Enhancement of full-spectrum photocatalytic activity over BiPO₄/Bi₂WO₆ composites

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Abstract: The full-spectrum photocatalyst is of important value for the practical use, which could absorb natural sunlight for photocatalytic degrading organic pollutants. $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts were prepared via ultrasonic-calcination method and had superior photocatalytic performance for degrading different kinds of organic pollutants under simulant sunlight irradiation. The apparent rate constant of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ on the degradation of methylene blue (MB) is 0.0305 min^{-1} , which is about 25.4 and 3.2 times of pure BiPO_4 and Bi_2WO_6 respectively. In the $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts, the core-hole structure of BiPO_4 as core and Bi_2WO_6 as hole was formed. During the photocatalytic process of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composites under simulant sunlight irradiation, the photo-generated electrons of BiPO_4 would inject to the conduction band of Bi_2WO_6 , and the photo-generated holes on Bi_2WO_6 could transfer to the valence band of BiPO_4 , and then an effective charges separation was achieved. The interaction of BiPO_4 and Bi_2WO_6 not only expanded the range of absorption spectrum but also enhanced the separation efficiency of photo-generated charges, and further improved the photocatalytic performance.

Keywords: $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composites; Full-spectrum; Photocatalytic degradation

1. Introduction

Photocatalysis has an important value in environmental purification and energy use utilization in recent years. The study of full-spectrum photocatalyst is the key technology that makes the best use of natural sunlight to purify environment [1, 2]. Recently, much attention has been given to Bi-based photocatalysts [3]. As a visible photocatalyst, Bi_2WO_6 possesses many advantages such as high activity, stable property and so on, which ascribes to the structure that the octahedron of ceratoid WO_6 locates in the sandwich of $(\text{Bi}_2\text{O}_2)^{2+}$ and promote the quick separation of photo-generated charges. Bi_2WO_6 has attracted more attention on the photocatalytic degradation of organic pollutants, however it still need further improve the photocatalytic efficiency in practical use [4-7]. Bi_2WO_6 doped with noble metal cocatalyst such as Au[8], Ag[9, 10], Pt[11] or composited other semiconductor photocatalysts such as TiO_2 [12, 13], ZnO [14], AgBr [15], Ag_3PO_4 [16], BiVO_4 [17], Bi_2O_3 [18] and Co_3O_4 [19], C_3N_4 [20, 21] to further improve photocatalytic performance. BiPO_4 , as a high active ultraviolet photocatalyst, has been attached importance by more and more researchers recently. Our research groups prepared three kinds of crystal structure and different morphology BiPO_4 photocatalysts via various methods such as hydrothermal, solvothermal, reflux and calcination, the photocatalytic activity of monazite monoclinic BiPO_4 is much better than that of traditional P25 TiO_2 [22-26]. Because the band gap of BiPO_4 is very wide, which only is excited by ultraviolet under 300 nm wavelength. In order to expand the absorption range and improve the photocatalytic activity, BiPO_4 was composited with RGO[27], C_3N_4 [28, 29], BiOI [30, 31], BiOBr [32, 33], Ag_3PO_4 [34-36], Bi_2MoO_6 [37], BiVO_4 [38], AgBr [39], AgI [40] and so on.

Based on merits and shortcomings of BiPO_4 and Bi_2WO_6 photocatalysts, $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composites were prepared via ultrasonic-calcination method in this work. Under the simulant sunlight irradiation, the photocatalytic activity of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ on the degradation of different kinds of organic pollutants was evaluated. Moreover, physicochemical properties and the proposed enhancement mechanism of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ photocatalytic activity were also systematically investigated.

2. Experimental Section

2.1 Synthesis of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts

Monazite monoclinic BiPO_4 nanorods prepared via reflux was used as precursor[25]. Appropriate amount BiPO_4 was weighed and added into a beaker, then 4.85 g (10 mmol)

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 3.3 g (10 mmol) $\text{Na}_2\text{WO}_6 \cdot 2\text{H}_2\text{O}$ were added as 1:1 mole ratio, at last 900 ml deionized water was added. The mixture was ultrasonicated for 1.0 h and then vigorously stirred for 1.0 h. A white precipitate was obtained by centrifugation and washed with deionized water for 3 times. Finally, the product was dried at 120 °C for 12.0 h and then calcinated in the muffle furnace in air at 500 °C for 4.0 h. According to the addition amount of BiPO_4 , 0.5%, 1.0%, 3.0%, 5.0%, 8.0% and 10.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts were obtained respectively.

2.2 Evaluation of Photocatalytic Activity and Photoelectrochemical Performance

The photocatalytic activity of as-prepared $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts were evaluated by degradation of MB in aqueous solution under a 500 W simulant sunlight xenon lamp irradiation (Institute for Electric Light Sources, Beijing) with no or different wavelength band-pass filter. 25 mg photocatalyst was added into as-prepared 50 mL $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ MB aqueous solution. Before irradiation, the suspension was ultrasonically dispersed for 0.5 h and then magnetically stirred for 1.0 h in dark to ensure the establishment of adsorption–desorption equilibrium. At each given time intervals, 3.0 mL suspension was taken out and separated through centrifugation (4000 rpm, 10 min). The concentration of MB solution was analyzed at the absorption band maximum (663 nm) using a Hitachi U-3010 UV-Vis spectrophotometer. The methods for the photocatalytic degradation of methyl orange (MO), Rhodamine B (RhB) and phenol were the same as above, but the concentration of phenol was $5.0 \text{ mg} \cdot \text{L}^{-1}$. The concentration of phenol is monitored using HPLC analysis with a UV detector at 270 nm. The mobile phase was methanol and water as 6:4, and the flow rate was $1.0 \text{ mL} \cdot \text{min}^{-1}$.

The photocurrents and electrochemical impedance spectroscopy (EIS) of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ photocatalysts were performed on CHI-660B electrochemical system (Shanghai, China) using a standard three-electrode cell under simulant sunlight irradiation. The ITO/samples with 20 mm×45 mm was acted as a working electrode, a standard calomel electrode (SCE) was used as reference electrode and a platinum wire was used as the counter electrode. ITO/ $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ was prepared by a dip–coating method: 6 mg $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ photocatalyst was suspended into 0.75 mL ethanol to make slurry, which was then dip–coated onto ITO glass electrode. The as–prepared electrodes were dried under ambient conditions for about 12.0 h and then calcinated at 120 °C for 5.0 h in air. Unless otherwise stated, the intensity of light at the film electrode was $1.5 \text{ mW} \cdot \text{cm}^{-2}$ and $0.1 \text{ mol} \cdot \text{L}^{-1}$ Na_2SO_4 electrolytes were used. The photoelectric responses of the sample as light-on and light-off were measured

at 0.0 V. The electrochemical impedance spectroscopy (EIS) was carried out at the open circuit potential, and a sinusoidal ac perturbation of 5 mV was applied to the electrode over the frequency range of 0.05-10⁵ Hz.

2.3 Materials Characterization

The crystallinity and purity of BiPO₄/Bi₂WO₆ samples were characterized by X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer (Cu K α =1.5418 Å, tube voltage=40 kV, tube current=20 mA) at a scan rate of 2°·min⁻¹ in the 2 θ range from 10° to 65°. The Ultraviolet–Visible diffuse reflectance spectroscopy (UV–Vis DRS) of BiPO₄/Bi₂WO₆ photocatalysts were performed on Hitachi U-3010 spectrophotometer equipped with an integrated sphere attachment in the range of 200 to 800 nm, and BaSO₄ was used as reference. The particle sizes of BiPO₄/Bi₂WO₆ samples were measured on the HITACHI HT7700 transmission electron microscopy (TEM) with an accelerating voltage 100 kV. The EDS mapping and the lattice planes and fringes of BiPO₄/Bi₂WO₆ were obtained from the high-resolution transmission electron microscope (HRTEM, JEM 2010F), and it was operated at an accelerating voltage of 200 kV. The Raman spectrum was measured at room temperature using HORIBAR 800 microscopic confocal Raman spectrometer in the range of 2000 cm⁻¹ to 4000 cm⁻¹, and the excitation wavelength was the 514.5 nm from an Ar⁺ laser with 30 mW output power. The electron spin resonance (ESR) signals of radicals spin-trapped by spin-trap reagent 5,5'-dimethyl-1-pyrroline-N-oxide(DMPO) were examined on a Bruker model ESR JES-FA200 spectrometer equipped with a Quanta-Ray Nd:YAG laser system as the irradiation source (λ = 365 nm). Magnetic parameters of the radicals detected were obtained from direct measurements of magnetic field and microwave frequency.

3. Results and Discussions

3.1 Photocatalytic activity and photocurrent response

BiPO₄ and Bi₂WO₆, as two kinds of Bi³⁺ oxy-acid salt photocatalysts, have been attached great importance by more and more researchers in recent years [8, 11, 18, 22, 29]. BiPO₄ possesses superior ultraviolet photocatalytic performance, and Bi₂WO₆ possesses excellent visible activity. Before irradiation, the suspensions of MB over BiPO₄, Bi₂WO₆ and BiPO₄/Bi₂WO₆ composite photocatalysts were ultrasonically dispersed for 0.5 h and stirred in the dark for 1.0 h to get the adsorption-desorption equilibrium. The initial concentration of MB is 1.0×10⁻⁵ mol·L⁻¹, the initial photocatalytic reaction concentration of MB over BiPO₄ and Bi₂WO₆ is 0.98×10⁻⁵ mol·L⁻¹ and 0.85×10⁻⁵ mol·L⁻¹ after reaching the

adsorption-desorption equilibrium (Fig.1), which indicated that Bi_2WO_6 had more adsorption capacity of MB than BiPO_4 . At the same time, the adsorption capacity of MB over $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts gradually decreased with the content of BiPO_4 increasing. The initial photocatalytic reaction concentration of MB over 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ is $0.92 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. So the adsorption of MB over photocatalysts in this work wouldn't affect greatly the evaluation of photocatalytic performance. Under simulant sunlight irradiation, the photocatalytic activities of BiPO_4 and Bi_2WO_6 on the degradation of MB were very low. The apparent rate constant k of BiPO_4 on the photocatalytic degradation of MB was only 0.0012 min^{-1} , the photocatalytic activity of Bi_2WO_6 on the degradation of MB was higher ($k=0.0095 \text{ min}^{-1}$) as a visible photocatalyst. $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ (BPW in Fig) composite photocatalysts possessed better photocatalytic performance on the degradation of MB under simulant sunlight irradiation. When the content of BiPO_4 was under 5.0%, the photocatalytic activity of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composites increased gradually with increasing the content of BiPO_4 . The photocatalytic performance of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ was the best and its apparent rate constant k was 0.0305 min^{-1} , which was about 25.4 and 3.2 times of pure BiPO_4 and Bi_2WO_6 respectively. When the content of BiPO_4 exceeded 5.0%, the photocatalytic activity of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composites decreased gradually with the content of BiPO_4 increasing, the above result was accorded with literatures [24, 30, 34, 37]. Because the high content of BiPO_4 would reduce the absorption properties of Bi_2WO_6 under simulant sunlight conditions, which further decreased the photocatalytic performance of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$. The photocatalytic activity of 10% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ was lower than that of pure Bi_2WO_6 .

Fig.1 The adsorption and and apparent rate constants of photocatalytic degradation MB over BiPO₄, Bi₂WO₆ and BiPO₄/Bi₂WO₆ (500W Xenon lamp, [MB]= $1.0\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$)

Fig.2 Photocatalytic activity of 5.0%BiPO₄/Bi₂WO₆ depended on wavelength

Fig.3 Photocatalytic degradation of different kinds of organic pollutants over Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ under simulant sunlight condition (500W Xenon lamp, 25mg photocatalyst, $[\text{MO}] = 1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $[\text{RhB}] = 1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $[\text{phenol}] = 5.0 \text{ ppm}$)

Wavelength dependent photocatalytic activities of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ were also measured in order to study its light absorption properties and the best excitation wavelength under simulant sunlight irradiation with band-pass filter. As can be seen from Fig. 2, 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ had higher photocatalytic activity at 380 nm than that at 365 nm and 420 nm. Which demonstrated that 380 nm was the best excitation wavelength. With wavelength increasing above 420 nm the photocatalytic performance of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ were all very low, because long wavelength didn't excite its photo-generated charges.

$\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts were investigated to degrade different kinds of organic pollutants popularly. Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ were selected to degrade cationic dye MO, anionic dye RhB and neutral colorless reagent phenol under simulant sunlight condition (Fig. 3). 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ exhibited better photocatalytic performance on the degradation of these organic pollutants than pure Bi_2WO_6 . The above results showed that $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts had no-selectivity and could effectively degrade different kinds of organic pollutants [26, 41].

Fig.4 Photocurrent responses of BiPO₄, 5.0% BiPO₄/Bi₂WO₆ and Bi₂WO₆

under simulant sunlight irradiation

During the photocatalytic process, the separation and transfer of photo-generated charges are the important step that determines photocatalytic efficiency. The photocurrent responses of photocatalyst on the ITO conductive glass under light irradiation could demonstrate the separation and transfer efficiency of photo-generated electrons and holes [42, 43]. The transient photocurrent responses of BiPO₄, 5.0% BiPO₄/Bi₂WO₆ and Bi₂WO₆ at light-on and light-off were reversible and stable (Fig. 4). Due to a little ultraviolet in the simulant sunlight, the photocurrent response of BiPO₄ was very weak. The photocurrent of Bi₂WO₆ was much better than that of BiPO₄. The photocurrent of 5.0% BiPO₄/Bi₂WO₆ was the highest (26 μ A) and about 2.5 times as high as that of pure Bi₂WO₆. The enhancement of photocurrent of 5.0% BiPO₄/Bi₂WO₆ composite photocatalyst indicated that the intimate interaction was existed between BiPO₄ and Bi₂WO₆ interface, which improved the separation of photo-generated electrons and holes and further enhanced BiPO₄/Bi₂WO₆ photocatalytic performance [13, 16, 29, 42].

3.2 Characterization of BiPO₄/Bi₂WO₆ composites

As can be seen from the TEM images that precursor BiPO₄ was nanorod (Fig. 5a) [25] and pure Bi₂WO₆ was nanosheet (Fig. 5b) [44, 45]. The morphology of 1.0% BiPO₄/Bi₂WO₆ composite photocatalyst was the same as that of Bi₂WO₆ nanosheet, there was no big

difference (Fig. 5c). With increasing the content of BiPO_4 , it can be seen that the core-hole structures of Bi_2WO_6 nanosheet produced around BiPO_4 nanorod were gradually formed from the TEM images of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts (Fig. 5c and f). The TEM image of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ obviously displayed that core-hole structure of Bi_2WO_6 nanosheet formed around BiPO_4 nanorod (Fig. 5e). With the content of BiPO_4 further increasing, the TEM image of 8.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ showed a part of bare BiPO_4 nanorod (Fig. 5f). It was indicated that too much content of BiPO_4 would destroy the core-hole structure of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts and further decreased its absorption efficiency and photocatalytic performance.

Fig.5 The TEM images of BiPO_4 , $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composites and Bi_2WO_6

(a, BiPO_4 ; b, Bi_2WO_6 ; c, 1.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$; d 3.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$; e, 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$; f, 8.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$)

The core-hole structure of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ was further demonstrated by the EDS mapping and HRTEM images (Fig.6 and Fig.7). The elemental composition and mapping of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ were examined by EDS mapping (Fig.6). Bi, P, W, O elements were all existed in 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalyst. P element distributed the main body of BiPO_4 nanorod, but W element distributed the margin of BiPO_4 nanorod and a part of W elements were enriched on the surface of BiPO_4 nanorod. The Fig.7a was the HRTEM image of Bi_2WO_6 , the lattice fringes of 0.193 nm, 0.273 nm and 0.318 nm belonged to the lattice plane

of Bi_2WO_6 orthorhombic (JPCDS 079-2381) (202), (002) and (131). From the HRTEM image of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$, the (200) lattice plane of BiPO_4 about 0.330 nm lattice dispace ascribed to monazite monoclinic (JPCDS 089-0287) was coated by the (002) and (131) lattice plane of Bi_2WO_6 . Moreover, the heterojunction was formed between the (002), (131) lattice plane of Bi_2WO_6 and the (200) lattice plane of BiPO_4 .

Fig.6 The EDS mapping of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$

Fig.87 HRTEM images of Bi_2WO_6 (a) and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ (b)

In order to investigate the valance bond interaction between BiPO_4 and Bi_2WO_6 in $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts, the characteristic Raman spectra of samples were tested. Bi_2WO_6 has five characteristic Raman spectra, which located in 826 cm^{-1} , 792 cm^{-1} , 718 cm^{-1} , 433 cm^{-1} and 298 cm^{-1} respectively(Fig.8). 826 cm^{-1} and 792 cm^{-1} were ascribed to the symmetric and anti-symmetric stretching modes of terminal O-W-O, the peak of 718 cm^{-1}

was anti-symmetric bridging mode associated with the tungstate chain. Moreover, the peak of 433 cm^{-1} was ascribed to anti-symmetric mode of WO_6 octahedral, the Raman peak of 298 cm^{-1} was assigned to translational modes of simultaneous motions of Bi^{3+} and WO_6^{6-} [46-48]. The Raman spectrum of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ included the all characteristic peaks of Bi_2WO_6 . Among them, the 298 cm^{-1} peak of Bi_2WO_6 produced a red shift to 301 cm^{-1} , but the peaks located at 826 cm^{-1} , 792 cm^{-1} , 718 cm^{-1} produced a little blue shift. It was indicated that BiPO_4 changed the chemical bond energy of Bi_2WO_6 in the $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts. There was chemical bond interaction between BiPO_4 and Bi_2WO_6 . Moreover, the characteristic Raman peaks of BiPO_4 located at 414 cm^{-1} , 572 cm^{-1} , 1006 cm^{-1} and 1079 cm^{-1} appeared in the Raman peaks of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ [26]. The composite of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ didn't change the crystal structure of BiPO_4 and Bi_2WO_6 , and the all characteristic peaks of Bi_2WO_6 orthorhombic (JPCDS 079-2381) appeared. With increasing the content of BiPO_4 , the characteristic peaks of its monazite monoclinic (JPCDS 089-0287) were gradually demonstrated (Fig. S1).

Fig.8 Raman spectra of Bi_2WO_6 , 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ and BiPO_4

Fig.9 UV-Vis spectra of Bi_2WO_6 , 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ and BiPO_4

The UV-Vis spectra of BiPO_4 , Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ were showed in Fig. 9. The absorption band edge of precursor BiPO_4 was about 320 nm (Fig. 9a) [25]. Bi_2WO_6 , as a visible photocatalyst, its absorption band edge was about 460 nm. In the range of 200-450 nm, the strong absorption of Bi_2WO_6 ascribed to the charge transfer from O^{2-} to W^{6+} [4, 10]. The absorption band edge of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalyst was about 385 nm, which induced an obvious red shift compared to BiPO_4 and a blue shift compared to Bi_2WO_6 . The above results illustrated that there was chemical interaction between Bi_2WO_6 and BiPO_4 interface, which improved the separation and transfer of photo-generated charges. According to the calculated Tauc's plot, the band gaps of Bi_2WO_6 , 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ and BiPO_4 were 2.7 eV, 3.2 eV and 3.9 eV respectively (Fig. 9b).

3.3 Proposed enhancement mechanism of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ photocatalytic activity

The separation of photo-generated electrons and holes played a very important role during the photocatalytic process of decomposition of organic pollutants, which could be evaluated by the typical electrochemical impedance spectra (EIS) [21, 26, 29, 41]. Under simulant sunlight irradiation and in dark, The EIS Nyquist plots of BiPO_4 , Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ were presented in Fig. 10. The arc radius on the EIS spectra reflects the solid state interface layered resistance and the surface charges transfer resistance. The smaller arc radius on the EIS Nyquist plot indicates a more efficient separation of the photo-generated electrons and holes, and vice versa. The Nyquist arc radii of 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ were all smaller than that of BiPO_4 and Bi_2WO_6 , which illustrated that $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalyst had smaller electric resistance and higher efficiency

of charges separation than BiPO_4 and Bi_2WO_6 . Thus, 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ photocatalyst has higher separation efficiency of photo-generated charges and better photocatalytic activity.

Fig.-10 The EIS response of Bi_2WO_6 , 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ and BiPO_4 thin film electrodes in dark and under simulant sunlight irradiation

The main oxidative species of semiconductor photocatalysts could be verified by the trapping experiments of active species, usually using ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) as hole scavengers, tertiary butyl alcohol (t-BuOH) as hydroxyl radical scavengers and purging N_2 as $\cdot\text{O}^{2-}$ radical scavenger. The oxidative species on the photocatalytic degradation of MB over Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ were shown in Fig. 411. When the N_2 was purged the photocatalytic activity of Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ didn't changed, which indicated that $\cdot\text{O}^{2-}$ radical wasn't the main oxidative species. The photocatalytic performance of Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ changed slightly by addition of t-BuOH, suggesting that $\cdot\text{OH}$ radical played an assistant role on the photocatalytic degradation of MB over Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$. Moreover, the ESR spin-trap technique was used to monitor the oxidative species generated by Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ with DMPO in water and Methyl alcohol under light irradiation (Fig. S2). The result of ESR further demonstrated that there was no $\cdot\text{O}^{2-}$ radical in the system of Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$. However, the intensity of $\cdot\text{OH}$ radical in 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ system was much higher than that of Bi_2WO_6 . The photocatalytic

activity of Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ decreased greatly by addition of EDTA-2Na, which improved that photo-generated holes are the main oxidative species of Bi_2WO_6 and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$.

Fig.11 The plots of photocatalytic degradation of MB over Bi_2WO_6 (a) and 5.0% $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ (b) with the addition of hole, $\cdot\text{O}^{2-}$ and $\cdot\text{OH}$ radical scavenger under simulant sunlight irradiation

Fig.12 The proposed mechanism of charges separation and enhancement of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ photocatalytic activity

Based on the above results, a proposed enhancement mechanism of charges separation and photocatalytic process over $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ was inferred in Fig.12. During the photocatalytic process of $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composites under simulant sunlight

irradiation, Bi_2WO_6 could absorb visible light to form photo-generated holes that transited to the valance band of BiPO_4 , at the same time BiPO_4 could absorb ultraviolet to form photo-generated electrons that transited to the conduction band of Bi_2WO_6 . The interaction of BiPO_4 and Bi_2WO_6 not only expanded the range of absorption spectrum but also enhanced the separation and transfer efficiency of photo-generated charges, and then further improving the photocatalytic performance. According to the result of main oxidative species detection, the photo-generated holes of BiPO_4 valance band could degrade the organic pollutants directly or react with water to form $\cdot\text{OH}$ radical that further decompose organic pollutants.

4. Conclusions

In this work, $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts were prepared via ultrasonic-calcination method. Compared with pure BiPO_4 and Bi_2WO_6 , $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ has superior photocatalytic performance for degrading different kinds of organic pollutants under simulant sunlight irradiation. In the $\text{BiPO}_4/\text{Bi}_2\text{WO}_6$ composite photocatalysts, the core-hole structure of BiPO_4 as core and Bi_2WO_6 as hole was formed. The photo-generated electrons of BiPO_4 would inject to conduction band of Bi_2WO_6 , and the photo-generated holes on Bi_2WO_6 could transfer to the valance band of BiPO_4 , and then an effective charges separation was achieved. The interaction of BiPO_4 and Bi_2WO_6 not only expanded the range of absorption spectrum but also enhance the separation efficiency of photo-generated charges, which then improve the photocatalytic performance.

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*Graphical Abstract