Construction of MIL-125-NH$_2$@BiVO$_4$ Composites for Efficient Photocatalytic Dye Degradation

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Cite This: ACS Omega 2022, 7, 26201−26210

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ABSTRACT: The design and construction of a photocatalyst with a heterostructure are a feasible and effective way to enhance the catalytic performance. Herein, a specially designed composite based on MIL-125-NH$_2$ and BiVO$_4$ was prepared and used for wastewater treatment. In the hybrid MIL-125-NH$_2$@BiVO$_4$. MIL-125-NH$_2$ was uniformly dispersed on the BiVO$_4$ surface. There is a high affinity between MIL-125-NH$_2$ and BiVO$_4$ due to the lattice defects. Under visible light irradiation, the catalytic activity of the as-prepared composite was evaluated by the degradation of various dyes such as malachite green, crystal violet, methylene blue, and Congo red. Nearly 98.7, 99.1, and 41.0% of the initial MG, MB and Cr(VI) were respectively removed over the optical sample of BVTN-5, demonstrating that the hybrid holds great promise for practical applications. Moreover, the composites can be recycled and reused with good stability after five consecutive cycles. The mechanism was proposed and discussed in detail. This work will shed light on the construction of MOF-based composites for efficient photocatalysis.

INTRODUCTION

Worldwide, the wastewater produced by increasing industrial activities has become a serious threat for the environment and human health. Among the contaminants, the toxic Cr(VI) and dye-containing substances have emerged as a huge global challenge and attracted extensive interests. Most of the chromium from the groundwater originates from natural sources and anthropogenic activities. Cr(III) is the dominant species in natural water, while Cr(VI) is believed to be a solely anthropogenic pollutant. The United States Environmental Protection Agency (US EPA) Guidelines for Carcinogen Risk Assessment have classified hexavalent chromium as one of the 17 chemicals posing the greatest threat to human beings. In addition, a concentration of Cr(VI) in drinking water exceeding 0.1 mg·L$^{-1}$ is considered to be carcinogenic through a mutagenic mode action. Therefore, various methods have been proposed for wastewater remediation, including absorption, membrane-based separation, and catalytic reduction. Restricted by low removal efficiencies, high energy consumption, and high cost, it is difficult to meet the requirements of practical application. Very recently, semiconductor photocatalysis has been considered as a promising and environmentally benign technique that can convert the organic pollutants into nonhazardous components under visible light. Many efforts have been dedicated to the design and preparation of high-performance photocatalysts toward environmental remediation. To date, numerous photocatalysts such as metal oxides, inorganics, noble metals, and polymers have been applied for light-driven pollutant elimination. Nevertheless, the rapid recombination of photogenerated carriers and the suboptimal utilization of solar energy still bring a huge hindrance to the application of photocatalysts. To improve the photocatalytic efficiency, some researchers developed several bismuth-based metal oxide-based photocatalysts, including BiOX (X = Cl, Br, I), Bi$_3$WO$_6$, BiVO$_4$, Bi$_2$Ti$_3$O$_12$, BiFeO$_3$, Bi$_5$S$_3$, Bi$_3$FeTi$_3$O$_12$, CaBi$_2$O$_4$, etc. All of them exhibit excellent capability in light of their outstanding efficiency and the enhanced charge transfer in photocatalysis. As bismuth vanadate (BiVO$_4$) possesses the characteristics of low cost, suitable band gap, good stability, and nontoxicity, it has attracted great interest since the pioneering work conducted by Kudo et al. Restricted by the limited surface area, poor adsorption capacity, and low ability to separate photogenerated electron–hole pairs, pure BiVO$_4$ shows an undesirable photocatalysis performance. Various types of BiVO$_4$-based composites such as n-BiVO$_4$@p-MoS$_2$ (76.5% Cr(VI), 69.2% CV, 60 min), Cu$_2$O/BiVO$_4$ (100% CV, 91% RhB, 73% MO, 120 min), Bi$_2$O$_3$/BiVO$_4$ (70% α-DCB, 6 h), Au-(BiOCl/BiVO$_4$) (67% MO, 240 min), and V$_2$O$_5$/BiVO$_4$ (92% MB, 180 min) are synthesized to overcome such defects. Besides, metal–organic frameworks (MOFs), composed of metal units and organic ligands with...
large pore sizes, high surface areas, structure adaptability, and flexibility, are attractive porous crystal materials and have been found to have a huge potential in the photocatalytic field. Prior studies demonstrated that MOFs possess a semiconductor-like property and can be directly used as photocatalysts. Taking MIL-125-NH$_2$ as an example, it could be stimulated by ultraviolet light with a small band gap energy at about 2.6 eV in which metal clusters serve as the conduction band (CB) and organic linkers play the role of the valence band (VB). Unfortunately, MIL-125-NH$_2$ suffers from weak visible light response and low efficiency.

Herein, by combining the advantages of BiVO$_4$ and MIL-125-NH$_2$, a MIL-125-NH$_2$@BiVO$_4$ composite was prepared via a facile hydrothermal method. In the hybrid, BiVO$_4$ serves as the support/matrix for MIL-125-NH$_2$ coating. The element substitution in lattice substantially promoted the stability of composites. Effects of Ti/Bi molar ratio on the structure and property of composites were investigated. Under visible light irradiation, photocatalytic removal of various pollutants was conducted, and results showed that the as-prepared composites exhibited high efficiency.

This work provides a facile approach for the design and preparation of high-performance photocatalysts for water treatment.

**EXPERIMENTAL SECTION**

**Materials.** Bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O, 99%), ammonium metavanadate (NH$_4$VO$_3$, 99%), nitric acid (HNO$_3$, Sinopharm Chemical Reagent Co., Ltd.), 2-amino-terephthalic acid (H$_2$ATA, 98%), titanium isopropoxide (TTIP, 95%), methanol (MeOH), and N,N-dimethylformamide (DMF, 99.8%) were obtained from Shanghai Macklin Biochemical Co., Ltd., and utilized as received without further treatment.

**Synthesis of MIL-125-NH$_2$@BiVO$_4$ Composites.** The BiVO$_4$ particles were synthesized via a hydrothermal method modified from a previous study and nominated as BV. For the synthesis of MIL-125-NH$_2$@BiVO$_4$ composites with varying molar ratios, a solvothermal method was used and is shown in Figure 1a. At first, 1 mmol of the BV was ultrasonically dispersed into the 40 mL mixture of DMF and MeOH (4:1, v/v). Subsequently, 2 mmol of H$_2$ATA was added slowly under violent agitation until it dissolved completely, and then 1 mmol of TTIP was added dropwise to the suspension.
After vigorous stirring for 30 min, the resultant solution was transferred into a Teflon-lined autoclave and kept under 423 K for 16 h. After that, the precipitates were collected by centrifugation and washed several times with DMF and MeOH. Finally, the obtained dark yellow sample was dried under a vacuum oven at 333 K overnight. The final product was referred to as BVTN-5. Based on the procedure mentioned above, BVTN-n (n = 1, 2, 3, 4, 5, 6) composites were synthesized, while the numerical suffixes represent the molar ratio of Ti/Bi (1:19, 1:5, 1:4, 1:2, 1:1, 2:1). For comparison, pure MIL-125-NH₂ was collected under the same conditions in the absence of BiVO₄ and denoted as TN.

**Characterization.** The X-ray diffraction (XRD) patterns were recorded by an Ultima IV equipped with Cu Kα radiation at a scanning angle (2θ) range of 5 to 80° and scanning rate of 10°·min⁻¹, while AXS UltraDLD was employed to achieve X-ray photoelectron spectroscopy (XPS) to determine the elemental composition and the chemical states on the surface of the prepared samples. The Fourier transform infrared spectroscopy (FT-IR) was documented using a VERTEX 80v by means of a KBr disk as the reference in the scanning range of 4000–400 cm⁻¹; Raman spectra were gained from DXRS32. Morphology and structure were observed by a scanning electron microscope (SEM) spectrophotometer (JSM-7600F), while the energy-dispersive X-ray spectroscopy (EDS) of the samples was also performed during the SEM measurement (INCA X-Act, Oxford Instruments). Moreover, the Brunauer–Emmet–Teller (BET) (BET-PMI2) method was used to determine gas adsorption isotherms and the specific surface area, whereas the average pore diameter and pore size distribution were analyzed by the Barrett–Joyner–Halenda (BJH) method, based on the foundation of N₂ adsorption–desorption isotherms. UV-2802 and UV-2600 were used to acquire the UV–vis absorption spectra as well as the UV–visible diffuse reflectance spectra (UV-DRS) of the specimens by taking BaSO₄ as reference. The photoluminescence (PL) spectra of the samples were excited at 365 nm and performed on a HORIBA Scientific fluorescence spectrophotometer (FluroMax-4). Photocurrent transient was studied using an electrochemical workstation (CHI-660E, Shanghai Chenhua, China) with the standard three-electrode system.

**Photocatalytic Experiment.** The catalytic activities of the samples were investigated in detail through the photocatalytic decomposition of various target organic pollutants including one typical dye, malachite green (MG), and Cr(VI) under visible light illumination. In addition, MB, CR, and CV were also selected to evaluate the performance of the prepared samples. The photocatalytic reaction was carried out under room temperature, and a 300 W Xe lamp (λ > 420 nm) (CEL-HXF300, light intensity: 100 mW·cm⁻²) was the light source. Experimental details are as follows: 40 mg of the as-prepared sample was dispersed into the 40 mL MG solution (75 mg·L⁻¹). To achieve an adsorption–desorption equilibrium, the suspension was magnetically stirred and maintained in the dark for 1 h before being irradiated with visible light. At given intervals of time, 3 mL of the reaction suspension was filtered with a 0.22 μm syringe filter to eliminate the residue particles, and the concentrations of filtrate were collected at the maximum absorption wavelength of the specific position (MG: 617 nm, CV: 590 nm, MB: 664 nm, CR: 496 nm, Cr(VI): 540 nm) by a UV–vis spectrophotometer. The concentrations of Cr(VI) were tested according to the 1,5-diphenylcarbazide (DPC) colorimetric method. Triple testing was performed for each sample for averaging the results to ensure the reproducibility of the results. To determine the stability of the prepared composite, the used material was collected and the same degradation experiment was performed for five cycles. The photocatalytic oxidation (PCO) efficiency of dyes and the photocatalytic reduction (PCR) efficiency of Cr(VI) were estimated by $\eta = (C_0 - C_t)/C_0 \times 100\%$, where $\eta$ represents the photocatalytic removal efficiency and $C_0$ and $C_t$ refer to the concentration of the dye or Cr(VI) before and after the reaction.

It is essential to gain more information on the band structures of the composite to explore the separation of photogenerated carriers over the heterostructures. The positions of the semiconductor’s VB and CB were calculated using the following empirical equations:¹⁹,²⁰

\[
E_{VB} = X + 0.5E_g + E^e
\]

\[
X = \left[ x(A)^a x(B)^b x(C)^c x(D)^d \right]^{1/(a+b+c+d)}
\]

\[
E_{CB} = E_{VB} - E_g
\]

where $E_{VB}$ and $E_{CB}$ are the VB and CB edge potential, respectively, while $E_g$ and $E^e$ correspond to the band-gap energy of the semiconductor and the energy of free electrons vs hydrogen (4.5 eV), with $X$ being the electronegativity of the semiconductor.²² The VB and CB values of BiVO₄ were calculated by the above formula (eqs 1, 2, and 3), and the photocatalytic mechanism of the MIL-125-NH₂@BiVO₄ composite to efficiently remove the dye is proposed in Figure 6 based on the band gaps of BiVO₄ and MIL-125-NH₂.

**RESULTS AND DISCUSSION.** As illustrated in Figure 1a, MIL-125-NH₂@BiVO₄ composites were obtained through the hydrothermal method. Prepared BiVO₄ was used as substrate for the deposition and in situ growth of MOF particles. The obtained powder is dark yellow in color.

To find out the crystal structure of the as-prepared samples, XRD patterns were explored and summarized in Figure 1b. The characteristic peaks of BV centered at 19.0, 28.8, 30.6, and 53.3° are matched well with the (011), (121), (040), and (161) faces of BiVO₄, confirming the successful synthesis of BiVO₄ (JCPDS Card No. 83-1699). Moreover, the narrow line widths indicate a high degree of crystallinity for the as-prepared BV. For the TN product, the sharp peaks are located at 6.8, 9.7, 11.7, 15.0, 16.6, 17.9, 19.0, and 22.5°, evidencing the effective preparation of MIL-125-NH₂.²⁶,²⁷ No peaks for any other phases or impurities are detected, and the diffraction peaks of BVTN-5 are consistent (those of BVTN-6 match well) with those of BV and TN.²² However, the signals attributed to MIL-125-NH₂ over BVTN-n (n = 1, 2, 3) composites are almost undetectable probably due to the low content of TN and the good distribution of TN in composites. The above data show a high degree of consistency with the previous literature.²⁸

FTIR spectra (Figure 1c) were determined to explore the functional groups in composites. The stretching vibration of the O–H bond near 3446 cm⁻¹ can be associated with the presence of water absorbed over the surface. Predictably, the absorption band at 700–900 cm⁻¹ is assigned to the asymmetric stretching and symmetric stretching vibration of the V=O bond.²⁹ In the spectrum of BV, the broad and strong peak of 731 cm⁻¹ is assigned to the asymmetric stretching of
VO$^{3-}$, revealing the successful synthesis of monoclinic sheelite BiVO$_4$ powder. This observation is consistent with the conclusion obtained from XRD analysis. Seen from the spectrum of the TN sample,$^{40,41}$ the bands at 1300–1600 cm$^{-1}$ are attributed to the stretching vibrations of the carboxylate group. C–N and N–H bonds at 1259 and 1626 cm$^{-1}$ are correlated with the linkers in the framework of MIL-125-NH$_2$. Moreover, the characteristic absorption of 400–800 cm$^{-1}$ belongs to O–Ti–O. BVTN-$n$ shows the same adsorption bands as BV and TN, further proving the presence of BiVO$_4$ and MIL-125-NH$_2$ in the composite.

The Raman spectra (Figure S1) provide further information on the local structure and bonding states. The Raman signal of BV exhibited a monoclinic phase.$^{42}$ Besides, the V–O bond length was calculated to be 1.69 Å according to the empirical expression $\nu = 21.349e^{-1.9176R}$, wherein $\nu$ and $R$ are the peak positions of the group’s stretching mode and the bond length, respectively.$^{43}$ The peak of the composite was consistent with two monomer materials, supporting the successful complexation of BV and TN.

Figure 2 displays the XPS analysis of the prepared BV, TN, and BVTN-5 samples. The relevant peaks were calibrated with the C 1s signal of contaminant carbon.$^{22}$ The typical survey spectrum depicted in Figure 2a confirms the presence of Bi, Ti, O, V, N, and C elements in BVTN-5, which is in agreement with the EDS analysis results. As presented in Figure 2b, the binding energies at 533.2, 531.8, 530.4, and 529.6 eV were show in the high resolution of O 1s. These peaks can be ascribed to the signals of O from the adsorbed H$_2$O or surface hydroxyl group, C=O, lattice oxygen for BiVO$_4$ and MIL-125-NH$_2$, respectively.$^{44}$ Additionally, two signal peaks at 401.8 and 399.2 eV exhibited in Figure S2 are associated with the $-\text{N}=$ or $-\text{NH}^-$ and $-\text{NH}_2$ groups of the organic linkers.$^{45,46}$ In the high-resolution spectrum of the C 1s orbital (Figure S2), the peaks located at 284.8, 285.3, 286.4, and 288.8 eV could be ascribed to C–O, C–N–O, C–O, and C==O bonds, which were mainly derived from H$_2$ATA linkers and benzoic rings, confirming that MIL-125-NH$_2$ was formed instead of TiO$_2$. For bismuth and titanium, they are in good accordance with those in previous researches.$^{33,34}$ The typical peaks centered at 164.5 and 159.3 eV in the Bi 4f spectrum (Figure 2c) correspond to Bi 4f$^{5/2}$ and Bi 4f$^{7/2}$, and the splits at 164.4 and 458.5 eV are assigned to Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ (Figure 2d), manifesting that the Bi and Ti species in BVTN-5 exist in the form of Bi$^{3+}$ and Ti$^{4+}$ oxidation state. Meanwhile, the Ti 2p$_{1/2}$ peak has a broad bump because of the overlap between Bi 4d$^{3/2}$ at 466.4 eV and Ti 2p$_{1/2}$ at 464.4 eV.$^{24}$ Compared with the pristine BV, the presence of TN on the BV caused the band of Bi$^{3+}$ to shift toward low energy, suggesting that Bi$^{3+}$ has been doped into the lattice of TN.$^{47}$ Besides,

**Figure 2.** XPS spectra of BV, TN, and BVTN-5 samples: (a) survey scan, (b) O 1s, (c) Bi 4f, and (d) Ti 2p spectra.
Figure 3. SEM images of (a) BV, (b) TN, and (c, d) BVTN-5 at different resolutions.

Figure 4. (a, b) Photocatalytic oxidation of 10 mg·L⁻¹ MG solution via the as-prepared samples. (c) Effect of MG concentration on the reduction over BVTN-5. (d) Simultaneous photocatalytic removal ability of dye mixture via the as-prepared BVTN-5 samples (75 mg·L⁻¹ MG, 75 mg·L⁻¹ CV, 75 mg·L⁻¹ MB). Reaction conditions: 40 mg catalysts, 40 mL solution, λ > 420 nm, pH ~6, room temperature.
BV can work as an electron producer; thus, electrons can transfer to TN, thereby enhancing the charge density around Ti\(^{4+}\). A similar situation has been reported by Zhao et al.\(^{44}\) XPS results provide sufficient evidence for the formation of MIL-125-NH\(_2\)@BiVO\(_4\) composites via the hydrothermal method.

SEM images were used to illustrate the morphology of the materials. As revealed in Figure 3a, pure BiVO\(_4\) exhibited a structure of aggregated branch-like dendrite shape with a length size in the 50–300 nm range and a unique backbone about 1–2 μm long, while bare MIL-125-NH\(_2\) (Figure 3b) had a tablet-like morphology. However, compared with the smooth surface of pristine BiVO\(_4\) stick structures wrapped with the smaller size MIL-125-NH\(_2\) were observed for the BVTN-5 composite in Figure 3c,d. Elemental mapping analysis was performed on the BVTN-5 composite for further confirmation. Figure S3 unambiguously confirms the presence of Ti and Bi elements in the sample. In addition, the actual molar ratio of Ti/Bi in the prepared BVTN-5 was obtained by ICP-OES. The actual amount of Ti/Bi in the position is quite similar to the nominal values (0.98). The actual contents of BiVO\(_4\) (33.1%) and MIL-125-NH\(_2\) (66.9%) in BVTN-5 were evaluated by TG analysis (Figure S4). Thermogravimetric analysis revealed two regions of significant weight losses in BVTN-5. The surface adsorbed water was lost to evaporation at the first stage of loss below 120 °C. And the second weight loss between 300 and 400 °C belongs to structural disintegration.\(^{50,51}\) It is believed that BVTN-5 almost shows chemical stability up to 300 °C.

**Photocatalytic Results.** The photocatalytic performance of the sample was tested with MG as the target pollutant. A dark adsorption was operated for 1 h before the light was turned on to achieve the adsorption desorption equilibrium. Besides, the blank examination was set for verifying the direct photolysis of MG. As shown in Figure 4a, the total removal efficiency generally has a positive correlation with the content of TN in BVTN-\(n\) composites. BVTN-5 presented an efficiency of MG (10 mg L\(^{-1}\)) removal (93.6%) close to TN (95.1%). It is also clear that the BVTN-5 composite exhibited a higher photocatalytic performance than that of the pristine BV (40 mg, 68.1%) and BV/TN mixture (BV: 13.24 mg, TN: 26.76 mg, 85.9%), which is indicative of the formation of the desired heterostructure (Figure 4b), matching well with the conclusion of DRS. From XPS, ICP, BET, SEM, and photocatalytic reaction test results, the specific surface area of the sample and the content of TN on the surface play a key role in the photocatalytic performance. The photocatalytic efficiency of BVTN-6 is arguably unsatisfactory as a result of the excessive TN prompting greater adsorption performance than photocatalytic performance. It is inferred that excess loadings possibly hinder photogenerated electron transfer and reduce the accessibility of active sites, which is detrimental to the photocatalytic performance. To survey the influence of coexisting ions, MG is also dissolved in tap water and conducted under the same experimental conditions. BVTN-5 shows a striking removal efficiency without distilled water (92.6%, 3 h) (Figure 4b). BVTN-5 is hence chosen for the follow-up research.

To evaluate the effect of initial MG concentration in the photocatalytic activity, the concentration versus removal efficiency is plotted (Figure 4c). It is obvious that 75 mg L\(^{-1}\) reaches the maximum movement efficiency (95.5%) of BVTN-5 in 3 h. To some extent, the removal efficiency gradually increased with concentration until the concentration of 75 mg L\(^{-1}\), which is driven by the concentration difference. Contrarily, a too high concentration causes the saturation of dye accumulated on the photocatalyst surface; there is not enough time to degrade them into small molecules.\(^{52,53}\) The catalytic performance of this work is comparable with other MOF-based photocatalysts (Table S1).

Whether BVTN-5 can achieve the selective degradation of cationic or anionic pollutants is illustrated in Figure S5. BVTN-5 performed better in cationic dyes (MG, MB, CV) than the anionic dye (CR). To discuss the selectivity of different kinds of dyes, the variation in zeta potential of the BVTN-5 photocatalyst in aqueous dispersion has been carried out, and the results are shown in Figure S6. With the increase in the value of pH within the pH range tested, the zeta potential of the composite becomes more negative. The zero-point charge (pH\(_ZPC\)) was determined to be at ca. 2.7. It is clear that the surface of BVTN-5 was negatively charged when the pH value was above 2.7, contributing to an electrostatic attraction effect between BVTN-5 and the cationic pollutant.\(^{54}\) Thus, the cationic dye can be selectively accumulated onto the surface and rapidly degraded by the migrated photogenerated electron, leading to the superior removal efficiency compared to the anionic dye.\(^{29}\)

In real industrial activities, multicomponent dyes or heavy metal ions along with dye are often discharged inevitably, so it is of great significance to treat different kinds of pollutant mixture systems simultaneously. As shown in Figure 4d, a mixture containing MG, MB, and CV (the concentration of both pollutants was controlled as 75 mg L\(^{-1}\)) can be efficiently degraded (88.7/99.2/80.3%, 3 h) after irradiation with the presence of BVTN-5 conducted in neutral media without acid adjustment, giving the persuasive proof that construction of the inherent heterostructure boasted a remarkable photocatalytic ability.

The ability of products to remove other binary system and ternary system pollutants is displayed in Figure S5 (the concentration of Cr(VI) and dyes was fixed at 10 and 75 mg L\(^{-1}\), respectively). To some extent, it could be seen from the result that the final removal efficiency of the mixed dye solution is slightly lower than that of the individual dye solution; on the contrary, there is a mutual promotion in the photocatalytic removal of Cr(VI) and dye binary system (MG/CV (95.8/97.6%), MB/CV (82.1/89.6%), MG/MB (96.6/96.9%), CV/Cr(VI) (97.6/55.2%), CR/Cr(VI) (97.1/62.5%), MG/MB/Cr(VI) (98.7/99.1/41.0%), 3 h). Meanwhile, the single removal of CV, MB, CR, CV, and Cr(VI) over BVTN-5 is reported to be 97.9, 97.6, 58.2, 97.9, and 15.1%, respectively. It is reckoned that the dye molecules compete for the available active sites of catalysts in the targeted multicomponent system, and hence, the dye removal percentage was reduced. By the way, it is well known that the pH value is a crucial prerequisite in the removal efficiency of Cr(VI).\(^{29,50}\) BVTN-5 presented better performance under the acidic conditions (Cr(VI) (20.5%), MG/MB/Cr(VI) (71.4/81.7/57.1%), 3 h, pH ~2).

Additionally, Kyung et al.\(^{55}\) reported that a complex intermediate can be formed in the mixture of dyes and Cr(VI). No new absorption peak for the intermediate was detected from UV–vis, indicating that dyes and Cr(VI) stably existed in the solution. Furthermore, the product after photocatalytic process was monitored through XPS to analyze the valence state of Cr on the photocatalysts (Figure S7). According to the high-resolution spectrum of Cr 2p, discernible peaks that appeared at 576.7 and 586.2 eV correlate with Cr 2p\(_{3/2}\) and Cr 2p\(_{1/2}\) of Cr(III), respectively.
It is disclosed that the BVTN-5 composites efficiently detoxify harmful Cr(VI) into innoxious Cr(III) under visible light. The stability and recyclability of the catalysts play a decisive role in real applications. The used catalyst was collected by centrifugation (8000 rpm) and regenerated by ethanol (50 mL, 50%, v/v). After drying at 60 °C, the recovered catalysts were used for the next cycle under the same conditions. As illustrated in Figure 5a, the sample still maintained prominent removal efficiency after five cycles. XRD (Figure 5b) and FTIR results (Figure S8) of the used BVTN-5 exhibited no obvious deviation, confirming that the structure integrity composition was well preserved. In addition, it was found that BVTN-5 can maintain its original structure after five times of the cycling test (Figure S9). Moreover, the ICP detection of the solution after photocatalytic activity demonstrates that the leaching of the Ti$^{4+}$ ions can be nearly ignored, suggesting that the sample has excellent stability for the photocatalytic degradation of pollutants.

The optical properties of BV, TN, and the BVTN-5 composite were investigated by UV−vis DRS. From the results depicted in Figure 5c, the addition of MIL-125-NH$_2$ led to a red shift by the BiVO$_4$ based composite. The degradation activity of the composite is substantially boosted because of the increase in visible light response. The band gap energy ($E_g$, eV) value of different samples can be estimated using the Tauc plot method,

\[
(\alpha h\nu)^{1/n} = A(h\nu - E_g)
\]

where $\alpha$, $h\nu$, and $A$ represent the absorption coefficient, the photon energy, and the constant, respectively, while the $n$ value depends on the characteristics of the transition, i.e., direct or indirect.

According to Figure 5d, the band gap for the BV, TN, and BVTN-5 is calculated to be 2.3, 2.7, and 2.4 eV, respectively. Collectively, it can be deduced that combining TN with BV to form the intimate heterointerface can narrow the band gap and enhance visible light absorption, endowing the composites with favorable optical properties. The charge separation extents for products are presented to investigate the photocatalytic mechanism (Figure S10). The decreased intensity represents the low recombination of electron−hole pairs. BVTN-5 showed a larger PL quenching effect compared to the bare samples, demonstrating the improved charge separation. Photocurrent-response spectra were investigated and required in Figure S11. It can be observed that BVTN-5 bared outstanding photocurrent density among the three materials.
suggeting the higher efficient separation of photogenerated carriers.

**Mechanism of the Enhanced Photocatalytic Property.** Generally, a plurality of reactive species was expected in photocatalytic degradation contribution. Radical quenching experiments were executed to definitely investigate the oxidizing substance produced in the photocatalytic removal of MG over BVTN-5 (Figure S12). Ethylenediaminetetraacetic acid disodium (EDTA-2Na, 0.2 mmol·L⁻¹), AgNO₃ (0.2 mmol·L⁻¹), tertiary butanol (TBA, 0.2 mmol·L⁻¹), and p-benzoquinone (BQ, 0.2 mmol·L⁻¹) were applied for the capture of holes (h⁺), electrons (e⁻), hydroxyl radicals (·OH), and superoxide anion radicals (·O₂⁻), respectively. The predominant reactive species in the process was relation to h⁺, for the corresponding removal efficiency decrease strongly. There was a slight increased with the scavengers’ addition of BQ and AgNO₃. By consuming O³⁻ and e⁻ selectively, the separation of photocarriers was promoted and h⁺ increased.

As discussed above, the compete and synergistic for the available active sites leading a reduce or promote in photocatalytic activity plausibly. We can attribute the removal ability of dyes without irradiation to the adsorption of MG (75 mg·L⁻¹) on the surface of BVTN-5 (Figure S13). Moreover, the photolysis of dyes cannot be neglected under visible light (Figure S11); the involved photolysis steps were presumed in eqs 5, 6, 7, 8, and 9. During the photolysis process, dye can be excited into dye* and then oxidized by O₂ to degraded products. Meanwhile, with the irradiation, Cr(VI) acts as photo-induced electron acceptor, and dyes serve as a hole scavenger, which could hence hinder the photogenerated carriers’ recombination and enormously promote the simultaneous removal of Cr(VI) and dyes.

\[
\text{Dye} + h_0 \rightarrow \text{dye}^* + e^- \quad (5)
\]

\[
\text{dye}^* + O_2 \rightarrow \text{intermediates} \rightarrow \text{degraded products} \quad (6)
\]

\[
\text{BVTN} - 5 h_0 h^+ + e^- \quad (7)
\]

\[
\text{Cr(VI)} + e^- \rightarrow \text{Cr(III)} \quad (8)
\]

\[
\text{Dye} + h^+ \rightarrow \text{intermediates} \rightarrow \text{degraded products} \quad (9)
\]

**CONCLUSIONS**

In summary, a series of novel visible-light driven MIL-125-NH₂@BiVO₄ composites with different molar ratios of Ti/Bi were successfully synthesized and characterized. They show broad use in strong photocatalytic activity under visible irradiation in the degradation of different dyes (MG (95.5%), MB (97.6%), CV (97.9%), CR (58.2%)) or simultaneous removal of different pollutant (MG/MB/Cr(VI) (98.7/99.1/41.0%)) mixture systems in a neutral medium, and the optimal molar ratio of Ti/Bi is 1:1. It was found that the recombination of photogenerated electrons and holes in BiVO₄ significantly inhibited with the presence of MIL-125-NH₂, leading to the enhanced photocatalytic activity. In addition, the products also have excellent stability and recyclability. This is a report on the utilization of the MIL-125-NH₂@BiVO₄ composite, which can remove organic dyes and Cr(VI) in a neutral media simultaneously. Besides, we hope that this work can bring a new insight into the treatment of wastewater in real practice.

**ASSOCIATED CONTENT**

* Supporting Information
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01862.

  Figure S1, Raman spectra; Figure S2, C 1s and N 1s spectra; Figure S3, SEM-EDS elemental mapping; Figure S4, TG curves; Figure S5, simultaneous photocatalytic removal ability of mixture pollutants; Figure S6, zeta potential measurement; Figure S7, Cr 2p spectrum; Figure S8, FTIR spectra; Figure S9, SEM images; Figure S10, PL spectra; Figure S11, transient photocurrent spectra; Figure S12, free radical capture results in the photocatalytic removal; Figure S13, removal performance in dark; Table S1, comparison of various photocatalysts’ efficiency; and additional references (PDF)

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Notes
The authors declare no competing financial interest.

Acknowledgments
This work was supported by the National Natural Science Foundation of China (21606133) and Jiangsu Provincial Natural Science Foundation of China (BK20160922). We also would like to acknowledge the support received from Advanced Analysis & Testing Center, Nanjing Forestry University, for sample tests.

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