



Enhancement of photocatalytic activity over NaBiO₃/BiOCl composite prepared by an in situ formation strategy

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ABSTRACT

NaBiO₃/BiOCl composite photocatalysts with heterostructure have been prepared by a novel in situ formation approach, by using NaBiO₃ and hydrochloric acid aqueous solutions as the raw materials. Under visible light ($\lambda > 400$ nm) irradiation, the photocatalytic activity of Rhodamine B over NaBiO₃/BiOCl photocatalysts has been evaluated. The results demonstrate that the combination of NaBiO₃ and BiOCl has a higher photocatalytic activity compared with single NaBiO₃ or BiOCl photocatalyst, due to more effective photo-excited electron-hole separation by the heterojunction semiconductor structure and also higher absorption capacity of NaBiO₃.

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1. Introduction

Photocatalysis technology, which enables the solar energy to purify water and air [1], is highly expected to be an ideal “green” technology for water/air treatment. Until now, semiconductor combination, which constructs a heterojunction interface between two types of semiconductors with matching energy band gaps, has been widely applied because it enhances the photogenerated charge carriers separation, thus achieving better efficiency for the decomposition of the organic compounds in wastewater. Previously, many heterostructured semiconductors, such as Cu₂O/TiO₂ [2,3], Bi₂O₃/TiO₂ [3], CdS/TiO₂ [4], Fe₂O₃/TiO₂ [5], FeTiO₃/TiO₂ [6], MoS₂(WS₂)/TiO₂ [7], CuAlO₂/TiO₂ [8], Si/TiO₂ [9], Co₃O₄/BiVO₄ [10], Bi₂O₃/BaTiO₃ [11], WO₃/CuBi₂O₄ [12], CaFe₂O₄/PbBi₂Nb₂O₉ [13] have been reported as photocatalysis systems.

NaBiO₃, first reported by Kako et al. [14], is a new efficient photocatalyst under visible light irradiation. The photocatalytic removal and transformation of polycyclic aromatic hydrocarbons (PAHs) and sodium pentachlorophenate (PCP-Na) over NaBiO₃ have also been systematically studied [15,16]. Our previous works [17,18] demonstrate that, in the presence of halogen hydride, NaBiO₃ can be corroded to Bi-based oxyhalides crystals which have received lots of interests due to their potential applications in decompos-

ing organic compounds for environmental remediation [19–21], photo-electrochemical conversion [22] and splitting water into hydrogen and oxygen gases [23]. Herein, we develop a new strategy for the in situ preparation of NaBiO₃/BiOCl composite photocatalysts with heterojunction structure to enhance the photocatalytic activity.

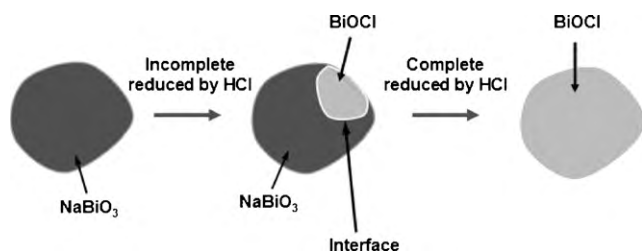
2. Experimental

2.1. Materials and preparation

Ultrapure water from the Milli-Q system (Millipore, USA) was used in this experiment. All chemicals (purchased from Sinopharm Chemical Reagent Co., Ltd.) were analytical grade and used as received without further purification. The preparation method for NaBiO₃/BiOCl composites is as follows. 3 g NaBiO₃·2H₂O powders were immersed into 20 mL of water and 40 mL of absolute ethanol while being stirred at room temperature. After NaBiO₃ were dispersed in the water–ethanol solution, for the synthesis of BiOCl and NaBiO₃/BiOCl composite photocatalysts with different NaBiO₃:BiOCl molar ratio of 7.1%, 14.1% and 25.3%, 18, 10, 8.5 and 7 mL of HCl aqueous solutions (7.2 wt%) was added, respectively. After stirring for 40 min, the resulted products were separated by centrifugation, washed by absolute ethanol, and dried at 80 °C for 6 h in air before further characterizations and photocatalytic activity evaluations. Scheme 1 gives the illustration of the in situ preparation of NaBiO₃/BiOCl composite photocatalysts.

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Scheme 1. Illustration of the in situ preparation of $\text{NaBiO}_3/\text{BiOCl}$ composites.

2.2. Characterization and optical properties measurement

The crystal structures of the samples were analyzed by X-ray diffractionmeter (XRD, Bruker D8 ADVANCE). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopic (EDX) measurements were performed using a JSM 7401 field emission gun-scanning electron microscope. The N_2 adsorption–desorption analysis was measured on a NOVA 4000 (Quantachrome Corporation) instrument. Visible light diffuse reflectance spectroscopy (visible-light-DRS) was measured at room temperature on a Hitachi U-3010 spectrophotometer.

2.3. Batch sorption experiments and chemical analysis

For measuring the sorption isotherms, in dark condition, 0.08 g of BiOCl and $\text{NaBiO}_3/\text{BiOCl}$ composite photocatalysts were transferred to flasks (250 mL), containing 200 mL of Rhodamine B (Rh. B) aqueous solution with different initial concentrations. These flasks were then transferred into an incubator shaker and shaken (at 150 rpm) for 48 h at a temperature of $25 \pm 2^\circ\text{C}$ to reach the adsorption–desorption equilibrium. Once the equilibrium was reached, the solid photocatalysts were separated by centrifuging at a speed of 4000 rpm for 15 min and the equilibrium concentration of Rh.B was detected by an UV–vis spectrometer at a wavelength of 554 nm.

2.4. Photocatalytic activity

The photocatalysis experiments of the samples were carried out in an XPA-Photochemical Reactor (Xujiang Electromechanical Plant, Nanjing, China). A Xenon lamp (500 W) was used as the light source. To ensure that the irradiation of the light system takes place only within the visible-light wavelengths, 2 M NaNO_2 aqueous solution was used to remove the radiation below 400 nm [24]. The photocatalyst dosage in the experiment was 0.4 g/L (initial concentration of Rh.B solution is 7.5 ppm) and the reaction temperature was kept at $20 \pm 2^\circ\text{C}$ by a water cooler machine (Lab Tech Company, USA). The slurry of reaction mixture was taken out and centrifuged at the speed of 4000 rpm for 15 min before the concentration determination.

3. Results and discussion

3.1. Characterization

Fig. 1 gives the XRD patterns (a), EDX patterns (b) and visible-light-DRS (c) of the pure phase of BiOCl and $\text{NaBiO}_3/\text{BiOCl}$ photocatalysts with different compositions. The XRD and EDX results demonstrated that the molar ratio of NaBiO_3 (JCPDS card no. 30-1161) and BiOCl (JCPDS card no. 82-0485) crystals in the $\text{NaBiO}_3/\text{BiOCl}$ composite photocatalysts can be well controlled by inducing different amounts of hydrochloric acid aqueous solutions. NaBiO_3 is an indirect transition semiconductor with the bandgap of 2.3–2.6 eV [14–16], indicating its visible light adsorption property. However, BiOCl is a type of wide bandgap semiconductor, the

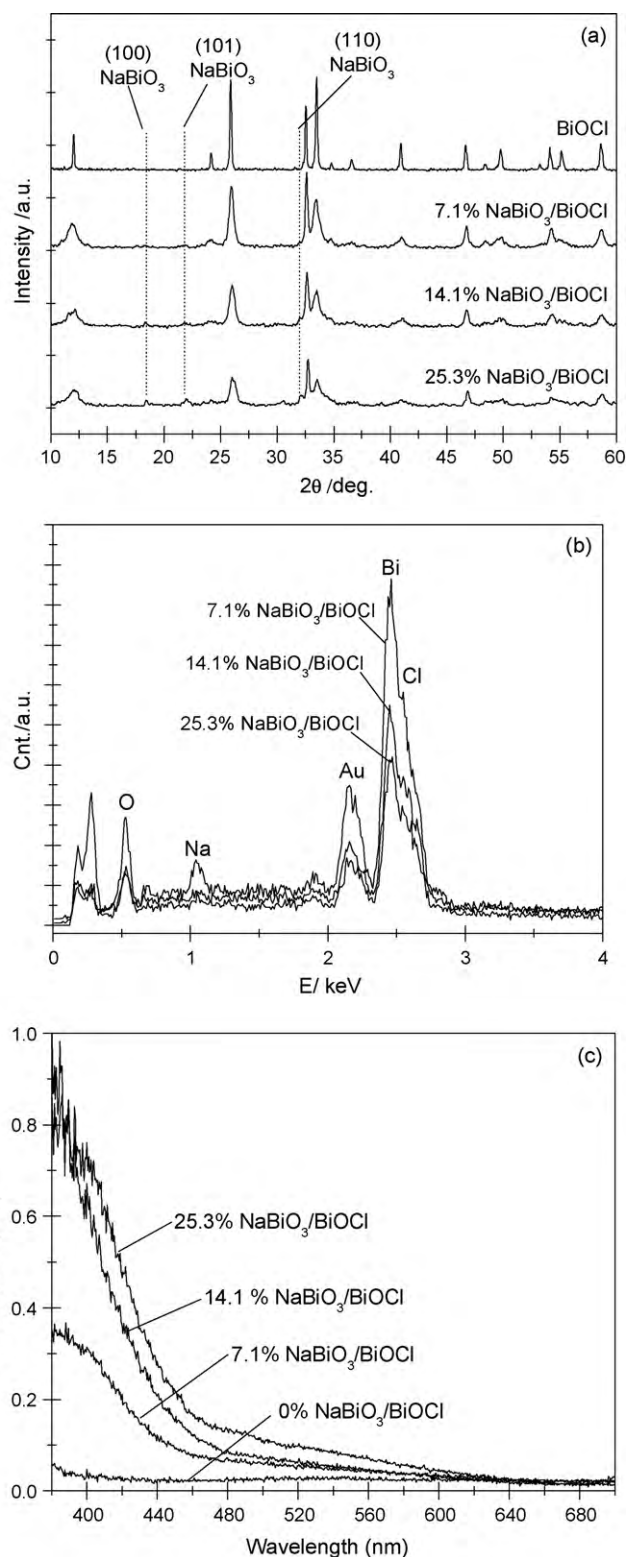


Fig. 1. XRD patterns (a), EDX patterns (b) and visible-light-DRS (c) of $x\%$ $\text{NaBiO}_3/\text{BiOCl}$ composites.

band gap range of which is 3.2–3.4 eV, according to the previous reports [20,21]. Therefore, it could be found that the visible-light-absorption ability of $\text{NaBiO}_3/\text{BiOCl}$ composite photocatalysts can be improved by increasing the molar ratio of NaBiO_3 to BiOCl because of the visible-light responsibility of NaBiO_3 . According to Kako et al., the long tail from Fig. 1(c) up to 620 nm could be possibly ascribed to the existence of lattice defects in NaBiO_3 crystal [14].

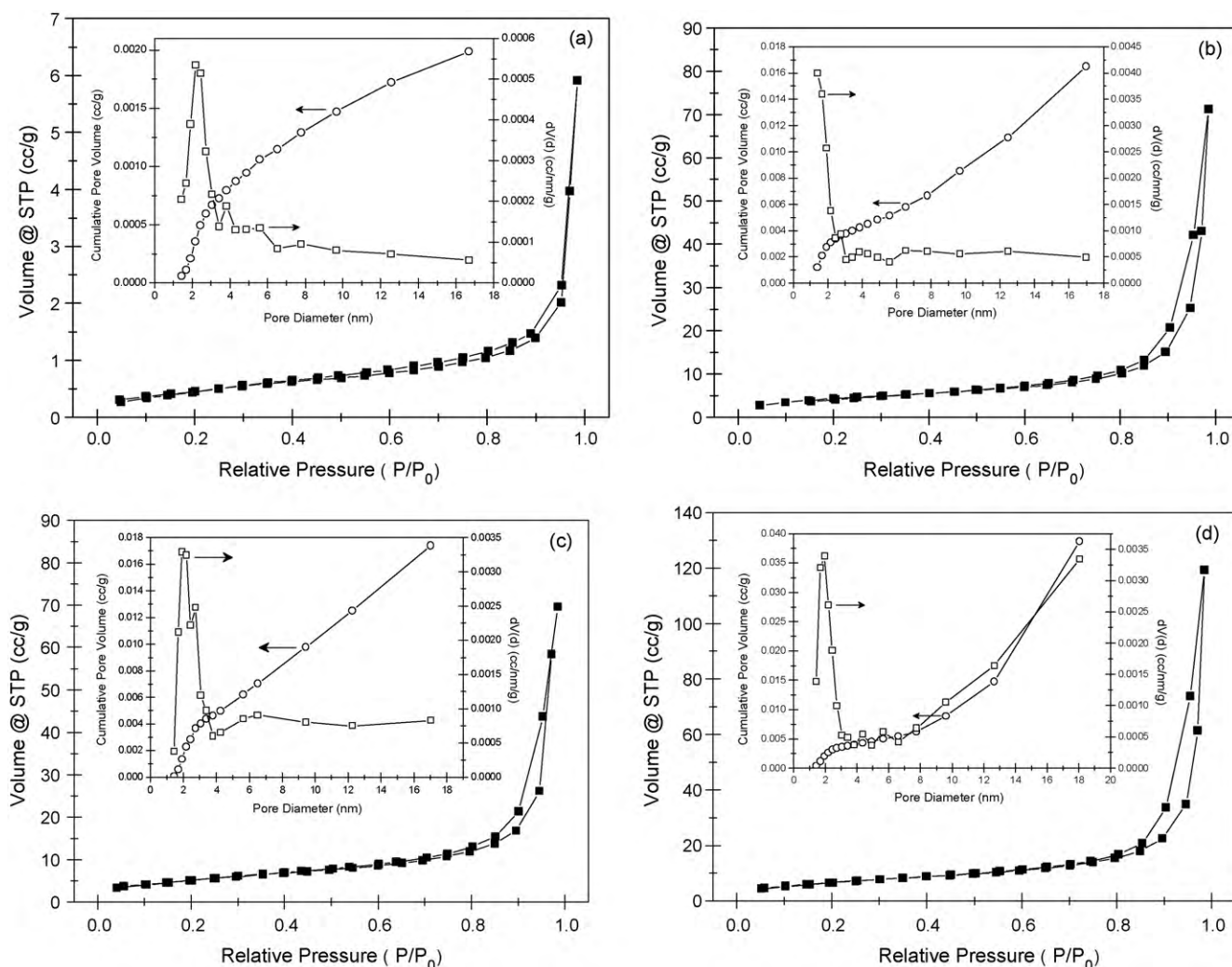


Fig. 2. N₂ adsorption–desorption isotherms and BJH pore size distributions from adsorption branch for the 0% NaBiO₃/BiOCl (a), 7.1% NaBiO₃/BiOCl (b), 14.1% NaBiO₃/BiOCl (c) and 25.3% NaBiO₃/BiOCl composites.

Fig. 2 shows the plots of nitrogen adsorption–desorption isotherms and BJH pore size distribution of BiOCl and the series NaBiO₃/BiOCl composite photocatalysts. It can be seen that both samples have sorption isotherms with a capillary condensation range starting at about $P/P_0 = 0.6$ – 0.7 , extending to almost $P/P_0 = 1.0$. This suggests the textural porosity of the samples and it is deduced that the porous structure could be caused by the stacking of the sheet-like structure of the composite photocatalysts (Fig. 3).

3.2. Sorption isotherms

In order to evaluate the sorption capacity of the catalysts, and to understand the interactions between the catalysts and the molecules of the selected pollutant (namely, Rhodamine B), sorption isotherms of Rhodamine B molecules on BiOCl and the series NaBiO₃/BiOCl photocatalysts were investigated. The Langmuir and Freundlich equations, were adopted to describe the experimental data, which can be expressed respectively as,

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

$$q_e = K_F C_e^{1/n} \quad (2)$$

where q_e represents the equilibrium sorption amount (mg/g), C_e is the equilibrium concentration (mg/L) of Rhodamine B in solution, q_m is the maximum sorption capacity (mg/g), K_L is the sorption

equilibrium constant (L/mg), K_F is a constant representing the sorption capacity ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$), and n is a constant depicting the sorption intensity.

As given in Fig. 4 and Table 1, the sorption isotherms of Rhodamine B on the BiOCl and NaBiO₃/BiOCl photocatalysts can be better fitted by the Langmuir model than the Freundlich model. It should be noted that the Langmuir equation is obtained based on the assumption of monolayer coverage, and thus the better fitting results of the sorption of Rhodamine B on the NaBiO₃/BiOCl photocatalysts implying the possible occurred monolayer sorption. From the q_m value (obtained through the Langmuir model) and the specific surface area of NaBiO₃/BiOCl photocatalysts, the area covered by one Rh.B molecule (σ) can be calculated, as shown in Table 2. Such a small σ value suggests that condensed monomolecular layer of Rh.B covers over the NaBiO₃/BiOCl surface. On the other hand, the plateau regions in the sorption isotherms of Rh.B on such NaBiO₃/BiOCl composite photocatalysts could be the result of the condensed liquid being filled in these pores. Because of the microporous and mesoporous structure of the composites, the sorption saturation of the Rh.B molecule monolayer on the surface of the NaBiO₃/BiOCl composite photocatalysts could not be the actual reason of the plateau regions in the sorption isotherms, although the sorption isotherm results can be well modeled by Langmuir equation. Meanwhile, on the basis of the results obtained through the Langmuir model, it is surprising to find out that the sorption capac-

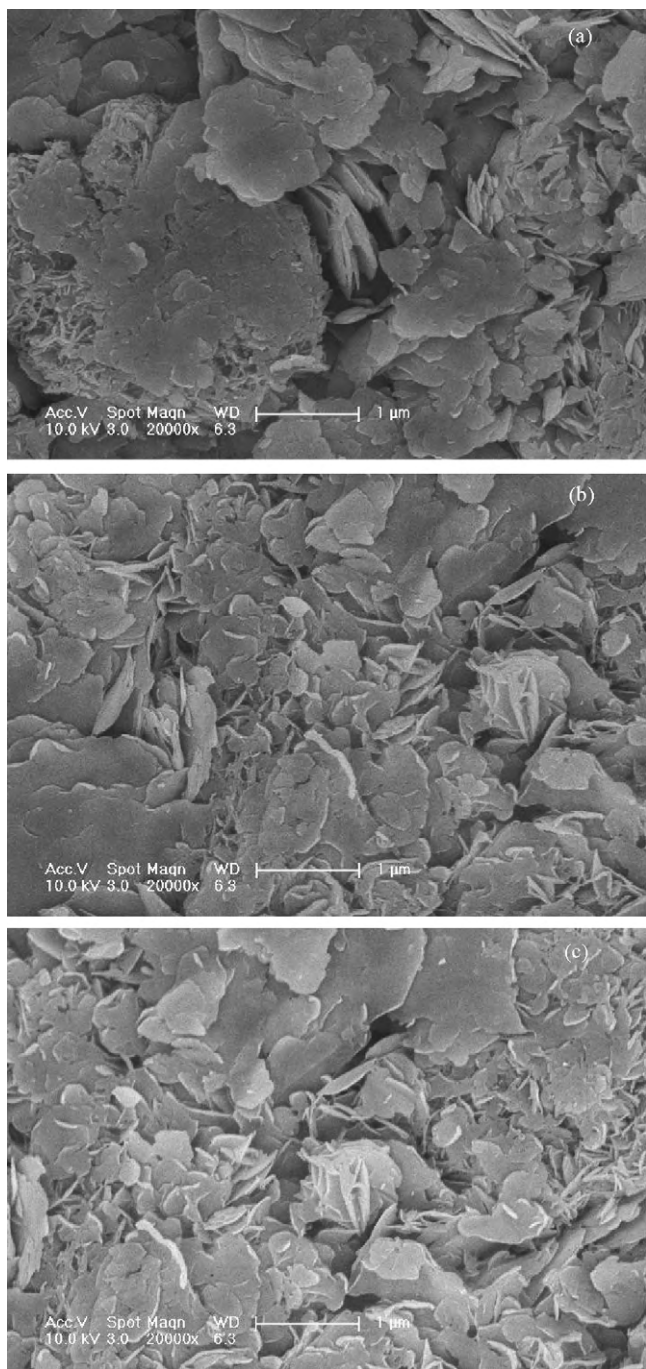


Fig. 3. SEM image of 7.1% (a), 14.1% (b) and 25.3% (c) $\text{NaBiO}_3/\text{BiOCl}$ composites.

ity of Rhodamine B on the $\text{NaBiO}_3/\text{BiOCl}$ photocatalysts was over 27–131 times as large as that on the pure BiOCl phase, possibly due to the larger sorption capacity of NaBiO_3 catalyst [14].

Table 1

Calculated equilibrium constants using the Langmuir and Freundlich equations for Rh.B sorption on pure phase of BiOCl and series $\text{NaBiO}_3/\text{BiOCl}$ photocatalysts.

$x\%$	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	r^2	K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$)	n^{-1}	r^2
0%	0.82622	0.16201	0.97871	0.86683	0.59709	0.97457
7.1%	22.33727	0.61821	0.91824	14.86787	0.37883	0.84794
14.1%	91.15282	2.71264	0.97042	23.35725	0.20274	0.95575
25.3%	108.39389	2.26955	0.96216	31.63199	0.23211	0.86552

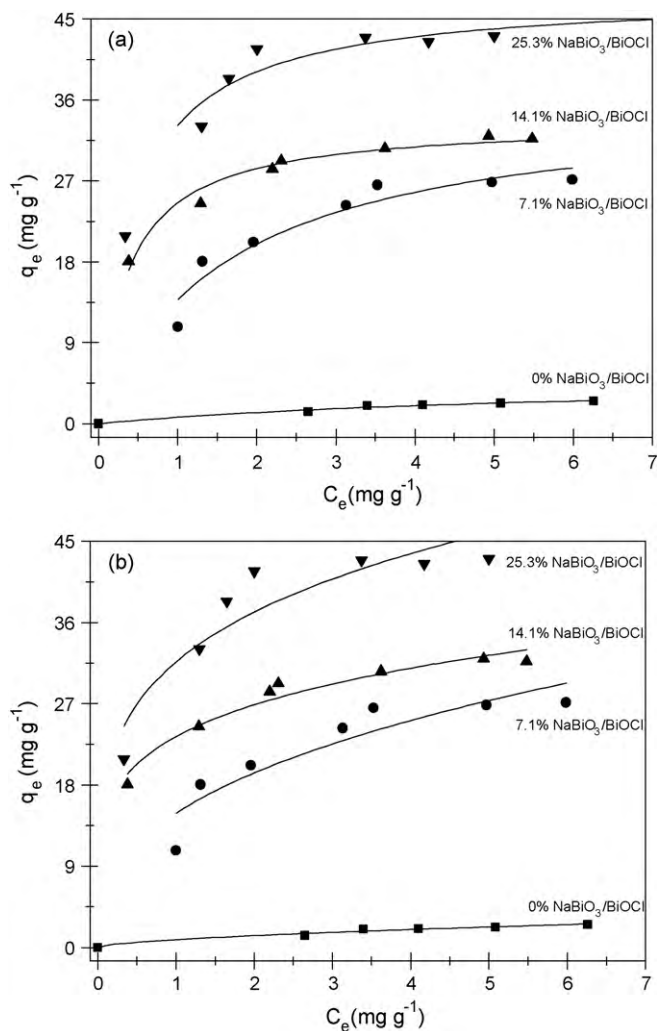


Fig. 4. Sorption isotherms of Rh.B on the BiOCl , 7.1% $\text{NaBiO}_3/\text{BiOCl}$, 14.1% $\text{NaBiO}_3/\text{BiOCl}$ and 25.3% $\text{NaBiO}_3/\text{BiOCl}$ composites at 25 °C and modeling using the Langmuir (a) and Freundlich equation (b).

Table 2

Some interface parameters of pure phase of BiOCl and $\text{NaBiO}_3/\text{BiOCl}$ composites obtained from the N_2 adsorption–desorption isotherms, BJH pore size distribution results and Langmuir fitting.

$x\%$	q_m (mmol g^{-1})	a ($\text{m}^2 \text{g}^{-1}$)	σ (m^2)	D_a (nm)	V_p ($\text{cm}^3 \text{g}^{-1}$)
0%	0.00172	1.748	0.16×10^{-23}	20.92	$9.14\text{E}-03$
7.1%	0.04663	15.802	0.49×10^{-23}	27.9	$1.10\text{E}-01$
14.1%	0.19029	19.091	1.66×10^{-23}	22.55	$1.08\text{E}-01$
25.3%	0.22628	24.508	1.53×10^{-23}	30.12	$1.85\text{E}-01$

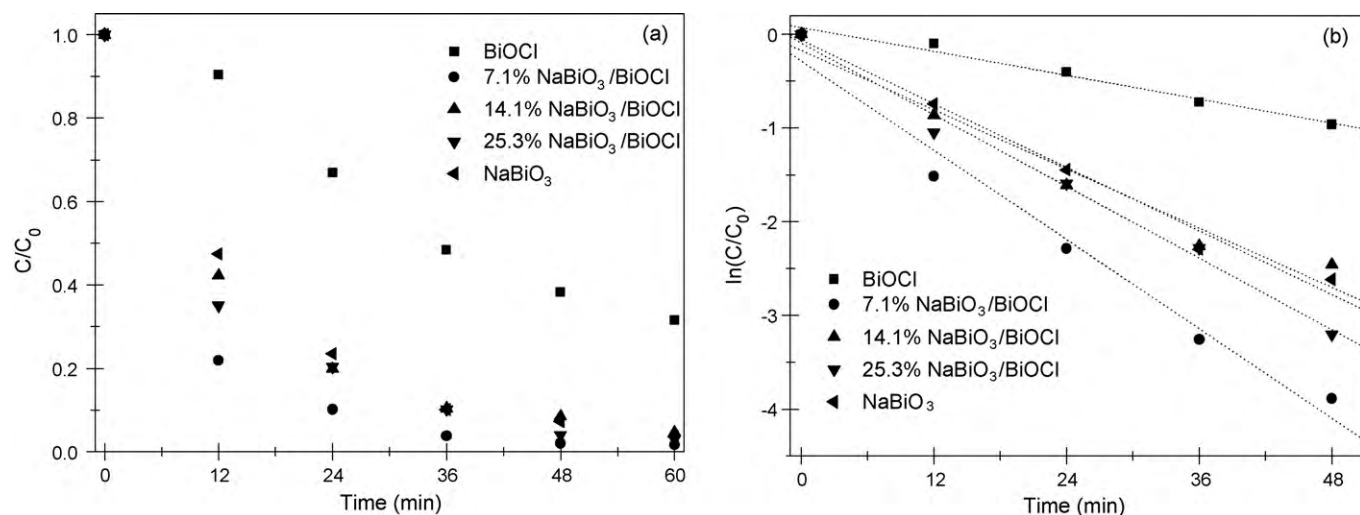


Fig. 5. Rh.B photocatalytically decomposed over pure phase of BiOI, NaBiO₃ and NaBiO₃/BiOI composites as a function of irradiation time and the pseudo first-order reaction kinetics.

3.3. Photocatalytic activity evaluation

Fig. 5 exhibits the photocatalytic activities of Rh.B dye on BiOI and NaBiO₃/BiOI photocatalysts. In comparison with the BiOI, the NaBiO₃/BiOI photocatalysts showed an improved photocat-

alytic activity under visible light irradiation. After 60 min of visible light irradiation, the removal efficiency of Rh.B by NaBiO₃/BiOI composite photocatalysts and NaBiO₃ were over 90%. The results also proved that the Rh.B molecules can be decomposed over the wide bandgap BiOI semiconductor (degradation efficiency was

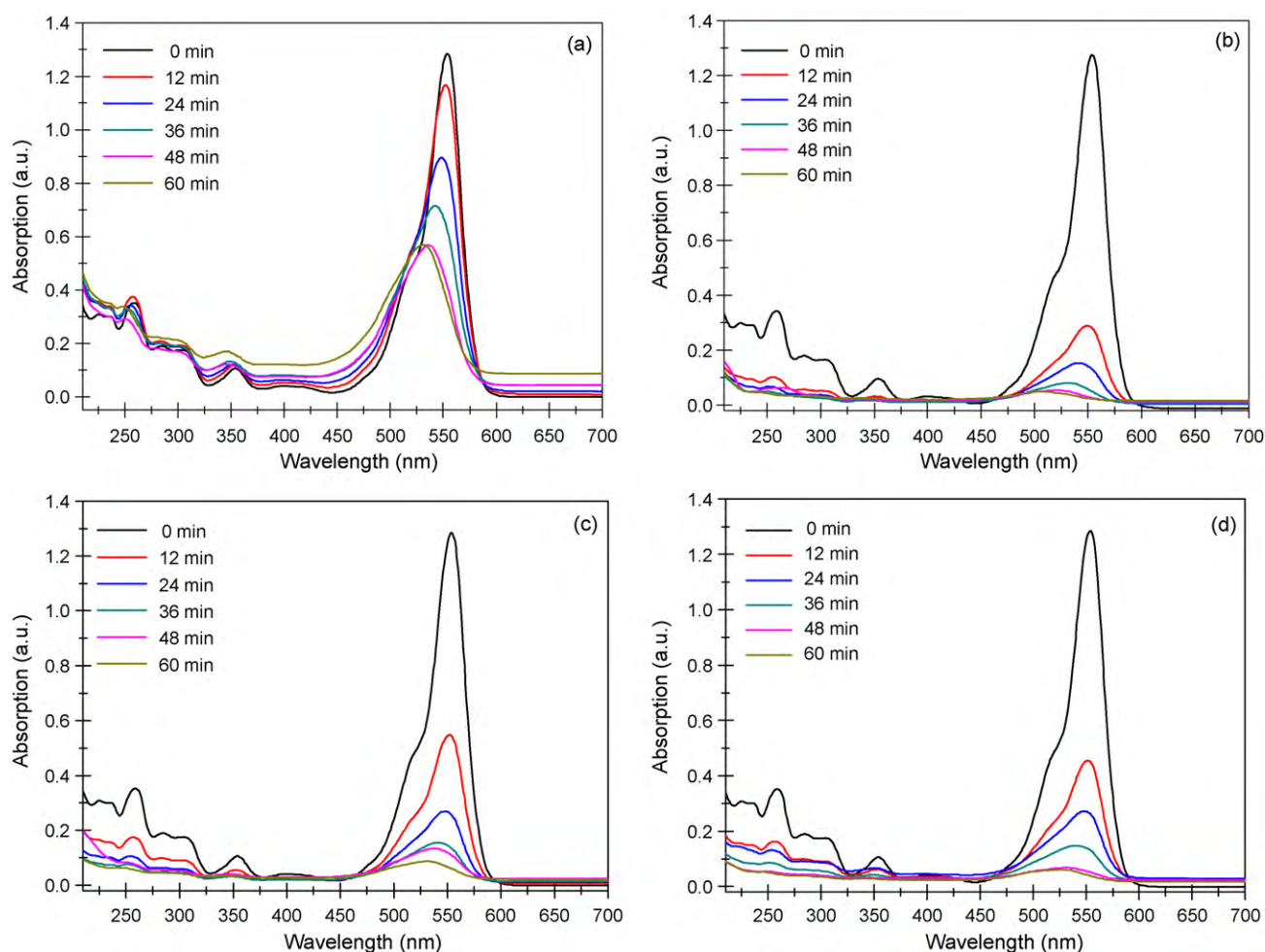


Fig. 6. UV-vis spectral changes of Rh.B aqueous solutions by using photocatalysts of BiOI (a) 7.1% NaBiO₃/BiOI (b), 14.1% NaBiO₃/BiOI (c) and 25.3% NaBiO₃/BiOI composites (d).

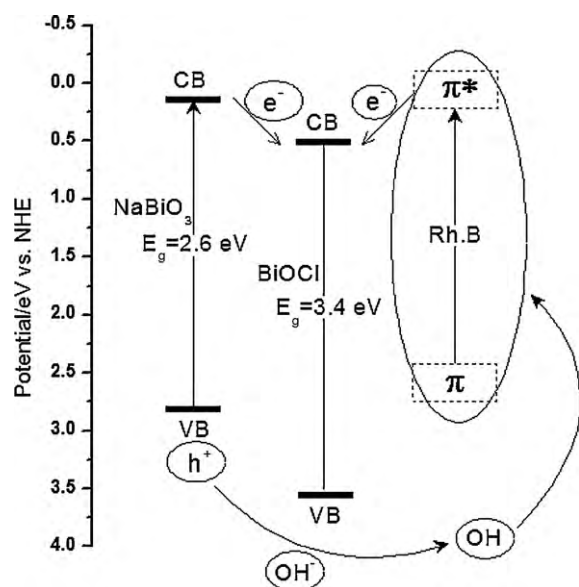


Fig. 7. Energetic diagram of NaBiO₃/BiOCl heterojunction.

~41%), possibly due to the effect of Rh.B dye sensitization on BiOCl semiconductor compounds [23].

The UV–vis spectra variations of Rh.B aqueous solutions (Fig. 6) show an obvious decrease in major absorption band at 554 nm. A concomitant wavelength shift of the band to shorter wavelengths ($\lambda_{\text{max}} = 506 \text{ nm}$) could be observed apparently, demonstrating the intermediate products of de-ethylated Rh.B molecules were formed during the photocatalysis [25]. The result further demonstrates that the Rh.B molecules were effectively decomposed during the photocatalysis. From the discussion above, it is noted that the final decomposition efficiency (after 1 h) of BiOCl after combination with a small amount of NaBiO₃ could be as high as the pure NaBiO₃ photocatalyst. On the other hand, the pseudo first-order reaction kinetics of Rh.B decomposition under visible light irradiation was investigated and the K_r values were determined, the results of which are listed in Table 3. The result shows that photocatalytic reaction rates of series NaBiO₃/BiOCl composite photocatalysts were higher than that of pure NaBiO₃ and BiOCl photocatalyst, although the final removal efficiencies over NaBiO₃/BiOCl and NaBiO₃ photocatalysts were similar. This result is very important because it proves that the combination of NaBiO₃ and BiOCl can effectively improve the photocatalytic performance and result in a synergistic effect of “1 + 1 > 2”.

The valence and conduction band edge (VB and CB) of BiOCl and NaBiO₃ semiconductors at the point of zero charge was calculated based on an atom's Mulliken electronegativity [26] and the predicted band edges were shown in Table 4. The predicted band edge potentials of BiOCl and NaBiO₃ suggest that the VB (or CB) potential of BiOCl are more positive (or negative) than those of NaBiO₃. It can be speculated that if under visible light irradiation, only NaBiO₃ semiconductor will be activated, the electrons generated to their conduction band are injected into the CB of inactivated BiOCl and the photogenerated holes from NaBiO₃ are not able to migrate to BiOCl, resulting in an effective electron-hole separation. Fig. 7 provides illustrations of interparticle electron transfer behavior under simulated solar light and visible light ($\lambda > 400 \text{ nm}$) irradiation. Moreover, the superior photocatalytic activity of NaBiO₃/BiOCl composite photocatalysts upon visible light irradiation can be partially attributed to the high sorption capacity of NaBiO₃.

The XRD patterns of the series NaBiO₃/BiOCl blend photocatalysts after photocatalysis was also investigated and the results (given in Fig. 8) show that the XRD patterns were almost similar to

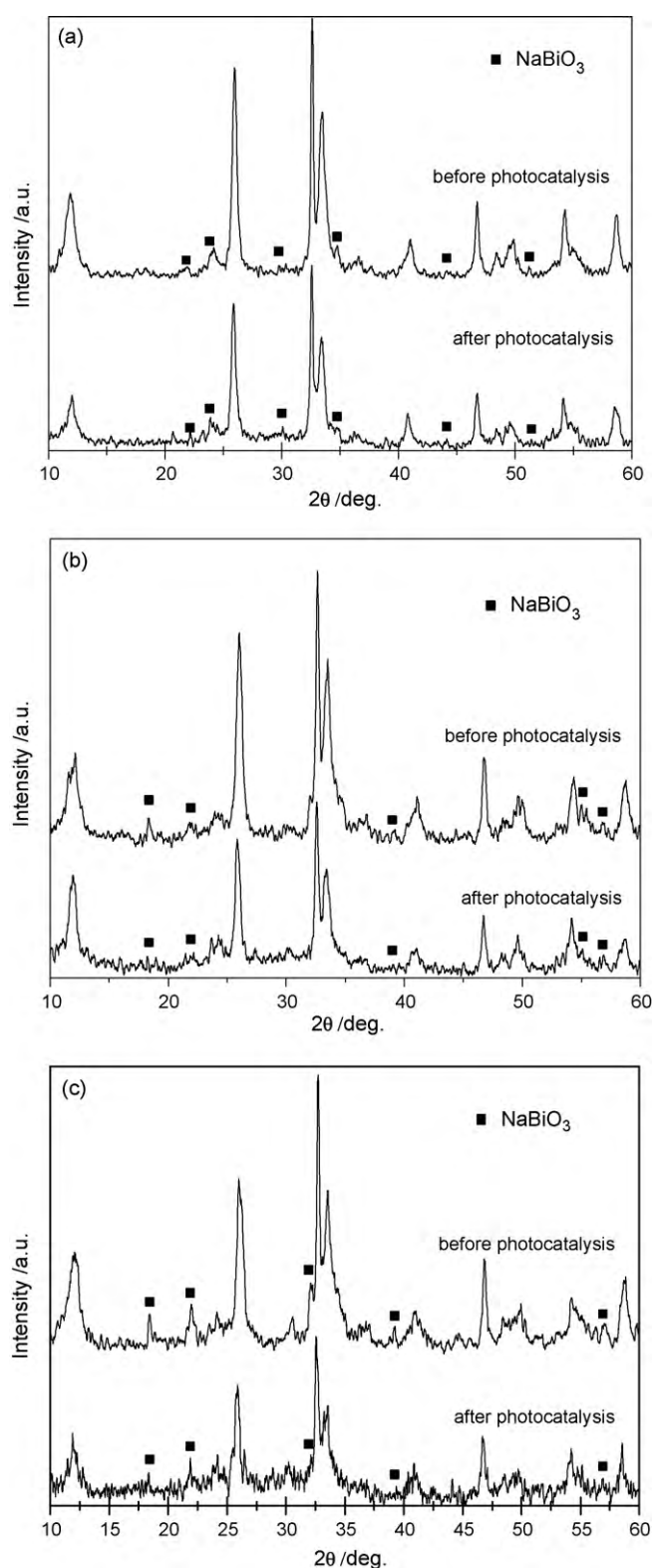


Fig. 8. XRD patterns of 7.1% NaBiO₃/BiOCl (a), 14.1% NaBiO₃/BiOCl (b) and 25.3% NaBiO₃/BiOCl composite photocatalysts (c) before and after photocatalysis.

those of the NaBiO₃/BiOCl photocatalysts before being used, suggesting the good chemical stability of the as-prepared NaBiO₃/BiOCl composite photocatalysts. As a type of heterogeneous photocatalysts, the NaBiO₃/BiOCl composite photocatalysts can be easily recycled by a simple filtration. Moreover, the sedimentation rate of series NaBiO₃/BiOCl composite photocatalysts in water was

Table 3

Photocatalytic kinetic results by using different catalysts.

	BiOCl	7.1% NaBiO ₃ /BiOCl	14.1% NaBiO ₃ /BiOCl	25.3% NaBiO ₃ /BiOCl	NaBiO ₃
K_r (min ⁻¹)	0.02123	0.07937	0.05663	0.06373	0.05253
r^2	0.9784	0.97575	0.96144	0.98985	0.98514

Table 4Absolute electronegativity, estimated band gap, calculated conduction band (CB) edge and valance band (VB) edge of BiOCl and NaBiO₃.

Catalyst	Absolute electronegativity (X /eV)	Estimated band gap (E_g /eV)	Calculated CB edge (E_{CB} /eV)	Calculated VB edge (E_{VB} /eV)
BiOCl	6.35901	3.19 ^a /3.4 ^b [ref]	0.26401/0.15901	3.45401/3.55901
NaBiO ₃	5.49579	2.3 ^a /2.6 ^b [ref]	-0.15421/0.30421	2.14579/2.90421

^a Estimated results.^b From references.

roughly calculated as $\sim 0.18 \text{ cm s}^{-1}$, however, sedimentation rate of P25 which is a well known photocatalyst and has been widely studied for wastewater treatment, was only about $\sim 0.004 \text{ cm s}^{-1}$. These results show good separability, which is an advantage for wastewater treatment.

4. Conclusions

NaBiO₃/BiOCl composite photocatalyst has been obtained by an in situ preparation approach, using NaBiO₃ and HCl aqueous solutions as the raw materials. An enhanced photocatalytic activity of NaBiO₃/BiOCl composite photocatalysts has been observed. Based on an atom's Mulliken electronegativity, it is found that effect of efficient charge separation on the NaBiO₃/BiOCl interface plays a key role for the catalytic enhancement. This study also showed the chemical stability and good separability of the as-prepared NaBiO₃/BiOCl composites.

Acknowledgements

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