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Investigation of adsorption and photocatalytic activities of *in situ* cetyltrimethylammonium bromide-modified Bi/BiOCl heterojunction photocatalyst for organic contaminants removal†

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Bi/BiOCl heterojunction was prepared *via* a hydrothermal method, using cetyltrimethylammonium bromide (CTAB) as a stabilizing agent. The structure and chemical properties of Bi/BiOCl with the three different CTAB contents were thoroughly analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), field-emission scanning electron microscope (FESEM), high resolution transmission electron microscope (HRTEM), UV-vis diffuse reflectance spectra (UV-vis DRS), zeta potential, and carbon element analysis, the results indicates that there are some important interactions between CTAB and Bi/BiOCl, resulting in decreasing the band gap of Bi/BiOCl with the increase of CTAB content. Two typical dyes, rhodamine B (RhB) and methyl orange (MO) which has different surface charges, were choosed as the target pollutants. Under the visible light ($\lambda = 420$ nm), the photocatalytic efficiency of Bi/BiOCl with a higher CTAB (Bi/BiOCl-a) was 3.72-fold more than that of Bi/BiOCl with a lower CTAB (Bi/BiOCl-c) to remove RhB. Bi/BiOCl heterojunction alone exhibited a poor degradation capability for the MO such as 5% of MO photodegradation with Bi/BiOCl-c. In contrast, MO removal efficiency by the Bi/BiOCl-a was 100%. Hence, the CTAB could play an important role to enhance the removal of dyes. Firstly, CTAB could absorb the target pollutants near the surface of Bi/BiOCl due to the electrostatic attraction and dispersion interaction; then Bi/BiOCl could degrade the pollutants *via* the *in situ* h^+ or $\cdot O^{2-}$ under the visible light. The proposed mechanism was supported by the FTIR and adsorption analysis.

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Introduction

Semiconductor-based photocatalysis has been considered as a promising and green chemical technology by using solar energy for the removal of harmful organic pollutants from water.^{1–3} In past several decades, TiO_2 has been the most widely used photocatalyst for organic water contaminants degradation.^{4–6} Niu *et al.* reported that TiO_2 /polypropylene composite is highly active for complete photodegradation of organic dyes and some permanent organic pollutants.⁷ Recently, BiOCl has been extensively investigated because of its physicochemical stability and layered structures. BiOCl is an excellent photocatalyst with unique optical properties and has a tetragonal

structure with lattice constants of $a = b = 0.389$ nm and $c = 0.789$ nm.² It is of a layer structure, Bi_2O_2 slabs interleaved by double slabs of Cl atoms in the tetragonal matlockite structure. It can often be used to decompose organic compounds into inorganic substances for purifying the textile dye polluted wastewater. For example, Zhang *et al.* reported that the photocatalytic activity of BiOCl was higher than that of TiO_2 on the degradation of methyl orange (MO) dye.³ Some studies also have confirmed that BiOCl exhibits a better performance than TiO_2 under UV light illumination for some dyes in aqueous solution.^{8–10} But for photocatalytic systems, the high rate of electron-hole recombination is due to the high band gap (3.4 eV).¹¹ Many methods are adopted to improve separation of the electron-hole pair, such as hierarchical nanostructures,^{12–14} halogen-mixing solid solutions,¹⁵ and crystal-facet control.¹⁶ Yet, the nanocomposites of metal-BiOCl heterojunctions have been a more effective strategy to solve the problem.¹⁷ The incorporation of metal nanoparticles in BiOCl, such as gold and silver, can effectively promote its photocatalytic performance, which serves as an electron trap, so that the charge transfer between BiOCl and metal substantially improves the electron-hole separation.^{18,19}

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In the synthesis of metal-BiOX ($X = \text{Cl}, \text{Br}, \text{I}$), large amounts of surfactants are often used,^{11–14} because surfactants play a key role in metal nanoparticles formation such as interaction with metal precursors and stability of metal species.²⁰ Thus, surfactants cannot be completely removed because of the interaction between metal nanoparticles and surfactant molecules.^{21,22} Only thermal and oxidative methods can successfully remove the stabilizing molecules, but reduce the catalytic capability.²³ Many researchers adopted washing method to remove surfactant molecules from the photocatalysts, but a few surfactant molecules may be left to affect the photocatalytic properties of catalysts, which is rarely reported. In consideration of the unique interaction, surfactant molecules should affect the photochemical properties of those photocatalysts. For instance, Shukla *et al.* reported that different cationic surfactants functionalized WO_3 nanoparticles showed a higher photocatalytic property for the degradation of highly toxic but immensely used azo dye than WO_3 alone under visible light.²⁴ Yu *et al.* reported that CTAB@BiOCl exhibited a higher adsorption capacity than the BiOCl alone and maintained a good photocatalytic activity.²⁵ These remaining surfactant molecules can affect the photochemical properties of photocatalysts, which required a further investigating.

Herein, Bi/BiOCl photocatalysts with different CTAB contents were prepared in ethanol. The influence of CTAB on the structure and chemical properties of Bi/BiOCl was also studied by XRD, XPS, FTIR, zeta potential and FESEM-mapping. The mechanism on how to remove dyes on the Bi/BiOCl with different CTAB contents under the visible light irradiation was further discussed. It found that removal efficiencies of dyes were increased more with the increase of CTAB content.

Experimental section

Materials

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, AR), cetyltrimethylammonium bromide (CTAB, AR), concentrated hydrochloric acid (HCl, 37%), rhodamine B (Rh B), methyl orange (MO), and absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the aqueous solutions were prepared by using ultrapure water (Mill-Q Biocel, 18 M Ω).

Preparation of Bi/BiOCl and BiOCl

Bi/BiOCl nanosheets were synthesized by a previously reported method.²⁴ In a typical procedure, 3 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added to 5 mL $\text{C}_2\text{H}_5\text{OH}$ containing 0.3 g CTAB. The mixture solution was stirring at room temperature before white slurry was formed. Then 0.5 mL HCl was dropwise added with stirring for a while. The above mixture was poured into a 100 mL Teflon-lined stainless autoclave to perform hydrothermal process at 180 °C for 5 h. The resulting precipitate was collected and washed using absolute ethanol and deionized water to remove the surfactant (Fig. 1), and then freeze-dried under vacuum. The sample was defined as Bi/BiOCl-a when the obtained product was washed using 150 mL absolute ethanol and 150 mL

Fig. 1 Schematic diagrams of CTAB change in Bi/BiOCl with the increase of washing frequencies.

deionized water under the aid of vortex; the sample was defined as Bi/BiOCl-b when 300 mL absolute ethanol and 300 mL deionized water were used under the aid of vortex; the sample was defined as Bi/BiOCl-c when Bi/BiOCl-a was dialyzed with deionized water till the conductivity of solution is equal to that of deionized water.

Preparation of BiOCl was the same as that of Bi/BiOCl, except that 5 mL $\text{C}_2\text{H}_5\text{OH}$ dissolving 0.3 g CTAB was replaced by 5 mL ultrapure water and samples was washed 6 times.

Photocatalytic activity measurement

The photocatalytic activities of samples were evaluated in terms of the photodegradation of dyes under visible light irradiation at ambient temperature. 50 mg of photocatalyst was added into a 100 mL of 25 mg L^{-1} dye aqueous solution to undergo a stirring in the dark for 30 min. After reaching a complete adsorption-desorption equilibrium (around 30 min), it was exposed to visible light irradiation offered by 250 W Xe lamp with a 420 nm cut-off filter under continuous stirring. The vertical distance between lamp and liquid level was 15 cm. A small quantity of liquid was sampled at desired time to measure variation of the concentration of dye in the solution. The concentrations of RhB and MO were determined from the absorbance at the wavelength of 554 nm and 464 nm respectively by an UV-visible spectrophotometer (UV-2990, Shimadzu, Japan).

Adsorption experiments

Batch adsorption experiments were carried out to evaluate the removal efficiency of Bi/BiOCl for MO in solution. Bi/BiOCl-a was placed in a beaker containing 100 mL 25 mg L^{-1} MO solution, followed by agitation at 150 rpm on a mechanical shaker under ambient and dark conditions. The effect of contact time on removal performance of Bi/BiOCl-a for MO was analyzed by drawing the samples at an arbitrary time period from 0 to 2 h and 0.15–0.5 g L^{-1} of Bi/BiOCl-a. The MO concentration was analyzed by UV-visible spectrophotometer (see in the above section).

Characterization

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (X'Pert PRO MPD, PANalytical) using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 mV and 40 mA, respectively. The data was recorded in a 2θ range of 5–90°. Infrared spectra were measured *via* KBr squash method using an ATR-FTIR spectrophotometer (Nicolet 8700, Thermo Fisher

Scientific, USA). Field-emission scanning electron microscope (FESEM) (SU-8020, Hitachi Limited, Japan) equipped with the energy-dispersive X-ray spectrometer, and high resolution transmission electron microscope (HRTEM) (JEM 2100F, Japan) were employed to characterize the morphology and crystalline structure of particles. The UV-vis diffuse reflectance spectra (UV-vis DRS) of the samples were recorded on a UV-vis spectrometer (U-3900, Hitachi, Japan) with an integrating sphere using BaSO₄ as the reference. The surface chemical composition of catalysts was analyzed by X-ray photoelectron spectroscopy (ESCALAB 250Xi Al K α , Thermo Fisher Scientific). BET surface areas were analyzed using a full automatic analyzer (ASAP2020HD88, Micromeritics Instrument Corp). Zeta potentials were analyzed by Zetasizer Nano size (Zetasizer2000, Malvern, UK).

Results and discussion

Characterization and chemical component analysis

XRD patterns of as-prepared BiOCl and Bi/BiOCl_s are shown in Fig. 2. Compared with pure tetragonal BiOCl (JCPDS file no. 06-0249)^{26,27} and pure Bi (JCPDS file no. 44-1274)^{26,28} (ref. Fig. S1[†]), the characteristic peaks of Bi/BiOCl_s exhibit the diffraction peaks of BiOCl tetragonal phase and Bi rhombohedral phase, but some diffraction peaks of Bi metal are difficult to be detected, except a few weak peaks. With the increase of washing frequency, the intensities of {001}, {002}, {003} peaks of BiOCl become stronger, indicating that {001}, {002}, {003} facets grow up. And peak intensity of Bi becomes weaker, which is probably attributed to Bi oxidation. In addition, some unknown diffraction peaks were detected from XRD patterns of Bi/BiOCl-a and Bi/BiOCl-b at round 7.5°, 15.0°, 18.7°, which are behind the XRD patterns of CTAB in Fig. S1.[†] This suggests that those unknown peaks may be resulted from CTAB as a template. Carbon element contents in Bi/BiOCl_s and BiOCl were analyzed by the elemental analyzer, which are summarized in Table 1. The carbon contents in Bi/BiOCl-a, Bi/BiOCl-b, and Bi/BiOCl-c were

Table 1 Carbon content and surface analysis of Bi/BiOCl_s and BiOCl

Samples	C (% wt)	Molar ratio of surface elements		Surface area (m ² g ⁻¹)
		Bi/O	Bi/Cl	
Bi/BiOCl-a	16.49	0.80	0.77	3.12
Bi/BiOCl-b	9.50	0.79	0.83	3.22
Bi/BiOCl-c	0.32	0.68	1.08	7.41
BiOCl	<0.1	0.74	0.91	2.84

16.49%, 9.50% and 0.32%, respectively. This suggests that CTAB could be left in the Bi/BiOCl_s.

The morphology and structure of samples were characterized by field emission scanning electron microscopy (FESEM). The high-magnification FESEM image of Bi/BiOCl_s in Fig. S2(c)–(h)[†] shows that Bi/BiOCl_s exhibit sheets-like structure with plenty of plates. The length of plates is varied from hundreds of nanometers to several micrometers, and thickness of plates is about 20–30 nm. In addition, the FESEM image of BiOCl (Fig. S2a and b)[†] is similar with that of Bi/BiOCl_s. Chemical element mapping analysis (Fig. 3a, b and S3[†]) reveals that the elements including Bi, Cl, O, C and N are uniformly distributed over the Bi/BiOCl_s. The SEM-EDS (Fig. 3c) further confirms that Bi/BiOCl-b contains Bi, O, and Cl with an atomic Bi : Cl ratio of 1.06, which is agreed with XPS results (Table 1). The high-resolution TEM images revealed in Fig. 4 that some small circular nanoparticles were dispersed on the surface of BiOCl. In addition, the resolved lattice fringes of 0.227 nm in Fig. 4a was coincided with the fringe spacing of the (1 1 0) lattice plane of the rhombohedral Bi metal nanoparticles.

The porous structure and specific surface area of Bi/BiOCl_s were further studied by the nitrogen adsorption-desorption experiments (Fig. S4[†]). All the samples display type II adsorption-desorption isotherms, which are typical characteristics of macroporous materials.²⁹ These macropores result from stacking sheets. This is confirmed by FESEM images. The BET specific surface areas of BiOCl-a, Bi/BiOCl-b, and Bi/BiOCl-c were 3.12 m² g⁻¹, 3.22 m² g⁻¹, 7.41 m² g⁻¹ (Table 1), which is consistent with previous literature reports,^{13,30} indicating that specific surface areas increase with the decrease of CTAB contents.

Fig. 5a shows the FT-IR spectra of CTAB, Bi/BiOCl-a, Bi/BiOCl-b and Bi/BiOCl-c samples. The main adsorption bands of CTAB were observed at wave numbers (2920 cm⁻¹, 2860 cm⁻¹, 1480 cm⁻¹, 1458 cm⁻¹, 1430 cm⁻¹, 960 cm⁻¹, 905 cm⁻¹, 720 cm⁻¹). Bands at 2920 cm⁻¹ and 2860 cm⁻¹ are attributed to CH₂ symmetric and antisymmetric vibrations.^{31,32} Bands at 1430 cm⁻¹ and 1480 cm⁻¹ are assigned to the anti-symmetric and symmetric modes of vibrations of the head group methylene moiety (N⁺-CH₃), respectively.^{33,34} Band at 1458 cm⁻¹ arises from the CH₂ scissoring modes.³³ Bands at 960 cm⁻¹ and 905 cm⁻¹ can be assigned to the C-N⁺ stretching modes.^{33,34} Band at 720 cm⁻¹ corresponds to the rocking mode of the methylene (-CH₂)_n chain.^{33,35} For IR spectra of Bi/BiOCl_s, the peaks at 3540 cm⁻¹ and 1630 cm⁻¹ could be assigned to O-H stretching mode and vibration mode of the water molecules.³⁶ The IR

Fig. 2 XRD patterns of BiOCl, and Bi/BiOCl-a, b and c.

Fig. 3 FESEM image (a), EDS-mapping (b) and EDS (c) of Bi/BiOCl-b.

Fig. 4 HRTEM images of Bi/BiOCl-a (a) and Bi/BiOCl-b (b).

spectra of Bi/BiOCl show many same peaks with that of CTAB, such as 2920 cm^{-1} , 2860 cm^{-1} , 1480 cm^{-1} , 960 cm^{-1} , 905 cm^{-1} , 720 cm^{-1} . And the intensities of these peaks become weaker or disappear with the increase of washing frequency, indicating that CTAB content is reduced. This also shows that a few CTAB is left in the Bi/BiOCl, affecting Bi/BiOCl chemical properties.

Fig. 5b shows the zeta potential values of Bi/BiOCl as a function of pH. Bi/BiOCl-a presents positive charge ($52 \pm 3\text{ mV}$) for a whole pH, and Bi/BiOCl-b also shows positive charge, ranging from $52 \pm 3\text{ mV}$ at acidic medium to $40 \pm 2\text{ mV}$ at basic medium. However, zeta potential of Bi/BiOCl-c decreases from 25 mV to -5 mV with the increase of pH (3.6–8.2), producing an IEP at $\text{pH} \sim 7.0$. Thus, it is indicated that higher CTAB in the Bi/BiOCl samples can increase obviously surface charge density, probably resulting from $-\text{C}-\text{N}^+$ group. This result also agrees with FTIR analysis, such as the decrease of peak intensity of the $\text{C}-\text{N}^+$ stretching modes with the increase of washing frequency.

The UV-vis DRS spectra of Bi/BiOCl-a, Bi/BiOCl-b, and Bi/BiOCl-c samples were measured by a UV-vis spectrometer (Fig. 6). A steep increase of the absorption at 432 nm of wavelengths can be assigned to the intrinsic band gap absorption of Bi/BiOCl-a. UV-vis DRS of Bi/BiOCl samples exhibit a blue shift and reduced photoabsorption in the visible light range with the decrease of CTAB content in samples. For example, the intrinsic band gap absorption of Bi/BiOCl-c appears at 383 nm . The enhanced photoabsorption in the visible light range can be attributed to the presence of CTAB.

X-ray photoelectron spectroscopy (XPS) was performed in order to investigate the surface compositions and chemical

Fig. 5 FTIR spectra of CTAB and Bi/BiOCl-a, b and c samples (a) and zeta potential of Bi/BiOCl-a, b and c samples as a function of pH (b).

Fig. 6 UV-vis diffuse reflectance spectra of Bi/BiOCl-a, b and c samples.

states of Bi/BiOCl. Fig. 7f shows the presence of Bi, O, Cl, C, N peaks in Bi/BiOCl, and the corresponding binding energy values are listed in Table 2. In Fig. 7a, the high-resolution Bi 4f spectrum for Bi/BiOCl-c (BiOCl) exhibits two individual peaks at 159.4 eV (159.4 eV) and 164.7 eV (164.8 eV), assigned to the binding energies of Bi 4f_{7/2} and Bi 4f_{5/2}.³⁷ For Bi/BiOCl-a or Bi/BiOCl-b, the peaks of Bi 4f_{7/2} and Bi 4f_{5/2} shift to lower binding energy at 159.0 eV and 164.3 eV, 158.9 eV and 164.2 eV, respectively, which could be due to a deficiency in oxygen.³⁸ The O 1s peak at around 530.1 eV (530.2 eV) for Bi/BiOCl-c (BiOCl) (Fig. 7b) is characteristic of O species in the bismuth-oxygen bond of BiOCl lattice, and the O 1s peak at 531.5 eV (531.9 eV) can be ascribed to the O species in oxygen-deficient regions.^{37–39} For Bi/BiOCl-a and Bi/BiOCl-b, the main peaks of O 1s shifts to low binding energy of 529.7 eV and 529.6 eV, respectively, which could be assigned to oxygen adsorption state,⁴⁰ indicating that CTAB could be adsorbed on these samples due to electric attraction interaction of C-N⁺ and oxygen exposure. The Cl 2p spectrum for Bi/BiOCl-c (BiOCl) is resolved into two peaks

located at 198.1 eV (198.2 eV) and 199.7 eV (199.8 eV) (Fig. 7c), which are ascribed to the binding energies of Cl 2p_{3/2} and Cl 2p_{1/2}, respectively.⁴¹ For Bi/BiOCl-a or Bi/BiOCl-b, the peaks shift at lower binding energy with 197.8 eV and 197.6 eV, respectively, indicating that N-Cl bond could appear, which is reported by Catherine *et al.*⁴² The N 1s peaks of Bi/BiOCl-a, Bi/BiOCl-b, and Bi/BiOCl-c were at 402.4 eV, 402.2 eV and 403.1 eV (Fig. 7d), which is attributed to the positively charged nitrogen (N⁺) in CTAB.⁴³ The C 1s spectra of Bi/BiOCl could be fitted with a main band at 284.7 eV or 284.8 eV (Fig. 7e), attributed to C-C or C-H bond, and include that another peak at 286.0 eV or 285.8 eV could be associated to C-N bond.⁴⁴ These correspond to binding energy of CTAB with 284.7 eV and 285.5 eV.

Photocatalytic activity

Rhodamine-B (RhB) with a positive charge and Methyl Orange (MO) with a negative charge were chosen respectively as the typical organic pollutants to evaluate the photocatalytic activities of Bi/BiOCl under the visible light. The photodegradation of RhB with Bi/BiOCl is shown in Fig. 8. Adsorption/desorption equilibrium was achieved between Bi/BiOCl and RhB solution before visible-light irradiation, and adsorption was about 10–20% (Fig. 8a). In order for a better comparison, blank experiment was also performed under the same condition, finding that degradation efficiency of RhB was extremely low. The photodegradation of RhB for Bi/BiOCl-a, Bi/BiOCl-b and Bi/BiOCl-c was 99.4%, 98.4%, 58.7%, respectively, after 120 min of irradiation. To quantitatively investigate the reaction kinetics of RhB degradation, experimental data was fitted by a pseudo-first-order model (Fig. 8b). The corresponding reaction constants (*k*) (Fig. 8c) of Bi/BiOCl-a, Bi/BiOCl-b and Bi/BiOCl-c were 0.0223 min^{−1}, 0.0177 min^{−1}, 0.006 min^{−1}, respectively, indicating that Bi/BiOCl-a shows a better photocatalytic activity than Bi/BiOCl-b and Bi/BiOCl-c. This also suggests that CTAB has a large influence on the chemical properties of Bi/BiOCl, enhancing RhB degradation with Bi/BiOCl.

Fig. 7 High-resolution XPS spectra (a, Bi 4f; b, O 1s; c, Cl 2p; d, N 1s; e, C 1s) and survey XPS spectra (f) of CTAB, BiOCl, and Bi/BiOCl-a, b and c samples.

Since RhB is a positive organic dye, its removal mainly depends on photocatalytic activity. To further demonstrate chemical adsorption properties of Bi/BiOCl, MO was chosen, as shown in Fig. 8d. During the degradation, the unpromoted photolysis of MO is regarded as negligible. MO concentration almost keeps constant after 10% of MO amount is adsorbed on the Bi/BiOCl-c. In contrast, MO removal efficiency with Bi/BiOCl-a and Bi/BiOCl-b are almost 100% after adsorption in dark. This indicates that CTAB in the Bi/BiOCl can enhance the MO adsorption.

Photocatalytic mechanism

To further investigate the reaction mechanism between Bi/BiOCl and dyes, IR spectra of products after MO and RhB photocatalytic degradation are compared in Fig. 9. The main peaks in the spectrum of MO are as following (Fig. 9a): peaks at 1598 cm^{-1} , 1515 cm^{-1} and 1443 cm^{-1} corresponding to the vibration mode of C=C on benzene skeleton; peak at 1362 cm^{-1} corresponding to the vibration mode of aromatic C-N; peak at 1108 cm^{-1} corresponding to the vibration mode of 1,4 positions

Table 2 Binding energy of Bi 4f, O 1s, Cl 2p, N 1s, C 1s for different samples^a

Samples	Binding energy (eV) of surface elements									
	Bi 4f		Cl 2p		O 1s		N 1s		C 1s	
Bi/BiOCl-a	164.3	159.0	199.4	197.8	531.9	529.7	402.4	399.7	286.0	284.7
Bi/BiOCl-b	164.2	158.9	199.2	197.6	532.2	529.6	402.2	399.4	285.9	284.8
Bi/BiOCl-c	164.7	159.4	199.7	198.1	531.5	530.1	403.1	399.7	286.8	284.8
BiOCl	164.8	159.4	199.8	198.2	531.9	530.2	—	—	—	—
CTAB	—	—	—	—	—	—	402.2	—	285.5	284.7

^a “—” represents undetected.

Fig. 8 Photodegradation of RhB or MO with Bi/BiOCl: (a) the change of RhB concentration; (b) pseudo-first-order kinetic model fitting curves of RhB photodegradation; (c) pseudo-first-order kinetic reaction rate constants (k) of RhB photodegradation; (d) the change of MO concentration (Bi/BiOCl-a, b and c dosage: 0.5 g L^{-1} ; RhB or MO initial concentration: 25 mg L^{-1}).

substituted on aromatic compounds; peaks at 1031 cm^{-1} and 1005 cm^{-1} corresponding to the vibration mode of sulfonate; peaks at 744 cm^{-1} , 690 cm^{-1} and 615 cm^{-1} corresponding to the vibration mode of outside surface deformation of C–H with five adjacent hydrogen atoms. Peak at 1031 cm^{-1} is red-shifted by 4 cm^{-1} in the Bi/BiOCl, supporting that sulfonate group of MO is interacted with the surface of Bi/BiOCl.^{45,46} In addition, most peaks of MO appear in the IR spectra of products after MO

reaction with Bi/BiOCl-a and Bi/BiOCl-b, indicating that MO is adsorbed on the Bi/BiOCl-a and Bi/BiOCl-b. But these characteristic peaks are hard detected in the IR spectrum of Bi/BiOCl-c reaction with MO, which indicates that MO is almost no adsorbed on the Bi/BiOCl-c. Moreover, the peaks intensity at 962 cm^{-1} , 905 cm^{-1} , 720 cm^{-1} belonging to CTAB are decreased, indicating that CTAB may be leached from Bi/BiOCl.

Fig. 9 FTIR spectra of MO, RhB and products after MO (a)/RhB (b) removal via Bi/BiOCl-a, b and c.

Fig. 9b shows the IR spectra of RhB reaction with Bi/BiOCl. Compared with products after MO reaction with Bi/BiOCl, IR peak intensity of RhB with Bi/BiOCl is quite weaker and broader, such as round 1582 cm^{-1} , 1465 cm^{-1} , 1379 cm^{-1} , 1334 cm^{-1} , 756 cm^{-1} , which suggests that RhB adsorption amount is much less. In addition, peaks at 962 cm^{-1} , 905 cm^{-1} , 720 cm^{-1} that belongs to CTAB are much broader, indicating that MO can prevent better CTAB leaching from Bi/BiOCl than RhB.

In consideration of strong adsorption interaction between MO and Bi/BiOCl-a/b, MO adsorption experiment on Bi/BiOCl-a was carried out to investigate the MO removal process on the Bi/BiOCl-a with CTAB in Fig. 10. The MO adsorption process includes three procedures: first, fast step takes extremely shorter time, depending on intensively electric attraction; secondly, slow step takes several minutes to one hour, depending on electrostatic attraction and dispersion interaction; thirdly, an equilibrium step. This indicates that CTAB

content in the Bi/BiOCl has significant influence on the MO adsorption.

Based on the above information obtained, a possible reaction mechanism of MO or RhB removal on the CTAB modified Bi/BiOCl is proposed in Fig. S5,† as following: first, organic pollutant molecules may be adsorbed nearby the surface of Bi/BiOCl, because of the electrostatic attraction and dispersion interaction. Secondly, under visible light illumination, the electrons in the VB of BiOCl are excited to oxygen vacancies states and then holes remain in the VB of BiOCl.²⁴ The electrons are further transferred to nearby Bi nanoparticles, and then trapped by the O_2 to form reactive $\cdot\text{O}^{2-}$.^{47,48} Finally, organic molecules adsorbed onto the surface of Bi/BiOCl may also be oxidized into other organic compounds *via* h^+ or $\cdot\text{O}^{2-}$ radicals.

Conclusions

A Bi/BiOCl heterojunction was prepared *via* a hydrothermal method, using CTAB as a stabilizing agent. The chemical interaction between CTAB and Bi/BiOCl was explained by FTIR, XPS and XRD, such as N^+-Cl or N^+-O binding, which directly affect the band gap of Bi/BiOCl. The MO removal efficiency was increased with the increase of CTAB content in the Bi/BiOCl nanocomposites due to adsorption, which is confirmed by FTIR, zeta potential and adsorption experiments. For RhB removal, the photocatalytic efficiency of Bi/BiOCl-a with a higher CTAB content was 3.72-fold more than that of Bi/BiOCl-c with a lower CTAB content under 420 nm visible light, due to synergy between CTAB adsorption and photocatalytic oxidation. Therefore, it can be found that CTAB in the Bi/BiOCl has a key pole in the dyes removal.

Conflict of interest

The authors declare no competing financial interest.

Fig. 10 MO adsorption process on Bi/BiOCl-a (Bi/BiOCl-a dosage: $0.05\text{--}0.5\text{ g L}^{-1}$; MO initial concentration: 25 mg L^{-1}).

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