Synthesis of Bi₇F₁₁O₅/BiOCl nanosheets by a simple post-synthesis method and the improved charge separation by the heterojunction

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Abstract

The Bi₇F₁₁O₅/BiOCl heterojunction is prepared by a simple hydrothermal method using BiOCl and NH₄F as the precursors. It is found that under ultraviolet light irradiation ($\lambda \leq 420$ nm), the activity of Bi₇F₁₁O₅/BiOCl is 3.3 and 6.4 times higher than that of BiOCl and Bi₇F₁₁O₅ for the degradation of methyl orange (MO), respectively. The high activity is mainly attributed to the greatly improved the separation and transfer efficiency of charges. This simple post-synthesis method is useful to develop efficient photocatalysts.

Keywords: BiOCl/Bi₇F₁₁O₅; heterojunction; charge separation; photocatalysis

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1. Introduction

As an advanced oxidation technology, photocatalysis has attracted much attention [1-3]. However, the low quantum efficiency and light utilization efficiency limit its practical applications [4-6]. Among the reported photocatalysts, bismuth-based compounds [7-9] have been intensively investigated due to the outstanding optical and photocatalytic properties. However, their photocatalytic activities are still not high enough to meet practical requirements. Thus, many attempts have been made to improve the photocatalytic activity of photocatalysts by morphology or active planes control [10-12], metal or non-metal doping (*e.g.*, Fe, F etc.) [13,14], co-catalyst modification (*e.g.*, Cr, Bi etc.) [15,16], and semiconduction coupling [17-20].

In particular, semiconduction coupling is one of the effective methods to enhance the generation and separation of photo-generated carries, thus improving the photocatalytic activities, including $\text{Bi}_2\text{O}_2\text{CO}_3/\text{BiOCl}$ [17], $\text{Fe}_2\text{O}_3/\text{BiOCl}$ [18], $\text{g-C}_3\text{N}_4/\text{BiOCl}$ [19], $\text{TiO}_{2-x}/\text{BiOCl}$ [20], and so on. In this work, the $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ heterojunction is prepared by a simple post-synthesis approach. The results show that $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ heterojunction shows the significantly improved photocatalytic activity.

2. Results and discussion

2.1. Crystal phase and morphology analysis

The preparation, characterization, theory calculation and activity test are provided in electronic supporting information (ESI). Fig. 1 shows that the phase-pure BiOCl , $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ and $\text{Bi}_7\text{F}_{11}\text{O}_5$ have formed, on base of the standard card JCPDS No. 06-0249 (BiOCl) and No. 50-0003 ($\text{Bi}_7\text{F}_{11}\text{O}_5$). Their scanning electron

microscope (SEM) images are shown in Fig. S1 (ESI). The BiOCl sample is composed of 4-7 μm microspheres assembled by the nanosheets (Fig. S1a, ESI). After hydrothermal treatment with NH_4F , the microspheres have gradually broken into nanosheets (Fig. S1(b,c), ESI). It is interesting that BiOCl can be converted to $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ and $\text{Bi}_7\text{F}_{11}\text{O}_5$ merely by adjusting the added amount of NH_4F . Table S1 (ESI) shows that the BET areas (5.0 and 3.9 m^2/g) of the $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ and $\text{Bi}_7\text{F}_{11}\text{O}_5$ samples are significantly smaller than that (16.5 m^2/g) of the BiOCl sample. The microspheres of BiOCl have broken into nanosheets for the $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ and $\text{Bi}_7\text{F}_{11}\text{O}_5$ samples, which may result in the decreased BET areas [18].

Typically, the $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ sample is characterized by the high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) patterns (Fig. 2). It seems that $\text{Bi}_7\text{F}_{11}\text{O}_5$ nanosheets distribute on BiOCl nanosheets (Fig. 2a). In Fig. 2(b), the clear diffraction spots correspond to the (200) and (110) Bragg reflections of BiOCl, and the diffraction rings correspond to (112) and (004) Bragg reflections of $\text{Bi}_7\text{F}_{11}\text{O}_5$, respectively. Additionally, the included angle between (110) and (1-10) is 90° , indicating that the zone axis is [001] direction. This result is constant with the reports [21,22]. The SAED patterns reveal the single crystalline nature of BiOCl and the polycrystalline nature of $\text{Bi}_7\text{F}_{11}\text{O}_5$. Moreover, Fig. 2(c) shows the lattice fringe images of the $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ sample. The lattice spacing of 0.274 nm is well indexed to (110) crystal plane of BiOCl, and the lattice spacings of 0.231 and 0.340 nm match (004) and (112) planes of $\text{Bi}_7\text{F}_{11}\text{O}_5$, respectively. The results demonstrate that a heterojunction has formed between BiOCl and $\text{Bi}_7\text{F}_{11}\text{O}_5$ due to their matched energy bands, which will be further discussed in the latter sections.

2.2. UV-DRS, EIS and theory calculation

Fig. S2(a) (ESI) displays the UV–visible diffuse reflectance spectra (UV-DRS) of the samples. All the samples exhibit the light absorption in UV light ranges. The absorption edges of BiOCl and Bi₇F₁₁O₅ are determined to be 374 and 324 nm, respectively. Compared with BiOCl, Bi₇F₁₁O₅ shows an obvious blue-shift, indicating a wide band gap. The band gap energy (E_g) of a semiconductor can be calculated by equation (1) as follows [23].

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (1)$$

where α , h , ν , E_g and A represent absorption coefficient, Plank constant, light frequency, band gap energy and a constant, respectively. Among them, n is determined by the optical transition type of a semiconductor ($n=1$ for a direct optical transition and $n=4$ for an indirect optical transition) [24]. The values of n are 4 and 1 for BiOCl and Bi₇F₁₁O₅, respectively [8,9,25]. The band gap energies of BiOCl and Bi₇F₁₁O₅ are determined to be 3.32, and 3.83 eV, respectively.

The conduct band and valence band positions of a semiconductor can be calculated by the following empirical formula (2,3) [26]:

$$E_{VB} = \chi - E^e + 0.5 E_g \quad (2)$$

$$E_{CB} = E_{VB} + E_g \quad (3)$$

where χ is the absolute electronegativity of a semiconductor, which is defined as the geometric mean of the absolute electronegativity of constituent atoms; E^e is the energy of free electrons on the hydrogen scale (*ca.* 4.5 eV); E_{CB} and E_{VB} are the conduct and valence band potentials, and E_g is band gap. Herein, the calculated E_{CB} and E_{VB} values of BiOCl and Bi₇F₁₁O₅ are summarized in Table S2 (ESI). It is obvious that the CB and VB of Bi₇F₁₁O₅ down shift and the band gap become wider, compared with BiOCl.

Further, the calculated band gap of BiOCl is 2.61 eV by Density Functional Theory (DFT) (Fig. S2b, ESI). The band gap of Bi₇F₁₁O₅ has been calculated to be 3.81 eV by Hu et al [9]. The calculation result by DFT is slightly smaller than the experimental results, which is a common feature of DFT calculations [27]. Fig. S2c (ESI) shows that the VB top of BiOCl is mainly composed of the O 2p and Cl 3p orbits, and its CB bottom is mainly composed of Bi 6p and a part of O 2p orbits. Hu et al. have reported that F 2p and O 2p orbits mainly contribute to the VB of Bi₇F₁₁O₅, and Bi 6p orbit mainly contributes to the CB [9]. The results show that BiOCl and Bi₇F₁₁O₅ have the matched energy bands, thus a heterojunction can form.

Besides, Fig. S2d (ESI) shows the electrochemical impedance spectroscopy (EIS) spectra of the samples. It is well known that the smaller arc radius indicates a higher electrical conductivity that will favor for an efficient electron transfer [28,29]. The arc radius of the samples follow the order of BiOCl < Bi₇F₁₁O₅/BiOCl << Bi₇F₁₁O₅, namely, the conductivity order is BiOCl > Bi₇F₁₁O₅/BiOCl >> Bi₇F₁₁O₅. The different conductivities of the samples may be mainly relative to their crystal structures. The simulated equivalent electric circuit from EIS data consists of a solution resistance (R_s), a constant phase element (CPE) accounting for electrical double-layer capacitance, a charge-transfer resistance (R_{ct} , also called Faraday resistance), and a Warburg impedance (W) for the diffusion and insertion of Na⁺ ion into active materials. Their resistances (R_s) of electrolyte solution are measured to be about 4 Ω , suggesting that R_s is not susceptible to the surface condition of electrode. However, the R_{ct} values of BiOCl, (36%) Bi₇F₁₁O₅/BiOCl and Bi₇F₁₁O₅ are calculated to be 3, 9 and 33 Ω , respectively. This clearly demonstrates the charge-transfer resistance (R_{ct}) of BiOCl is smaller than Bi₇F₁₁O₅.

Additionally, the PL spectrums of the samples with the excitation wavelength of

325 nm are shown in Fig. S3 (ESI). It is widely accepted that the stronger PL intensity, the higher recombination rate of electron and hole of the photocatalytic semiconductors [30-32]. From the PL results, we can see that the PL intensity of phase-pure Bi₇F₁₁O₅ is stronger than that of pure BiOCl, indicating that the recombination rate of electron and hole of Bi₇F₁₁O₅ is faster than BiOCl. The results agree with the activity order.

2.3. Photocatalytic activities

Fig. 3(a,b) shows the degradation curves and reaction kinetic curves of methyl orange (MO) dye under UV light irradiation ($\lambda \leq 420$ nm). Their degradation activities follow the order of Bi₇F₁₁O₅/BiOCl > BiOCl > Bi₇F₁₁O₅. After irradiation 30 min, 80% of MO has been degraded by Bi₇F₁₁O₅/BiOCl, but only 17% and 21% of MO are degraded by Bi₇F₁₁O₅ and BiOCl, respectively. The degradation rate constants (k_a) are given in Table S1 (ESI). The degradation rate constant ($k_a=0.0642$ min⁻¹) of Bi₇F₁₁O₅/BiOCl sample is 6.42 and 3.28 times higher than those of Bi₇F₁₁O₅ ($k_a=0.0100$ min⁻¹) and BiOCl ($k_a=0.0196$ min⁻¹), respectively. It is obvious that the Bi₇F₁₁O₅/BiOCl sample shows the highest activity amongst. Moreover, we also have investigated the influence of combination ratio between Bi₇F₁₁O₅ and BiOCl on the photocatalytic performance, which is discussed in ESI (Table S3 and Fig. S4,). The results show that the photocatalytic activity of the samples would decrease with the increase of the molar ratio of Bi₇F₁₁O₅ to BiOCl.

From Table S1 and Fig. S2(a,d) (ESI), the BiOCl sample has a higher BET area (16.5 m²/g), a stronger light absorption and a higher conductivity than the Bi₇F₁₁O₅/BiOCl sample, but the activity of BiOCl is much lower than that of Bi₇F₁₁O₅/BiOCl. This suggests that the BET area, light absorbance and conductivity

may not be the main factors affecting the photocatalytic activity. We assume that its high activity may be mainly relative to the formation of $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ heterojunction. It is well known that photocatalytic activity is strongly dependent on the separation and transfer of photogenerated charges [33,34]. The conduct band (CB) and valence band (VB) are 0.49 and 3.81 eV for BiOCl , whereas 1.2 and 5.03 eV for $\text{Bi}_7\text{F}_{11}\text{O}_5$, respectively. Therefore, an efficient $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ heterojunction can form due to the matched energy bands (Fig. 3c). The photogenerated electrons and holes can be effectively separated by the interfacial electrical conductivity, thus improving the photocatalytic activity. Further more, the good stability of $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ can be confirmed by the cycle experiment (Fig. S5, ESI).

In addition, we have also investigated the main oxidative species of the samples during the process for the degradation of MO. Herein, we employ ammonium oxalate and isopropyl alcohol (IPA) as the hole scavenger and the radical scavenger, respectively. As is shown in Fig. S6 (ESI), we can see that the photocatalytic activities of BiOCl , $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ and $\text{Bi}_7\text{F}_{11}\text{O}_5$ only decrease slightly when adding ammonium oxalate. When adding IPA, however, the photocatalytic activities of BiOCl , $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ and $\text{Bi}_7\text{F}_{11}\text{O}_5$ obviously decrease. The results demonstrate that the holes are the major oxidative species for degradation of MO over BiOCl , $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ and $\text{Bi}_7\text{F}_{11}\text{O}_5$.

3. Conclusions

The $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ heterojunction can be prepared by the simple post-synthesis method. It shows an improved photocatalytic activity due to the separation and transfer of charges by the heterojunction. The reported post-synthesis method could be extended to the other photocatalysts.

Electronic supporting information

The experimental section can be vialable via www.elsevier.com.

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Fig. 1

Fig. 1 X-ray diffraction (XRD) patterns of the samples.

Fig. 2

Fig. 2 High-resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAED) patterns of $\text{Bi}_7\text{F}_{11}\text{O}_5/\text{BiOCl}$ sample: (a) TEM; (b) SAED; (c) Lattice fringe images.

Fig. 3

Fig. 3 (a) Degradation curves and (b) reaction kinetic curves of methyl orange (MO) over the samples under ultraviolet light irradiation ($\lambda \leq 420$ nm); (c) Schematic diagram of Bi₇F₁₁O₅/BiOCl heterojunction

Graphic abstract