A facile synthesis of heterojunctional BiVO₄/Bi₅O₇I with enhanced photocatalytic activity for organic dyes degradation

Zhuomin Qiang¹, Jinqiu Huang¹, Chengyu Yang¹, Feng Li^{1,*}, Taohai Li¹, Marko Huttula², Zhongjia Huang^{3,*}, and Wei Cao^{2,*}

¹College of Chemistry, Key Lab of Environment Friendly Chemistry and Application in Ministry of Education, Xiangtan University, Xiangtan, 411105, China.

²Nano and Molecular Systems Research Unit, P. O. Box 3000, University of Oulu, FIN-90014, Finland

³School of Mechanical and Automotive Engineering, Anhui Polytechnic University, Wuhu, 241000, China

Abstract

Photocatalysis technology has risen to effectively degrade the hardly-degraded organic pollutants in recent years and the photocatalysts play an important role in striding the obstacles of the visible light response. Herein, a high-efficiency BiVO₄/Bi₅O₇I heterojunctional photocatalysts have been purposefully designed by controlling the reactant ratios and ultrasonic time of reaction at room temperature. Photocatalytic experimentals confirm that the prepared optimal BiVO₄/Bi₅O₇I composites displayed enhanced photocatalytic ability to degrade rhodamine B (RhB) and quinoline blue (QB) under visible light irradiation. Furthermore, the photocatalysts exhibits high photostability and reusability proved by four consecutive cycling experiments. A possible mechanism of p-n heterojunctional BiVO₄/Bi₅O₇I composites enhanced the photocatalytic performance was discussed in detail on the basis of the reactive species trapping experiments in photocatalytic degradation process.

Keywords: BiVO₄/Bi₅O₇I; Ionic-liquid; Photocatalytic; Visible light; Ultrasonic

E-mails: fengli_xtu@hotmail.com; Wei.Cao@oulu.fi; hzj@ahpu.edu.cn

1. Introduction

With the rapid development of water treatment technology, it appears more and more important in utilizing natural resources to remove hazardous pollutants without additional manmade energy or chemicals. The natural water circulation process, however, is helpless in front of industrial wastewater where large amount of organic dyes are discharged of which is chemically stable and hardly degraded without using external treatments [1]. From the point of energy efficiency view, solar energy is the most abundant and cleanest form within human's disposal. However, for the light source in photocatalytic water purification, its application cannot circumvent the barrier set up by the intrinsic spectral distribution, since the low-energy photons can hardly excite semiconductor catalysts. Furthermore, the only few photocatalysts of low bandgap for sunlight photocatalysis suffer from either high electron-hole combination rate, or complicated synthetic routes [2]. Under those circumstances, designing new-typed photocatalyst and novel synthesis are urgently demanded.

Among various photocatalysts, the bismuth-based nanocrystals have attracted considerable attentions due to variations of chemical composition and unique electronic structures [3-5]. For instance, bismuth vanadate (BiVO_4) is an n-type semiconductor with a narrow band gap about 2.4 eV [6], for which low band gap and chemically stable natures enable its visible-light photocatalytic ability in sunlight and visible light harvesting for water splitting and purifications [7]. Meanwhile, the investigation indicates that the catalytic activity is greatly influenced by its crystal structures [8]. The monoclinic scheelite BiVO_4 shows the strongest photocatalytic activity compared with other crystalline phases including tetragonal zircon and tetragonal scheelite [9-13]. Even so for the pure BiVO_4 , the poor charge transport and high recombination rate of the photogenerated pairs lead to inferior chemical activity under visible light, setting blockages in the photocatalytic applications [14-16].

It is generally agreed that heterojunctional structures can promote separations of the (e^- - h^+) charge pairs and enhance the catalytic performances [17]. Once the p-n junction has been formed, the inner electric field between the inner surface of two semiconductors not only facilitate the separation efficiency of photoinduced electron-hole pairs [18, 19], but also accelerate charge transfer through the heterojunction interface [20]. For that reason, the BiVO_4 has also been engineered to combine with lattice matchable complexes either containing Bi (e.g. BiOI [21] Bi_2O_3

[22]) or XO_4 ion groups (Ag_3PO_4 [23] Ag_3VO_4 [24]). Though photocatalytic performances have been enhanced, these heterojunctional complexes suffer from either high synthetic costs for practical applications or relatively unsatisfied decontamination rates due to competing charge migrations [25-27]. In this instance, the similar systems in bismuth compounds were investigated. The $\text{Bi}_5\text{O}_7\text{I}$ may be a suitable heterojunctional partners due to its microstructures, p-type nature [28] and visible light photocatalytic activity to deal with various organic pollutants [29-31]. Similar to the BiVO_4 , the pure $\text{Bi}_5\text{O}_7\text{I}$ also suffers from a certain degree of inhibition due to its deficient light absorption and low transfer efficiency. Many ways have been proved valid to improve its catalytic performances, for instance, ions doping [32], or morphology modification [30, 33], and heterojunction synthesis [34]. Despite the homologous complexes of $\text{Bi}_5\text{O}_7\text{I}/\text{Bi}_2\text{O}_3$ [35], $\text{AgI}/\text{Bi}_5\text{O}_7\text{I}$ [36], or $\text{Ag}/\text{AgBr}/\text{Bi}_5\text{O}_7\text{I}$ [37] have formed, the p-n heterojunctional design has never been reported by using the p-type $\text{Bi}_5\text{O}_7\text{I}$ to join with the n-type BiVO_4 counterpart.

In this paper, a ingenious $\text{BiVO}_4/\text{Bi}_5\text{O}_7\text{I}$ n-p heterojunction was designed and synthesized by a wet method using ultrasonic at room-temperature. Moreover, the photocatalytic activities of the sample was evaluated by degradation experiment for rhodamine B (RhB) and quinoline blue (QB) under visible-light irradiation, which suggests the designed $\text{BiVO}_4/\text{Bi}_5\text{O}_7\text{I}$ n-p heterojunctions have outstanding photocatalytic performance. In addition, the photocatalytic mechanism of the $\text{BiVO}_4/\text{Bi}_5\text{O}_7\text{I}$ heterojunction was proposed and explicated.

2. Experimental Section

2.1 Materials

The $\text{K}_6\text{V}_{10}\text{O}_{28}\cdot 9\text{H}_2\text{O}$ was employed as the vanadium source. It was firstly prepared via a route as shown in the literature [38]. $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ was purchased from Shantou Xilong Chemical Factory, and 1-ethyl-3-methylimidazolium iodide ([EMIM]I) Hengyang Kaixin Chemical Factory. Rhodamine B (RhB) and quinoline blue (QB) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai China). All of the chemical reagents were of analytical purity and used without further purification.

2.2 Preparation of $\text{BiVO}_4/\text{Bi}_5\text{O}_7\text{I}$ composite

The whole synthesis was performed through an ultrasonic method under different synthesis conditions. In a typical procedure, $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ (2.42 g, 5 mmol) was

dissolved in deionized water (10 mL) and successively stirred 20 min to form a suspension. Meanwhile, a certain amount of [EMIM]I and $K_6V_{10}O_{28} \cdot 9H_2O$ were also dissolved in deionized water (10 mL) and successively stirred for 20 min to form an emulsion, which was slowly added into the suspension. The mixture was kept stirring for 20 min and put into ultrasonic reactor radiated with ultrasound for 1 hour. After the reaction, the resulting product was alternately washed with deionized water and absolute ethanol for three times, and then the cleaned products were put into a vacuum drying oven and dried at 70 °C for 24 h.

Synthesis of the binary $BiVO_4/Bi_5O_7I$ composite is not straightforward, but needs tries of adjusting reaction conditions. The molar ratios of $K_6V_{10}O_{28} \cdot 9H_2O$ and [EMIM]I were first varied during the synthesis process. They were fixed to 1 : 0, 3 : 1, 3 : 2, 1 : 1, 2 : 3, 1 : 3 and 0 : 1, and sample prepared were labeled as S1, S2, S3, S4, S5, S6 and S7 consequentially. Parameters were tabulated in Table 1. We characterized the as-prepared samples, and found heterojunction is formed at the ratio of 2 : 3 (see later context). On this basis, the ultrasonic time was then tuned ranging from 0 to 120 min. These samples were labeled as S5-0, S5-20, S5-40, S5-60 and S5-120 corresponding to ultrasonic time for 0 min, 20 min, 40 min, 60 min and 120 min, respectively.

Table 1 The amounts of $K_6V_{10}O_{28} \cdot 9H_2O$ and [EMIM]I used in the preparation of samples.

Samples	$K_6V_{10}O_{28} \cdot 9H_2O/g$	[EMIM]I/g	$K_6V_{10}O_{28} \cdot 9H_2O/[EMIM]I$ (mol:mol)	The relative content of [EMIM]I (%)
S1	0.677	0	1:0	0
S2	0.510	0.297	3:1	25
S3	0.400	0.476	3:2	40
S4	0.338	0.600	1:1	50
S5	0.270	0.714	2:3	60
S6	0.169	0.892	1:3	75
S7	0	1.19	0:1	100

2.3 Characterizations

The crystal structures were examined by X-ray diffraction (XRD, MiniFlex II diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm)). Morphologic determination was carried out by scanning electron microscopy (SEM) on JEOL JSM-6700F, and the transmission electron microscopy (TEM) on JEOL, JEM-2010F. The element composition and surface chemical state of the as-prepared product was analyzed by the X-ray photoelectron spectroscopy (XPS, TOM, ESCALAB 250Xi). The UV-vis diffuse reflectance spectra were obtained with a UV-visible spectrophotometer (Perkin-Elmer, USA). The electrochemical impedance spectroscopy (Mott-Schottky plots) was performed on an electrochemical workstation (CHI660E) in a typical three-electrode system.

2.4 Photocatalytic activity measurement

Photocatalytic activities were evaluated by the degradation of RhB and QB in aqueous solution under visible light irradiation. In the experimental setup, a 300 W Xe lamp with a cutoff filter ($\lambda = 365$ nm) was employed as the light source. In a typical process, 50 mg of photocatalyst was dispersed into a solution containing 50 ml of RhB or QB aqueous solution ($C=10$ mg L $^{-1}$). Before irradiation, the mixture solution was stirred in darkness for 30 min to attain the adsorption-desorption equilibrium. The suspension was stirred and exposed to the visible-light irradiation. During the photocatalysis, a certain amount of suspension was taken out and centrifuged to separate solid particles at given time intervals. The concentration of RhB and QB was determined by UV-vis spectrometer (UV-2550, Shimadzu) in the range of 200-800 nm.

2.5 Scavenging experiments for reactive oxidative species

To study photocatalytic mechanism, the scavenging experiments were conducted during QB discoloration process. Benzoquinone (BQ), tert-butyl alcohol (t-BuOH) and potassium iodide (KI) were added and employed as superoxide ($\bullet\text{O}_2^-$) scavenger, hydroxyl radical ($\bullet\text{OH}$) scavenger and hole (h^+) scavenger. In a typical experiment, 50 mg of photocatalyst together with different scavengers was dispersed in 50 mL of QB aqueous solution, and the flowing process was similar to the photocatalytic degradation process of QB.

3. Results and Discussion

3.1 Impact of reactant contents on microstructure and morphology

We first studied the as-prepared samples prepared with variation of reactant contents but the same ultrasonic time. The crystal information of the as-synthesized samples is investigated by XRD patterns which were depicted in Figure 1a, b for samples S1-S6. As shown in Fig. 1a, when $[\text{EMIM}]\text{I} < 25\%$, the diffraction peaks of the products are assigned to these from the tetragonal phase (JCPDS NO. 14-0133) and the monoclinic phase (JCPDS NO. 14-0688) of the BiVO_4 . This indicates the as-prepared products (S1 and S2) are pure BiVO_4 , but have mixed phases. However, compared with the sample S1, the proportion of the tetragonal BiVO_4 in S2 is larger. The XRD results also denote that though the addition of $[\text{EMIM}]\text{I}$ can alter crystalline phase, it is still not sufficient to introduce iodine compound into the system. In Fig. 1b, the XRD patterns of the samples (S3, S4 and S5) are significantly different from these of pure BiVO_4 (S1 and S2). A series of characteristic diffraction peaks of monoclinic-phase $\text{Bi}_5\text{O}_7\text{I}$ (JCPDS NO. 38-0669) are observed besides the diffraction peaks of tetragonal BiVO_4 . In addition, the diffraction peak observed at 28.8° doesn't belong the tetragonal BiVO_4 nor the monoclinic $\text{Bi}_5\text{O}_7\text{I}$. In fact, this diffraction peak is in good agreement with (-121) lattice plane of the monoclinic BiVO_4 . The relative content of $\text{Bi}_5\text{O}_7\text{I}$ in the products also gradually increases with the $[\text{EMIM}]\text{I}$ in the reaction as its characteristic diffraction peaks show in the Fig.1. In all, samples S3-S5 are the composites consisting of tetragonal BiVO_4 , monoclinic BiVO_4 and monoclinic $\text{Bi}_5\text{O}_7\text{I}$. However, when the relative content of $[\text{EMIM}]\text{I}$ increase to 75 % (S6), two extra peaks located at 19.7° and 45.6° turn out in addition to the diffraction peaks of BiVO_4 and $\text{Bi}_5\text{O}_7\text{I}$. These peaks correspond to the ones of (-111) and (-231) lattice plane of monoclinic Bi_2O_3 . Thus excess amount of $[\text{EMIM}]\text{I}$ can result in the generation of the Bi_2O_3 impurity. If relative content of $[\text{EMIM}]\text{I}$ in reactants reaches 100 % in S7 without using $\text{K}_6\text{V}_{10}\text{O}_{28}\cdot 9\text{H}_2\text{O}$ during the synthesis, only BiOI is found as the final product. This shows that $\text{K}_6\text{V}_{10}\text{O}_{28}\cdot 9\text{H}_2\text{O}$ is indispensable for the

Fig. 1. XRD patterns of the samples S1 and S2 (a), S3-S6 (b).

generations of BiVO_4 and $\text{Bi}_5\text{O}_7\text{I}$. The results above suggest that the relative content of ionic liquid $[\text{EMIM}]\text{I}$ in the reagents has significant influences on the preparation of $\text{BiVO}_4/\text{Bi}_5\text{O}_7\text{I}$ composite. The crystalline phase of the obtained samples can be conveniently controlled by varying the amount of ionic liquid $[\text{EMIM}]\text{I}$ in the reactants.

The SEM images of the samples (S1-S6) were depicted in Figure 2 a-f. As shown in Fig 2a, b, S1 and S2 (pure BiVO_4) are composed of two types of microspheres. One has the diameter $\sim 3\text{-}5\text{ }\mu\text{m}$ and another less than $1\text{ }\mu\text{m}$. This is in line with the XRD results where two different crystal structures were found for the samples (Fig.1a). As shown in Fig. 2c-e, when the relative content of ionic liquid $[\text{EMIM}]\text{I}$ in the reactants tuned to 40 % and 60 %, the samples (S3, S4 and S5) are provided with a rod-like structure of $\text{Bi}_5\text{O}_7\text{I}$ with $2\text{-}3\text{ }\mu\text{m}$ in diameter and $5\text{-}10\text{ }\mu\text{m}$ in length beside microspherical BiVO_4 . The relative content of rod-like structure gradually enhance with $[\text{EMIM}]\text{I}$ portion, in consistence with the results of XRD as shown in Fig. 1a. From the SEM image of S6 in Fig. 2f, it is found that the products are mainly composed of rod-like structure ($\text{Bi}_5\text{O}_7\text{I}$), but in a larger diameter. Surface of these microrods are further covered with irregular nanoparticles, indicating the formation of Bi_2O_3 impurity due to the excessive amount of $[\text{EMIM}]\text{I}$.

Fig. 2. SEM images of samples S1 (a), S2 (b), S3 (c), S4 (d), S5 (e) and S6 (f).

3.2 Crystal and morphologic features of BiVO₄/Bi₅O₇I heterojunction

The above results show pure BiVO₄/Bi₅O₇I complexes require stringent preparation conditions with relative contents of ionic liquid [EMIM]I ranging from 40 % to 60 % during the synthesis. Following this discovery, we further processed refined synthesis under the same reagent ratio of S5 but varied ultrasonic time. The XRD was surveyed for the samples of S5-sequences which shown in Figure 3a-b. Below 40 minutes of ultrasound radiation, the as-prepared samples have standard diffraction peaks of the tetragonal phase BiVO₄ (JCPDS NO. 14-0133) and the tetragonal phase BiOI (JCPDS No. 10-0445) as shown in Fig.3a. No characteristic peaks of other impurities are observed, demonstrating that the as-synthesized samples (S5-0, S5-20 and S5-40) are only composed of BiVO₄ and BiOI. However, the BiVO₄ vary in phases. When the ultrasonic time of reaction increases from 40 min to 60 min, the tetragonal phase BiOI in products transforms into the monoclinic Bi₅O₇I besides the generation of monoclinic BiVO₄. We attribute this to the effect of catalysis of K₆V₁₀O₂₈•9H₂O or its product in reaction that promotes the occurrence of a reaction where BiOI is further decomposed to Bi₅O₇I during preparation process. When the ultrasonic time reaches 120 min, the XRD pattern of S5-120 (Fig. 3b) is consistent with that of S6 (Fig.1b), demonstrating that products also contains Bi₂O₃ impurity besides BiVO₄ and Bi₅O₇I. Therefore, pure BiVO₄/Bi₅O₇I complexes can only be obtained at the ultrasonic time of reaction time ranging from 60 min to 120 min on the base of S5.

Fig. 3. XRD patterns of the samples S5-0, S5-20 and S5-40 (a), S5-60 and S5-120 (b).

Figure 4a-d exhibit the SEM images of the S5-sequence samples, from S5-0, S5-20, S5-40, S5-60 to S5-120. A morphological evolution was found from S5-0, S5-20 to S5-40. The sheet-like nanostructures of BiOI in Fig. 4a gradually grown to smoother aggregations in Fig. 4b, and reaches microspheres in S5-40 are mainly

composed of many microspheres. This also suggests that the amount of BiOI decrease along with ultrasonic time of reaction ranging from 0 min to 40 min. When the ultrasonic time increased to 60 min, the sheet-like nanostructure disappeared and S5-60 (Fig. 4d) mainly consisted of the rod-like structures. Such a morphology is completely different from these of S5-0, S5-20 and S5-40. The crystallinity is also comparably better. Finally, when the ultrasonic time increased to 120 min, the morphology of S5-120 (Fig. 4e) mainly assembled with the rod-like structures was similar to that of S6 (Fig. 2f). The results above indicated that the analysis of SEM images of all samples are in good agreement with that of XRD patterns.

Fig. 4. SEM images of samples: S5-0 (a), S5-20 (b), S5-40 (c), S5-60 (d) and S5-120 (e).

The interfacial region of $\text{BiVO}_4/\text{Bi}_5\text{O}_7\text{I}$ composite from sample S5 is elucidated through TEM and High Resolution Transmission Electron Microscopy (HRTEM). In Figure 5a and b clarified the coexistence of the long rod structures with diameter of ca. 1 μm and irregular microparticles with diameter of ca. 600 nm. In addition, there are some nanosheets with thickness of ca. 100 nm in S5. In HRTEM images of Fig. 5c-d, two lattice planes were merged together. One has the lattice spacing of 0.34 nm, corresponding to the (310) lattice plane of $\text{Bi}_5\text{O}_7\text{I}$, and another spanning 0.309 nm, to the (-121) lattice plane of the monoclinic phase BiVO_4 . The HRTEM results are consistent to the XRD conclusion, where sample S5 was identified as the $\text{BiVO}_4/\text{Bi}_5\text{O}_7\text{I}$ composite. The monoclinic phase of $\text{Bi}_5\text{O}_7\text{I}$ and the tetragonal phase of BiVO_4 coexisted in the sample.

Fig. 5. The TEM images of sample S5 (a, b), the HRTEM images of sample S5 (c, d).

3.3 Chemical states and optical absorption properties

Compositional and chemical determination of the sample S5 was carried out via XPS. Figure 6a shows an XPS survey where only adventitious carbon peak was found at 284.8 along with other peaks from elements in the designed complex. The C1s is employed in the energy calibration. The two peaks located at 164.4 eV and 158.8 eV (Fig. 6c) are assigned to Bi 4f_{7/2} and 4f_{5/2}. The I 3d peak is found at 630.0 eV and 618.4 eV (Fig. 6d), and the 2p_{3/2} peak of the V⁵⁺ in BiVO₄ at 516.3 eV (Fig. 6e). Peaks at 532.0 eV and 529.6 eV belong to the O, with the one of 532.0 eV from the V-O bond, and another one from Bi-O bond (Fig. 6f) [39]. The above results prove S5 is composed of Bi, I, V and O, and no other impurity stays in the BiVO₄/Bi₅O₇I composite.

Fig. 6. XPS spectra of BiVO₄/Bi₅O₇I composite. (a) the entire XPS spectra of the sample, (b) C 1s, (c) Bi 4f, (d) I 3d, (e) V 2f and (f) O 1s.

The band gap energy is one of the key factors that influence the photocatalytic performance of semiconductor photocatalyst. The band gap E_g of all the samples can be estimated by UV-vis diffuse reflectance spectra in the range of 200-800 nm. Figure 7a, b shows UV-vis diffuse spectra of the as-synthesized samples, and all the samples show visible light absorption. Among these samples, the sample S5 exhibits high absorption in the visible-light region from 400 nm to 600 nm. It is well known that the migration direction of the photo-generated charge depends on the band structure of semiconductors. According to the absorption spectra in Fig. 7a and b, the band gap energy (E_g) of as-synthesized samples are usually assessed from the Tauc plot conforming to the following formula: $ah\nu = A(h\nu - E_g)^n$, where α , ν , E_g and A are absorption coefficient, light frequency, band gap energy, and a constant, respectively. Among them, n is decided by the type of optical transition of a semiconductor ($n = 1$ for a direct transition and $n = 4$ for an indirect transition). As reported formerly, the n values of BiVO_4 [6] and $\text{Bi}_5\text{O}_7\text{I}$ [28] are 1 and 4, respectively. Fig. 7c, d show the Tauc plots for the calculation of the band gap energy of these samples. The BiVO_4 and $\text{Bi}_5\text{O}_7\text{I}$ possessed band gap energies of 2.54 and 2.03 eV, respectively, while the other composites showed values in the range of 1.60 - 2.85 eV, showing a strong absorption capability to visible light. The Mott-Schottky tests were applied to verify the semiconductor type and flat band potential of the pure BiVO_4 and $\text{Bi}_5\text{O}_7\text{I}$. As shown in Fig. 7e, f, a positive slope and negative slope of the Mott-Schottky plots for BiVO_4 and $\text{Bi}_5\text{O}_7\text{I}$ indicated that BiVO_4 and $\text{Bi}_5\text{O}_7\text{I}$ are n-type and p-type semiconductors, respectively [40]. The E_{FB} of BiVO_4 and $\text{Bi}_5\text{O}_7\text{I}$ was calculated to be -0.40 and 1.36 V (vs. Ag/AgCl), which can obtain the potentials of conduction bands (CB) for BiVO_4 and valence band (VB) for $\text{Bi}_5\text{O}_7\text{I}$ ($E = E_{\text{FB}} + 0.0591\text{pH} + 0.198$). It thus appears that the E_{CB} of BiVO_4 and E_{VB} of $\text{Bi}_5\text{O}_7\text{I}$ are calculated to 0.21 eV and 1.97 eV (vs. NHE) by the equation. The potentials of valence band (VB) edges can be calculated by $E_{\text{CB}} = E_{\text{VB}} - E_g$. Therefore, according to the above equations, the E_{VB} value of the BiVO_4 and the E_{CB} of $\text{Bi}_5\text{O}_7\text{I}$ are calculated to 2.75 eV and -0.06 eV, respectively.

Fig. 7. UV-vis diffuse reflectance spectra of (a) the samples prepared by the proportion of the amount of reactants, (b) the samples synthesized by varying the ultrasonic time of reaction, Tauc plots of (c) the samples prepared by the proportion of the amount of reactants, (d) the samples synthesized by varying the ultrasonic time of reaction, Mott-Schottky curves of (e) BiVO₄, (f) BiOI.

3.4 Photocatalytic properties

The photocatalytic performances of the as-synthesized samples are evaluated using RhB and QB as the target dyes under visible-light irradiation. Figure 8a,b respectively display the curve graph of RhB and QB degraded by the samples S1-S7 under visible-light irradiation. After irradiated under visible light for 180 min, the degradation efficiencies of S2, S3, S4, S5, S6 and S7 for Rh B are 73 %, 88 %, 97 %, 98 %, 94 % and 90 %, respectively. S4 and S5 exhibit faster degradation effect on RhB compared with other samples. Although the degradation efficiency of S7 increases to 90 % after 180 min, it was obvious that the high degradation efficiency is attributed to the surface adsorption property for RhB. However, S1 (pure BiVO₄) almost exhibited no degradation effect on RhB. As shown in Fig. 8b, S1 and S2 basically had no effect on QB, in contrast, after exposed under visible light for 75 min, the degradation efficiencies of S3, S4, S5, S6 and S7 for QB reached 52 %, 63 %, 80 %, 98 % and 92 %. The results above fully demonstrate that S5 exhibits best photocatalytic property for RhB and QB among all the samples.

Fig. 8. Time-course variation of C/C_0 of RhB (a) and QB (b) degraded by the samples (S1-S7) under visible-light irradiation.

Photocatalytic reactivity of the S5-sequence samples was also measured. The results are depicted in Figure 9 for these synthesized in different ultrasonic time. After irradiated under visible-light irradiation for 180 min, the degradation efficiencies of S5-60 and S5-120 for RhB increased to 100 %, implying that S5-60 and S5-120 exhibit better photocatalytic activities compared to S5-0, S5-20 and S5-40 (Fig. 9a). As shown in Fig. 9b, S5-60 also possessed best degradation and photocatalytic effect on QB under visible-light irradiation. The results above indicate that the diversities of the photocatalytic efficiency of samples synthesized by changing the ultrasonic time mainly resulted from the different generated products and the high adsorption efficiency attributed to large specific surface area. Therefore, the $\text{BiVO}_4/\text{Bi}_5\text{O}_7\text{I}$ composite (S5) exhibits better photocatalytic activities compared to the $\text{BiVO}_4/\text{BiOI}$ composite (S5-0, S5-20 and S5-40).

Fig. 9. Time-course variation of C/C_0 of RhB (a) and QB (b) degraded by the samples synthesized by varying the ultrasonic time of reaction under visible-light irradiation.

In order to study the photocatalytic stability and reproducibility of the samples, the sample S5 is tested for photocatalytic degradation of RhB and QB repeatedly over 4 cycles (Figure 10). After 4 times recycling experiment, the photocatalytic efficiencies of S5 for RhB and QB are 75 % and 70 % respectively. Obviously, the

sample (S5) still exhibits a good photocatalytic activity after 4 cycles. The photocatalyst is stable.

Fig. 10. Photocatalytic degradation of RhB (a) and QB (b) by recycling the photocatalyst under visible light.

3.5 Photocatalytic mechanism

To further explore the mechanism of photodegradation of QB, the scavenging experiments were carried out. Various scavengers such as benzoquinone ($\bullet\text{O}_2^-$ quencher), tert-butyl alcohol ($\bullet\text{OH}$ quencher) and KI (h^+ quencher) were introduced to identify reactive sites in the QB degradation process with S5 as the catalyst [41, 42]. As shown in Figure 11, the degradation efficiency of QB was almost not inhibited upon addition of tert-butyl alcohol, implying the role of $\bullet\text{OH}$ during the degradation of QB can be negligible. On the contrary, the degradation rate was obviously decreased after a certain amount of benzoquinone or KI was added into the photocatalytic reaction system. Therefore, $\bullet\text{O}_2^-$ and h^+ are the two main active species during the photocatalytic process of QB using $\text{BiVO}_4/\text{Bi}_5\text{O}_7\text{I}$ composites as catalysts under visible-light irradiation.

Fig. 11. Time course of the photodegradation of QB over the as-prepared $\text{BiVO}_4/\text{Bi}_5\text{O}_7\text{I}$ (S5) in the presence of various radicals scavengers.

On the base of the above results, a possible mechanism of the photodegradation of QB for BiVO₄/Bi₅O₇I composites is proposed and illustrated in Scheme 1 [43, 44]. The CB values of BiVO₄ and Bi₅O₇I are 0.21 and -0.06 eV, respectively and their VB values are 2.75 and 1.97 eV, respectively. Bi₅O₇I is a p-type semiconductor with the fermi level (E_F) close to its VB while BiVO₄ is a n-type semiconductor with the E_F close to its CB. When the BiVO₄ microspheres contact with the Bi₅O₇I microrods, a p-n junction could form between them. The construction of the BiVO₄/Bi₅O₇I p-n heterojunction can contribute to adjust the relative position of their energy bands. Eventually, the valence band bottom of BiVO₄ becomes lower in energy than that of Bi₅O₇I after their Fermi levels reached equilibrium state. Under the irradiation of visible light, BiVO₄ and Bi₅O₇I can be both excited and produce the photogenerated electrons and holes. The photogenerated electrons can transfer from CB of Bi₅O₇I to CB of BiVO₄ and the holes can transfer from VB of BiVO₄ to VB of Bi₅O₇I. Thus the photogenerated charge carriers can be effectively separated. Furthermore, the n-p interface of BiVO₄/Bi₅O₇I can accelerate electron transfers from the electron-rich BiVO₄ site to the hole-enriched iodines site. The CB of BiVO₄ can provide a platform to reduce the O₂ molecules producing the active •O₂⁻ radicals, and then induce the QB degradation or interact with H₂O to produce •OH radicals. The holes from VB of Bi₅O₇I can directly oxidize QB to form CO₂. Finally, the as-synthesized BiVO₄/Bi₅O₇I composite would decompose QB into CO₂ under visible-light irradiation.

Scheme 1 The possible photocatalytic reaction mechanism of the BiVO₄/Bi₅O₇I (S5) composite under visible-light irradiation.

4. Conclusions

To summarize, we have designed and successfully synthesized a n-p heterojunctional BiVO₄/Bi₅O₇I photocatalysts employed in effective water

purification under visible light. Raw reactants were selected to [EMIM]I, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{K}_6\text{V}_{10}\text{O}_{28} \cdot 9\text{H}_2\text{O}$ and an ultrasonic assistant method was developed for sample synthesis. Despite simpleness for room-temperature wet method, it is the necessary to control stringent proportion of the amount of reactants and ultrasonic reaction time for successful preparation of the $\text{BiVO}_4/\text{Bi}_x\text{O}_y\text{I}$. The as-prepared $\text{BiVO}_4/\text{Bi}_5\text{O}_7\text{I}$ photocatalyst exhibited superior photocatalytic efficiency for degradation of RhB and QB under visible-light irradiation compared with the non-heterojunctional candidates. Besides virtue of charge separations for (e^- - h^+) migration in most heterojunctions, the p-n nature of the present complex would facilitate capture and retain of the charges. It is hoped that the work will be served as a prototypical p-n semiconductor photocatalysts design along with its possible utility in water decontamination via sun-visible-light photocatalysis.

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