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Fabrication of Bi$_2$MoO$_6$ Nanosheets/TiO$_2$ Nanorod Arrays Heterostructures for Enhanced Photocatalytic Performance under Visible-Light Irradiation

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Abstract: Bi$_2$MoO$_6$/TiO$_2$ heterostructures (HSs) were synthesized in the present study by growing Bi$_2$MoO$_6$ nanosheets on vertically aligned TiO$_2$ nanorod arrays using a two-step solvothermal method. Their morphology and structure were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Excellent visible-light absorption was observed by UV–Vis absorption spectroscopy, which was attributed to the presence of the Bi$_2$MoO$_6$ nanosheets with a narrow-band-gap. The specific surface area and pore volume of the photocatalysts were significantly increased due to the hierarchical structure composed of Bi$_2$MoO$_6$ nanosheets and TiO$_2$ nanorods. The photoluminescence and photoelectrochemical characterizations showed improved separation and collection efficiency of the Bi$_2$MoO$_6$/TiO$_2$ HSs towards the interface charge carrier. The photocatalytic analysis of the Bi$_2$MoO$_6$/TiO$_2$ HSs demonstrated a significantly better methylene blue (MB) degradation efficiency of 95% within 3 h than pristine TiO$_2$ nanorod arrays under visible-light irradiation. After three photocatalytic cycles, the degradation rate remained at ~90%. The improved performance of the Bi$_2$MoO$_6$/TiO$_2$ HSs was attributed to the synergy among the extended absorption of visible light; the large, specific surface area of the hierarchical structure; and the enhanced separation efficiency of the photogenerated electron-hole pairs. Finally, we also established the Bi$_2$MoO$_6$/TiO$_2$ HSs band structure and described the photocatalytic dye degradation mechanism. The related electrochemical analysis and free-radical trapping experiments indicated that h$^+$, O$_2^-$ and -OH have significant effects on the degradation process.

Keywords: Bi$_2$MoO$_6$; TiO$_2$ nanorod arrays; heterostructure; photodegradation; solvothermal method

1. Introduction

Light- and catalysis-assisted removal of pollutants and water electrolysis are popular processes because of their environmental friendliness. Titanium dioxide (TiO$_2$) is a popular photocatalyst because of its favorable electron mobility, resistance to photocorrosion, low cost, and low toxicity [1–4]. Nevertheless, its poor solar-light utilization, due to its band-gap value (3.0–3.2 eV) and high photo-charge-carrier recombination rate [5,6], limit the extensive application of anatase and rutile. These drawbacks were somewhat successfully overcome by TiO$_2$ dye-sensitization, doping, and coupling with other metals and their oxides [7–10]. The most promising method is the combination of TiO$_2$ with materials possessing narrow band-gaps. The resulting heterostructures (HSs) demonstrate an extended (to the visible-light spectrum) optical absorption and increased separation of charge carriers [11–14].

Bismuth (III)-containing oxides, such as Bi$_2$O$_3$, BiOI, BiOCl, BiVO$_4$, Bi$_4$Ti$_3$O$_{12}$, and Bi$_2$WO$_6$, have attracted much interest due to their superior photocatalytic and physicochemical performances [15–18]. Importantly, Bi$_2$MoO$_6$ is a layered oxide with an Aurivillius
structure that possesses visible-light-driven photocatalytic activity for water and organic electrolysis and decomposition [19,20]. Interestingly, some studies reported that coupling Bi$_2$MoO$_6$ with TiO$_2$ yielded HSs with enhanced photocatalytic performance. For instance, the flake-like Bi$_2$MoO$_6$ grown on TiO$_2$ films demonstrated excellent significant visible-light self-cleaning properties [21], which were attributed to the synergy between the individual components of these HSs, including superhydrophilicity and effective charge-carrier separation [21]. Pan et al. [22] reported that Bi$_2$MoO$_6$/TiO$_2$ HS microspheres exhibited excellent photocatalytic activity towards phenol and nitrobenzene decomposition under visible light. Zhang et al. [23] prepared Bi$_2$MoO$_6$/TiO$_2$ HSs with two different morphologies using Bi$_2$MoO$_6$ nanoparticles and nanosheets. Both morphologies efficiently degraded organic pollutants because of the extended visible-light-absorption capability of Bi$_2$MoO$_6$ and excellent separation of charge carriers driven by the photo-induced potential differential of the Bi$_2$MoO$_6$/TiO$_2$ heterojunction [21–24]. A summary of Bi$_2$MoO$_6$-based photocatalysts and their photocatalytic performance is illustrated in Table S1 in the Supplementary Materials.

As is widely accepted, enhancement in the surface area could contribute to improving the photocatalytic performance because photodegradation is typically a surface-based process [25]. In this respect, one-dimensional (1D) nanomaterials, including nanowires, nanotubes, and nanorods, have attracted extensive attention because of their large aspect ratio, chemical stability, and unique geometrical morphologies, offering direct pathways for charge transport. On the one hand, nanomaterials with aligned 1D morphologies possess a short diffusion and transport path for holes, along with their radial directions. Simultaneously, their long axes are the preferred channels for electron transfer as well as optical scattering and adsorption [13,14]. Lindquist et al. [26] used Fe$_2$O$_3$ nanorod arrays as anodes in a photoelectrochemical (PEC) cell to address issues of the PEC system and improve its efficiency. Recent studies also demonstrated superior photocatalytic, photovoltaic, and PEC properties of the aligned 1D nanostructures in addition to their recyclable and reusable characteristics, unlike their bulk or randomly shaped (not aligned) counterparts [27–30]. On the other hand, nanomaterials with nanosheet morphologies could favor the adsorption of pollutants during photodegradation [31]. However, dispersed Bi$_2$MoO$_6$/TiO$_2$ nanoparticles have downsides owing to their tendency to agglomerate during the reaction and to the difficulty in separating and fully recovering them from the reaction mixture. Few studies have been published on HSs-containing Bi$_2$MoO$_6$ and 1D TiO$_2$ (Bi$_2$MoO$_6$/TiO$_2$ nanobelts, nanotubes, and nanorods) and their photocatalytic performance. Therefore, to further address and explore this topic, a strategy was developed to embed the photocatalytic species on a high surface area material [32,33]. In this context, we developed a simple hydrothermal/solvothermal method to synthesize HSs containing Bi$_2$MoO$_6$ nanosheets and TiO$_2$ nanorod arrays grown on an FTO surface in advance. The crystallinity, structure, morphology, band structure, and optical properties of these HSs were thoroughly analyzed. Our Bi$_2$MoO$_6$/TiO$_2$ HSs exhibited excellent photocatalytic activity in the visible-light region due to the combination of the Bi$_2$MoO$_6$ light-absorption and charge-separation efficiency of the Bi$_2$MoO$_6$/TiO$_2$ heterojunction.

2. Materials and Methods

2.1. Materials

All chemicals used in this study were of analytical grade, purchased from Sinopharm Chemical Reagent Co., Tianjing, China and used as received. FTO (SnO$_2$:F conducting glass), used as a substrate, was acquired from Kejing Materials Technology Co., Hefei, China. Deionized (DI) water, which was used throughout all experiments, was prepared in our laboratory using the water purifying system RC–K2 (Ruicheng Technology Co., Ltd., Beijing, China).

2.2. Preparation of TiO$_2$ Nanorod Arrays

TiO$_2$ nanorod arrays were grown on an FTO substrate hydrothermally [13,14]. First, a 1:1 (by volume) mixture of hydrochloric acid (HCl, AR, 36.0–38.0%) and DI water with
a specific Ti(OC₄H₉)₄ (AR, 98.0%) content was prepared. Then, the above solution was transferred to a Teflon pot, in which a rectangular piece of FTO, with the conducting layer facing down, was placed against the wall of the Teflon pot. Prior to the synthesis, the FTO was ultrasonicated in DI water, then in acetone, and finally in ethanol. The hydrothermal reaction was performed in a Teflon-lined, stainless-steel autoclave for 6 h at 453 K. The resulting product was TiO₂ nanorod arrays grown on the FTO pieces.

2.3. Synthesis of the Bi₂MoO₆/TiO₂ Composites

Bi₂MoO₆/TiO₂ composites were synthesized solvothermally [34–36]. The stepwise synthesis protocol is shown in Figure S1 in the Supplementary Materials. First, Bi(NO₃)₃·5H₂O (AR, 99.0%) and Na₂MoO₄·2H₂O (AR, 99.0%) (at 2:1 mole ratio) were dissolved in a mixture of ethylene glycol (EG, AR, 99.5%) and ethanol (C₂H₅OH, AR, 99.7%) (at 1:1 volume ratio) under constant stirring. Then, the resulting clear mixtures were placed into a 50 mL Teflon-lined, stainless-steel autoclave containing an FTO substrate coated with TiO₂ nanorod arrays. The reaction was conducted at 433 K for 14 h. Under these conditions, several Bi₂MoO₆/TiO₂ composites were prepared with different amounts of Bi₂MoO₆ by varying the mass of the raw materials, as shown in Table S2. The corresponding samples were marked as BMT-1, BMT-2, BMT-3, and BMT-4. In addition, pure Bi₂MoO₆ nanosheets (without TiO₂) were also synthesized under the same conditions.

2.4. Characterization

The phase structures of the as-prepared products were analyzed by X-ray diffraction (XRD) performed using a D8 Advance (Bruker Corp., Karlsruhe, Germany) instrument equipped with Cu Kα radiation as an X-ray source. The sample morphologies were inspected using scanning electron microscopy (SEM) performed with a JSM-7100F (Hitachi Corp., Tokyo, Japan) instrument. The elemental composition and valence-band potential (EᵥB) were obtained using X-ray photoelectron spectroscopy (XPS) performed with an ESCALAB 250 (Thermo Scientific (Shanghai) Corp., China) instrument equipped with Al Kα radiation as an X-ray source. The ultraviolet-visible (UV–Vis) absorption spectra were recorded by a UV2600 (Shimadzu (China) Corp., Shanghai, China) spectrophotometer. The Brunauer–Emmett–Teller (BET) specific surface areas (S.metro) and pore volume of the as-prepared samples were estimated from the nitrogen adsorption–desorption isotherms that were recorded by a nitrogen adsorption apparatus (ASAP 2020, Micromeritics Instruments Corp., Atlanta, GA, USA) at 77 K. Electron spin resonance (ESR) signals of the radicals’ spin were recorded by a E500 spectrometer (Bruker Corp., Karlsruhe, Germany). The 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was selected as a free radical scavenger to capture -OH and -O₂⁻ species. Photoluminescence (PL) emission spectra were measured at room temperature using a FluoTime-300 spectrophotometer (PicoQuant Co., Berlin, Germany) under a 325 nm laser as an excitation source.

2.5. Photocatalytic Activity

Methylene blue (MB) was used as a compound representing organic pollutants and other organic dyes. MB is chemically stable and difficult to decompose. The photocatalytic degradation was tested in a MB aqueous solution (1.0 × 10⁻⁵ mol·L⁻¹, 50 mL) using a 1 × 1 cm² FTO substrate containing the Bi₂MoO₆/TiO₂ HSs. A blank sample (without any catalysts) and TiO₂/FTO nanorod arrays were also used for comparison for the photocatalytic MB degradation experiments. AM 1.5 G simulated solar light (with 100 mW/cm² fluence) was provided by a 300 W Xe PLS-SXE300D (Perfectlight Technology Co., Beijing, China) lamp. Prior to the photocatalytic experiments, the aqueous solutions containing MB and photocatalysts were kept in the dark for 30 min to establish an adsorption/desorption equilibrium. Absorption spectra of MB aqueous solutions, at a wavelength of 664 nm, were collected using a UV–Vis spectrophotometer at specific intervals, which revealed the
changes in MB content after irradiation. The dye degradation efficiency was calculated by the formula below [37]:

\[ X = \frac{C}{C_0} \times 100\% \]

where \( C_0 \) and \( C \) are MB contents at times 0 and \( t \), respectively.

2.6. Assessment of PEC Performance

The PEC performance of our samples was tested using a CHI660E (Chenhua Instruments Inc., Shanghai, China) electrochemical workstation equipped with a three-electrode (Pt foil as a counter, calomel as a reference, and working electrodes) configuration. In addition, 0.5 M Na\(_2\)SO\(_4\) served as an electrolyte. The effective area of the working electrodes was 1.5 cm\(^2\). Electrochemical-impedance-spectroscopy (EIS) was performed with a 5 mV amplitude AC voltage in the 10 Hz–1 MHz range. Mott–Schottky plots of pure TiO\(_2\) and Bi\(_2\)MoO\(_6\) were recorded at 1000 Hz. The light source was the same as in the photocatalytic experiment.

3. Results and Discussion

3.1. X-ray Diffraction (XRD)

As shown in Figure 1, synthesized TiO\(_2\), Bi\(_2\)MoO\(_6\), and Bi\(_2\)MoO\(_6\)/TiO\(_2\) composite films possessed good crystallinity according to the XRD results. The XRD pattern revealed diffraction peaks at 36.2°, 54.3°, and 62.8°, attributed to (101), (211), and (002) crystal planes of rutile TiO\(_2\), respectively (PDF card number 21-1276). The XRD patterns of Bi\(_2\)MoO\(_6\)/TiO\(_2\) revealed TiO\(_2\) and FTO peaks, as well as peaks at 28.2°, 32.5°, 46.7°, and 55.5°, that were attributed to (131), (200)/(002), (202), and (133) planes of the orthorhombic koechlinite phase of Bi\(_2\)MoO\(_6\), according to PDF card number 76-2388. These results confirmed the formation of Bi\(_2\)MoO\(_6\)/TiO\(_2\) composites. XRD peaks of Bi\(_2\)MoO\(_6\) observed in the Bi\(_2\)MoO\(_6\)/TiO\(_2\) spectra became sharper and narrower as the initial Bi\(_2\)MoO\(_6\) amount was increased, while the XRD peaks of TiO\(_2\) became less intense. No other changes in the crystalloid structure were observed as the initial materials used were changed.

![XRD patterns of pristine TiO\(_2\)/FTO, Bi\(_2\)MoO\(_6\), and BMT-1, BMT-2, BMT-3, and BMT-4 samples.](image-url)
3.2. X-ray Photoelectron Spectroscopy (XPS)

XPS of the BMT-3 composites revealed the presence of Bi, Mo, Ti, and O elements (see Figure 2a). Some carbon was also observed due to environmental and instrument contamination. The high-resolution Bi 4f XPS spectrum showed two peaks at 158.0 and 163.3 eV (see Figure 2b), which were assigned to the spin-orbit splitting peaks of Bi 4f7/2 and Bi 4f5/2, respectively [38]. Thus, Bi in Bi2MoO6/TiO2 existed as Bi3+. Two strong peaks at 232.3 and 235.5 eV, corresponding to Mo 3d5/2 and Mo 3d3/2 spin-orbit components of Mo6+, respectively [39] (see Figure 2c), were observed in the high-resolution Mo 3d XPS spectrum. The peaks at 457.5 and 463.2 eV matched the binding energies of Ti 2p3/2 and Ti 2p1/2 states, respectively (see Figure 2d). Thus, Ti was present as Ti4+ in the Bi2MoO6/TiO2 composites. The fitting of the high-resolution O 1s XPS spectrum revealed three peaks at 528.9, 529.4, and 531.1 eV (see Figure 2e), which corresponded to Bi-O, Mo-O, and Ti-O bonds, respectively [22,38]. Thus, these results confirmed the coexistence of Bi2MoO6 and TiO2 in the synthesized HSs.

Figure 2. (a) XPS fully scanned spectrum of the BMT-3 composite, and high-resolution XPS of (b) Bi 4f, (c) Mo 3d, (d) Ti 2p, and (e) O 1s. The circle symbol represent the experimental data, the black lines represent the fitting curves, and the colored lines represent the multimodal fitting curves.
3.3. Morphologies

SEM showed that the diameters of the bare TiO$_2$ nanorods were 200 nm (see Figure 3a). Moreover, the nanorods were vertically aligned and uniformly distributed on the FTO substrate. Pure Bi$_2$MoO$_6$ nanosheets exhibited laminar and irregular, sheet-like morphology (see Figure 3b). SEM of the Bi$_2$MoO$_6$/TiO$_2$ composites showed that some Bi$_2$MoO$_6$ nanosheets adhered to the TiO$_2$ nanorods (see Figure 3c–f). Additionally, as the initial Bi/Mo content was increased, the Bi$_2$MoO$_6$ nanosheets increased in number and began to aggregate. The sample (BMT-3, shown in Figure 3e) with appropriate initial Bi/Mo content showed the growth of dispersed Bi$_2$MoO$_6$ nanosheets around TiO$_2$ nanorods. Instead, a serious agglomeration of Bi$_2$MoO$_6$ was observed, as shown in Figure 3f. These findings suggest that the initial concentration of the materials used significantly affected the Bi$_2$MoO$_6$/TiO$_2$ composite morphology.

![Figure 3. SEM images of (a) pristine TiO$_2$ nanorod arrays, (b) pure Bi$_2$MoO$_6$ nanosheets, and Bi$_2$MoO$_6$/TiO$_2$ composites denoted as (c) BMT-1, (d) BMT-2, (e) BMT-3, and (f) BMT-4.](image-url)
It is widely known that the photocatalytic activity of catalysts is significantly influenced by the specific surface area and pore volume of photocatalysts due to the presence of surface-reactive sites [40]. The nitrogen adsorption–desorption isotherms of the TiO$_2$, Bi$_2$MoO$_6$, BMT-3, and BMT-4 samples are shown in Figure S2 in the Supplementary Materials. The similar adsorption–desorption curves revealed strong N$_2$ adsorption–desorption performance, which indicated the existence of capillary condensation in the large mesopores in the samples. The $S_{BET}$ and pore volume of TiO$_2$, Bi$_2$MoO$_6$, BMT-3, and BMT-4 HSs are listed in Table S3. Interestingly, the coupling of TiO$_2$ and Bi$_2$MoO$_6$ significantly increased the $S_{BET}$ and pore volume (the maximum value for BMT-3 are 88.2 m$^2$/g and 0.18 cm$^3$/g, respectively) compared to the pure Bi$_2$MoO$_6$ (26.0 m$^2$/g and 0.05 cm$^3$/g, respectively). Combined with the photocatalytic experiment results we can deduce that the high $S_{BET}$ and pore volume of BMT-3 played significant roles in enhancing photocatalytic performance.

3.4. Optical Properties

The UV–Vis spectra of TiO$_2$ nanorod arrays showed that they were adsorbed, as expected, in the ultraviolet region at 400 nm (see Figure 4a), which is mainly accounted for by absorption within the rutile band-gap [41]. The absorption intensity of Bi$_2$MoO$_6$ was relatively mild and peaked at ~450 nm. Thus, a slight extension to the visible-light region was observed in comparison to TiO$_2$. The absorption edges of the Bi$_2$MoO$_6$/TiO$_2$ composites exhibited a certain degree of red-shift, which indicates the extension of the material’s absorption towards visible light. The band-gap energies of the TiO$_2$, Bi$_2$MoO$_6$, and Bi$_2$MoO$_6$/TiO$_2$ HSs were calculated from the Kubelka–Munk function, plotted against the photon energy (see Figure 4b). The band-gap values of TiO$_2$ and Bi$_2$MoO$_6$ were equal to 3.1 and 2.77 eV, respectively. Moreover, the band-gap values of the BMT-1, BMT-2, BMT-3, and BMT-4 composites were 2.88, 2.85, 2.81, and 2.79 eV, respectively. Furthermore, the photogenerated electron-hole pairs were excited due to the extension of absorption into the visible-light region, favoring enhanced PEC and photocatalytic performance.

Figure 4. (a) UV–Vis absorption spectra: (b) Kubelka–Munk plots of pristine TiO$_2$ nanorod arrays, pure Bi$_2$MoO$_6$, and Bi$_2$MoO$_6$/TiO$_2$ composites; and (c) PL spectra of TiO$_2$ and Bi$_2$MoO$_6$/TiO$_2$ HSs photocatalysts.
Photoluminescence (PL) emission spectra have been widely employed to reveal the separation efficiency of the photo-induced electrons and holes in the composite semiconductors [42]. The PL spectra of the as-prepared TiO$_2$, BMT-3, and BMT-4 samples in the present study are shown in Figure 4c. The strongest emission intensity peak observed in pure TiO$_2$ nanorods corresponded to the band-gap transition. A significant decrease in fluorescence of Bi$_2$MoO$_6$/TiO$_2$ (BMT-3 and BMT-4) was observed, indicating a lower photoelectron-hole recombination in Bi$_2$MoO$_6$/TiO$_2$ than in TiO$_2$. Moreover, the similar fluorescence intensity of BMT-3 and BMT-4 indicated similar separation performance of the photo-induced electrons and holes in the BMT-3 and BMT-4 samples. The migration and recombination efficiencies of the photo-induced carriers in all samples were further revealed by EIS characterization.

3.5. Photocatalytic Properties

The relationship between residual MB contents and irradiation time, with and without photocatalyst, is shown in Figure 5a. Figure 5b shows the fitting curves of the kinetics of MB photodegradation. The degradation of MB in the presence of TiO$_2$ and Bi$_2$MoO$_6$/TiO$_2$ obeyed the pseudo-first-order kinetics and could be expressed as $\ln(C/C_0) = k(t-t_0)$, where $k$ is the reaction rate constant [43,44]. The rate constants and the corresponding correlation coefficients (R-Square) of different photocatalysts and the blank sample are given in Table S4, which were calculated by linear fitting $-\ln(C/C_0)$ to irradiation time ($t$). The values of R-Square are close to 1, which reveal a good correlation to the pseudo-first-order reaction kinetics. MB degradation without catalysts was negligible under visible light, with a $k$ value of 0.000538 min$^{-1}$ (see Figure 5b). In contrast, the reaction rate constant of MB decomposition in the presence of TiO$_2$ nanorods was 0.00113 min$^{-1}$, which was attributed to the photon-trapping effect caused by the morphology of the TiO$_2$ nanostructure [13,14]. However, the photocatalytic performances of the Bi$_2$MoO$_6$/TiO$_2$ HSs were significantly better. Thus, the presence of Bi$_2$MoO$_6$ in the composite played a significant role. The photocatalytic ability of Bi$_2$MoO$_6$/TiO$_2$ (BMT-4) was lower for samples with higher Bi$_2$MoO$_6$ content because of the recombination of the photogenerated electron-hole pairs inside the numerous Bi$_2$MoO$_6$ nanosheets [44]. From the viewpoint of practical application, it is important to evaluate the stability of the as-prepared catalyst. Comparison of the XRD pattern of the Bi$_2$MoO$_6$/TiO$_2$ (BMT-3) before and after the photocatalytic reaction (performed three times with the same catalyst) showed that, even after three cycles, the positions and intensities of the XRD peaks remained almost the same (Figure 5c), which confirmed the excellent stability of the Bi$_2$MoO$_6$/TiO$_2$ composite catalysts. The stable activity was further validated by repeating the photocatalytic degradation processes thrice, as shown in Figure 5d. The three degradation curves showed a similar trend in each running cycle, which indicated that the Bi$_2$MoO$_6$/TiO$_2$ photocatalyst exhibited high and stable activity for degradation.

To investigate the mechanisms underlying the photo-oxidation ability, ESR technology was used to detect active free radicals. The ESR signals of BMT-3 dispersed in the DMPO solution are shown in Figure S3. No ·OH ESR signals were generated in darkness; however, a set of four feature peaks with an intensity ratio of 1:2:2:1 were observed after light illumination (see Figure S3a), attributed to DMPO-·OH adducts. Similarly, no ·O$_2^-$ signals were generated in the dark, and six peaks of DMPO-·O$_2^-$ were observed in the ESR spectra (see Figure S3b) with illumination. These results demonstrated that ·O$_2^-$ and ·OH are both active species, and their synergistic effect significantly promoted the photocatalytic degradation of MB.
In contrast, the reaction rate stability of the combination of the photogenerated electron-hole pairs inside the numerous nanorod arrays and Bi$_2$MoO$_6$ HSs was significantly better. Thus, the presence of these nanostructures played a significant role. The photocatalytic ability of Bi$_2$MoO$_6$/TiO$_2$ HSs was attributed to the photon trapping effect caused by the morphology of the nanosheets and the amount of Bi$_2$MoO$_6$ in the composite played a critical role. The amount of Bi$_2$MoO$_6$ in the BMT-3 sample exhibited optimal stability and reproducibility due to the presence of Bi$_2$MoO$_6$/TiO$_2$ HSs. The heterojunction of the Bi$_2$MoO$_6$/TiO$_2$ HSs showed a reverse ZnO type and its interfacial interaction with TiO$_2$, which enhanced the separation and transfer efficiency of the electron-hole pairs photogenerated in the Bi$_2$MoO$_6$/TiO$_2$ HSs. The heterojunction of the Bi$_2$MoO$_6$/TiO$_2$ interface suppressed the charge recombination, thereby producing more (re)active species, which resulted in a high photocurrent response and photocatalytic activity.

3.6. PEC Analysis

The PEC performance of the Bi$_2$MoO$_6$/TiO$_2$ HSs was compared to that of pure TiO$_2$ nanorod arrays and Bi$_2$MoO$_6$. For this purpose, we recorded the photocurrent as a function of time ($I$–$t$ curves) by alternating exposure to darkness and visible light (see Figure 6a). All samples exhibited similar photocurrent responses. No photocurrent was observed in the dark, which confirmed the absence of any electrochemical processes. A minimal photocurrent response was observed for the TiO$_2$ nanorod array, and a significant one for the Bi$_2$MoO$_6$/TiO$_2$ HSs. The BMT-3 sample exhibited optimal stability and reproducibility of the photocurrent response since the Bi$_2$MoO$_6$/TiO$_2$ HSs, and the amount of Bi$_2$MoO$_6$ was the most favorable out of all the BMT samples. The separation and collection efficiency of interface charges were further studied by EIS (see Figure 6b). Typically, the semicircles in the corresponding Nyquist plots corresponded to Faradic reactions. It has been established that the semicircle radius is negatively correlated with the charge transfer efficiency [45,46]. In our study, the semicircle diameters for the Bi$_2$MoO$_6$/TiO$_2$ HSs were significantly smaller than those obtained for Bi$_2$MoO$_6$ and TiO$_2$. This data confirms the lower interfacial charge-transfer resistance and fast charge-transfer process of our composite Bi$_2$MoO$_6$/TiO$_2$ HSs due to the presence of Bi$_2$MoO$_6$ and its interfacial interaction with TiO$_2$, which enhanced the separation and transfer efficiency of the electron-hole pairs photogenerated in the Bi$_2$MoO$_6$/TiO$_2$ HSs. The heterojunction of the Bi$_2$MoO$_6$/TiO$_2$ interface suppressed the charge recombination, thereby producing more (re)active species, which resulted in a high photocurrent response and photocatalytic activity.
light illumination (see Figure S3a), attributed to DMPO·OH adducts. Similarly, no signals were generated in the dark, which confirmed the absence of an interface charge recombination, thereby producing more (re)active species, which resulted in a high photocatalytic degradation of MB.

The PEC performance of Bi$_2$MoO$_6$/TiO$_2$ HSs was investigated. Mott–Schottky plots revealed the flat-band potential of TiO$_2$ and Bi$_2$MoO$_6$ (Figure 6c). A gap between $E_{VB}$ and flat-band potential can be inferred from the XPS–valance band (XPS–VB) plots, as shown in Figure S4. Thus, the calculated $E_{VB}$ values of TiO$_2$ and Bi$_2$MoO$_6$ were 2.4 and 1.68 V, respectively. Moreover, the conduction band potential ($E_{CB}$) of TiO$_2$ and Bi$_2$MoO$_6$ were calculated to be −0.7 and −1.09 V, respectively. Based on these results, the band alignment of the Bi$_2$MoO$_6$/TiO$_2$ was established, as shown in Figure 7. The $E_{CB}$ and $E_{VB}$ of TiO$_2$ were more positive than those of Bi$_2$MoO$_6$. Accordingly, it is highly likely that Bi$_2$MoO$_6$/TiO$_2$ HSs possess staggered band

**Figure 6.** (a) The transient photocurrent response; (b) Nyquist plots of pristine TiO$_2$, Bi$_2$MoO$_6$, and Bi$_2$MoO$_6$/TiO$_2$; (c) Mott–Schottky plots of pristine TiO$_2$ and Bi$_2$MoO$_6$.

The Mott–Schottky plots of TiO$_2$ and Bi$_2$MoO$_6$ are shown in Figure 6c. The positive slopes of both compounds imply that they are n-type semiconductors. The flat-band potential ($V_{fb}$) can be calculated by the Mott–Schottky equation [42]:

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N_d} \left[ (V - V_{fb}) - \frac{kT}{e} \right]$$

where $C$ is the capacitance at the interface with the electrolyte, $e$ is the electronic charge, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon$ is the sample dielectric constant, $N_d$ is the charge-carrier concentration, $V$ and $V_{fb}$ are the applied and flat-band potentials, $k$ is the Boltzmann’s constant, and $T$ is the temperature [47]. The $V_{fb}$ could be calculated from the intercept of the $1/C^2$ curve (plotted as a $V$ function) with the $x$-axis [48]. The $V_{fb}$ values for the pure TiO$_2$ and Bi$_2$MoO$_6$ were equal to −0.35 and −0.58 V (vs. a normal hydrogen electrode, NHE), respectively.

### 3.7. Energy Band Alignment and Photocatalytic Mechanism

In order to explain the photocatalytic process, the energy band alignment of the Bi$_2$MoO$_6$/TiO$_2$ HSs was investigated. Mott–Schottky plots revealed the flat-band potential of TiO$_2$ and Bi$_2$MoO$_6$ (Figure 6c). A gap between $E_{VB}$ and flat-band potential can be inferred from the XPS–valance band (XPS–VB) plots, as shown in Figure S4. Thus, the calculated $E_{VB}$ values of TiO$_2$ and Bi$_2$MoO$_6$ were 2.4 and 1.68 V, respectively. Moreover, the conduction band potential ($E_{CB}$) of TiO$_2$ and Bi$_2$MoO$_6$ were calculated to be −0.7 and −1.09 V, respectively. Based on these results, the band alignment of the Bi$_2$MoO$_6$/TiO$_2$ was established, as shown in Figure 7. The $E_{CB}$ and $E_{VB}$ of TiO$_2$ were more positive than those of Bi$_2$MoO$_6$. Accordingly, it is highly likely that Bi$_2$MoO$_6$/TiO$_2$ HSs possess staggered band
alignment. Visible-light irradiation excites Bi$_2$MoO$_6$ molecules, generating electron-hole pairs. At the same time, a large band-gap prevents TiO$_2$ molecules from being excited by visible-light irradiation. In this case, the electrons travel from the conduction band of the Bi$_2$MoO$_6$ to TiO$_2$, which suppresses electron-hole pair recombination by the internal field of the Bi$_2$MoO$_6$/TiO$_2$ heterojunction since the $E_{CB}$ of Bi$_2$MoO$_6$ is relatively more negative. The separated electrons can react with O$_2$ molecules, forming $\cdot$O$_2^-$ radicals since the corresponding redox potential is equal to $-0.046$ V and more positive than the $E_{CB}$ of TiO$_2$. Subsequently, the H$_2$O molecules are transformed into $\cdot$OH radicals after trapping an electron. Both photogenerated holes, together with $\cdot$O$_2^-$ and $\cdot$OH radicals, can react with MB molecules, damaging their structures. We believe that this process, based on the interfacial charge transfer, is indeed feasible. The reaction mechanism and chemical equations of the above processes are proposed as follows and can be found in the previous literature [23,38,49,50].

$$\text{Bi}_2\text{MoO}_6 + \text{hv} \rightarrow \text{Bi}_2\text{MoO}_6 (e^- + h^+)$$

$$\text{Bi}_2\text{MoO}_6 (e^- + h^+) + \text{TiO}_2 \rightarrow \text{Bi}_2\text{MoO}_6 (h^+) + \text{TiO}_2 (e^-)$$

$$\text{TiO}_2 (e^-) + \text{O}_2 \rightarrow \text{TiO}_2 + \cdot \text{O}_2^-$$

$$\cdot \text{O}_2^- + \text{H}_2\text{O} \rightarrow \cdot \text{HO}_2 + \text{OH}^-$$

$$\cdot \text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \cdot \text{OH}$$

$$\text{H}_2\text{O}_2 \rightarrow 2 \cdot \text{OH}$$

$$\text{Bi}_2\text{MoO}_6 (h^+) + \text{MB} \rightarrow \text{degraded products}$$

$$\cdot \text{O}_2^- + \text{MB} \rightarrow \text{degraded products}$$

$$\cdot \text{OH} + \text{MB} \rightarrow \text{degraded products}$$

Figure 7. The band structures of the Bi$_2$MoO$_6$/TiO$_2$ HSs and postulated photocatalytic mechanism of dye degradation.
4. Conclusions

In summary, the Bi$_2$MoO$_6$/TiO$_2$ HSs were synthesized through a simple two-step solvothermal process by growing Bi$_2$MoO$_6$ nanosheets on TiO$_2$ nanorod arrays. The Bi$_2$MoO$_6$/TiO$_2$ HSs exhibited enhanced photocatalytic activity for MB degradation under visible-light irradiation, and BMT-3 achieved the highest degradation rate of $k = 0.015$ min$^{-1}$ among all samples. The enhancement was attributed to the heterojunction structures established by the close contact between the Bi$_2$MoO$_6$ nanosheets and the TiO$_2$ nanorods. The results of the UV–Vis absorption spectra show an extended absorption to visible light after coupling Bi$_2$MoO$_6$ with TiO$_2$. The results of N$_2$ adsorption–desorption isotherms show a significantly increased $S_{BET}$ and pore volume compared to the pure Bi$_2$MoO$_6$ due to the hierarchical structure of the Bi$_2$MoO$_6$/TiO$_2$ HSs. The results of PL and PEC characterization of the Bi$_2$MoO$_6$/TiO$_2$ HSs reveal improved separation efficiency and enhanced migration rate of photogenerated electron-hole pairs. Thus, the synergy between Bi$_2$MoO$_6$ and TiO$_2$ was identified as the crucial factor leading to the improved photocatalytic performance. Furthermore, the reusability and chemical stability of Bi$_2$MoO$_6$/TiO$_2$ HSs is demonstrated by photocatalytic cycle test. Finally, the mechanism and process of the dye photodegradation were discussed. The $h^+\cdot O_2^-$, and $\cdot$OH radicals were validated as being active species that react with MB dye molecules. The results of this work suggest that Bi$_2$MoO$_6$/TiO$_2$ HSs are promising candidate materials for wastewater treatment. Collectively, our current strategy can help in the synthesis and photocatalytic application of other heterostructures in the future.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12030574/s1. Table S1: Bi$_2$MoO$_6$-based photocatalysts and their photocatalytic performance; Table S2: The abbreviations of products with different amounts of Bi$_2$MoO$_6$ by varying the mass of raw materials in precursor solution; Table S3: $S_{BET}$, Pore Volume, and Mean Pore Diameter of TiO$_2$, Bi$_2$MoO$_6$, BMT-3, and BMT-4 samples; Table S4: Pseudo-first-order rate constants and corresponding R-Square values of different samples; Figure S1: Stepwise synthesis protocol of TiO$_2$ nanorod arrays and Bi$_2$MoO$_6$/TiO$_2$ HSs; Figure S2: N$_2$ adsorption–desorption isotherms (a) and the corresponding pore-size distribution curves (b) of TiO$_2$, Bi$_2$MoO$_6$, BMT-3, and BMT-4 samples; Figure S3: The ESR signals of $\cdot$OH (a) and $\cdot$O$_2^-$ radicals (b) of BMT-3 photocatalysts; Figure S4: XPS valence-band spectra of TiO$_2$ and Bi$_2$MoO$_6$.

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