Charge Transport Properties of Cu2S/BiVO4 Composite Photocatalyst

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Abstract. The Cu2S/BiVO4 composite photocatalysts had been synthesised by a simple solution adsorption method. The obtained samples were characterised by means of field emission scanning electron microscope (SEM), X-ray diffraction patterns (XRD), UV-visible absorption spectrum techniques and transient photovoltage spectra (TPV). The results showed that the Cu2S nanoparticles were evenly loaded on the surface of the dumbbell-like BiVO4 composites. Compared with pure BiVO4, Cu2S/BiVO4 composites had better photocatalytic activity. Furthermore, the photogenerated charge transport properties of Cu2S/BiVO4 composites were investigated by means of TPV technique. The interface between BiVO4 and Cu2S enhanced the separation efficiency of photogenerated charge carriers, thus, the photocatalytic activity of Cu2S/BiVO4 composites was enhanced.

1. Introduction

As an ideal green technology, photocatalytic degradation of organic pollutants has attracted continuous interest for its potential applications in environmental cleaning and solar energy utilization [1, 2]. BiVO4 has great application prospects in the wide of photocatalysis due to its nontoxic, stable, suitable energy band structure and high photocatalytic activity [1-4].

It is known that there are three crystalline phases of BiVO4, tetragonal zircon phase (z-BiVO4), tetragonal scheelite phase (t-BiVO4) and monoclinic scheelite phase (m-BiVO4), in which m-BiVO4 shows the best photocatalytic activity because of its narrow band gap (2.4 eV)[5-7]. The preparation methods of monoclinic BiVO4 include solid reaction method, hydrothermal method and ultrasonic strengthening method etc. [8]. Nonetheless, monoclinic BiVO4 synthesized by the traditional method has the disadvantages of poor photoelectron transfer rate, poor adsorption performance and poor separation and recombination of photoelectric charge carriers, which leads to low photocatalytic efficiency [9]. However, further research on the improvement of BiVO4 photocatalytic activities is still indispensable. Many efforts have been made on the improvement of activities, including the construction of heterojunction. Wang and co-worker prepared g-C3N4/ {010} interface BiVO4 Z...
photocatalyst by ultrasonic dispersion method. The degradation rate of g-C₃N₄/010 facets of BiVO₄ interface Z-scheme photocatalysts can reach the highest 88.3% within 30 min under visible light irradiation, and the mineralization ability (96.03%) is about 2.24 as high as that of BiVO₄ (42.83%) [10]. Won-Chun Oh et al. research shows that the interface between BiVO₄, GO and PVDF can be fully contacted by hydrothermal method and ultrasonication method. Using a simple modification strategy, the BiVO₄ can be improved in accordance with the photocatalytic activity of the catalyst, and the degradation rate reaches 90% [11]. A. Malathi study found that BiFeWO₆ not only acts as a good electron acceptor in the BiFeWO₆/BiVO₄ composite, but also effectively prevents the separation of photogenerated electron-hole pairs and increases the photocatalytic degradation efficiency of the BiFeWO₆/BiVO₄ composite [12]; The 3D heterojunction structure was constructed by a simple hydrothermal method, and the visible light absorption range of BiVO₄, Bi₂S₃ and MoS₂ was successfully expanded. The photocatalytic degradation rate of BiVO₄/Bi₂S₃/MoS₂ heterojunction to RhB, methylene blue (MB) and malachite green (MG) by visible light irradiation was 97%, 93% and 94%, respectively [13].

2. Experimental

2.1. Fabrication of Cu₂S/BiVO₄
Cu₂S/BiVO₄ composites were synthesized by solution adsorption method. Bi (NO₃)₃·5H₂O (99.99% Sinopharm) and NaVO₃ (99.99% Sinopharm) were used as Bi and V source with molar ratio of 1:1. In a typical synthesis, the aqueous solution which marked as solution A was prepared by dissolving Bi (NO₃)₃·5H₂O (0.001 mol) in 5 mL deionized water and HNO₃ (68% Xilong Chemical Co.) of 0.3 mL. At the same time, NaVO₃ (0.001 mol) was dissolved in 5 mL deionized water under vigorous stirring, and the resultant solution was marked as solution B. When solution A and B were clear, two solutions were mixed and 9.7 mL of deionized water also added mixed solution. After stirring for 1 min, the resulting suspension was added into a glass bottle. The bottle was sealed and heated to 80 °C for 1 h. Then, Solution C (Cu₂S 5mg/L of ammonium hydroxide; Cu₂S/BiVO₄ molar ratio: 0.1, 0.5, and 1.0) add into the bottle gas. The bottle was also sealed and heated to 80 °C for 2 h. The precipitate was collected and washed with ethanol and distilled water several times. Then, the sample was dried in a vacuum at 80 °C for 4 h. The composite photocatalysts were marked as 0.1 Cu₂S/BiVO₄, 0.5 Cu₂S/BiVO₄, and 1.0 Cu₂S/BiVO₄. For comparison, the single BiVO₄ sample without Cu₂S was also prepared via the same solvothermal method.

2.2. Characterization
The crystalline structures of the samples were characterized by a powder X-ray diffraction (XRD, X’Pert Powder) with Cu Kα radiation in the range of 10–60°. The morphologies were observed on the field emission scanning electron microscopy (FESEM, Merlin Compact, and Carl Zeiss). The adsorption spectra were obtained using a UV-vis spectrophotometer (UV 3600, Shimadzu). Charge transport properties of samples were recorded by the transient photovoltage (TPV) with a 500 MHz digital phosphor oscilloscope (TDS 5054, Tektronix). The TPV measurement was carried out under air atmosphere at room temperature.

2.3. Photocatalytic activity test
Photocatalytic activities of Cu₂S/BiVO₄ composites were evaluated by degradation of RhB under the irradiation of the simulated solar irradiation, 500 W Xenon lamp was used as light source. The solution included a measured amount of 20 mg photocatalyst and 20 ml of 10 mg/L concentrated RhB. Before illumination, the reaction system was stirred in the dark for 30 min to establish an adsorption-desorption equilibrium. During the light irradiation, 1 mL of suspensions was centrifuged to remove the photocatalyst every 30 min. Then the concentration of RhB supernatants was analyzed by a UV-vis spectrophotometer.
3. Results and Discussion

![Figure 1](image.png)

**Figure 1.** XRD patterns of Cu₂S/BiVO₄ composites, BiVO₄ and Cu₂S.

The XRD patterns of as prepared BiVO₄ and different ratios Cu₂S/BiVO₄ composites are shown in Fig. 1. The diffraction peak of BiVO₄ is heterophase and composed of monoclinic scheelite (JCDS #14-0688) and tetragonal scheelite (JCDS #14-0133). No diffraction peak of Cu₂S is found in the Cu₂S/BiVO₄ composites, which is probably because that a little amount of Cu₂S was loaded on BiVO₄.

![Figure 2](image.png)

**Figure 2.** FESEM image of (a) BiVO₄, (b) 0.1 Cu₂S/BiVO₄, (c) 0.5 Cu₂S/BiVO₄, (d) 1.0 Cu₂S/BiVO₄.

![Figure 3](image.png)

**Figure 3.** (a) DES analysis and (b) FESEM images of 0.1 Cu₂S/BiVO₄, (c) mapping of Bi element, (d) mapping of V element, (e) mapping of O element, (f) mapping of Cu element, (g) mapping of S element.

The morphology of the BiVO₄ and Cu₂S/BiVO₄ composites is shown in Fig. 2. As shown in Fig. 2a, BiVO₄ displays the dumbbell-like morphology with a length of about 5 μm. The FESEM images of
as prepared different loaded Cu2S/BiVO4 composites are also dumbbell-shaped (shown in Fig. 2b, 2c and 2d). Cu2S nanoparticles is evenly distributed on the surface of BiVO4. With the increasing of Cu2S percent, more and more Cu2S nanoparticles are adsorbed on the surface of BiVO4, as shown in Fig. 2d. Moreover, the EDS data (shown in Fig. 3a) and element mapping images of Bi, V, O, Cu, S (Fig. 3c-g) of 0.1 Cu2S/BiVO4 composite can clearly confirm that Cu and S element are existent and uniformly dispersed on dumbbell-like BiVO4, which can proved successful preparation of Cu2S/BiVO4 composites.

The UV-vis absorption spectra of Cu2S/BiVO4 composites, BiVO4 and Cu2S are carried out and shown in Fig. 4. The data shows that Cu2S exhibits strong light absorption in the range of 200-800 nm, indicating that Cu2S has a strong visible light response. The absorption edge of BiVO4 is extended to about 650 nm due to phase transition between tetragonal and monoclinic phase of heterophase BiVO4 [14], it is consistent with the result of XRD. The absorption intensity of Cu2S/BiVO4 composites is increased with the loaded number of Cu2S. Furthermore, in comparison with BiVO4, Cu2S/BiVO4 composites display red shift of optical bandgap due to the existence of Cu2S, thus it is beneficial to photocatalytic degradation in the whole UV-vis band.

Figure 4. UV–vis absorption spectra of Cu2S/BiVO4 composite, BiVO4 and Cu2S.

Figure 5. Evolution of RhB concentration during its photocatalytic degradation for Cu2S/BiVO4 composite, BiVO4 and Cu2S.

Fig.5 shows the catalytic degradation efficiency of RhB Cu2S/BiVO4 composite under simulated sunlight irradiation. Among them, the photocatalytic degradation effect of 0.1 Cu2S/BiVO4 composite, 0.5 Cu2S/BiVO4 composite, 1.0 Cu2S/BiVO4 composite, BiVO4 is reach 90%, 45%, 50%, and 22% in 3 hour, respectively. However, pure Cu2S has no catalytic effect. The catalytic degradation effect of
0.1 of Cu$_2$S/BiVO$_4$ composite is 4 times that pure BiVO$_4$ and 9 times that Cu$_2$S. With the increase of the content of supported Cu$_2$S, the catalytic effect of the composite decreases gradually, which is due to the fact that supported 0.1 Cu$_2$S/BiVO$_4$ composite is beneficial to the separation of photogenerated electron-hole pairs.

The TPV measurements are implemented to research the kinetics properties of photogenerated charge carries of BiVO$_4$, Cu$_2$S and Cu$_2$S/BiVO$_4$ composites. As shown in Fig. 6, the photovoltaic signal of BiVO$_4$ and Cu$_2$S is negative, indicating that the photogenerated electron/hole transport toward the surface/bulk of BiVO$_4$ and Cu$_2$S. The Cu$_2$S and heterophase BiVO$_4$ are characterized by p-type semiconductor property [15]. With the increase of Cu$_2$S content in Cu$_2$S/BiVO$_4$ composites system, the photovoltage signal of Cu$_2$S/BiVO$_4$ composites gradually changes from negative signal to positive signal, indicating that the charge transport mechanism of composites will change with the increase of Cu$_2$S content, from the dominant of the initial electrons to the dominant of the final holes. It is probably related to energy band location and interface between Cu$_2$S and BiVO$_4$. When the content of Cu$_2$S is low (0.1 Cu$_2$S/BiVO$_4$), Under irradiation, BiVO$_4$ and Cu$_2$S will be excited and generate electron-hole pairs, conduction band (CB)-electrons of BiVO$_4$ easily flow into the CB edge of Cu$_2$S, valence band (VB)-holes of BiVO$_4$ will be inhibited transport toward VB-Cu$_2$S owing to the unmatched surface band bending of composite. In Fig. 6, it can be seen that the photovoltage intensity of 0.1 Cu$_2$S/BiVO$_4$ composite is the strongest, which possesses the effective separation of photogenerated electron-hole pairs, corresponding to its highest photocatalytic activity, corresponding to its highest photocatalytic activity. With the increase of Cu$_2$S content (0.5 Cu$_2$S/BiVO$_4$ and1.0 Cu$_2$S/BiVO$_4$), the surface band bending of VB-Cu$_2$S is leveled, VB-holes of BiVO$_4$ are injected VB-holes of Cu$_2$S, holes are dominated in catalytic degradation. Furthermore, BiVO$_4$ provides the number of photoinduced charge carriers in the Cu$_2$S/BiVO$_4$ composite system, while the interface between BiVO$_4$ and Cu$_2$S enhances the separation efficiency of photogenerated charge carriers.

![Figure 6. TPV of Cu$_2$S/BiVO$_4$ composites, BiVO$_4$ and Cu$_2$S. The wavelength and intensity of excitation pulse are 532 nm and 50 J.](image)

4. Conclusion
The Cu$_2$S/BiVO$_4$ composite photocatalyst is synthesized by a simple solution adsorption method. The Cu$_2$S nanoparticles are supported on the surface of the dumbbell like BiVO$_4$ to form a Cu$_2$S/BiVO$_4$ composite. The catalytic activity of the composite catalysts were higher than pure Cu$_2$S and BiVO$_4$ under the simulated sunlight. The photocatalytic degradation of BiVO$_4$ loaded with 0.1 Cu$_2$S was the best. It was proved that the interface between Cu$_2$S/BiVO$_4$ composite improves the effective separation of photogenerated electron-hole pairs of the composite.

Acknowledgments
The work was supported by The Scientific Research Fund of Heilongjiang Academy of Sciences (No. KY2020GJS02). Corresponding authors: dqhe2015@163.com, 13946165731@163.com.
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