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ORIGINAL ARTICLE

Synthesis and Photocatalytic Activity of Polyhedral $BiVO_4$

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Abstract: Polyhedral $BiVO_4$ was prepared by hydrothermal-calcination two-step method. The physicochemical properties of polyhedral $BiVO_4$ were characterized by XRD, TG/DTA, SEM and UV-vis DRS. The photocatalytic properties of the samples were investigated by using 10 mg/L methylene blue (MB) as the target degradant. The experimental results showed that the prepared polyhedral $BiVO_4$ is monoclinic. The morphology is about 10 μm polyhedral block. The pure phase $BiVO_4$ has strong visible light absorption capacity. Under visible light irradiation, the prepared $BiVO_4$ can degrade 90% of MB within 40 min. Moreover, the photocatalytic performance was further improved by forming a $BiVO_4$/BiOCl heterojunction, and the kinetic reaction rate was 1.5 times that of the pure phase $BiVO_4$.

Keywords: Material Science; $BiVO_4$; $BiVO_4$/BiOCl; Photocatalytic

Introduction

With the development of industry, environmental problems caused by wastewater discharge have received more and more attention in the past few decades. In order to remove organic pollutants from wastewater, the traditional methods are mainly adsorption or biodegradation, but they cannot remove organic pollutants quickly and effectively.[1-3] In order to achieve better results, people try to use sunlight as energy, in the appropriate half conductor photocatalyst can degrade organic pollutants into harmless compounds.[4-6] Photocatalytic degradation of organic pollutants has the advantages of environmental protection, energy saving and high efficiency compared with traditional methods, and has been extensively studied.

External light response cannot utilize the visible light with the most energy in the solar light, so a more suitable visible light catalyst is needed for degradation reaction.[7-8] $BIVO_4$ is environmentally friendly due to its narrow forbidden band width, suitable valence band position, stable chemical properties is widely used in photocatalytic degradation of organic pollutants.[9-10] But $BIVO_4$ has a low photocatalytic activity due to its low efficiency of photo-generated electron-hole separation and easy recombination, which affects its application in photocatalysis. In order to improve the photocatalytic efficiency of $BIVO_4$, different researchers have carried out a lot of research on controlling morphology[11], ion doping[12], and constructing heterojunction[13].

In this paper, we have successfully prepared polyhedral massive $BiVO_4$ by hydrothermal -calcination method, which has good optical and photocatalytic properties. $BiVO_4$/BiOCL heterojunction structure has been synthesized by changing the ratio of raw materials to make the catalytic performance of 45 has been further improved.

1. Experimental part

1.1 Chemical raw materials

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Vanadium chloride (VCL_3) was purchased from Shanghai saen chemical technology Co., Ltd. Anhydrous bismuth nitrate ($bi(no_3)_35h_2o$) was purchased from guoyao chemical reagent Co., Ltd. Methylene blue ($C_{16}H_{18}CLN_3S_3H_2O$) was purchased from Tianjin Zinko Fine Chemical Research Institute. Terephthalic acid (H_2 BDC) and absolute ethanol were purchased from Beijing Chemical Reagent Company. All chemicals are analytically pure and have not been further purified.

1.2 $BIVO_4$ preparation

Bivo 4 was synthesized by hydrothermal-calcination two-step method. The experimental synthesis process is as follows:

Hydrothermal synthesis step: dissolve 8 mmol VCL_3 and 4 mmol h2 BDC in 20 mL anhydrous ethanol, after 55 is stirred evenly, continue to add 11.2 mmol $bi(no_3)_35h_2o$, continue to stir 30 min, put the mixed solution into a 50 mL teflon lined reaction kettle, 120 ℃ temperature hydrothermal reaction 48 h, cool to room temperature, and use the intermediate product deionized water and absolute ethyl alcohol are alternately washed and dried overnight in a 80 ℃ drying oven to obtain a calcined precursor. Calcination step: placing the precursor obtained by hydrothermal synthesis in the previous step in a crucible, placing the precursor in a muffle furnace, and adding 5 ℃/min.

The heating rate of is increased from room temperature to 450 ℃, and the polyhedron $BIVO_4$ is obtained by keeping the temperature at 450 ℃ for 2h.

1.3 Material characterization

The phase composition, purity and crystallinity of the sample were determined by a PANalytical XPert PRO MPD diffractometer with Cu Kα radiation (λ= 0.15405nm). The tested working current was 40 mA ,the tested working voltage was selected as 40 kV ,and the scanning speed was 5 min-1. In order to obtain the size and morphology information of the material, SEM analysis was performed using a Hitachi S4800 scanning electron microscope with an operating voltage of 10 kV and a current of 10 mA. In order to obtain a suitable calcination temperature for the precursor, Germany is used.

The TG/GTA6300 comprehensive thermal analyzer of 65 NETZSCH company performs thermogravimetric (TG) and differential thermal (DSC) analysis at the heating rate of 5 ℃/min, the atmosphere is air. The absorbance of the material was characterized by TU-190T UV-visible diffuse reflection from Beijing general instruments Co., Ltd. In addition, the real content of Bi, v and o in the synthesized catalyst was tested by SEM-EDS.

1.4 Photocatalytic performance test

The 300 W xenon lamp was used as the light source, and the ultraviolet light below 420 nm was filtered out by a filter to serve as the simulated visible light source.

Experimental steps: weigh 0.05 g catalyst, add it to 50 mL and 10 mg/L methylene blue solution, stir under dark conditions mix for 0.5 h to reach the adsorption-desorption equilibrium. After the light is turned on, centrifuge the 4 mL solution every 20 min and test the supernatant with an ultraviolet-visible spectrophotometer.

The concentration of methylene blue was determined by monitoring the ultraviolet-visible absorption spectrum of the reaction solution. The ultraviolet-visible spectrophotometer uses TU-190T and uses a fixed sample cell to contain the test solution. Select 300-800 nm for the wavelength range to be tested and scan. The tracing step is set to 1 nm and the spectral bandwidth is set to 1 nm. The scanning mode is Abs absorbance, and the whole test is conducted at room temperature.

2. Results and discussions

2.1 Representation

The successful synthesis of polyhedron $BIVO_4$ is influenced by reaction temperature, reactant addition ratio and other factors. In this experiment, 80 carried out thermogravimetric-differential thermal analysis on the hydrothermal precursor in order to initially obtain the appropriate calcination temperature of the precursor. Figure 1 is the thermogravimetric-differential thermal curve of the front drive. It can be seen from Figure 1 that 30-350 ℃ mainly refer to the removal of water in the precursor. In the range of 350-410 ℃, there is a sharp endothermic peak, and the

rapid weight loss is about 20%, which is analyzed as the decomposition of terephthalic acid in the precursor.[14] After 410 ℃, the weight does not change any more, indicating that most of terephthalic acid is completely decomposed to generate $BIVO_4$. According to the thermogravimetric curve, the calcination temperature of the precursor is determined to be 450℃.

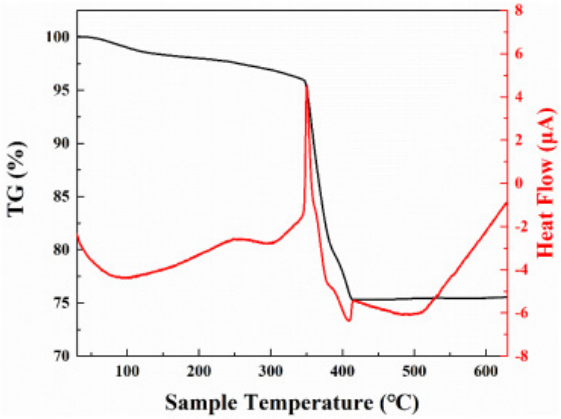

Figure 1. TG-DSC curves of the precursor.

During the preparation of precursor, the addition of raw materials must be strictly controlled, and the final calcined product can be controlled by changing the addition of V/Bi. As shown in Figure 2, when the V/Bi (amount ratio of substances) in the reactant is strictly controlled at 1.4, the final calcined product is pure monoclinic phase $BiVO_4$, which is very matched with the XRD results of $BiVO_4$ prepared by different methods in other literatures.[15-16] When the ratio of V/Bi changes, the calcined product can successfully synthesize monoclinic phase BiVO 4, but other substances V_2O_5 or BiOCl appear. When the V/Bi ratio reaches 1.2, the calcined product is mainly monoclinic phase $BIVO_4$, but there is a V_2O_5 phase (denoted as $BIVO_4/V_2O_5$). When the V/Bi ratio reaches 1.6, the calcined product is mainly monoclinic phase BIVO4, but there is a BiOCl phase (marked BIVO4/BIOCL).

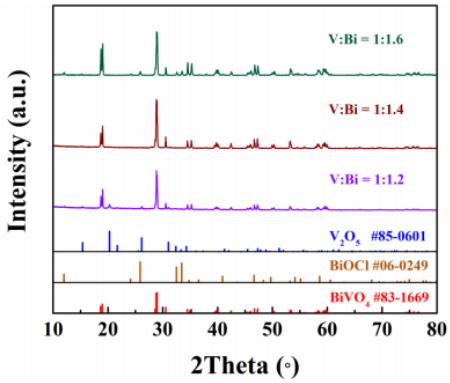

Figure 2. XRD pattern of the synthesized sample.

Figure 3a is a scanning electron microscope picture of pure phase $BIVO_4$. the prepared $BIVO_4$ is a massive polyhedron, most of which is angular and about 10 μm in size. The obtained $BIVO_4/V_2O_5$ is a sheet-like spherical shape with a diameter of about 200-400 nm. (Figure 3b) It can be seen from Figure 3c that the bivo4/biocl product is similar to bivo4 in microscopic morphology and is a massive polyhedron with a size of about 10-15 μm. The element bi can be seen through EDS: v: o has a ratio of about 1:1:4, which is very close to the element ratio of the molecular formula of bivo4, further confirming the successful preparation of bivo4.

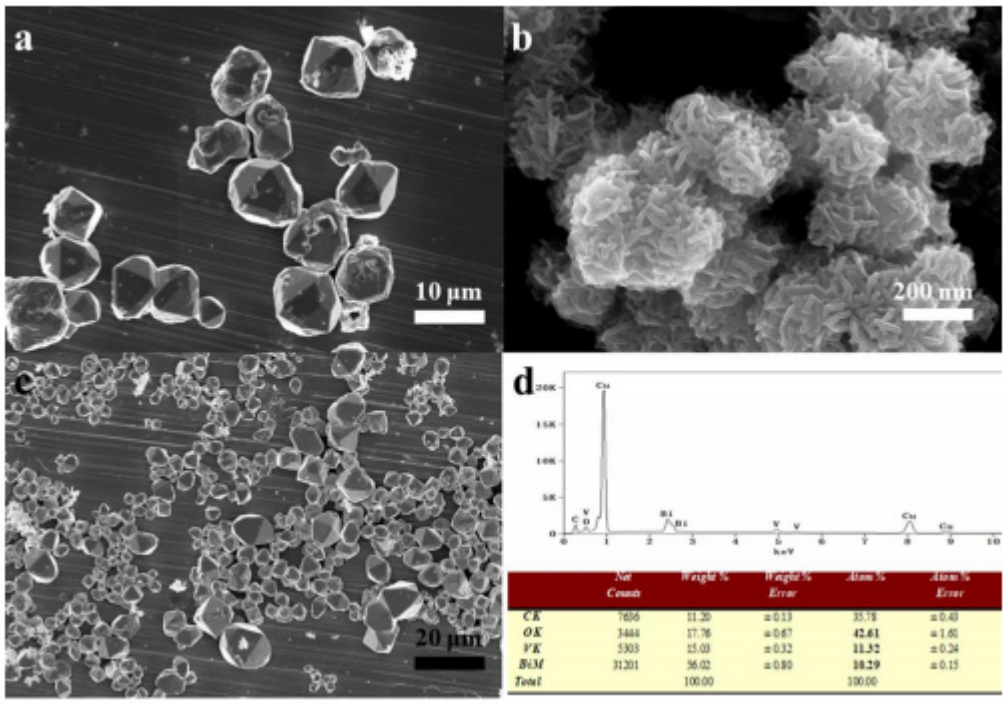

Figure 3. SEM images of (a) $BiVO_4$; (b) $BiVO_4/V_2O_5$; (c) $BiVO_4$/BiOCl and EDS images of $BiVO_4$.

Absorption is an important factor that determines the performance of photocatalyst. In order to measure the absorption of three different synthesized products $BIVO_4$, $BIVO_4/V_2O_5$ and BIVO4/BIOCL, the absorbance of the three materials was measured by ultraviolet-visible diffuse reflection, and the forbidden band width was calculated. As can be seen from Figure 4a, bivo4/biocl has the strongest absorbance in the ultraviolet-visible range, while $bivo_4/v_2o_5$ has the weakest absorbance.

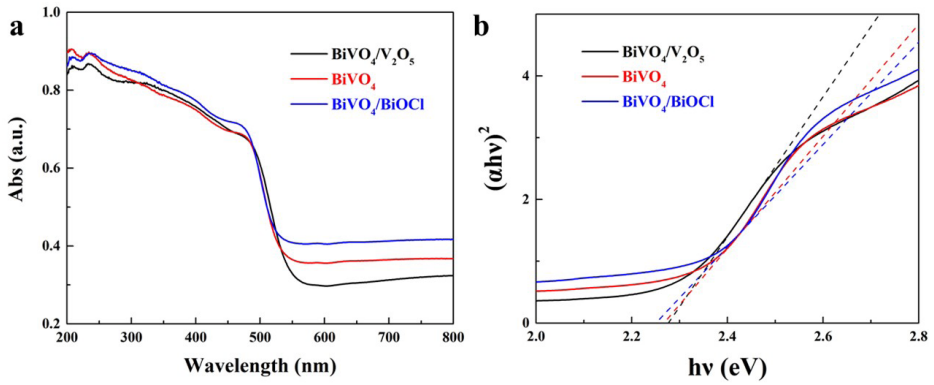

Figure 4. (a) UV-vis diffuse reflectance spectrum and (b) (αhv)2 - hv plots of the $BiVO_4$,$BiVO_4/V_2O_5$and $BiVO_4$/BiOCl.

2.2 Photocatalytic performance test

In order to explore the photocatalytic performance of three different materials, methylene blue solution of 10 mg/L was selected as the target pollutant in this experiment to compare the degradation performance of three different materials under visible light. The degradation rate of methylene blue of the three materials in 100 min under visible light irradiation is shown in Figure 5a.

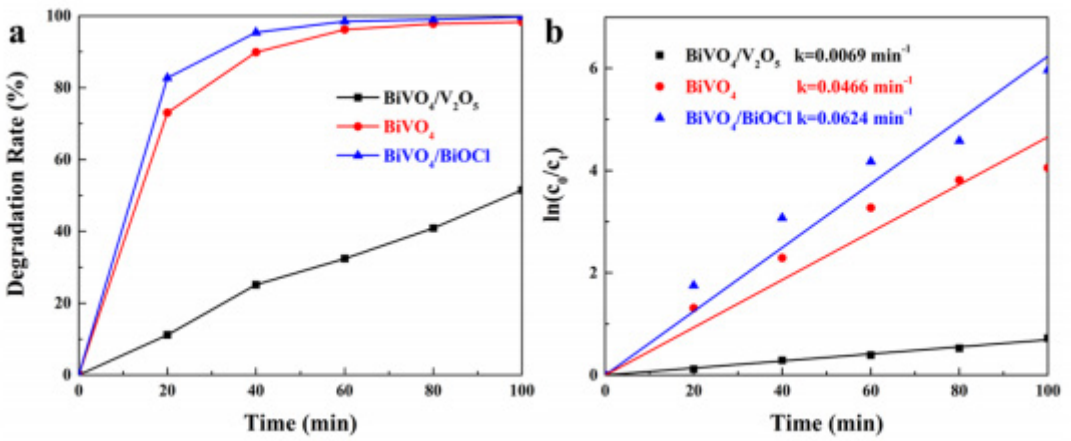

Figure 5. (a) Degradation efficiency and (b) kinetic process of MB degradation over $BIVO_4/V_2O_5$, BiVO4 and 130 $BiVO_4$/BiOCl.

The improvement of photocatalytic performance of $BIVO_4$/BIOCL compared with $BIVO_4$ can be attributed to the formation of heterojunction. Compared with a single $BIVO_4$, the formation of heterojunction effectively enhances the separation of photo-generated electron-hole pairs, inhibits the recombination of electron-holes during migration, and greatly improves photocatalytic activity. However, the relatively low photocatalytic performance of $BIVO_4/V_2O_5$ can be revealed from the relevant literature. The obvious excess of V_2O_5 in the[17] $BIVO_4/V_2O_5$ compound blocks light for $BIVO_4$ and cannot excite the catalyst to generate electron holes. The active substances for photocatalysis are greatly reduced and the photocatalytic performance is obviously reduced.

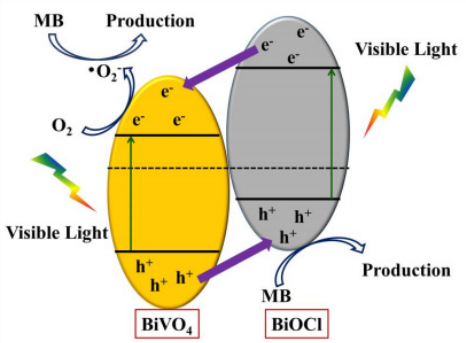

Figure 6. MB degradation mechanism over $BiVO_4$/BiOCl.

Figure 6 shows the electron transfer mechanism in the photocatalytic process of $BIVO_4$/BIOCL heterojunction. $BIVO_4$ itself has the disadvantages of low electron cavity separation efficiency and easy recombination during migration. The photocatalytic activity can be effectively improved by recombination with BiOCl to form a heterojunction structure. $Bivo_4$ electrons (e_-) migrate from valence band to conduction band and in conduction band under excitation of visible light holes (h_+) are left on the BiOCl. similarly, valence and conduction band holes are formed on the biocl and electrons are enriched. The formation of heterojunction makes Holes in the valence band of bivo4 migrate to the valence band of BiOCl and electrons in the BiOCl guide band migrate to the guide band of bivo4, respectively forms hole enrichment on the valence band of BiOCl and electron enrichment on the conduction band of $BiVO_4$. In the hole enrichment region, sub Methylene blue is oxidized and degraded, and oxygen (O_2) is reduced to superoxide radicals (O_-) in the electron-rich region to degrade methylene blue.

3. Conclusion

In this paper, polyhedral $BiVO_4$ photocatalyst is prepared by hydrothermal-calcination two-step method, and the samples are characterized and photo-catalytic properties are tested. The results show that the synthesized product is monoclinic, with a polyhedral block shape of 10 μm in size, has strong absorption ability to visible light, and can degrade 90% methylene blue within 40 min. $BiVO_4$/BiOCL heterojunction was successfully prepared by changing the ratio of raw material V/Bi, which improved the photocatalytic activity of the catalyst. And the kinetic reaction rate

reaches 1.5 times of that of single $BiVO_4$ and the degradation efficiency within 40 min reached 95%.

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