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Synthesis of novel p-n heterojunction m-Bi₂O₄/BiOCl nanocomposite with excellent photocatalytic activity through ion-etching method

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ABSTRACT

A novel p-n heterostructure photocatalyst m-Bi₂O₄/BiOCl was successfully synthesized through a facile ion-etching method. Via adjusting the added volume of HCl solution, a series of different ratios of composite photocatalysts were obtained. The as-prepared samples of physical, chemical and optical characteristics were examined by X-ray diffraction, scanning electron microscope, transmission electron microscope, energy dispersive X-ray spectroscopy, selected-area electron diffraction, Fourier transform infrared absorption, Raman microscope, N₂ adsorption-desorption, X-ray photoelectron spectroscopy and UV-vis spectrum technologies. The photocatalysts showed high degradation rate and complete mineralization ability for methyl orange and tetracycline solution under visible light. The reaction rate constant of m-Bi₂O₄/BiOCl for methyl orange was 52.28 times higher than that of BiOCl. The characterization presented a good stability of materials. Furthermore, the photocurrent response test certified that the heterostructure effectively accelerated the separation and migration of photo-generated carriers. The scavenger experiments evidenced that hole (h⁺) and superoxide radical (•O₂⁻) were the primary active radicals. A possible photocatalytic mechanism was proposed. This work provided an alternative photocatalyst applied to water environmental remediation.

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1. Introduction

Recently, photocatalysts as a kind of favorable and green media for environmental remediation have drawn much attention due to the important roles that they play. Among these photocatalysts, bismuth-based semiconductors are considered to be environmental friendly photocatalysts to purify pollutants. Some photocatalysts, such as Bi₂O₃ [1,2], BiPO₄ [3,4], Bi₂WO₆ [5,6], BiOM (M = Cl, Br or I) [7–9] and BiVO₄ [10,11],

etc., are widely applied to degrade dyes, phenol, other organic pollutants, and even photocatalytic removal of NO [12–15].

BiOCl, as a p-type and novel ternary semiconductor, has a unique layer structure, whose internal [Bi₂O₂]²⁺ layers interleave double Cl⁻ slabs [16,17]. This interaction structure induces the formation of a strong internal electric field, leading to promoting the transformation of photo-generated carriers and effectively suppressing their recombination [18–20]. Moreover, the Bi 6s, O 2p and Cl 2p orbitals hybridize and its conduction

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band (CB) was consisted of Bi 6s and Bi 6p orbitals. According to existing reports, the large dispersed Bi 6s orbital is beneficial to strengthening the mobility of photo-induced carries [7,21].

The large band gap energy of BiOCl (~ 3.4 eV) merely adsorbs UV light, limiting the application of BiOCl. That seeking new ways to modify photocatalytic performance of BiOCl is one of main directions of photocatalytic research. Li et al. [22] synthesized ultrathin BiOCl nanosheet using ethanol and water as solvents and Polyvinylpyrrolidone as surfactant. Mi et al. prepared ultrathin nanosheet photocatalyst of Fe(III) modified BiOCl with exposure of active (001) facet [23]. These ultrathin BiOCl nanosheets decrease the transferring path length of carriers from interior to surface and prolong the life of charge carries, leading to enhancing the absorption for vis-light and photocatalytic activity of photocatalysts. Both BiOCl/Ag₂CO₃ hybrids [24] and synthesized BiOCl/BiPO₄ via electrochemical anodization method [25] improved photocatalytic activity of BiOCl. However, these photocatalysts have some shortcomings, for instance, high cost of raw materials, complicated operation, low efficiency and poor adaptability to environment and so on.

In addition, forming heterojunctions between different semiconductors has been certified to be a useful method to promote photocatalytic activity of BiOCl. For instance, BiOCl/SnO₂ [26], BiOCl/Bi₂S₃ [27], Bi₂O₂CO₃/BiOCl [28] and g-C₃N₄/BiOCl [29] performed good photocatalytic ability in degrading organic pollutants. Both closely linked interface in heterojunctions and well-matched band structure can effectively inhibit the recombination of photo-generated carriers and speed up photocatalytic degradation for organic pollutants [30–32]. However, photocatalytic efficiency of BiOCl and charge transfer rate of related heterojunctions need to be further enhanced.

Nearly two years, a novel photocatalyst of monoclinic dibismuth tetroxide (m-Bi₂O₄) responding to visible light was constructed successfully [32–34]. The excellent property of m-Bi₂O₄ and m-Bi₂O₄-based compounds immediately caught the researchers' interest and achieved some good results. For example, Bi₂O₄/Fe₃O₄ hybrid nanocomposites were applied to degrade ibuprofen and Z-scheme g-C₃N₄/m-Bi₂O₄ catalyst was utilized to inactivate *E. coli* K-12 [35,36]. Heterostructure Bi₂O₂CO₃/Bi₂O₄ photocatalyst was used to decompose dyes and phenol [37].

The combination of photocatalysts with semiconductors is a trend to greatly heighten the photocatalytic performance [38]. Furthermore, ion-etching chemical method has indicated to be an efficient technology to synthesize semiconductor photocatalysts, such as bismuth-based photocatalysts [38,39], etc. Based on existing literature, no researches of m-Bi₂O₄/BiOCl compound are reported.

Given the superiorities and researches of BiOCl and m-Bi₂O₄, we synthesized m-Bi₂O₄/BiOCl photocatalyst by an ion-etching method. The degradation of methyl orange and antibiotic of tetracycline were examined under vis-light to characterize capability of novel m-Bi₂O₄/BiOCl photocatalyst. The aim is to enhance the photocatalytic performance of BiOCl and enlarge its absorbance range to sun light. Furthermore, the degradation mechanism of m-Bi₂O₄/BiOCl photocatalyst was also proposed.

2. Experimental

2.1. Chemicals and materials

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), methyl orange (MO) and isopropanol (IPA) were gained from Macklin Reagents (shanghai) Co., Ltd. Sodium bismuthate hydrate (NaBiO₃·2H₂O), 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL), sodium oxalate (Na₂C₂O₄), hydrochloric acid (HCl, 36 wt%–38 wt%) and tetracycline were obtained from Aladdin Reagents (Shanghai). The above reagents were all analytical grade.

2.2. Synthesis of m-Bi₂O₄

The m-Bi₂O₄ sample was prepared via hydrothermal method based on reported literature [40]. Typically, certain amount of NaBiO₃·2H₂O was distributed in 90 mL ultrapure water with sonication for 0.5 h. It was vigorously stirred for 1 h at room temperature, then was putted into a 150-mL autoclave and heated to 433 K for 12 h. The resulted products were gathered through centrifuging and washing. The m-Bi₂O₄ sample was dried at 333 K for 12 h under vacuum.

2.3. Synthesis of m-Bi₂O₄/BiOCl

Ion-etching method to synthesize m-Bi₂O₄/BiOCl complex was based on previous literature [41,42]. The synthetic route followed as: 1 mmol/L m-Bi₂O₄ was dispersed in 10 mL absolute ethanol with ultrasound. Some volume of diluted HCl solution (1 mol/L) was added into suspension dropwise with magnetic stirring. Then the above solution was stirred continuously for 3 hours and ultrasonically treated for 1 hour. Then the product was dried at 333 K for 20 h in a vacuum oven after filtration and washing.

In this experiment, the relative ratio of m-Bi₂O₄ and BiOCl were controlled by adjusting the volume of diluted HCl solution. Thus, the various products of m-Bi₂O₄/BiOCl were denoted as BiOCl-1, BiOCl-1.5 and BiOCl-2, respectively, based on the volumes of used HCl solution of 1, 1.5 and 2 mL. Pure BiOCl was synthesized by adding excessive HCl. Fig. 1 was the schematic diagram of prepared m-Bi₂O₄/BiOCl photocatalyst.

2.4. Sample characterizations

The structure properties of as-prepared photocatalysts were checked by powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer, USA). Transmission electron microscopy (TEM, JEM-2100, Japan) and field emission scanning electron microscopy (FE-SEM, Phenom, USA) equipped with energy dispersive X-ray spectroscopy detector (EDX) were used to detect the morphology and elemental content.

The valence states and composition were conducted via X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, USA). Specific surface area (BET) was measured through N₂ adsorption-desorption instrument (Micromeritic TriStarII 3020, USA). Fourier transform infrared spectrometer (FT-IR, Thermo, Ni-

Fig. 1. Schematic diagram of synthetic procedure.

colet-6700, USA) was applied to detect the functional groups. UV-vis spectrum was obtained via an UV-vis-NIR Spectrophotometer (Shimadzu UV-3600, Japan). Photocurrent test was executed by using a CHI-660E electrochemical station equipped with a standard three-electrode.

2.5. Evaluation of catalyst performance

MO dye and tetracycline solution were selected to investigate the capability of above photocatalysts. The visible light source came from a Xenon lamp (CEL-HXF-300W), which equipped with a cut-off filter to ensure wavelength larger than 420 nm and was placed at 14 cm from liquid surface. The experimental device was showed in Fig. S1 (Supporting Information). The process of photocatalytic degradation was made as following: 50 mg samples were poured into 100 mL solution containing MO (10 mg/L) and tetracycline (30 mg/L). Before irradiation, the solution was magnetically stirred in the dark for 0.5 hour to achieve adsorption-desorption equilibrium.

During the process of vis-light irradiation, reaction solution was continually withdrawn approximately 5 mL at given time interval. Then it was centrifuged to dislodge photocatalysts and the remaining solution was analyzed via an UV-vis-NIR Spectrophotometer. The characteristic peaks for MO and tetracycline solution were at 464 and 357 nm, separately. The calculated degradation ratio (η , %) used the following formula:

$$\eta = (1 - \frac{C_t}{C_0}) \times 100\% \quad (1)$$

here, C_0 (mg/L) and C_t (mg/L) were the equilibrium concentration and instantaneous concentration of pollutants at any time t (min), respectively.

2.6. Active species trapping experiments

To gain insight probable mechanism of photocatalytic degradation, the diverse scavengers were applied to competitive experiments for the purpose of investigating the role of active radicals during the photocatalytic process. Generally, the active radicals involve hole (h^+), superoxide radical ($\bullet O_2^-$) and hydroxyl radical ($\bullet OH$) [43]. In the test, IPA, $Na_2C_2O_4$ and TEMPOL were utilized as scavengers for $\bullet OH$, h^+ and $\bullet O_2^-$, separately. MO solution was selected as pollutants and other conditions were the same as the degradation experiments.

3. Results and discussion

3.1. Characterization of materials

Fig. 2 was the XRD results of $m-Bi_2O_4$, BiOCl and $m-Bi_2O_4/BiOCl$ composites with different ratios and the three-dimensional map was displayed in Fig. S2 (Supporting Information). Pure $m-Bi_2O_4$ exhibited identical diffraction peaks corresponding to the monoclinic phase of Bi_2O_4 (JCPDS 83-0410, lattice constants: $a = 12.367 \text{ \AA}$, $b = 5.118 \text{ \AA}$ and $c = 5.567 \text{ \AA}$) [33,36]. With the increasing addition of HCl solution, new diffraction peaks appeared, indicating that new materials were produced. The peak intensities of 2θ of 26.86° and 29.52° indexed to (111) and (-311) planes were decreased. Besides, when the amount of HCl solution was excessive, the two peaks disappeared.

Simultaneously, comparing with the standard maps, the characteristic diffraction peaks indexed perfectly to the tetragonal phase of BiOCl (JCPDS 06-0249, lattice parameters: $a = b = 3.891 \text{ \AA}$, $c = 7.369 \text{ \AA}$) [44,45]. These peaks were detected at 2θ of 11.97° , 24.16° , 25.92° and 33.41° , corresponding to the (001), (002), (101) and (102) crystal planes [46,47]. The intensities of these peaks gradually became stronger when the amount of added HCl solution was varied from 1 mL to overdose. Moreover, no impure peaks were discovered, verifying high purity of products. The method of relative intensity ratio (RIR) was applied to quantitatively calculate the composition of multi-phase sample. When the sample and corundum ($\alpha-Al_2O_3$) are mixed in 50:50 by weight, the intensity ratio of its strongest peaks is defined as RIR value for sample phase [48]. When the two phases of a and b constitute one sample, their weight ratio can be calculated for each phase in compounds using the following formula:

Fig. 2. XRD patterns of $m-Bi_2O_4$, BiOCl and $m-Bi_2O_4/BiOCl$.

Table 1

Quantitative calculation of phase composition and crystallinity in m-Bi₂O₄/BiOCl samples based on XRD data.

Sample	Peak intensity		Weight ratio (wt%)		Crystallinity (%)
	<i>I_a</i> (BiOCl)	<i>I_b</i> (m-Bi ₂ O ₄)	BiOCl	m-Bi ₂ O ₄	
m-Bi ₂ O ₄	0	25889	0.00	100.00	93.21
BiOCl	11776	0	100.00	0.00	96.08
BiOCl-1	4574	9737	36.52	63.48	92.79
BiOCl-1.5	9752	6571	64.51	35.49	92.42
BiOCl-2	10373	1541	89.18	10.82	96.91

$$W_a = \frac{I_a}{I_a + (I_b / (RIR_b / RIR_a))} \quad (2)$$

$$W_b = \frac{I_b}{I_b + (I_a / (RIR_a / RIR_b))} \quad (3)$$

where, *W* and *RIR* represent the weight ratios and *RIR* values of phase a and phase b, respectively; *I* is the integrated intensity of strongest peak of phase a or phase b, respectively [49]. For m-Bi₂O₄ and BiOCl phase, the *RIR* values are 11.82 and 9.65

Fig. 3. SEM images of m-Bi₂O₄ (a), BiOCl (b), BiOCl-1 (c), BiOCl-1.5 (d) and BiOCl-2 (e); EDX (f), TEM (g), HR-TEM images (h) of BiOCl-1 sample.

according to PDF database, respectively. The calculated results of as-prepared samples were list in Table 1.

SEM measure was employed to examine the surface morphology of obtained catalysts. In the Fig. 3(a), the m-Bi₂O₄ was square shape and had a rough surface. For BiOCl (Fig. 3(b)), its nanoplate stacked layer by layer and the thickness reached 125.8 nm. The increasing of nanosheet thickness of BiOCl led to a much long moving path for charge carriers [22]. This corresponded with the lowest photocatalytic activity in the experiment described later.

For m-Bi₂O₄/BiOCl, with the increasing amount of HCl solution, the morphology of the complex changed, as displayed in Fig. 3(c)–(e). When 1 mL of HCl solution was added, BiOCl-1 sample began to appear nanosheet structure with a thickness of only 34 nm. The more amount of HCl solution was added, the more obvious the nanosheet was observed. The BiOCl-2 sample (Fig. 3(e)) completely become nanosheets and aggregated forming intimate contact.

EDX spectrum for BiOCl-1 was shown in Fig. 3(f) and the inserted picture was the corresponding part. It existed three elements of Bi, O and Cl. TEM and HR-TEM were presented in Fig. 3(g) and (h). The lattice fringes of 0.204 and 0.331 nm were corresponded to lattice planes of (221) and (111) of m-Bi₂O₄ and lattice spacing of 0.152 nm was ascribed to (114) plane of BiOCl. Fig. S3 was the selected-area electron diffraction (SAED) and its regular highlights indicated a single crystalline structure of BiOCl-1 sample.

3.1.1. FT-IR

FT-IR measurement was conducted to further identify the chemical composition and bonding of composites. Fig. 4 presented the characteristic peaks of the samples and the broad band at 3448 cm⁻¹ was caused by the stretching and deformation vibration of O–H group in physisorbed and/or chemisorbed H₂O [24]. This peak could be seen in every sample owing to the water sorption from air.

The range of absorption peaks of m-Bi₂O₄ were between 500 and 1000 cm⁻¹. The bands at 553 and 593 cm⁻¹ were designated to stretching vibrations of Bi–O bond [50]. Upon treatment

Fig. 4. FT-IR spectra of m-Bi₂O₄, BiOCl, BiOCl-1, BiOCl-1.5 and BiOCl-2 samples.

Fig. 5. Raman spectra of m-Bi₂O₄, BiOCl and BiOCl-1 samples.

with HCl solution, the intensities of the peaks diminished. When m-Bi₂O₄ was completely converted to BiOCl, the location of Bi–O bond stretching vibrations shifted to 531 cm^{−1}, which was valent symmetrical vibrations of Bi–O in BiOCl [51]. Based on the FT-IR and XRD results, it can be concluded that the compounds consisted of m-Bi₂O₄ and BiOCl.

3.1.2. Raman spectroscopy

Fig. 5 showed the structure information of m-Bi₂O₄/BiOCl. The Raman spectra of m-Bi₂O₄ had two bands at 122 and 308 cm^{−1}. BiOCl has a tetragonal P4/mmm space group and its vibrational modes can be depicted as:

$$\Gamma = 2A_g + B_g + 3E_g + 2A_u + 2E_u \quad (4)$$

here, A_g , B_g , and E_g are Raman actives and others are infrared actives [52,53].

BiOCl sample had two obvious peaks and one weak peak. Symmetric vibrations rather than asymmetric vibrations increased Raman bands. Therefore, the strong peak at 142 cm^{−1} was ascribed to A_{1g} internal Bi–Cl stretching vibration and 197 cm^{−1} was assigned to E_g internal Bi–Cl stretching vibration. The not readily noticeable and weak band at 395 cm^{−1} corresponded to E_g and B_{1g} band produced from oxygen motion atoms [54,55].

BiOCl-1 displayed three main characteristic bands at 123, 146 and 316 cm^{−1}. The peak at 197 cm^{−1} disappeared, suggesting that Cl[−] replaced some O^{2−} in the lattice to form Bi–Cl bonds. It can be drawn a conclusion that the m-Bi₂O₄/BiOCl complex was successfully synthesized.

3.1.3. BET analysis

Fig. 6 was the isotherms of three samples, and from Fig. 6(a) and (b), it can be known that the average pore sizes of m-Bi₂O₄ and BiOCl were 52.01 and 13.99 nm, respectively. Besides, the isotherm of BiOCl-1 sample can be classified to type-IV (Fig. 6(c)) and the shape of hysteresis loop was type H3 at relative high pressure, indicating a mesoporous structure (2–50 nm) [56,57]. The hysteresis loop shifted at $P/P_0 \approx 1.0$, suggesting that BiOCl-1 sample had a macroporous structure (large than 50 nm).

The BET specific surface areas of m-Bi₂O₄, BiOCl and BiOCl-1 were 17.87, 237.05 and 112.90 m²/g, respectively. The pore size were examined through BJH model from desorption branch of nitrogen adsorption-desorption isotherm. The average pore diameter was 18.96 nm for BiOCl-1, corresponding to the isotherm showed in the insert of Fig. 6(c). The small mesopores might be stem from the pores within the nanosheets, but large pores were owing to the existence of the space between the interlaced nanosheets [58,59].

3.1.4. XPS

Fig. 7 revealed the valence states and chemical composition of BiOCl-1. The survey spectra (Fig. 7(a)) stated clearly that BiOCl-1 sample consisted of only Bi, O and Cl elements, excluding the adventitious carbon species from XPS measurement, whose binding energy was at 284.6 eV. The two high-resolution peaks of Bi 4f were corresponding to the positions of Bi 4f_{5/2} and Bi 4f_{7/2} (Fig. 7(b)). The Bi 4f_{5/2} can be resolved into one bimodal peak at 164.59 and 163.76 eV. And the Bi 4f_{7/2} peak was resolved into other bimodal peak at 159.35 and 158.6 eV, which should be attributed to Bi (III) and Bi (V) on the basis of previous researches [40,60].

The banding energies of Cl 2p at 197.95 and 199.55 eV (Fig. 7(c)) were ascribed to the positions of Cl 2p_{3/2} and Cl 2p_{1/2} [61]. The peak of O 1s can be decomposed into two peaks at 529.84 and 530.86 eV (Fig. 7(d)), indicating that the two distinguishable models of O existed simultaneously in BiOCl-1. Between the two peaks of O 1s, one with low binding energy was the lattice oxygen and the other was attributed to the chemisorbed and physically adsorbed oxygen on the surface of catalysts [28,51]. Above all, the m-Bi₂O₄/BiOCl photocatalysts were prepared successfully.

3.1.5. UV-vis spectra

Fig. 6. Nitrogen adsorption-desorption isotherms and pore size distribution curves (inserted) of m-Bi₂O₄ (a), BiOCl (b), and BiOCl-1 (c).

Fig. 7. XPS spectra of BiOCl-1 catalyst: Survey spectra (a), Bi 4f (b), Cl 2p (c) and O 1s (d).

The optical performance of photocatalysts was displayed in Fig. 8. For pure m-Bi₂O₄, the absorption threshold wavelength was about 640 nm. In contrast, the BiOCl absorption cutoff wavelength was approximately 380 nm, demonstrating that the BiOCl sample only absorbed UV light. With the proportion increasing of m-Bi₂O₄ in the composite, the absorption edge red-

shifted monotonically and the absorption ability to visible light was enhanced. The colors of photocatalysts were changed with the increasing of used HCl solution. Initially, the color of m-Bi₂O₄ was dark brown, and then became yellow after adding HCl solution. Finally, BiOCl became white powder. The color change was as vivid as shown in Fig. 8(a).

Fig. 8. Different colors (a), UV-vis absorption spectra (b) and E_{bg} (c) of samples

The photocatalytic activity was deeply influenced by the band gap energy (E_{bg}) of semiconductor. The value of E_{bg} is calculated through following equation according to DRS data:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (5)$$

here, α , h , ν , and A are all constants and can be found in other literatures. According to previous research, n values of $m\text{-Bi}_2\text{O}_4$ and BiOCl were all 4 for indirect transition. E_{bg} were estimated through the plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ that were extrapolated to $(\alpha h\nu)^{1/2} = 0$ as illustrated in Fig. 8(b). The values of E_{bg} (Fig. 8(c)) were estimated approximately to 3.2, 2.0 and 1.87 eV for BiOCl , $m\text{-Bi}_2\text{O}_4$ and BiOCl-1 , respectively.

The path of migration and redox capability of photo-generated carriers were significantly affected by the location of band edge potentials. Generally speaking, the more positive of valence band (VB) position is, the stronger oxidation capability of holes becomes. On the contrary, the CB position is more negative, causing stronger reduction power of electrons. The potentials of VB and CB in semiconductors were determined by applying the electronegativity theory based on following empirical equations:

$$E_{VB} = X - E^e + 0.5E_{bg} \quad (6)$$

$$E_{CB} = E_{VB} - E_{bg} \quad (7)$$

here, X is the Mulliken electronegativity. E^e is free electron energy (~ 4.5 eV vs. NHE) [62]. The X value of BiOCl was 6.36 [27,63] and the VB values were 3.46 and 1.63 eV for BiOCl and

$m\text{-Bi}_2\text{O}_4$. Correspondingly, their CB values were 0.26 and -0.37 eV, separately.

3.2. Photocatalytic performance

The phenomenon of photocatalytic degradation was investigated by degrading MO and tetracycline under visible light. And the results were presented in Fig. 9(a) and (b). Blank experiment (without catalysts) showed that the performance of MO and tetracycline was stable and almost no degradation was occurred during the process of photolysis.

From Fig. 9(a) and (b), it can be seen that pure BiOCl photocatalyst had neglected degradation performance for MO. Although the concentration of tetracycline was decreased 30% by BiOCl , it might be attributed to the selective adsorption due to the largest surface area of BiOCl . And $m\text{-Bi}_2\text{O}_4$ had about 80% degradation for MO or tetracycline, owing to its narrow band gap.

Through adding HCl solution to acidify $m\text{-Bi}_2\text{O}_4$, the activity of $m\text{-Bi}_2\text{O}_4/\text{BiOCl}$ got obvious enhancement, and efficiency was also improved compared with BiOCl . The degradation efficiencies of BiOCl-1 reached 95% for MO within 10 min and 85.5% for tetracycline within 150 min. The results indicated that the BiOCl-1 had the best degradation performance.

Nevertheless, when the ratio of HCl and $m\text{-Bi}_2\text{O}_4$ was 2:1,

Fig. 9. Photocatalytic degradation of MO (a) and tetracycline (b) under visible light; Spectral changes of MO (c) and tetracycline (d) over BiOCl-1 catalyst.

the effect was reduced, which might since the BiOCl accounted for too much proportion in the complex and led to bad consequence.

The intensities of absorption spectra of MO and tetracycline diminished with time got by as displayed in Fig. 9(c) and (d). And the color of MO solution changed from yellow to colorless, as vividly inserted in the graph of Fig. 9(c).

To quantitatively describe the photocatalytic ability, the degradation kinetics followed equation:

$$-\ln \frac{C_t}{C_0} = kt \quad (8)$$

here, k (min^{-1}) is kinetic constant specified by the plot versus t (min). The fitted results were shown in Fig. S4 and meanwhile listed in Table S1.

All of the k values for MO and tetracycline were positive, as shown in Table S1. As the picture of Fig. S4(a) and (b) showed, all samples were fitted well and had very high correlation coefficient ($R^2 > 0.90$). Fig. S4(c) and (d) exhibited k values by histogram. The reaction rate constants of BiOCl-1, BiOCl-1.5 and BiOCl-2 were far greater than that of m-Bi₂O₄ and BiOCl, especially BiOCl-1 had the biggest rate constant, which was 52.28 times as much as BiOCl.

Compared with pure BiOCl, the composite photocatalyst of m-Bi₂O₄/BiOCl showed excellent photocatalytic degradation performance for MO and tetracycline. The excellent photocatalytic capability of m-Bi₂O₄/BiOCl might be ascribed to p-n heterogeneous structure, large BET values and favorable band gap energies.

3.3. Mineralization

In fact, good photocatalytic effects do not indicate complete degradation for organic pollutants, for some intermediate products can be produced [36]. So, to further versify the degradation of organic pollutants over as-prepared photocatalysts, the values of total organic carbon (TOC) were determined and the results are shown in Fig. 10.

From the data in Fig. 10, it can be seen that BiOCl had very low degradation efficiencies for MO and tetracycline under

visible light. However, after combined with Bi₂O₄, m-Bi₂O₄/BiOCl (BiOCl-1) had much high photocatalytic effect and the degradation efficiencies for MO and tetracycline reached 96.6% and 93.9%, respectively, which indicated a high removal efficiencies of TOC to the two pollutants.

The above results also stated that there were a large number of intermediate products being produced during the process of photocatalysis. And these intermediate products were completely decomposed into H₂O and CO₂ within a given time.

3.4. Stability of photocatalyst

The photocatalyst of BiOCl-1 after reaction was filtered and washed with ethanol and water for several times. Then it was put into an oven to dry. The XRD and FT-IR technologies were employed to investigate the stability of the as-prepared photocatalysts before and after the reaction. It is vividly seen from the XRD pattern (Fig. 11(a)) that the diffraction peaks have not be changed and no impure peaks appeared, suggesting a stable crystal structure. Moreover, the vibration peaks of photocatalyst BiOCl-1 after reaction (Fig. 11(b)) were the same as those before reaction, demonstrating an excellent chemical structure. These results indicated that the synthetic photocatalyst of BiOCl-1 had a good stability.

3.5. Photocatalytic mechanism

To explore the mechanism and value the roles of reactive oxygen species (ROS) in photocatalysis, the selective addition of scavengers' analysis was implemented. IPA was used as scavenger for $\bullet\text{OH}$, Na₂C₂O₄ for h^+ and TEMPOL for $\bullet\text{O}_2^-$. The amount of these scavengers was 1 mmol/L. As showed in Fig. 12, when adding IPA, the degradation efficiency of MO was little lower than no scavenger, revealing that $\bullet\text{OH}$ played a part of role during the process of degradation. The activity was inhibited obviously with addition of TEMPOL, which demonstrated that $\bullet\text{O}_2^-$ was also important for photocatalytic process [64,65]. Besides, the addition of Na₂C₂O₄ thoroughly suppressed the degradation performance for MO, suggesting that h^+ played a

Fig. 10. Mineralization of MO and tetracycline over BiOCl-1 under visible light irradiation.

Fig. 11. XRD (a) and FT-IR (b) spectra of BiOCl-1 sample before and after photocatalytic reaction.

more critical role.

The contribution of $\bullet\text{O}_2^-$ and h^+ to the degradation of MO were 39.3% and 90.9%, respectively. The kinetic fit and data were showed in Fig. S5 and Table S2. Those data fitted well and the k values for no scavenger, IPA, TEMPOL and $\text{Na}_2\text{C}_2\text{O}_4$ were 29.02×10^{-2} , 17.32×10^{-2} , 7.61×10^{-2} and $0.31 \times 10^{-2} \text{ min}^{-1}$, respectively. The additive scavengers suggested that the dominant active species were $\bullet\text{O}_2^-$ and h^+ during the process of photocatalytic degradation. They could directly or indirectly oxidize MO to non-toxic substances.

Separated and migratory efficiency of photo-generated carriers as chief factors, greatly influence the photocatalytic performance of photocatalysts. The transient photocurrents were measured by photocurrent response experiments. Generally, the stronger intensity of current signal is, the higher separated efficiency of photo-generated carriers will be.

As revealed in Fig. 13, the photocurrents responded rapidly via light on-off cycles under visible light. BiOCl failed to produce photo-induced carriers under visible light, therefore the current signal was weak. The main reason was that its large band gap needed higher energy to be excited. The m-Bi₂O₄ sample with decent photocurrent density was not enough high. However, BiOCl-1 sample demonstrated the highest photocurrent density,

corresponding to the best photocatalytic activity as revealed by the test.

In the view of results analysis, a possible photocatalytic mechanism for m-Bi₂O₄/BiOCl was put forward in Fig. 14. The type of semiconductor for BiOCl and m-Bi₂O₄ were p-type and n-type respectively. Thence the electronic concentration in BiOCl was lower than that in m-Bi₂O₄. Moreover, the Fermi level (E_f) of m-Bi₂O₄ was close to the CB and it lied closely to the VB for BiOCl. Before contacting, the CB and VB of BiOCl were lower than those of m-Bi₂O₄.

Once the two semiconductors contacted, the band alignment between the two semiconductors led to establishing a p-n heterojunction. Charge redistribution occurred and the electrons transferred from m-Bi₂O₄ to BiOCl, resulting in a negative region in the vicinal region of BiOCl in the heterojunction, while the holes transferred from BiOCl to m-Bi₂O₄, creating a positive region in the m-Bi₂O₄ nearby the junction. The Fermi level of m-Bi₂O₄ down-shifted and that of BiOCl moved up until the E_f equilibrated [25,66,67]. Simultaneously, the energy band position of BiOCl shifted upward whereas m-Bi₂O₄ shifted downward accompanying with the Fermi level.

Consequently, the band structures bending in the opposite direction took place in the charge region, forming a corre-

Fig. 12. Influence of scavengers for the degradation of MO over BiOCl-1 with different scavengers.

Fig. 13. Photocurrent response experiments for m-Bi₂O₄, BiOCl and BiOCl-1 samples.

Fig. 14. The p-n junction formation by energy band bend and the probable photocatalytic mechanism for m-Bi₂O₄/BiOCl photocatalyst.

sponding internal electric field (E_{internal}). Upon the semiconductors were excited, the internal electric field accelerated the separation of carriers and drove it to different directions. The sites of oxidation and reduction were spatially separated [11,68]. Thence, the photo-excited electrons and holes transferred across the interface and internal electric field, extending the mobile path and prolonging the electronic lifetime.

According to above analysis, when the m-Bi₂O₄/BiOCl was irradiated by visible light, m-Bi₂O₄ was motivated to produce electron-hole pairs and then the holes were left on VB since the electrons were transferred from VB to CB. However, BiOCl could not response because of large band gap. Through charge redistribution, the CB and VB of BiOCl were higher than that of m-Bi₂O₄. The photo-generated holes were streamed to VB of BiOCl under the internal electric field force. These holes directly captured organics and then oxidized them.

The electrons on CB of m-Bi₂O₄ reacted with surface adsorbed oxygen [O_2]_{ad} and reduced them to $\bullet\text{O}_2^-$ species, which could reacted with pollutants. Some $\bullet\text{O}_2^-$ also further reacted with e^- and H^+ to generate $\bullet\text{OH}$, following the formulas below:

Therefore, the redox reaction carried out separately. This p-n heterojunction mode enhanced separation of electron-hole pairs, prolonged lifetime of carriers and facilitated photocatalytic degradation, causing an excellent photocatalytic activity over m-Bi₂O₄/BiOCl composite.

4. Conclusions

The heterostructure m-Bi₂O₄/BiOCl photocatalyst was successfully synthesized through an ion-etching method. The ratio of m-Bi₂O₄ to BiOCl was controlled by adjusting the volume of HCl solution. The experimental results certificated that as-prepared photocatalysts displayed high degradation rate and complete mineralization ability for MO and tetracycline solution under visible light. The degradation efficiencies for MO and tetracycline reached 96.6% and 93.9%, respectively. Moreover, the as-prepared photocatalysts showed good stabil-

ity.

The p-n heterojunction separated carriers effectively and enhanced photocatalytic activity. Furthermore, the reactive oxygen species trapping experiment revealed that h^+ and $\bullet\text{O}_2^-$ were primary radicals responsible for photocatalysis. The study proposed a strategy to design a heterostructure photocatalyst for treating water environmental issues.

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Graphical Abstract

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Synthesis of novel p-n heterojunction m-Bi₂O₄/BiOCl nanocomposite with excellent photocatalytic activity through ion-etching method

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A novel photocatalyst of p-n heterojunction m-Bi₂O₄/BiOCl was synthesized to degrade methylene orange and tetracycline. Under visible light, the m-Bi₂O₄/BiOCl showed excellent photocatalysis and mineralization ability for methylene orange and tetracycline within short irradiation time.

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离子刻蚀法制备具有高效催化性能的m-Bi₂O₄/BiOCl p-n异质结催化剂

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摘要: 光催化技术作为一种绿色的环境修复方法而备受关注, 它直接利用太阳光作为能源, 可有效地降解有机污染物. 铋系化合物具有化学稳定性强、抑制光腐蚀、无毒和来源广泛等优点, 被认为是一种环境友好的光催化剂, 广泛用于降解染料、苯酚和其他有机污染物. BiOCl具有独特的内部结构, 可形成内电场促进电子和空穴的移动, 抑制其复合. 但是BiOCl本身带隙能过大, 只能被紫外光激发, 对光的利用率较低, 限制了其在环境治理中的应用. 近两年来发现, m-Bi₂O₄带隙能小, 可吸收大波长的可见光, 催化性能好. 为充分发挥m-Bi₂O₄的优异性质, 改善BiOCl的性能, 本文将BiOCl与m-Bi₂O₄复合制得新型催化剂, 降低催化剂的带隙能, 增强对光的吸收, 提高量子效率, 促进光生载流子的分离, 抑制电子-空穴复合, 从而提高催化剂性能, 加速降解反应进程.

本文通过离子刻蚀法制备具有p-n异质结的m-Bi₂O₄/BiOCl复合催化剂, 通过调节HCl的加入量制得不同比例的催化剂, 并考察了其在可见光下催化降解MO (甲基橙) 的性能. 结果表明, m-Bi₂O₄/BiOCl复合催化剂在可见光下表现出优异的光催化降解MO和四环素的性能, 反应10 min内可降解95%的MO, 反应150 min内四环素的降解率为85.5%; 该复合催化剂对MO和四环素的光降解效率分别是纯BiOCl的52.3和4.9倍. 活性自由基捕获实验表明, 空穴在光催化降解过程中起最主要的作用, 其次是超氧自由基, 羟基自由基对降解反应也起到一定的作用.

采用XRD, SEM, EDS, TEM, SAED, FT-IR, Raman, XPS, BET, UV-vis和光电流等表征方法分析了催化剂的结构、形貌、化学组成、元素价态、孔结构、带隙能、光学性质和载流子复合效率. 结果表明, 与BiOCl的斜四方体相比, m-Bi₂O₄/BiOCl复合催化剂呈现纳米片状结构, 氯离子进入晶格的内部, 颜色也由BiOCl原来的深褐色变为黄色. m-Bi₂O₄/BiOCl为介孔结构, 比表面积为112.90 m²/g, 其吸收波长红移, 由紫外光扩展至可见光区域, 带隙能也由3.2降低为1.87 eV, 能带弯曲形成p-n异质结, 提高了电子-空穴的转移效率, 抑制其复合; m-Bi₂O₄/BiOCl的光电流密度高于m-Bi₂O₄和BiOCl, 电子-空穴的分离效率更高, 因而其催化性能更优越.

关键词: 四氧化二铋; 光催化; 甲基橙; 四环素; 降解机理

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