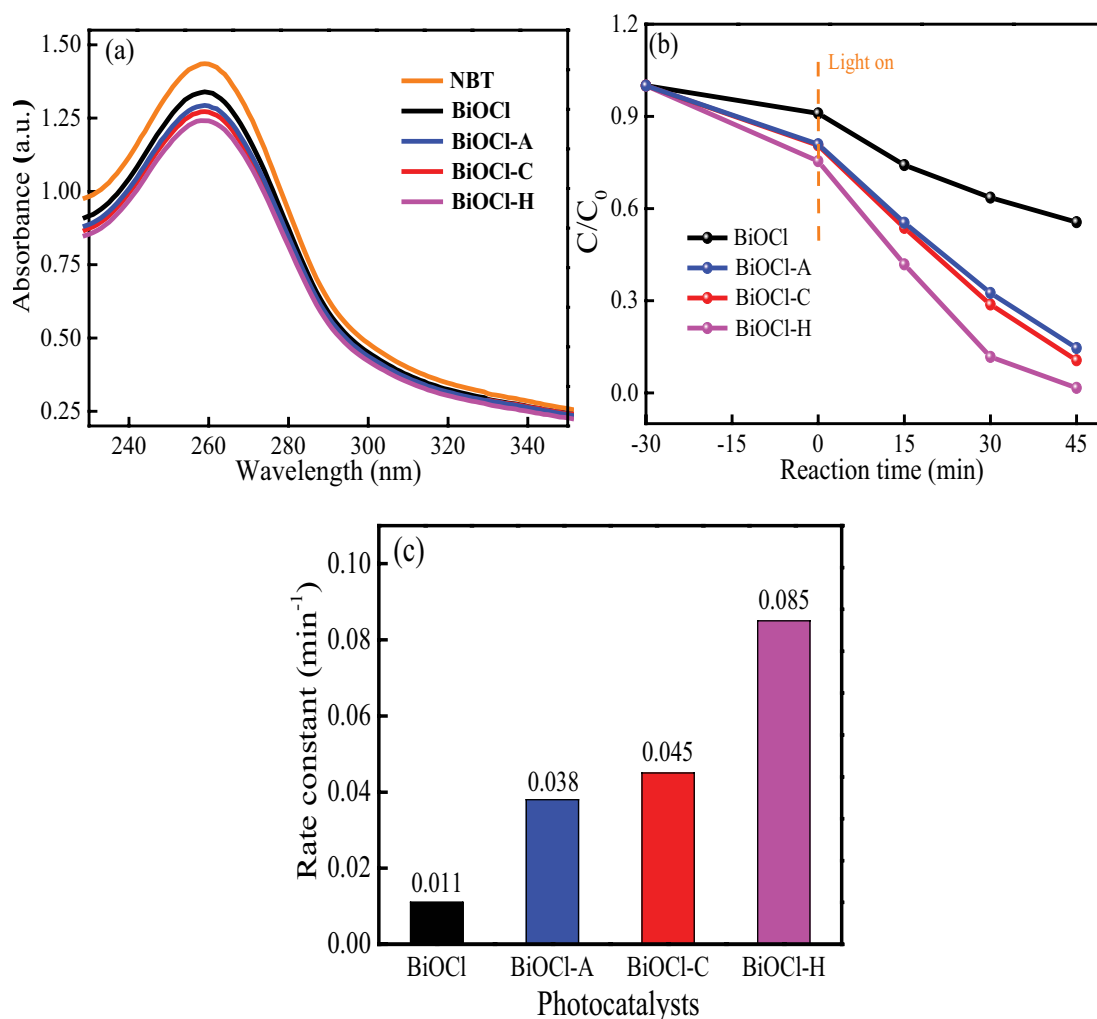


Fig. 7. The absorbance of NBT in different photocatalytic systems (a), abatement of RhB with the irradiation time (b), and photocatalytic decay rate constants of RhB over the different photocatalysts (c).

of BiOCl and promoting the content of surface hydroxyl on the surface of BiOCl prepared using ionic liquids as chlorine source. This result demonstrates that BiOCl-H, BiOCl-C and BiOCl-A have more opportunities than BiOCl in which the reaction of photoinduced holes oxidizes the hydroxyl groups to yield $\cdot\text{OH}$. Generally, the enhanced $-\text{OH}$ level on the surface of the photocatalyst is beneficial to the photocatalytic activity, which can be confirmed by the results of the photocatalytic activity test.

The absorbance of the NBT solution in the different photocatalytic systems after illumination was examined to study the level of superoxide radicals ($\cdot\text{O}_2^-$) [39], and the results were shown in Fig. 7a. The results demonstrate that the yield of superoxide radicals is relatively low and the difference is not obvious among the different photocatalytic systems. The superoxide radicals may be induced by the oxygen vacancies on the surface of the catalysts, which needs to be further explored.

In order to evaluate the photocatalytic activity of the prepared samples, the photocatalytic performance evaluation was carried out using RhB as a model pollutant, and the results were shown in Fig. 7b. Our previous study has well demonstrated that the photolysis of RhB under simulated sunlight irradiation for 1 h can be totally ignored [40]. In the process of photocatalytic reaction, the degradation of RhB accords well with a first-order kinetic model. As shown in Fig. 7c, degradation rate constant of RhB over BiOCl-A, BiOCl-C and BiOCl-H is 3.45, 4.09 and 7.72 times of that of over the reference BiOCl, respectively. The results suggest that the trend of photocatalytic activity of BiOCl, BiOCl-A, BiOCl-C and BiOCl-H matches well with the results of SPS and photocurrent, which demonstrates that separation rate of photoinduced carriers plays a significant role in influencing the photocatalytic performance.

4. Conclusions

In this demonstration, thin sheet-like BiOCl photocatalyst with enhanced photocatalytic activity was prepared using ionic liquids as chlorine sources. Ionic liquids can reduce the surface tension of the suspension system of BiOCl, improve the surface properties of BiOCl and greatly promote the photocatalytic efficiency. BiOCl photocatalysts prepared using ionic liquids as chlorine source have higher separation efficiency of photoinduced carriers and higher surface hydroxyl content than the reference BiOCl, which is attributable to the improvement of photocatalytic activity. Using ionic liquids as a chlorine source can remarkably boost the photocatalytic activity of BiOCl.

Acknowledgments

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