

BiVO₄/BiPO₄ 复合物的制备及可见光催化性能

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摘要: 采用水热法合成出具有不同 V、P 物质的量之比的 BiVO₄/BiPO₄ 复合物。 n_V/n_P 分别为: 0.1/9.9、0.5/9.5、1/9、3/7、5/5。采用 XRD、FE-SEM、EDS、拉曼、可见光光度计、漫反射以及电化学等测试手段对 BiVO₄/BiPO₄ 复合物进行表征。在可见光条件下降解亚甲基蓝来评价 BiVO₄/BiPO₄ 复合物的光催化活性。结果显示, 当 $n_V/n_P < 3/7$ 的时候, BiVO₄/BiPO₄ 复合物的光催化活性随着 BiVO₄ 含量的增加而增加, 当 $n_V/n_P = 3/7$ 的时候, 复合物具有最佳的光催化性能, 反应速率常数 k 为 0.005 1 min⁻¹, 是纯 BiPO₄ 的 23.2 倍。BiVO₄/BiPO₄ 复合物的光催化机制主要是由于 BiVO₄ 的加入, 提高了电子-空穴的分离率, 进而提高了光催化活性。

关键词: 水热法; BiVO₄; BiPO₄; 光催化活性; 电子-空穴对

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Preparation of BiVO₄/BiPO₄ Composites With Enhanced Visible-Light-Driven Photocatalytic Properties

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Abstract: BiVO₄/BiPO₄ composites with different n_V/n_P molar ratios were synthesized by a simple one-pot hydrothermal method. The n_V/n_P molar ratios were 0.1/9.9, 0.5/9.5, 1/9, 3/7, and 5/5, respectively. The BiVO₄/BiPO₄ composites were characterized by X-ray diffraction, field emission scanning electron microscope, energy-dispersive spectroscopy, Raman spectrum, UV-Vis spectrophotometer, UV-Vis diffuse reflectance spectroscopy, and electrochemical impedance spectra. The photocatalytic activities of BiVO₄/BiPO₄ composites were evaluated by the degradation of methylene blue (MB) under visible light irradiation ($\lambda > 420$ nm). When the ratios of the BiVO₄/BiPO₄ composites were less than 3/7, the photocatalytic activities of BiVO₄/BiPO₄ composites were enhanced with an increasing amount of BiVO₄. The result showed that the BiVO₄/BiPO₄ composite ratio for $n_V/n_P = 3/7$ possessed the highest photocatalytic activity. The BiVO₄/BiPO₄ composite ratio for $n_V/n_P = 3/7$ possessed the maximal k value of 0.005 1 min⁻¹. It is 23.2 times of the pure BiPO₄. The photocatalytic mechanism of the BiVO₄/BiPO₄ composites could be mainly ascribed to the existence of BiVO₄ which could accelerate the separation and migration efficiency of photogenerated carriers.

Keywords: hydrothermal; BiVO₄; BiPO₄; photocatalytic activity; electron-hole pairs

0 Introduction

Since the new century, environmental pollution became one of the toughest issues, and human beings

need to face it. Photocatalysts can replace the traditional pollutant control technology because of full use of sunlight, complete degradation without secondary pollution and other advantages. At present,

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TiO₂ was the most widely studied photocatalysts. Because of their outstanding photocatalytic activity^[1-4], TiO₂-based photocatalysts had been proven to be one of the promising photocatalysts. But TiO₂-based photocatalysts were hard to overcome the issue of high recombination rates of photogenerated electron-hole pairs. Therefore, how to carry out efficient photocatalytic materials had become an important issue of photocatalysts.

Currently, inorganic bismuth compounds (eg BiOX^[5], BiVO₄^[6-8], Bi₂WO₆^[9-10], Bi₂MoO₆^[11-12] and BiPO₄^[13-14]) were widespread concerned because of their high electron-holes separation rate. BiPO₄ was a new type of photocatalysts. BiPO₄ had been reported that had excellent photocatalytic activity under UV light than TiO₂ (P25) for the degradation of methylene blue (MB)^[15]. Zhu et al. reported PO₄³⁻ was favorable for the separation of photo-induced e⁻/h⁺ and PO₄³⁻ can improve the photocatalytic activity of BiPO₄^[16]. Due to the wide band gap, BiPO₄ had no visible light response. It must be the largest hindrance for the further applications of BiPO₄. Thus, it was an important mission to broaden the visible light absorption region of BiPO₄. Up to now, for obtaining visible light induced, much work had been done for BiPO₄, including C₃N₄/BiPO₄^[17], AgPO₄/BiPO₄^[18-19], BiOI/BiPO₄^[20], and Bi₂MoO₆/BiPO₄^[21]. BiVO₄ had a narrow gap-band energy (~2.4 eV) and had been considered to be one of the most promising photocatalysts. BiVO₄ was usually selected as a sensitizer photocatalyst because of its high visible-light response. BiVO₄ could degrade pollutants and evolve H₂ and O₂ under visible light ($\lambda > 420$ nm). However, as stated previously, the poor separation of photoinduced e⁻/h⁺ had a restriction on the photocatalytic activity of pure BiVO₄. Therefore, we envisaged that constructing BiVO₄/BiPO₄ heterostructured photocatalysts^[22-23], which could be a promising method to improve the photocatalytic performance and broaden the visible light absorption region of BiPO₄. However, until now, there were few reports about BiVO₄/BiPO₄ composites photocatalysts.

In this study, BiVO₄/BiPO₄ composites photocatalysts were synthesized by hydrothermal method. The

photocatalytic activities of BiVO₄/BiPO₄ composites were evaluated by the degradation of methylene blue (MB) under visible light ($\lambda > 420$ nm). Besides, detailed photocatalytic mechanism of the BiVO₄/BiPO₄ Composites had been discussed.

1 Experimental

1.1 Experimental drugs and equipment required for the experiment

All chemicals were analytical purity and were used without further purification. Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. Disodium phosphate dodecahydrate (Na₂PO₄·12H₂O) was obtained from Shenyang Federal Reagent Factory and ammonium metavanadate (NaVO₃) was obtained from Sinopharm Chemical Reagent Co., Ltd. Methylene blue (C₆H₁₈ClN₃S·3H₂O) was obtained from Tianjin Bodi Chemical Co., Ltd. Deionized water was used in all experiments.

The purity and crystallinity of pure BiPO₄, pure BiVO₄ and BiVO₄/BiPO₄ composites were characterized by X-ray diffraction (XRD) on Rigaku DMAX-Ultima⁺ diffractometer with Cu K α radiation ($\lambda = 0.154\ 06$ nm). Raman spectrum was excited with the 514 nm line of an Ar⁺ laser at an incident power of 20 mW. The morphologies of the samples were examined by a field emission scanning electron microscope (FE-SEM) with SUPRA 55 SAPHIRE. UV-Vis diffuse reflectance spectroscopy (DRS) measurements were measured using a TU-1901 UV-Vis spectrophotometer equipped with an integrating sphere attachment. The analysis range was from 200 to 800 nm, and BaSO₄ was used as a reflectance standard. Electrochemical experiments were performed in a flat cell having 0.1 mol·L⁻¹ Na₂SO₄ solution by a remote controlled potentiostat/galvanostat (VMP3 EG&G Princeton Research).

1.2 Preparation of photocatalysts

The BiVO₄/BiPO₄ composites with different BiVO₄ contents were synthesized by hydrothermal method. In a typical process, the precursor solution was prepared by dissolving 2 mmol Bi(NO₃)₃·5H₂O with 0.02 mmol NaVO₃, 1.98 mmol Na₂PO₄·12H₂O; 0.1 mmol NaVO₃,

1.9 mmol Na₃PO₄·12H₂O; 0.2 mmol NaVO₃, 1.8 mmol Na₃PO₄·12H₂O; 0.6 mmol NaVO₃, 1.4 mmol Na₃PO₄·12H₂O and 1 mmol NaVO₃, 1 mmol Na₃PO₄·12H₂O, respectively. Then the precursor solution was putted in 35 mL of distilled water. After stirring for 30 min, the resultant precursor solution was transferred into a 50 mL teflon-lined stainless steel autoclave. The autoclave was sealed and heated to 170 °C for 24 h and allowed to cool down to room temperature naturally. The precipitate was washed with absolute ethanol and distilled water for many times, respectively, and dried at 70 °C in air. In order to facilitate the expression, the composite ratios were named for $n_v/n_p=0.1/9.9$, 0.5/9.5, 1/9, 3/7, 5/5 as 0.1VP, 0.5VP, 1VP, 3VP, 5VP, respectively. For comparison, pure BiPO₄ sample was synthesized by adopting the method. BiPO₄ was synthesized by 2 mmol Bi(NO₃)₃·5H₂O and 2 mmol Na₃PO₄·12H₂O. The reaction process could be simply expressed as shown in Fig.1.

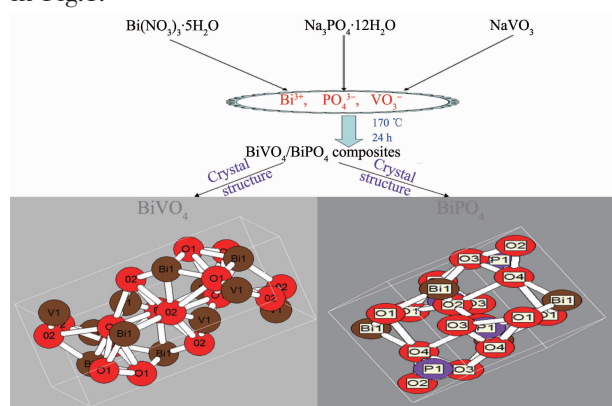


Fig.1 Reaction process and the crystal structure of BiVO₄ and BiPO₄

1.3 Photocatalytic activity tests

To carry out the photocatalytic activity of pure BiPO₄ and BiVO₄/BiPO₄ composites, the sample of 50 mg was suspended in a MB dye aqueous solution (100 mL, 10⁻⁵ mg·L⁻¹). After stirring for 30 min to reach an equilibrium adsorption state in the dark, the solution was irradiated with a 500 W Xe arc lamp. The lamp provided visible light ($\lambda > 420$ nm) with a cut off filter. At given time intervals, the solution (4 mL) was sampled and centrifuged. Then, the filtrates were analyzed by recording variations of the absorption

band maximum (664 nm) in a UV-Vis spectra of MB by using a TU-1901 UV-Vis spectrophotometer.

The degradation efficiency was calculated as follows^[24]:

$$n = \frac{A_0 - A}{A_0} \times 100\% \quad (1)$$

Where C_0 was the absorbance of original methylene blue (MB) solution and C was the absorbance of the methylene blue (MB) solution after visible light irradiation for 180 min. According to the Langmuir-Hinshelwood kinetics model, the photocatalytic process of methylene blue (MB) could be expressed as the following apparent pseudo-first-order kinetics equation:

$$\ln \frac{C_0}{C} = kt \quad (2)$$

Where k was the apparent pseudo-first-order rate constant, C_0 was the original methylene blue (MB) concentration and C was methylene blue (MB) concentration in aqueous solution at time.

2 Results and discussion

2.1 Photocatalytic activity

The photocatalytic activities of the BiVO₄/BiPO₄ samples were measured on the degradation of methylene blue (MB) in deionized water under visible light irradiation ($\lambda > 420$ nm) in Fig.2. It can be seen that pure BiPO₄ had less visible light photocatalytic activity for methylene blue (MB) degradation, due to the wide band gap (300 nm) of BiPO₄. After the depositing of BiVO₄, BiPO₄ can degrade methylene blue (MB) under visible light, which showed that BiVO₄ was a good visible light sensitizer to BiPO₄. The efficient visible light absorption abilities of BiVO₄/BiPO₄ composites ensured that the BiVO₄/BiPO₄ composites generated sufficient electron-hole pairs under visible irradiation. In particularly, 3VP displayed the best photocatalytic activity. Fig.2a showed the degradation efficiency of BiVO₄/BiPO₄ composites and the rate constant k . It could be seen that 3VP could degrade 60.2% methylene blue (MB) by 3 h illumination. It was calculated that 3VP possessed the maximal k value of 0.005 1 min⁻¹ which

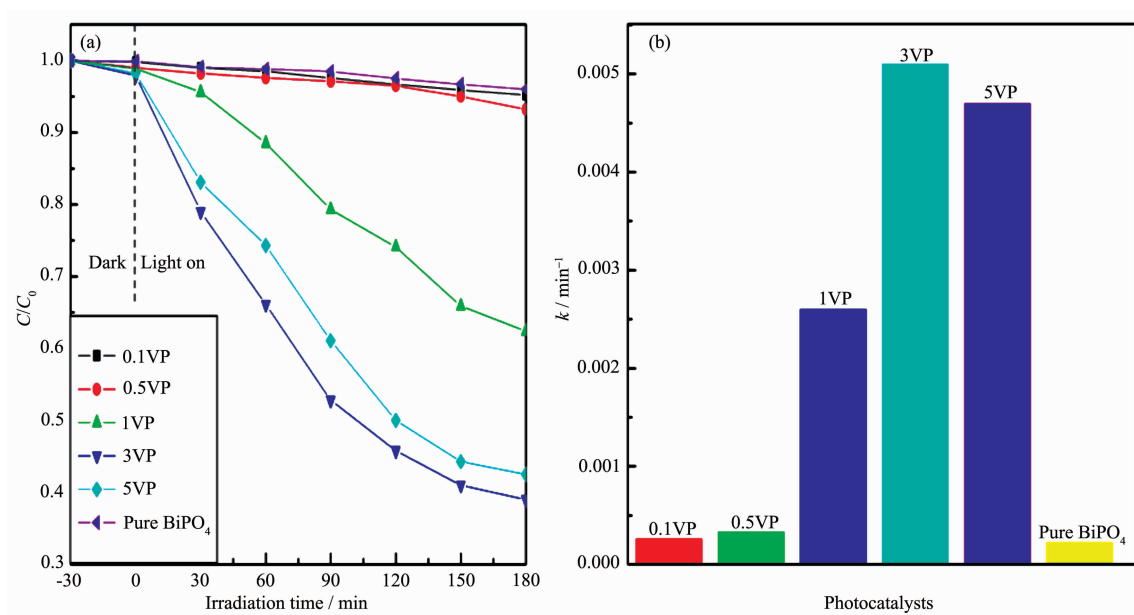


Fig.2 (a) Photodegradation efficiencies of MB as a function of irradiation time for different samples;
(b) Rate constant k of MB degradation for the as-prepared samples

was 23.2 times of the pure BiPO_4 in Fig.2b.

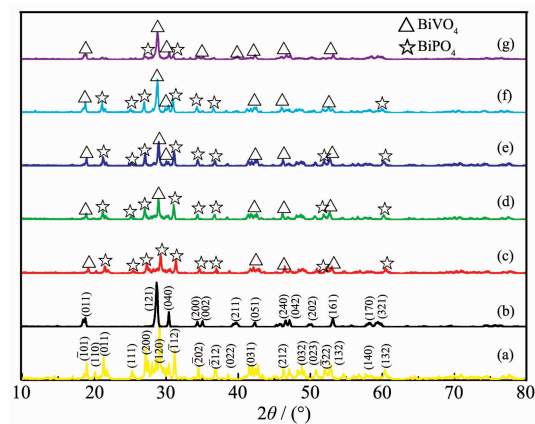
As reported in the previous literature^[25-29], generally, there was an optimal ratio of the two components in composite photocatalysts. When the component ratio of $\text{BiVO}_4/\text{BiPO}_4$ composites was changed that not only mainly affected the number of effective heterojunctions and also influenced the separation efficiency of $\text{BiVO}_4/\text{BiPO}_4$ composites. In case of the optimal content of 3VP, the most appropriate $\text{BiVO}_4/\text{BiPO}_4$ heterojunction was formed. The $\text{BiVO}_4/\text{BiPO}_4$ heterojunction could facilitate the high efficient separation of photoinduced electrons and holes, and endow the $\text{BiVO}_4/\text{BiPO}_4$ composite with higher photocatalytic activity under visible light irradiation ($\lambda > 420 \text{ nm}$).

2.2 Structural characterization

The purity and crystallinity of the $\text{BiVO}_4/\text{BiPO}_4$ composites were characterized by XRD. The Fig.3 showed the XRD patterns of the as-prepared BiPO_4 , BiVO_4 and $\text{BiVO}_4/\text{BiPO}_4$ composites. The $\text{BiVO}_4/\text{BiPO}_4$ composites exhibited a coexistence of both BiPO_4 and BiVO_4 phase. All the peaks for the samples were readily indexed to the monoclinic structure of BiPO_4 (JCPDS No.15-0767). As it could be seen in the pattern of BiVO_4 sample, the diffraction peaks could

be perfectly indexed to BiVO_4 phase (JCPDS No.21-0121). For the $\text{BiVO}_4/\text{BiPO}_4$ composites, all diffraction peaks of BiPO_4 were clearly observed, indicating that the solvothermal did not influence the crystal structure of BiPO_4 . When the n_v/n_p was 3/7, the strong characteristic diffraction peaks of sample BiPO_4 and monoclinic BiVO_4 were simultaneously found. With an increasing amount of BiVO_4 , more BiVO_4 diffraction peaks appeared.

To investigate the chemical bonding of the $\text{BiVO}_4/\text{BiPO}_4$ composites, Raman spectra were



(a) pure BiPO_4 ; (b) pure BiVO_4 ; (c) 0.1VP; (d) 0.5VP; (e) 1VP;
(f) 3VP; (g) 5VP

Fig.3 XRD patterns of the as-prepared samples

obtained and shown in Fig.4. The 3VP was selected for the study. In the Raman spectra, the observed intense band at 206 cm⁻¹ corresponded to the Bi-O stretching vibration^[30]. The band at 825 cm⁻¹ could be assigned to the symmetric vibration of V-O and the band at 323 cm⁻¹ could be assigned to the asymmetric stretching of VO₄³⁻^[31]. The ν_2 vibration of the PO₄³⁻ occurred at 362 cm⁻¹^[30].

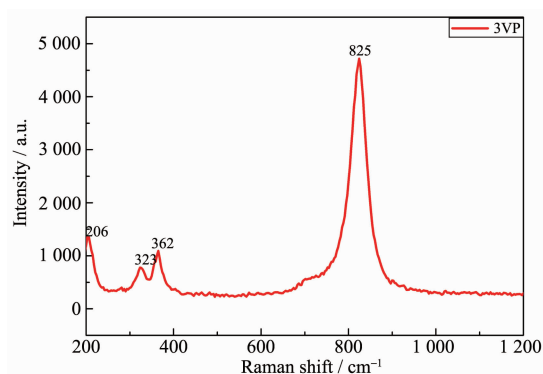


Fig.4 Raman spectrum of the as-prepared 3VP composite

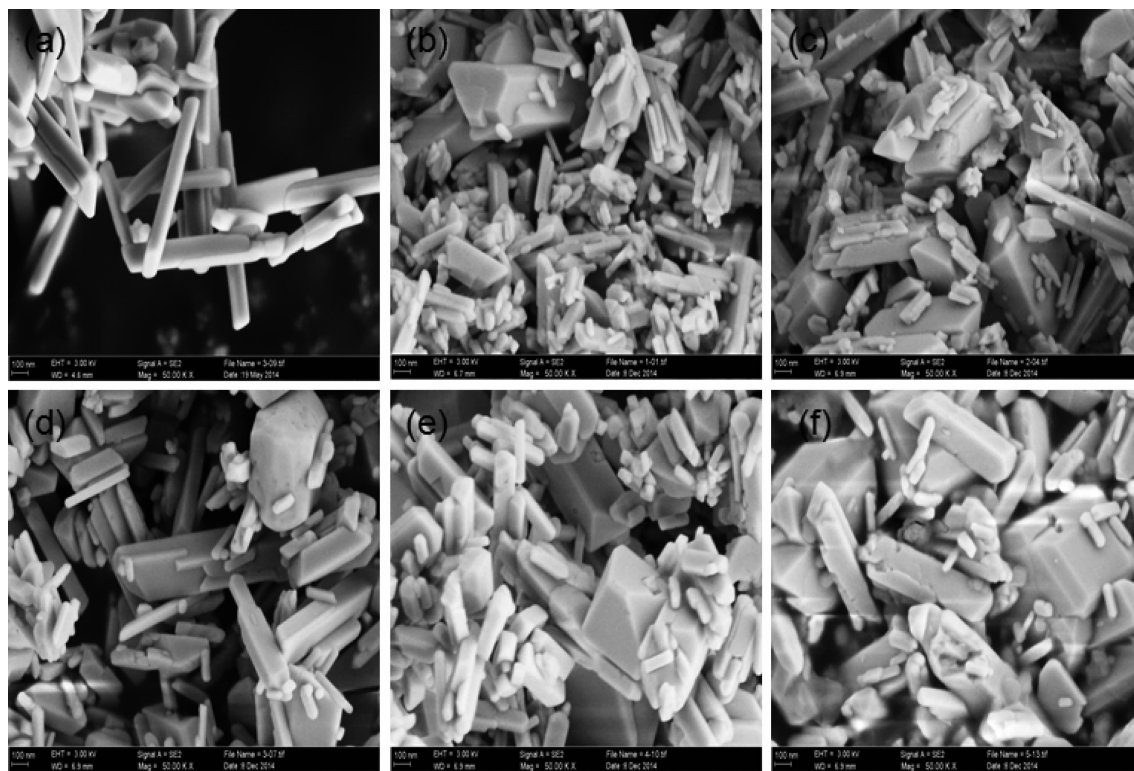
Combined with XRD results, all the evidences revealed the coexistence of both BiPO₄ and BiVO₄

phase.

2.3 Morphological analysis

The morphology and microstructure of the BiVO₄/BiPO₄ composites were characterized by FE-SEM. The FE-SEM images of the as-synthesized samples were given in Fig.5. The FE-SEM image (Fig.5a) of pure BiPO₄ showed that pure BiPO₄ had regular nanorods and had a clean surface. The nanorods had a length about 700 nm. After checking the relevant literature, pure BiVO₄ exhibited an irregular decahedron shape^[6-8]. Many irregular particles or particle aggregates of BiVO₄ were observed to adhere to BiPO₄ (Fig.5b, c, d, e, f). In Fig.5, it can be seen that with the increasing of the content of BiVO₄, the bulk morphology of the composite were increased, and the shape nanorods of the composite were decreased. When the n_V/n_P was 3/7, the composite had the best performance.

To determine the exact ratio of n_V/n_P , EDS was carried out to further identify the elemental composition of 0.1VP, 0.5VP, 1VP, 3VP and 5VP in Table 1. For example, the EDS pattern of the 3VP clearly indicated that, besides the V, Bi and O



(a) Pure BiPO₄; (b) 0.1VP; (c) 0.5VP; (d) 1VP; (e) 3VP; (f) 5VP

Fig.5 FE-SEM images of the as-prepared samples

Table 1 Characterization of the ratio of V/P

Sample	n_V/n_P (preparation process)	n_V/n_P (exact)
0.1VP	0.01	0
0.5VP	0.05	0.04
1VP	0.11	0.09
3VP	0.43	0.439
5VP	1	1.14

diffraction peaks corresponding to BiVO_4 , the P, Bi and O diffraction peaks coming from BiPO_4 were also observed, confirming that the samples were composed of both BiVO_4 and BiPO_4 . Meanwhile the molar ratio of n_V/n_P was 0.439, which was matched the ratio of the value of 3/7. The exact ratio of n_V/n_P was more or less the same as the one calculated from the preparation process.

2.4 Optical characterization

The optical absorption properties played a critical role in determining the photocatalytic performance of $\text{BiVO}_4/\text{BiPO}_4$ composites. The optical properties of pure BiPO_4 and 3VP were measured by UV-Vis diffuse reflectance spectra (DRS) in Fig.6. It could be clearly seen that BiPO_4 could merely respond to the UV light. The absorption band edge of BiPO_4 was around 300 nm. After the depositing of BiVO_4 , the light absorption of 3VP was significantly broadened to the visible light range around 460 nm. Compared with the pure BiPO_4 , 3VP photocatalyst showed a notable red-shift in the the absorption edge. This phenomenon may be due to the interaction between BiVO_4 and BiPO_4 , which subsequently resulted in a higher

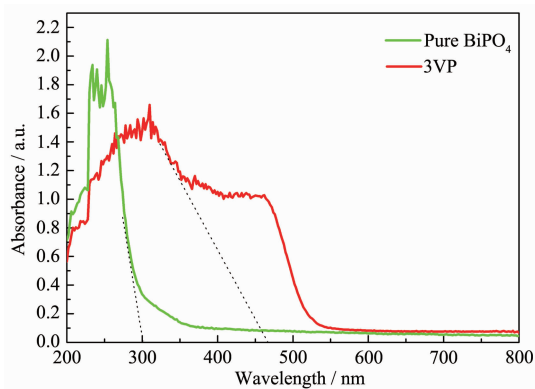


Fig.6 UV-Vis DRS of the as-prepared samples: pure BiPO_4 , 3VP

photocatalytic activity under visible light irradiation.

2.5 Electrochemical analysis

Electrochemical impedance spectra (EIS) measurements were conducted to investigate the separation efficiency of the photoinduced charge carriers and the charge transfer resistance. Fig.7 showed the EIS Nyquist plots of 3VP and pure BiPO_4 . It was known that when the diameter for arc radius was smaller, the charge transfer efficiency was higher^[32]. The diameter for arc radius of 3VP lighting was smaller than that of without lighting, which indicated a decrease in the charge-transfer resistance and led to an effective electron-hole pair separation. The radius of 3VP was smaller than that of pure BiPO_4 of lighting, implying that the charge transfer efficiency of 3VP was higher than that of pure BiPO_4 . Therefore, it could be concluded that the existence of BiVO_4 could accelerate the separation efficiency of photogenerated carriers of $\text{BiVO}_4/\text{BiPO}_4$ composites.

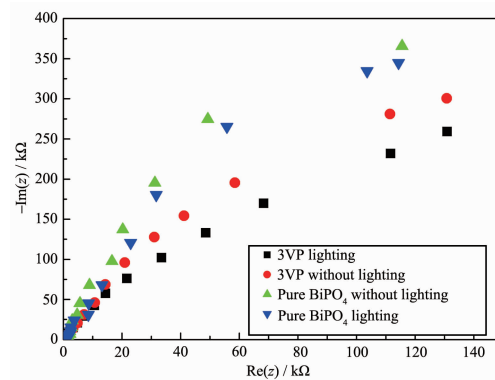


Fig.7 Nyquist plots for pure BiPO_4 , 3VP composite

2.6 Photocatalytic mechanism of $\text{BiVO}_4/\text{BiPO}_4$ composites

The enhancement of photocatalytic activity of $\text{BiVO}_4/\text{BiPO}_4$ composites was mainly due to the higher separation efficiency induced by the hybrid effect of BiVO_4 and BiPO_4 . A proposed schematic mechanism of the $\text{BiVO}_4/\text{BiPO}_4$ composites was shown in Fig.8. Through experiments, it was known that BiPO_4 had no or less visible light photocatalytic activity for MB degradation, which means that the electrons at the valence band (VB) of BiPO_4 could not inject into the conduction band (CB) of BiPO_4 under visible-light irradiation. After the depositing of BiVO_4 , at the

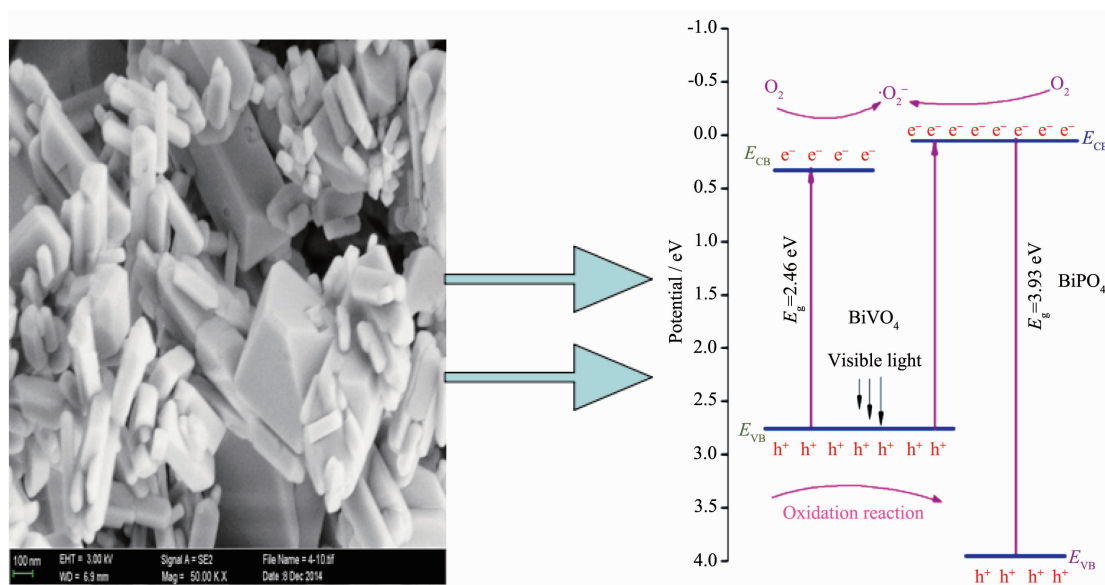
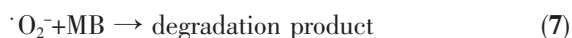
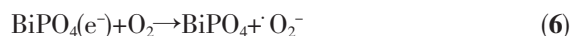
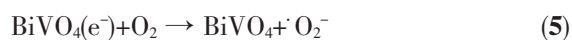
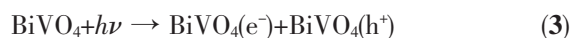


Fig.8 Schematic diagram of the separation and transfer of photogenerated charges in the BiVO₄/BiPO₄ composites under visible light irradiation

beginning of the reaction, photogenerated electron-hole pairs were formed on BiVO₄, under visible light irradiation ($\lambda > 420$ nm). The electrons at the VB of BiVO₄, not only could inject into the CB of BiVO₄, but also the CB of BiPO₄. The electrons injected into the CB of BiPO₄ not only revealed that BiPO₄ took part in the degradation of MB reaction under visible light irradiation and also led to a much reduced electron-hole recombination and improved the photocatalytic efficiency of the BiVO₄/BiPO₄ composites for MB degradation. The whole process was described as follows:



3 Conclusions

By the hydrothermal method, a series of BiVO₄/BiPO₄ were synthesized with different n_v/n_p . UV-Vis diffuse reflectance spectra could demonstrate that all the composites exhibited broad absorption in the visible region. The optimal n_v/n_p was 3/7. The k value was 0.005 min^{-1} which was 23.2 times of the pure

BiPO₄. The heterojunction structure of BiVO₄/BiPO₄ facilitated the efficient separation of photogenerated electron-hole pairs, greatly improving the photocatalytic efficiency of BiPO₄. The synthesized of BiVO₄/BiPO₄ composites provided a guideline for BiPO₄ transferred to visible light, increasing the utilization of sunlight.

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