

Novel visible-light-driven Pt/BiVO₄ photocatalyst for efficient degradation of methyl orange

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Abstract

Visible-light-induced Pt/BiVO₄ composite photocatalyst has been synthesized by the impregnation method. The composition, crystallinity and photo-absorption of the as-prepared samples were characterized by powder X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and UV–vis diffused reflectance spectroscopy. The results indicate that the visible light absorption of the Pt/BiVO₄ photocatalyst is greatly enhanced. The Pt element is present as PtCl₄ and disperses in the composite samples. Photocatalytic activities of the Pt/BiVO₄ samples were evaluated by the methyl orange decomposition under visible light irradiation. The results indicate that the photocatalytic efficiency is significantly improved after the Pt species was loaded. On the basis of experimental results, the mechanism of enhanced photocatalytic activity has been discussed.

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1. Introduction

Since the viewpoint of the solar energy utilization was brought forward, the development of visible-light-induced photocatalyst has attracted much attention [1–4]. Among various semiconductor photocatalysts, TiO₂ was found to be an efficient photocatalyst [5,6]. However, TiO₂ is only active under UV irradiation for its large band-gap energy of 3.2 eV [7–9]. To resolve this problem, doping TiO₂ with non-metal or metal atoms has received a lot of attention, such as TiO_{2-x}N_x [10], WO_x/TiO₂ [11], Ag/TiO₂ [12] and InVO₄/TiO₂ [13], etc., and the doped TiO₂ extends light absorption into visible light region. However, these dopants may also work as a recombination center between photo-generated carriers, which is usually discrete and inconvenient for the migration of electrons and holes. Apart from TiO₂, many single phased multi-component oxides like InVO₄ [14], Bi₂WO₆ [15], CaIn₂O₄ [16] and AgAlO₂ [17], etc., are also found to be active for degradation of organic contaminants or splitting of water under visible light irradiation.

In recent years, BiVO₄ has been demonstrated to be a good visible-light-driven photocatalyst [18–21]. However, the

activity of pure BiVO₄ still needs to improve due to its poor adsorptive performance and difficult migration of photo-generated electron–hole pairs [22]. There have few reports on the development of doping BiVO₄ to enhance photocatalysis under visible light irradiation. Recently, Kohtani et al. [23,24] reported that the Ag–BiVO₄ showed superior visible light activities in decomposing long-chain alkylphenols and polycyclic aromatic hydrocarbons. While, Long et al. [25] synthesized Co₃O₄/BiVO₄ composite photocatalysts, and found that the photocatalysts exhibited enhanced visible light photocatalytic activities on degradation of phenol.

In this paper, we report the preparation of visible-light-driven Pt/BiVO₄ photocatalysts for the first time. The photocatalytic activities of the Pt/BiVO₄ composite samples were compared on the decomposition of methyl orange under visible light irradiation.

2. Experimental

2.1. Synthesis of Pt/BiVO₄

All chemicals were reagent grade and used without further purification. A typical synthesis of Pt/BiVO₄ was shown in the following way: Bi(NO₃)₃·5H₂O and NH₄VO₃ were added to

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nitric acid solution and distilled water, respectively. And then mixed together, the pH value of the mixed solution was adjusted to 7 with ammonia. The mixture was stirred for 0.5 h at room temperature in air, and poured into a 100 mL Teflon-lined stainless reactor until 50% of the volume of the reactor was filled. The reactor was heated at 180 °C for 6 h under autogenous pressure. After cooling, the obtained samples were centrifuged and washed with distilled water. Finally the BiVO₄ sample was dried in a drying cabinet at 60 °C for 10 h.

The as-prepared BiVO₄ powder was added to 5 mL of distilled water containing an appropriate amount of H₂PtCl₆ in a ceramic dish. The suspension was stirred using a glass rod during evaporation of water under the irradiation of an infrared light. The resulting powder was collected and calcined in air at 400 °C for 0.5 h. The pure PtCl₄ was purchased from Shanghai Jiushan Chemical Company and used to compare the degradation of methyl orange with Pt/BiVO₄ samples.

2.2. Characterization

The X-ray diffraction (XRD) patterns were obtained on a DMAX-RB X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) measurements were done with a PHI Quantum 1600 XPS system with a monochromatic Mg K α source; all the binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. A diffuse reflectance UV–vis spectrophotometer (DRS, Shimadzu UV-3101) was used to obtain the absorption spectra of samples.

2.3. Photocatalytic activity

Visible light photocatalytic activities of the obtained photocatalysts were measured by the decomposition of methyl orange in an aqueous solution at ambient temperature. A 12-W energy saving lamp was used as the irradiation source. A cut-off filter was placed under the lamp to remove all wavelengths less than 400 nm. In each experiment, a 0.2 g amount of photocatalyst was added into 30 mL methyl orange solution with a concentration of 10 mg L⁻¹. At irradiation time intervals of every 3 h, the suspensions were collected, and then centrifuged (5000 rpm, 10 min) to remove the photocatalyst particles. The concentration of methyl orange was determined by a UV–vis spectrophotometer (Exact Science Apparatus Ltd. of Shanghai 722S).

3. Results and discussion

3.1. XRD patterns analysis

It was reported that the monoclinic BiVO₄ showed high photocatalytic activity under visible light irradiation [26]. Therefore, it is of great importance to control crystal form of BiVO₄ in order to obtain a visible-light-driven photocatalyst. To investigate the phase structures of the samples, their X-ray diffraction patterns were measured. Fig. 1 presents the XRD patterns of the pure BiVO₄ and Pt/BiVO₄ powders. The XRD analysis of the samples shows that all the samples are well crystallized, and the diffraction patterns are indexed to monoclinic BiVO₄ (JCPDS

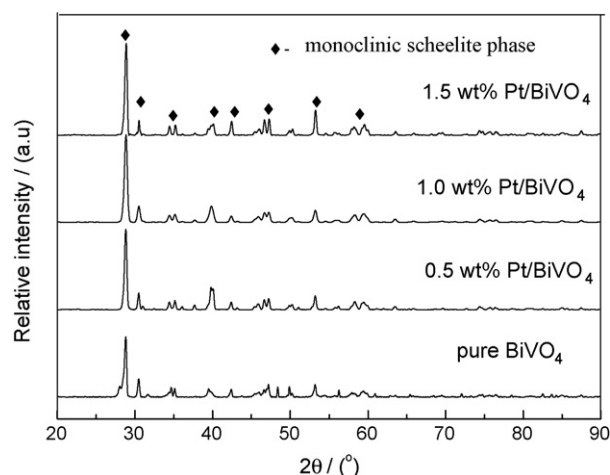


Fig. 1. XRD patterns of Pd/BiVO₄ composite photocatalysts.

83-1700). After the Pt species was doped, the intensity of the diffraction peaks in XRD patterns increase, indicating that the crystallinity of composite samples is enhanced. The result indicates that all samples are monoclinic scheelite structure, and the Pt doping does not influence the crystal structures of BiVO₄. No extra peaks except for monoclinic BiVO₄ are found. This phenomenon may be explained by the small amount of Pt species content (maximal 2.0 wt%) and highly dispersion in the samples.

3.2. XPS studies

To determine the chemical states of Pt species in the Pt/BiVO₄ composite particles, the X-ray photoelectron spectroscopy (XPS) of 1.0 wt% Pt/BiVO₄ was measured and shown in Fig. 2.

The Pt 4f orbital show splitting peaks at 72.3 and 75.4 eV, which is corresponding to the peaks of Pt⁴⁺ species. The peak of chlorine element is located 199.2 eV (Fig. 2b), which can be assigned to the Cl⁻ ions in the sample [27]. Based on the XPS results, the mole ratio of platinum and chlorine elements on the surface of composite samples is 1:4.1. So it can be deduced that the platinum doped in the composite photocatalyst is present in form of platinum chloride compound (PtCl₄).

3.3. Diffuse absorption UV–vis spectra

The color of the Pt/BiVO₄ composite samples is dark yellow and becomes darker by enhancing the Pt content. The optical absorption property of a semiconductor, which is relevant to the electronic structure feature, is recognized as the key factor in determining its photocatalytic activity. The UV–vis diffuse reflectance spectra of the samples are shown in Fig. 3. The steep shape of the spectrum indicates that the visible light adsorption is due to the band-gap transition. The band-gap absorption edge of pure BiVO₄ sample is determined to be 553 nm. The band-gap energy (E_g value) can be estimated to be 2.24 eV. After the Pt species was loaded, the visible light absorption of the composite samples is significantly enhanced, in agreement with the dark yellow color of the powder. The absorption edge shifts

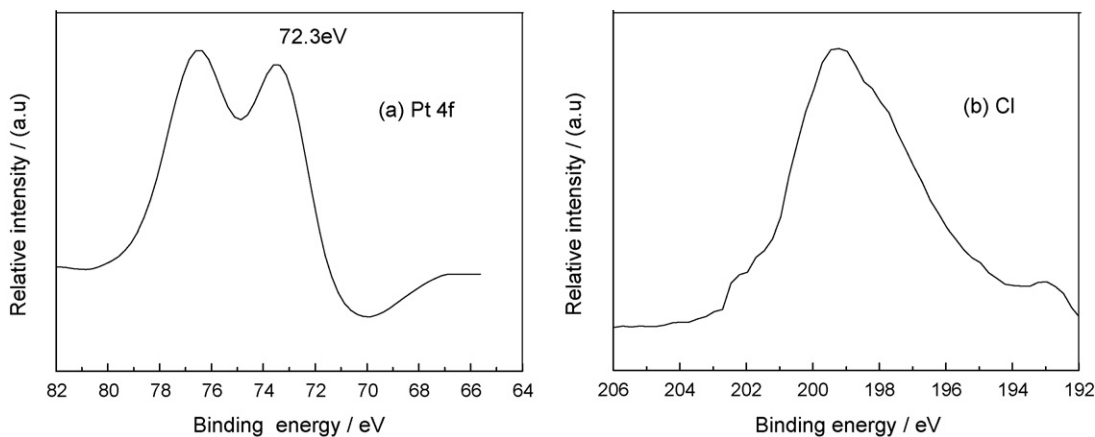


Fig. 2. High resolution XPS spectra of Pt and Cl elements on the surface of the Pt/BiVO₄ sample.

to red light. It is reported that the solid PtCl₄ particles has strong absorption in the visible light region with wavelength ranging from 400 to 700 nm, which can be assigned to the ligand field transition of the PtCl₄ modifier [28]. Therefore, the enhanced visible light absorption should be caused by the mutual effect of BiVO₄ and PtCl₄ species. It can be deduced that the Pt/BiVO₄ composite samples in this study should have good visible light photocatalytic activities.

3.4. Photocatalytic activity

The photocatalytic activities of Pt/BiVO₄ samples were evaluated by degradation of methyl orange under visible light irradiation. Temporal changes in the concentration of methyl orange were monitored by examining the variations in maximal absorption in UV–vis spectra at 500 nm. As a comparison, direct photolysis of methyl orange and methyl orange degradation over pure PtCl₄ samples were also performed under identical conditions. Fig. 4 shows the effect of Pt content on the photodegradation activity of methyl orange under visible light irradiation. A blank experiment in the absence of photocatalyst demonstrated that no obvious change in the methyl orange concentration was found. Fig. 4 also shows that photodegrada-

tion by pure PtCl₄ under the same illumination conditions was much slower than that by Pt/BiVO₄. The observation indicates that the pure PtCl₄ has a poor photoactivity in degradation of methyl orange though it has absorption in visible light region [28]. The decrease of methyl orange concentration in the presence of pure BiVO₄ is small, only about 42% in 15 h. The result indicates that the methyl orange can be degraded over BiVO₄ photocatalyst. The photocatalytic performance can be significantly improved when introducing Pt species; the reduction of methyl orange is 84.4% in the presence of 0.5 wt% Pt/BiVO₄ sample. The Pt content is an important factor for producing Pt/BiVO₄ with high activity. After being impregnated, the H₂PtCl₆ particles distribute on the surface of BiVO₄. By calcinations at 400 °C, the H₂PtCl₆ decomposed into platinum chloride species. The Pt(IV)Cl₄–BiVO₄ composite structure favors the migration of electron–hole pairs, and then leads to high photocatalytic activity. In our result, the photocatalytic activity of the Pt/BiVO₄ composite samples improve with increasing Pt content, the 2.0 wt% Pt/BiVO₄ sample exhibits the best activity, and the methyl orange concentration reduce as much as 100% in 15 h. This result is a great improvement when compared with the activity of pure BiVO₄. No obvious enhancement in the photocatalytic activity is observed when more Pt species was introduced.

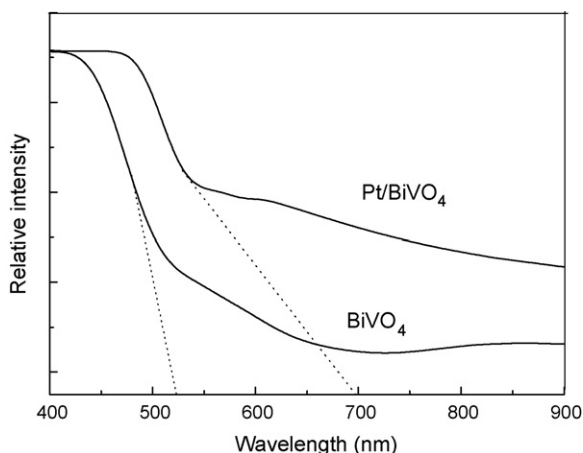


Fig. 3. UV–vis diffuse absorption spectra of different photocatalysts.

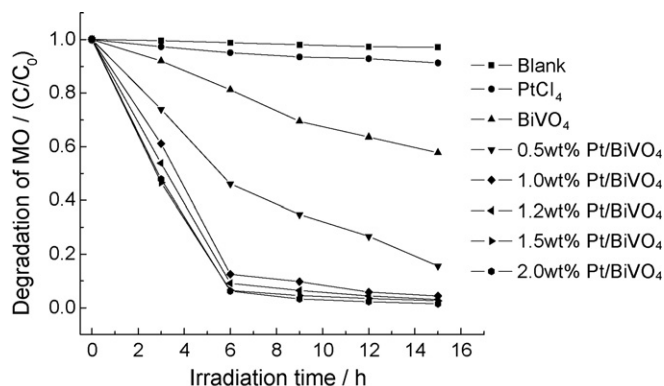


Fig. 4. Curves of photocatalytic degradation of methyl orange over Pt/BiVO₄ samples under visible light irradiation.

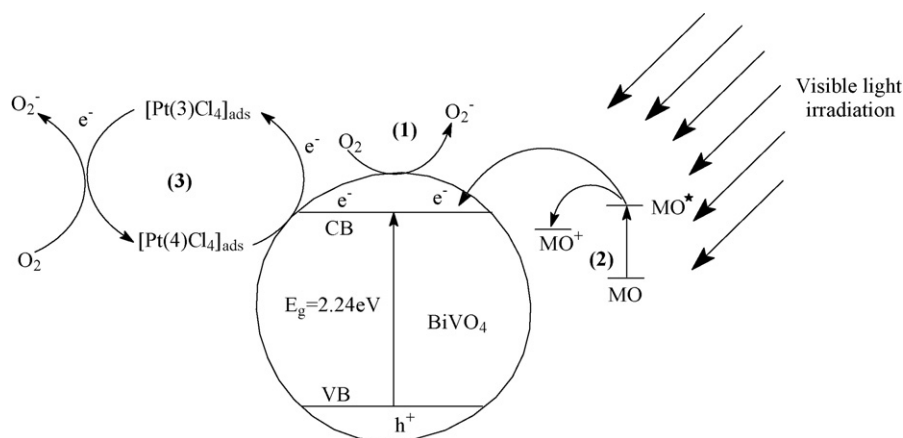


Fig. 5. The mechanism of methyl orange degradation over Pt/BiVO₄ composite photocatalysts under visible light irradiation.

The photoactivities of composite samples are significantly enhanced in the presence of low amount of platinum chloride distributed over pure BiVO₄ photocatalysts, while the pure PtCl₄ has poor photocatalytic performance. Based on the photocatalytic results, we proposed a working hypothesis on the visible light photocatalytic mechanism and depicted in Fig. 5. The methyl orange over Pt/BiVO₄ photocatalyst is degraded in three ways. The first one (part 1 in Fig. 5) is degraded by the photo-generated electrons in the BiVO₄ conduction band. The electrons in BiVO₄ valence band can be excited, and then transfer to conduction band under visible light irradiation [19]. The oxidative species •OH and photo-generated holes can decompose the methyl orange. However, the high recombination rate of photo-generated carriers leads to the low photoactivity of pure BiVO₄ [25]. The second way (part 2 in Fig. 5) is degraded by self-photosensitization of methyl orange molecules. The methyl orange molecules can be excited under visible light irradiation, which leads to electrons injection from the adsorbed dye species to the BiVO₄ conduction band [29,30]. The injected electrons react with the surface adsorbed O₂ molecules to yield the •OH radicals. The third one (part 3 in Fig. 5) is the photosensitization of Pt(IV)Cl₄ particles on the surface of BiVO₄. The platinum chloride can be excited in the visible light region and affords efficient charge transfer in the composite samples [28]. The Pt(IV)Cl₄ particles can act as electron traps and yield Pt(III)Cl₄ species. The labile Pt(III)Cl₄ intermediate will rapidly transfer an electron to the O₂ molecules and get the Pt(IV)Cl₄ species again. At the resulting oxidizing and reducing surface centers, oxidation of methyl orange and reduction of oxygen can occur, followed by mineralization. The holes still remain in the BiVO₄ valence band after migration of excited electrons. Therefore, the recombination of electron–hole pairs is restrained, and the photocatalytic activity can be improved greatly. When more Pt species is introduced, more active sites form, therefore the photocatalytic activity of Pt/BiVO₄ samples increase accordingly.

4. Conclusion

Novel Pt/BiVO₄ composite photocatalysts with visible light activities were prepared by the impregnation method. The

BiVO₄ particles retained monoclinic scheelite structures after the Pt species was doped. The visible light absorption of the Pt/BiVO₄ photocatalysts was enhanced greatly. XPS result revealed that the platinum doped in the composite photocatalyst is present in form of platinum chloride (PtCl₄). The photocatalytic experiments demonstrated that Pt species doping can effectively enhance the photoactivities of BiVO₄ samples in decomposition of methyl orange under visible light irradiation. The visible light photocatalytic mechanism was discussed based on the photocatalytic performance of the Pt/BiVO₄ samples.

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