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CuAlO₂/Bi₂WO₆: a novel p–n type composite with significantly enhanced visible-light photocatalytic reduction of Cr(VI)

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Abstract

The Bi₂WO₆ and CuAlO₂ powders were synthesized through the method of solid-state reaction. This study prepared the newly and highly effective p–n type CuAlO₂/Bi₂WO₆ photocatalysts that had diverse CuAlO₂ compositions by employing an environmentally friendly and economical approach. X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), photoluminescence (PL) emission spectra, and UV–vis diffuse reflectance spectroscopy were adopted to characterize the photocatalysts. The as-synthesized CuAlO₂/Bi₂WO₆ heterocatalyst was utilized to reduce toxic Cr (VI) ions into Cr (III) by means of photoreduction under visible light irradiation. When CuAlO₂ (1.0 wt.%) / Bi₂WO₆ was used, the Cr (VI) photoreduction rate constant was 4.7 times as many as that of pure Bi₂WO₆. The study also investigated how the ball milling time and CuAlO₂ composition affected the performance of CuAlO₂ / Bi₂WO₆. In addition, the stability of composite was investigated. The results revealed that the high conductivity of CuAlO₂, excellent crystalline quality, and the p–n heterojunction between CuAlO₂ and Bi₂WO₆ exerted a vital role in enhancing the photoreduction performance. This work explores the design of other new heterocatalysts, especially the p–n type composites containing CuAlO₂.

1. Introduction

The aggravating energy crisis and environmental deterioration have raised the demand for eco-friendly photocatalysts. Consequently, semiconductor photocatalysis, a green chemical method with great prospects in energy conversion and high efficiency to dispose of toxic pollutants in wastewater and atmosphere by using a suitable bandgap solid photocatalyst, has garnered significant research attention [1–5]. Despite the remarkable properties, TiO₂ does not meet the criteria of potential photocatalyst since it has a relatively wide bandgap and is just excited by UV light [6–8]. As a result, to make full use of visible light that takes up ca. 43% of the solar spectrum, designing and exploring the novel compounds that have effective photocatalytic performance in response to visible light is of great importance [9–11].

Bismuth tungstate (Bi₂WO₆) is one of the simplest aurivillius oxides, which may serve as a candidate n-type photocatalyst since it has good optical performances and favorable physicochemical properties, like non-linear dielectric susceptibility and ferroelectric piezoelectricity [12–16]. Nonetheless, regardless of the aforementioned properties, photo-absorption of wavelengths within ca. 450 nm and rapid charge-carrier recombination limit the use of pure Bi₂WO₆ as a photocatalyst. Consequently, many efforts have been made for enhancing photocatalytic performance of Bi₂WO₆ through forming porous structures in order to enhance the surface area [17, 18], loading co-catalysts [19–21], impurity doping [22–26], and coupling with other semiconductors to fabricate heterojunction nanostructures [27–32]. Particularly, the p–n heterostructure composites contribute to photogenerated electron migration via p–n junction due to the internal electric field and the tight connection between such interfaces [33–37]. CuAlO₂, one of the p-type semiconductors, has adequate optical transparency as well as excellent thermal and chemical stability. It is synthesized using non-toxic, cost-effective, and easily
obtainable materials, which can thus have gathered significant attention in the scientific community since 1997 [38–41]. Coupling p-type CuAlO2 with n-type Bi2WO6 will form a p–n heterojunction CuAlO2/Bi2WO6 photocatalyst with potential advantages, such as the enhancement of photogenerated electron–hole pairs separation and photocatalytic performance. To the best of our knowledge, there is no existing research regarding the photocatalytic performance of CuAlO2/Bi2WO6 composite.

In the present study, the solid-state reaction was used to synthesize Bi2WO6 and CuAlO2 compounds. This study synthesized the p–n heterocatalyst CuAlO2/Bi2WO6 via the ball milling method by doping CuAlO2 to Bi2WO6. X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), photoluminescence (PL) emission spectra, and UV–vis diffuse reflectance spectroscopy were applied in characterizing the photocatalyst. Besides, this work also adopted photoreduction of Cr2O72− (Cr (VI)) to evaluate its photocatalytic performance. The p–n heterocatalyst CuAlO2/Bi2WO6 showed significantly enhanced photocatalytic reduction activity in comparison to the pure Bi2WO6. The CuAlO2 composition and the ball milling time considerably affected its photocatalytic performance. Furthermore, we investigated the heterocatalyst stability. The designed p–n heterocatalysts in this work may potentially enhance charge transfer and suppress recombination.

2. Experimental

2.1. Materials

Bismuth oxide (Bi2O3), tungsten trioxide (WO3), aluminum oxide (Al2O3), cuprous oxide (Cu2O), and potassium dichromate (K2Cr2O7) were of analytical grade and provided by Shanghai and other China chemical reagent Ltd. The water utilized in this study was deionized water.

2.2. Sample preparation

CuAlO2 powders were prepared according to the method reported in the literature [42]. Briefly, we heat treated the stoichiometric mixture that contained Al2O3 and Cu2O under an N2 atmosphere at 1373 K for 10 h. The CuAlO2 powder crystallite diameter was around 100 nm calculated from the Scherrer equation. WO3 and Bi2O3 were utilized to be the raw materials to synthesize Bi2WO6 samples [43]. Thereafter, the Bi2O3–WO3 stoichiometric mixture was ground within the agate mortar for a while, followed by heating within the tubular furnace at 10°C min−1 and thermal treatment at 800°C for 24 h. After natural cooling to room temperature, the straw-yellow Bi2WO6 powder was ground in the agate mortar and gathered as the precursor for the preparation of the p–n junction photocatalyst CuAlO2/Bi2WO6.

2.3. Preparation of p–n heterojunction photocatalyst CuAlO2/Bi2WO6

This study prepared the CuAlO2/Bi2WO6 photocatalyst within the ND7–0.4 L ball mill (Tianzun Electronics Co, Ltd, Nanjing University). To be specific, agate balls at three diverse dimensions and Bi2WO6 powders (5.0 g) were added into the agate tank. Later, CuAlO2 at an appropriate mass was mixed with 2.0 ml H2O into the above agate tank. Following milled for 0–24 h at 400 rpm, the wet powders were dried in the air at 110°C. The CuAlO2 compositions varied as 0.2 wt.%, 0.5 wt.%, 1.0 wt.%, 3.0 wt.%, 5.0 wt.%, 10 wt.% and 20 wt.% to prepare diverse CuAlO2/Bi2WO6 samples. Finally, the synthesized samples were characterized and used for subsequent photocatalytic applications.

2.4. Material characterization techniques

A BRUKER D8 ADVANCE X-ray powder diffractometer was utilized to measure XRD in the presence of Cu Kα radiation (λ = 1.5406 Å) under room temperature at the emission current, accelerating voltage, and scanning speed of 40 mA, 40 kV, and 10° min−1, separately. A UV–3600 (SHIMADZU, Japan) UV–vis-NIR spectrophotometer that was loaded with the integrating sphere attachment was used for UV–vis diffuse reflectance spectroscopy. This study set the range of analysis at 190–700 nm, with BaSO4 being the reflectance control. TEM (JEOL-2010) and SEM (JEOL JSM–6610LV) were adopted to analyze sample microcrystalline structure and surface morphology at the accelerating and scanning voltages of 200 kV and 20 kV, respectively. The JASCO FP-6500 fluorescence spectrophotometer was utilized to record photoluminescence emission spectra at 430–530 nm.

2.5. Photocatalytic measurements

The decomposing Cr2O72− aqueous were measured in the presence of sample and visible light illumination to evaluate photocatalytic activities. Our experimental apparatus included an annular quartz tube and the unsealed beaker (150 ml, 5.5 cm in diameter) for reaction [44]. For the annular quartz tube, its empty chamber contained the 500 W Xenon lamp (Institute of Electric Light Source, Beijing) that had the maximal emission at around...
470 nm. A cutoff filter (λ > 400 nm, Instrument Company of Nantong, China) was used to control the wavelength of the visible light. The running water was passed via an inner thimble of the annular quartz tube in order to instantaneously eliminate the heat released from the lamp. During this process, the as-prepared photocatalyst (0.1 g) was mixed with 50 ml Cr$_2$O$_7^{2–}$ (6.5 mg l$^{-1}$) solution in the beaker at ambient temperature. The solution was continuously stirred with a magnetic stirrer throughout the reaction. The interval from the light source to reaction solution surface was 11 cm. Prior to irradiation, the solution was subjected to 20 min of ultrasonic vibration to ensure complete dispersion of the photocatalyst powder. This study collected 5 ml solution at regular intervals, followed by 6 min of centrifugation at 12000 rpm and filtering using the 0.2 μm Millipore filter before analysis. The photoreduction efficiency of Cr$_2$O$_7^{2–}$ was calculated according to equation (1) [44]:

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100$$

where $\eta$ represents photoreduction performance, $C_0$ stands for reaction content prior to illumination (mg l$^{-1}$), and $C_t$ indicates reactant content at the illumination time $t$ (mg l$^{-1}$).

### 2.6. Stability of the catalyst

In this study, five experimental cycles were used to investigate the CuAlO$_2$/Bi$_2$WO$_6$ heterocatalyst stability. The catalyst concentration and reactant volume utilized for every cycle were 2.0 g l$^{-1}$ and 50 ml, respectively. After irradiation for 20 min, the solid catalyst was centrifuged, rinsed and dried for the successive run.

### 3. Results and discussion

#### 3.1. Effect of heat treatment on the preparation of Bi$_2$WO$_6$

##### 3.1.1. Effect of different reaction temperatures

XRD was conducted to analyze the average crystallite size of the prepared samples and phase structure. In addition, the present study also extensively explored the impacts of diverse reaction temperatures on Bi$_2$WO$_6$ preparation. Diverse temperatures at 500 °C–1000 °C were set, and the reaction time was fixed at 6 h. Figure 1 depicts XRD patterns for Bi$_2$WO$_6$ samples.

Bi$_2$WO$_6$ showed a series of distinct peaks at 28.5°, 33.0°, 47.3°, 55.6°, 55.9°, 56.1°, and 58.8°, which can be indexed as (131), (002), (202), (191), (331), (133) and (262) diffraction planes, respectively [45]. The Bi$_2$WO$_6$ sample was well crystallized, and its diffraction peaks were consistent with Bi$_2$WO$_6$ orthorhombic crystal phase (JCPDS 39–0256). There was no distinct peak observed of Bi$_2$WO$_6$ prepared at 500 °C, and the calcined powder color was the same as that of the mixture before the heat treatment. However, as the preparation temperature of Bi$_2$WO$_6$ elevated to 600 °C, the strongest peak intensity (131) was significantly increased. Its diffraction peak intensity further increased significantly as the temperature was further raised to 700 °C, while the peak width was reduced slowly. Moreover, as observed on the XRD patterns for Bi$_2$WO$_6$ prepared at 500, 600, and 700 °C, the raw material peaks appeared due to the partial solid phase reaction between Bi$_2$O$_3$ and WO$_3$. At 800 °C,
diffraction peaks of only Bi₂WO₆ were found, and the color of the powder was also turned from yellow to straw yellow. And only the Bi₂WO₆ diffraction peaks were detected when the temperatures changed to 900 °C and 1000 °C. However, the strongest peak intensity (131) was significantly reduced. Meanwhile, the sintered product was extensively hard. This suggested that 800 °C was the optimum reaction temperature for the preparation of Bi₂WO₆.

3.1.2. Effect of different reaction time
We examined how the reaction time varying from 6 h to 24 h affected Bi₂WO₆ preparation at 800 °C. When reaction time increased within the range of 6–24 h, Bi₂WO₆ showed better nanocrystallinity, which was confirmed by the sharper shape and gradually increasing intensities of diffraction peaks (figure 2). At 24 h, those main peaks showed the highest intensities among the entire XRD patterns, thus indicating that 24 h was the best reaction time to prepare Bi₂WO₆ sample under 800 °C. This is mainly because calcination will enhance sample crystallinity, which enhances with the extension in thermal treatment time [46]. As a result, according to these observations, Bi₂WO₆ powders utilized in this study were prepared through solid-phase synthesis (24 h, 800 °C) using the Bi₂O₃-WO₃ stoichiometric mixture.

3.2. Characterization of the CuAlO₂/Bi₂WO₆ photocatalyst
3.2.1. XRD analysis
Figure 3 shows XRD patterns of CuAlO₂/Bi₂WO₆ samples with diverse CuAlO₂ compositions, pure Bi₂WO₆ and CuAlO₂. Pure CuAlO₂ could be indexed to the crystal plane (012) of rhombohedral with prominent diffractions peaks at 37.9° (JCPDS 35–1401) [47], and both Bi₂WO₆ and CuAlO₂ samples were well crystallized. Moreover, as CuAlO₂ (wt.%) was lower than 5.0, there existed no pure CuAlO₂ diffraction peak on XRD patterns. It suggests that CuAlO₂ showed high dispersion within the bulk phase. A weak diffraction peak corresponding to (012) plane of CuAlO₂ was observed for the composite containing 10 wt.% CuAlO₂, which is eventually improved when the CuAlO₂ density is 20 wt.%. Moreover, there was no new crystal phase on XRD patterns, indicating the two-phase composition of CuAlO₂/Bi₂WO₆ sample is merely Bi₂WO₆ and CuAlO₂.

3.2.2. SEM analysis
CuAlO₂ (1.0 wt. %)/Bi₂WO₆ photocatalyst was characterized at diverse ball milling time by SEM, which revealed the decrease in Bi₂WO₆ powder size with the increasing ball milling time (figures 4(a)–(c)). The EDS mapping was carried out to investigate the dispersion of two components (figure 4(d)). At the ball milling time of 6 h, the average grain diameter of the composite was approximately 200 nm, and the dispersion degree of the sample was much higher in comparison with that of the sample ball milled for 3 h.

3.2.3. TEM analysis
In this study, TEM and HR-TEM were performed for the interfacial characterization of CuAlO₂ (1.0 wt. %)/Bi₂WO₆ photocatalyst. Figure 5(a) shows a clear interface at the p–n junction of the photocatalyst CuAlO₂/Bi₂WO₆. Figure 5(b) shows the HR-TEM image matched with the rectangle region on TEM image. The left part exhibited Bi₂WO₆ (131) facets at the 0.312 nm interval. The right part depicted the CuAlO₂ (012) plane...
at the 0.237 nm interval. This confirms that the composite structure was obtained via Bi$_2$WO$_6$ and CuAlO$_2$ rather than a simple physical mixture of the two separated phases. Besides, the photoreduction activity under visible light irradiation of the composite is also much higher than that of the mixture of CuAlO$_2$ and Bi$_2$WO$_6$. It was also reported that the conductivity of CuAlO$_2$ is much higher than the other semiconductors and could be as high as 1 S cm$^{-1}$ [41], which could also improve the charge transfer efficiency. Conclusively, it can be said that the high conductivity, good crystallinity and the distinct interface of the composite contribute to photogenerated charge migration and fundamental for improving the photoreduction rate of Cr (VI).
3.2.4. UV–vis analysis
Figure 6 depicts UV–vis diffuse reflectance spectra for the pure Bi$_2$WO$_6$ and different CuAlO$_2$/Bi$_2$WO$_6$ photocatalysts with different CuAlO$_2$ composition. All the characterized photocatalysts were subjected to 6 h ball milling. Clearly, Bi$_2$WO$_6$ photo absorbs from UV light region to the visible light region with its absorption edge at around 450 nm and the corresponding bandgap is about 2.75 eV, which is in accordance with the prior study [45]. Bi$_2$WO$_6$ has distinct absorption within visible light, which is associated with the hybrid orbitals of Bi (6 s) and O (2p) transiting to W (5d) orbital [48]. In comparison with pure Bi$_2$WO$_6$, the CuAlO$_2$/Bi$_2$WO$_6$ heterocatalyst had extended range of absorption wavelength towards visible light region, along with enhanced absorption intensity. Since the range of photoexcited wavelength for the composite depends on and increases with the CuAlO$_2$ composition, which indicates that CuAlO$_2$ has an indirect absorption within visible region [38, 47] and thus can improve solar spectrum utilization. Similar result is presented in earlier report [49].

3.2.5. Photoluminescence emission spectra
The recombination of photoexcited electron-hole pair accounts for photoluminescence emission intensity, with a small value indicating the decreased recombination rate [50]. In this study, ultraviolet light at the wavelength of 300 nm was used to be the source of excitation to examine the PL emission spectra for different samples at 430–530 nm. The corresponding spectra are shown in figure 7. In the case of pure Bi$_2$WO$_6$, the strongest emission peak was detected at around 467 nm, which was associated with bandgap transition and showed the obvious redshift compared with that of ca. 450 nm acquired from figure 6. Re-absorption is responsible for such
redshift [51]. Clearly, PL spectra showed high sensitivity to CuAlO2 amount. For CuAlO2/Bi2WO6 composite, its PL intensity decreased relative to pure Bi2WO6, indicating that photogenerated charge carrier recombination between Bi (6 s) and O (2p, VB) hybrid orbital to empty W (5d) orbital was obviously suppressed within composite semiconductors [52]. However, excess CuAlO2 content also hindered the light absorption and weakened the photocatalytic performance. The sequence of photoluminescence emission intensity was decreased in agreement with the increase in photocatalytic activity. Thus, it can be concluded that only an appropriate range of composite composition can enhance the photocatalytic performance.

3.3. Photocatalytic activity of CuAlO2/Bi2WO6

3.3.1. Effect of CuAlO2 content
Photoreduction of Cr (VI) was conducted to evaluate the CuAlO2/Bi2WO6 composite visible-light photocatalytic performance, as depicted in figure 8. To facilitate comparison, this study also analyzed the photocatalytic performance of Bi2WO6 under the same conditions. According to the blank test, Cr(VI) content altered slightly in the presence of visible light irradiation, which indicated that the photoinduced self-decomposition was neglectable compared with different catalyst particles-induced photocatalysis. Additionally, based on the experimental results, CuAlO2 alone did not have distinct photocatalytic reduction performance in the presence of visible light irradiation. The CuAlO2/Bi2WO6 composite exhibited excellent visible-light
photocatalytic reduction properties in comparison to pure Bi$_2$WO$_6$. Furthermore, it improved remarkably with the increasing CuAlO$_2$ concentration and also showed a decrease tendency at higher CuAlO$_2$ levels, suggesting that 1.0 wt.% was the optimal CuAlO$_2$ concentration in the composite. The CuAlO$_2$(1.0 wt.%)/Bi$_2$WO$_6$ photocatalyst could reduce Cr(VI) by 93.0% in 150 min. In addition, the charge carrier trapping sites increase as the CuAlO$_2$ content increases to 1.0 wt.%, and it extends charge carrier lifespan and improves the overall photocatalytic reduction performance. While CuAlO$_2$(wt.%) exceeds 1.0, the highly concentrated dopant may serve as the electron and hole recombination center [53], thus gradually decreasing photocatalytic reduction performance, as confirmed from results of PL intensity.

To determine the photocatalytic reaction efficiency, this study applied the frequently used kinetic equations for data fitting. Then, a linear plot regarding $\ln\left(\frac{C_0}{C}\right)$ as a function of time was made, which verified the first-order kinetics. The kinetic equation was shown below [44, 53]:

$$\ln\left(\frac{C_0}{C}\right) = kt$$

where $C_0$ and $C$ denote the identical variables as those in equation (1) and $k$ represents the first-order rate constant (min$^{-1}$), whereas $t$ indicates irradiation time (min). Figure 9 shows the Cr (VI) reaction kinetics for diverse samples.

It was well observed from figure 9, that the photoreduction reaction of Cr(VI) followed the first-order kinetics equation. The corresponding values of $k$ for different CuAlO$_2$/Bi$_2$WO$_6$ samples and pure Bi$_2$WO$_6$ were calculated according to the kinetics model and shown in figure 10. The results demonstrated that the optimal CuAlO$_2$ concentration was 1.0 wt.% as confirmed already. The photoreduction rate constant of Cr(VI) for CuAlO$_2$(1.0 wt.%)/Bi$_2$WO$_6$ was 0.017 53 min$^{-1}$, and it was 4.7 times the one observed for pure Bi$_2$WO$_6$ (0.003 75 min$^{-1}$).

3.3.2. Effect of grinding time
The associations of photocatalytic reduction performance with ball milling time (0–24 h) were examined in every experiment under the conditions of 1.0 wt% CuAlO$_2$ content and 30 min illumination time. Obviously, ball milling time significantly influenced photocatalytic reduction performance (figure 11). The p–n heterocatalyst CuAlO$_2$/Bi$_2$WO$_6$ had significantly increased visible-light photocatalytic reduction performance compared with CuAlO$_2$/Bi$_2$WO$_6$ sample in the absence of ball milling. The photocatalytic reduction efficiencies were increased rapidly from 8.8% to 39.0% with the increasing ball milling time within 0–6 h. Nonetheless, when ball milling time exceeded 6 h, slowly decreased photocatalytic reduction performance was observed. This is due to the fact that couple CuAlO$_2$ with Bi$_2$WO$_6$ can form p–n heterocatalyst after undergoing ball milling, while the mixture of CuAlO$_2$/Bi$_2$WO$_6$ presents much lower activity because no p–n junction is formed in absence of ball milling. Based on the formed p–n heterojunction, the high conductivity of CuAlO$_2$ also helps to improve the transfer efficiency of the charge carriers. Additionally, it can be due to the increase in the active site number per unit photocatalyst weight, because of the increased photocatalyst specific surface area with the incremental ball milling time [54]. However, when ball milling time is further increased, the newly formed
surface possesses great surface energy with the tendency of agglomeration, consequently reducing the photocatalytic activity.

3.3.3. Stability of the catalyst
For a catalyst, its lifetime represents a vital variable in photocatalysis. Thus, it is of great importance to assess catalyst stability in the actual applications. For the determination of photocatalyst stability in photocatalytic reaction, we used CuAlO₂(1.0 wt.%)/Bi₂WO₆ sample with optimal photocatalytic performance for the repeated experiments. As a result, the photocatalytic performance was not lost even after the fifth cycle (Figure 12). At the same time, the CuAlO₂(5.0 wt.%)/Bi₂WO₆ composite was selected to be characterized by XRD patterns with different ground time. As shown in Figure 13, ‘★’ represents the strongest diffraction peak of CuAlO₂ and ‘★’ stands for the diffraction peaks of Bi₂WO₆. There is no sight of impurity phases in the patterns as the ground time increases from 3 h to 24 h. Consequently, the CuAlO₂/Bi₂WO₆ photocatalyst was highly stable in photocatalytic reaction.

4. Conclusions
The novel p–n type CuAlO₂/Bi₂WO₆ composite with significantly enhanced visible-light photocatalytic reduction of Cr(VI) was synthesized by the facile ball milling approach. The optimal CuAlO₂ content in the CuAlO₂/Bi₂WO₆ photocatalyst and the ideal ball milling time were determined to be 1.0 wt.% and 6 h, respectively. The rate constant value of Cr(VI) reduction over CuAlO₂(1.0 wt.%)/Bi₂WO₆ was 4.7 times as many...
as that of pure Bi$_2$WO$_6$. The CuAlO$_2$/Bi$_2$WO$_6$ photocatalyst was also highly stable in photoreaction. For CuAlO$_2$/Bi$_2$WO$_6$, the improved photocatalytic reduction activity might be ascribed to the high conductivity, favorable crystal morphology and well-defined composite interface. The present work can contribute to solving the insufficient catalytic performance and the reduced solar radiation conversion performance of Bi$_2$WO$_6$ in actual applications and explore the design of new heterocatalysts, especially for p–n heterojunction photocatalysts related to CuAlO$_2$.

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**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).
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