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Enhanced the Efficiency of Photocatalytic Degradation of Methylene Blue by Construction of Z-Scheme g-C₃N₄/BiVO₄ Heterojunction

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Abstract: Both non-metallic g-C₃N₄ and BiVO₄ are novel photocatalysts responsive to visible light, but their low charge separation efficiency restricts their inconspicuous photocatalytic activity. In this paper, direct Z-type g-C₃N₄/BiVO₄ photocatalyst was constructed by calcination and hydrothermal for the degradation of methylene blue. The existence of g-C₃N₄/BiVO₄ heterojunction was confirmed by the detailed study of its chemical structure and morphology by various characterization methods, such as X-ray diffraction (XRD), Scanning electron microscope (SEM), and X-ray photoelectron spectroscopy (XPS). The evaluation of photocatalytic performance showed that the MB degradation performance of 1.0-CN/BVO was significantly enhanced, which was 4.528 times and 2.387 times higher than pristine BiVO₄ and g-C₃N₄, respectively, which was mainly due to the enhanced light capture ability and effective electron transfer in the photocatalytic reaction. The 1.0-CN/BVO composite exhibited extremely catalytic stability and recyclability.

Keywords: g-C₃N₄/BiVO₄; photocatalysis; heterojunction; Z-scheme

1. Introduction

The use of visible light ($\lambda \ge 420$ nm) with abundant solar energy to degrade pollutants in aqueous solution is considered to be one of the most effective solutions to solve the energy and environmental crisis [1–3].

BiVO₄ has attracted extensive attention due to its nontoxicity, physical stability, relatively appropriate band gap, low preparation cost, and better photocatalytic application prospects [4,5]. There are primarily three crystal phases of BiVO₄ in nature, including monoclinic scheelite (ms-BiVO₄), tetragonal zircon (tz-BiVO₄), and tetragonal scheelite (ts-BiVO₄) [6–9]. The light utilization rate of tz-BiVO₄ and ts-BiVO₄ with a wide band gap (2.9 eV) [10,11] is low, mainly in the ultraviolet light region. While ms-BiVO₄ is a narrow band gap (2.4 eV) semiconductor [12,13], and thus exhibits the outstanding visible-light-driven photocatalytic behavior. However, the pristine ms-BiVO₄ presents poor charge-transport and weak surface adsorption characteristics, which restrict its wide photocatalytic application [7]. Heterojunction constructed by two semiconductors with matching band structure is an effective approach to suppress recombination of the photoexcited electron-hole pairs [14,15].

For the past few years, the two-dimensional layered nonmetallic graphite phase carbon nitrification $(g-C_3N_4)$ with a suitable band gap (2.7 eV) [16] can effectively degrade environmental pollutants under visible light, which has attracted extensive attention from researchers in different fields [17]. In addition, g-C₃N₄, with a suitable electronic structure, excellent physical and chemical stability, high surface area, many exposed active sites,



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). high photocarrier mobility, simple synthesis methods, and other outstanding features, has attracted extensive attention in both the research community and industry. It has been widely verified that the energy band of pristine $g-C_3N_4$ and $BiVO_4$ are perfectly matched to construct heterojunction composites [18,19]. The application of $g-C_3N_4/BiVO_4$ heterojunction can effectively deal with high a recombination rate of photogenerated electron-hole pairs, and exhibits the excellent ability of separation and transfer of electron-hole pairs [20,21].

Herein, the proposed Z-scheme $g-C_3N_4/BiVO_4$ heterojunction composites were constructed by thermal polymerization and showed outstanding photocatalytic performances for the degradation of methylene blue (MB) under visible light irradiation. The reasonable photodegradation mechanism was discussed in detail, according to the material characterization. This will provide a clear research strategy for the synthesis of efficient and practical heterojunction composites based on BiVO₄ in the field of visible light catalysis.

2. Experimental

2.1. Materials

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), ammonium metavanadate (NH₄VO₃), 36% acetic acid, ammonium hydroxide (NH₃·H₂O, 25%), ethyl alcohol (C₂H₅OH, 95%), and melamine were purchased from Sinopharm Chemical Reagents Co., Ltd (Xi'an, China). The methylene blue (MB, C₁₆H₁₈ClN₃S·3H₂O) were obtained from Shanghai Maikun Chemical Co., Ltd (Shanghai, China). All reagents involved in this work are all analytical grade and did not need further purification.

2.2. Synthesis of BiVO₄ and g-C₃N₄/BiVO₄ Composites

In a typical synthetic procedure (Schematic 1), firstly, 5 mmol Bi(NO₃)₃·5H₂O was put into 25 mL 36% acetic acid with stirring by magnetic force for 30 min at room temperature to obtain solution A for Bi source. An amount of 5 mmol NH₄VO₃ was added into 25 mL of deionized water and magnetically stirred at 60 °C for 30 min to obtain solution B for V source. For the next step, drop solution B into solution A and stir evenly, adding an appropriate amount of NH₃·H₂O to adjust the pH value of the solution to 7, and then stir vigorously with magnetic force for 2 h. After the mixture, orange solution was transferred into a 100 mL of Teflon-lined stainless-steel autoclave and introduced into an oven and maintained at 180 °C for 15 h. At the end of 15 h, the autoclave cooled naturally to room temperature. Finally, the obtained yellow products were separated by centrifugation, thoroughly cleaned with deionized water and anhydrous ethanol for 4 times, to remove impurities, and then the bright yellow pristine BiVO₄ was obtained after drying at 70 °C for 6 h, which was labeled as BVO.

The prepared 0.3 g BVO was fully mixed with 0.5, 1.0, and 1.5 g melamine, respectively, and then transferred into a ceramic crucible with a cover and heated to 600 °C at a rate of 5 °C per minute, maintained for 2 h (Scheme 1). After the reaction, it was naturally cooled to room temperature and the reaction products were ground into powder. The preparation of pristine g-C₃N₄ was the same as the above process, except that bismuth vanadate was not added, which was labeled as CN. The as-prepared g-C₃N₄/BiVO₄ samples were labeled as x-CN/BVO, where x stands for the different addition amount of melamine (x = 0.5, 1.0, and 1.5 g).



Scheme 1. Illustration of synthesis for x-CN/BVO composites.

2.3. Characterization

The XRD data were examined on a Shimadzu 6100 Diffractometer with Cu K α radiation (40 KV, 30 mA) (Shimadzu, Kyoto, Japan). The morphologies of as-prepared catalysts were investigated by using a Zeiss IGMA/VP (Carl Zeiss AG, Jena, Germany) emission SEM. The chemical composition and chemical status were obtained with XPS (Shimadzu AXIS-ULTRADLD spectrometer) (Shimadzu, Kyoto, Japan). UV–Vis diffuse reflectance spectra (DRS) of the samples were recorded using Shimadzu UV-3600 plus UV–Vis-NIR spectrophotometer (Shimadzu, Kyoto, Japan). Infrared spectra were recorded on a Fourier transform infrared (FT-IR, VECTOR-22) (BRUKER, Karlsruhe, Germany) spectrometer at room temperature by the standard KBr disk method.

2.4. Photocatalytic Degradation Experiments

The photocatalytic performance was studied by degrading methylene blue (MB) solutions under a 100 W 410 nm LED light array (CEL-LED 100) (CEAULIGHT, Beijing, China). For each degradation experiment, 30 mg of as-prepared catalyst were used to degrade 50 mL of MB solution ($30 \text{ mg} \cdot \text{L}^{-1}$). The distance between the light source and solution sur-face was 1 cm. The adsorption of MB molecules on the catalyst was related to the degradation performance of the catalyst. Therefore, before light irradiation, we first stirred the catalyst with the MB solution for 30 min to fully mix it to reach the equilibrium of adsorption and desorption. The time interval of irradiation was programmed to be 15 min. After a period of reaction, 5 mL of mixed solution was extracted and centrifuged to obtain a clear solution, which was used to detect the content of MB in the solution. The clean supernatant was measured by UV–Vis spectrophotometer (DH-2000, Ocean Optics) (Ocean Optics Asia, Shanghai, China) to analyze the degradation rate of MB.

3. Results and Discussion

3.1. XRD Analysis

XRD is the main technology to characterize the crystal structure and phase of the samples. The XRD results of the CN, BVO, and various heterostructure composite samples are presented in Figure 1, respectively. In the case of pristine CN, the diffraction intensity relatively weak peak at 12.86° is indexed as the (100) diffraction plane, which is characteristic of the in-plane structural repeat motif of tri-s-triazine [22,23]. Another strong diffraction peak at 27.50° is assigned to the (002) plane of CN, which is consistent with the interplanar stacking of aromatic systems [24]. For all BVO-based catalysts, the characteristic XRD peaks at 18.6°, 28.9°, 30.5°, 35.2°, 40.2°, 47.3°, 50.3°, 53.3°, and 58.5° are ascribed to the (110), (-121), (040), (002), (-112), (042), (202), (-161), (321) planes of ms-BiVO₄ (JCPDS card No. 14–0688) (a = 5.1971 Å, b = 5.0959 Å, c = 11.702 Å), respectively [25]. The XRD results of as-prepared material x-CN/BVO have almost no characteristic peak of CN. This may be because the high content of BVO and good crystallinity mask the characteristic peak of CN [26–28]. In addition, the absence of other characteristic peaks except BVO indicated that no excess substances were produced during the synthesis process. According to the XRD data, the dominant peak is at the position of $2\theta = 28.9^{\circ}$ and the Full Width Half Maximum (FWHM) is 0.519, 0.493, 0.500, and 0.483 of pristine BVO, 0.5-CN/BVO, 1.0-CN/BVO, and 1.5-CN/BVO. With the help of the Scherrer formula ($D = K \gamma / B \cos \theta$), the grain size of the samples can be determined, in which K is the Sheller constant (0.89), D is grain size, and γ is the wavelength of X-ray Cu-K α radiation (1.5406). The lattice sizes of the x-CN/BVO complexes with different amounts of CN hardly changed, and we can conclude that CN has almost no effect on the size of BVO.



Figure 1. The XRD patterns of as-prepared samples.

3.2. Morphology of Catalyst

The morphological characteristics of the samples were analyzed by SEM to study the morphological changes before and after combining, as depicted in Figure 2. Pristine CN is composed of a small number of irregular particles and nanosheets, which is the fold structure (Figure 2a). Figure 2b shows that pristine BVO is an irregular polygon with a smooth surface, showing the ideal crystallization state and high crystallinity, which identifies with the results of XRD. Interestingly, the morphology gradually changed into round and the surface was coated by CN, and became unsmooth with the addition of some CN nanosheets (Figure 2c). The shape and position mapped, respectively (Figure 2e–i), by the Bi, V, O, C, and N elements were basically consistent with the SEM image, which indicated that the five elements exist and CN was evenly distributed on BVO. The EDS patterns shown in Figure 2j indicated that the contents of the N element was less than others, which was consistent with the XRD and FT-IR (Figure S1, Supplementary Materials) results.

3.3. XPS Analysis

To better explore the interaction between CN and BVO, the surface chemical constitution and electronic states of 1.0-CN/BVO photocatalysts were verified by XPS measurements (Figure 3). As illustrated in Figure 3a, the XPS survey spectrum confirmed that the composites contained five elements: Bi, V, O, C, and N, and no characteristic peaks for other elements. The N 1s XPS spectrum was recorded in Figure 3b, where the two apparent peaks of binding energies of 400.0 and 397.6 eV were assigned to $N-(C)_3$ and C=N-C, respectively [27,29]. As observed in Figure 3c, the C 1s binding energy could be split into three peaks; the characteristic peak at 284.5 eV was due to the amorphous carbon on the surface of as-prepared samples. The other two peaks presented at 288.5 and 285.9 eV were indexed to sp² hybridized C (C-(N)₃). These characteristic peaks confirmed the existence of CN in the 1.0-CN/BVO. As shown in Figure 3d, the O 1s signals of 1.0-CN/BVO could be divided into 532.9, 529.6, and 531.7 eV assigned to the lattice oxide species (Bi-O bonds) and from the adsorbed oxygen species (hydroxyl groups), respectively. For the Bi 4f spectrum indicated in Figure 3e, the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ were associated with binding energies of 158.7 and 164.0 eV, respectively. From Figure 3f, the first V 2p peak at 524.0 eV belonged to $V 2p_{1/2}$, and the second at 516.3 eV referred to $V 2p_{3/2}$. According to the above analysis, the close binding between CN and BVO could be proved.



Figure 2. SEM image of (**a**) CN, (**b**) BVO, and (**c**) 1.0-CN/BVO; elemental mapping of 1.0-CN/BVO composite: (**d**) SEM image of 1.0-CN/BVO, (**e**) Bi, (**f**) O, (**g**) C, (**h**) V, (**i**) N, (**j**) EDS of 1.0-CN/BVO.



Figure 3. XPS spectra of 1.0-CN/BVO composite. (a) Survey spectra, (b) N 1s, (c) C 1s, (d) Bi 4f, (e) O 1s, (f) V 2p.

3.4. UV–Vis DRS and Band Structure Analysis

UV–vis spectroscopy is a widely recognized method to characterize the optical properties of semiconductors. As depicted in Figure 4a, the absorption edges of the pristine CN, BVO, and 1.0-CN/BVO corresponded to approximately 451.79, 526.67, and 586.82 nm, respectively, which is consistent with previous reports [27]. Compared with pristine CN and BVO, the absorptive capacity of 1.0-CN/BVO composite was greatly enhanced in the visible and ultraviolet light range, which was due to the formation of heterojunction and could lead to the generation of more charge carriers involved in the degradation of pollutants during the photocatalytic process. The following Tauc equation to estimate the band gap of CN, BVO, and 1.0-CN/BVO [30] was used:

$$\alpha h\nu = A(h\nu - E_{\alpha})^{\frac{1}{2}}$$

Herein, α , $h\nu$, A, and E_g are the optical absorption coefficient, photon energy, proportional constant, and the bandgap. The value of n is determined by the type of semiconductor, which is 1 for direct and 4 for indirect [31,32] (sm-BVO and platelike CN were determined to have a direct band gap like [27,33]). The curve fitting of $(\alpha h\nu)^2$ was extended as a straight line, and the intersection points of the straight line and the abscise were E_g of pristine CN, BVO, and 1.0-CN/BVO, respectively. It can be identified in Figure 4b that the band gap of pristine CN, BVO, and 1.0-CN/BVO is 2.75, 2.45, and 2.39 eV, respectively. Therefore, we could conclude that the visible light response of 1.0-CN/BVO heterostructure was stronger than that of BVO. The valence band (VB) and conduction band (CB) potentials can be estimated by the following empirical formula [24]:

$$E_{VB} = X - E_e + 0.5E_g$$
$$E_{CB} = E_{VB} - E_g$$

X is the electronegativity of semiconductor and E_e is a constant (4.5 eV, vs. NHE, pH = 7) [34]. X values for the CN and BVO were 4.64 and 6.04 eV, respectively [29]. The calculation based on the above formula showed that the VB potentials of CN and BVO were about 1.52 and 2.77 eV, respectively, and the CB potentials of CN and BVO were about -1.23 and 0.32 eV, respectively, which matched well with other works [35].



Figure 4. (a) UV–Vis spectrum and (b) band gaps (Eg) of pristine CN, BVO, and 1.0-CN/BVO composites.

3.5. Photocatalytic Degradation Performance

In order to assess the photocatalytic degradation performance for MB under visible light, the photocatalytic activity of the samples was evaluated. As shown in Figure S2 (Supplementary Materials), the photolysis of MB changed slightly during the light irradiation in the absence of the catalyst. As exhibited in Figure 5a, both pristine BVO and CN show relatively weak expression. However, the photocatalytic performance of the

x-CN/BVO composite was significantly enhanced, in which the decomposition of MB solution reached 93% after 75 min of visible light irradiation by 1.0-CN/BVO. In addition, the photocatalytic performance of a certain amount of catalyst for different concentrations of MB solution and the different amounts of catalyst for a certain concentration of MB solution were investigated. The results show that the higher the ratio of catalyst to MB concentration, the higher the photocatalytic efficiency (Figure S2, Supplementary Materials). To further obtain the degradation kinetics intuitively, pseudo-first-order model was used to fit the data, and the formula was as follows:

$$\ln(C_0/C) = kt$$

Herein, C₀, C, and k are the initial MB concentration (mg/L), the MB concentration at time t (mg/L), and the apparent pseudo-first-order rate constant (min⁻¹), respectively. The calculated MB degradation pseudo-first-order kinetic curve of the asprepared catalyst was shown in Figure 5b. The reaction constant k value of MB degradation of 1.0-CN/BVO was the highest, which was about 0.03808, 2.39 and 4.53 times of pristine BVO and CN. This outstanding performance (Table S1) confirmed that the enhanced photocatalytic activity of x-CN/BVO should be attributed to the introduction of CN. The k value of MB degradation in the prepared samples followed the sequence of 1.0-CN/BVO > 0.5-CN/BVO > 1.5-CN/BVO.

The photostability and recyclability are crucial indexes of the photocatalyst in practical and industrial applications. In this work, the stability measure of 1.0-CN/BVO was obtained through four repeated experiments in the same environment and equipment parameters. As displayed in Figure 5c, after four cycles of degradation of MB by 1.0-CN/BVO, the performance was slightly different from the first one. In addition, XRD pattern spectrum of the fresh and used 1.0-CN/BVO sample (in Figure 5d) showed that the crystalline structure of 1.0-CN/BVO phase did not change significantly after four cycles of repeated experiments, indicating that 1.0-CN/BVO was stable and effective.

3.6. Photocatalytic Mechanism

On the base of the above analysis, the enhancement on photocatalytic efficiency of x-CN/BVO catalysts for MB degradation can be obtained. According to the experimental and theoretical results [36], we calculated the conduction band and valence band energies of the samples. It was found that the LUMO and HOMO of MB are mismatched with the energy of BOV materials, so the photocatalytic process played a dominant role. In addition, before the photocatalytic experiment, we set up a 30 min dark reaction to achieve the balance of physical adsorption and desorption, and try to eliminate any other factors affecting the photocatalytic experiment. The plausible photocatalytic mechanism was shown in Scheme 2, in which the Z-scheme photocatalytic system is formed between CN and BVO. Layered CN is anchored on the facets of BVO through strong interfacial electrostatic interaction, resulting in a lot of charge accumulation at the contact interface. When x-CN/BVO heterostructure is used as a photocatalyst, visible light irradiation can stimulate the migration of CN and BVO electrons from VB to CB, leaving relatively stable holes in VB, thus forming electron-hole pairs. Attributing to the Z-scheme mechanism [37], the photogenerated electrons of CB from BVO (+0.32 eV), with little hindrance, migrated to VB of CN (+1.52 eV). The electrons from CB of CN were reacted again with oxygen to generate O_2^- species. Then, the O_2^- species presents more negative potential than O_2/O_2^- , the species preferentially reacted with MB [38]. The VB of BVO is 2.77 eV, which was more positive than CN's, so H_2O/OH^- can be oxidized to OH. Then, the OH species reacted with MB to produce degradation products. As shown in Figure S3 (Supplementary Materials), the photodegradation rates of MB are apparently depressed from 99.3% to 23%, 77% and 17% when BQ, IPA, and KI are being added into the reaction system, respectively. The results suggested that all the radicals of O_2^- , OH, and h^+ worked in MB degradation over 1.0-CN/BVO, and the O_2^- and h⁺ played the most dominate roles in photocatalysis reaction.



Figure 5. The removal efficiency of MB as a function of irradiation time and corresponding $\ln(C_0/C)$ curves of as-prepared (**a**,**b**); (**c**) cyclic test of photocatalytic degradation of MB by 1.0-CN/BVO. (**d**) XRD patterns of fresh and used 1.0-CN/BVO.



Scheme 2. Schematic illustration for x-CN/BVO Z-scheme heterojunction degradation MB.

4. Conclusions

In summary, the x-CN/BVO Z-scheme heterojunction photocatalyst composed of CN and BVO was successfully synthesized by calcination and hydrothermal methods. The as-prepared optimal photodegradation performance of 1.0-CN/BVO exhibits a wide photo response, high charge separation efficiency, and strong redox capacity at the same time [39]. The results displayed that the degradation of MB by1.0-CN/BVO was 4.528 and 2.387 times higher than that of pristine CN and BVO, respectively. In addition, the 1.0-CN/BVO com-

posite exhibits extremely catalytic stability and recyclability, indicating that the heterogeneous photocatalyst has huge potential for the removal of organic pollutants.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/coatings11091027/s1, Figure S1: FT-IR spectra of pristine CN, pristine BVO, and 1.0-CN/BVO, Figure S2: Under visible light irradiation, the removal rate of MB with different concentrations of 1.0-CN/BVO; check the photolysis of MB in the absence of the catalyst, Figure S3: Trapping experiments of active species during the photocatalytic degradation of MB over 1.0-CN/BVO sample under visible light irradiation, Table S1: The photocatalytic performance and catalytic efficiency were compared with other C_3N_4 , BiVO₄, and C_3N_4 /BiVO₄ materials.

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