 Preparation of \( \text{Ag}_3\text{PO}_4/\text{TiO}_2(\text{B}) \) Heterojunction Nanobelt with Extended Light Response and Enhanced Photocatalytic Performance

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Abstract: Photocatalytic degradation, as an emerging method to control environmental pollution, is considered one of the most promising environmental purification technologies. As Tibet is a region with some of the strongest solar radiation in China and even in the world, it is extremely rich in solar energy resources, which is ideal for applying photocatalytic technology to its ecological environment protection and governance. In this study, \( \text{Na}_2\text{Ti}_3\text{O}_7 \) nanobelts were prepared via a hydrothermal method and converted to \( \text{TiO}_2 \cdot x\text{H}_2\text{O} \) ion exchange, which was followed by high-temperature calcination to prepare \( \text{TiO}_2(\text{B}) \) nanobelts (“B” in \( \text{TiO}_2(\text{B}) \) means “Bronze phase”). A simple in situ method was used to generate \( \text{Ag}_3\text{PO}_4 \) particles on the surface of the \( \text{TiO}_2 \) nanobelts to construct a \( \text{Ag}_3\text{PO}_4/\text{TiO}_2(\text{B}) \) heterojunction composite photocatalyst. By generating \( \text{Ag}_3\text{PO}_4 \) nanoparticles on the surface of the \( \text{TiO}_2(\text{B}) \) nanobelts to construct heterojunctions, the light absorption range of the photocatalyst was successfully extended from UV (ultraviolet) to the visible region. Furthermore, the recombination of photogenerated electron–hole pairs in the catalyst was inhibited by the construction of the heterojunctions, thus greatly enhancing its light quantum efficiency. Therefore, the prepared \( \text{Ag}_3\text{PO}_4/\text{TiO}_2(\text{B}) \) heterojunction composite photocatalyst greatly outperformed the \( \text{TiO}_2(\text{B}) \) nanobelt in terms of photocatalytic degradation.

Keywords: photocatalyst; heterojunction; photocatalytic degradation; \( \text{TiO}_2(\text{B}) \) nanobelts

1. Introduction

The Qinghai–Tibet Plateau is the ecological security barrier of China and the origin of many rivers in China and South Asia. Therefore, it is of great significance to protect and manage its ecological environment [1–3]. As an emerging environmental pollution control technology, photocatalytic degradation is considered one of the most promising environmental purification technologies at present because of its advantages of mild reaction conditions, low secondary pollution, sustainability, and environmental friendliness [4–7]. Since Tibet is one of the regions with the strongest solar radiation in China and even the world, the abundant energy resource is ideal for applying photocatalytic technology to ecological environment protection and governance in Tibet [8–10]. \( \text{TiO}_2 \) is recognized as one of the best photocatalyst materials with stable properties, low cost, ease of access, non-toxicity and safety, and good resistance to photocorrosion. However, \( \text{TiO}_2 \) has a band gap as large as 3.2 eV and hence is photocatalytically active only under UV light, which
accounts for merely approximately 5% of solar radiation energy. Therefore, TiO₂ as a photocatalyst has a low utilization of solar radiation energy and insignificant photocatalytic performance [11–13]. However, combining TiO₂ with other narrow-band-gap semiconductor materials to construct heterojunctions can effectively enhance the photocatalytic performance of TiO₂. This is because, first, the introduction of narrow-band-gap semiconductors can extend the light-absorption range of TiO₂ from the UV region to the visible region, greatly increasing the material’s absorption range of the solar spectrum; second, the construction of heterojunctions can effectively promote the separation of photogenerated electrons and holes, thereby improving the quantum yield of photogenerated carriers participating in photocatalytic redox reactions [13–15]. Current studies show that the use of Ag₃PO₄ compounded with TiO₂ can effectively enhance TiO₂ photocatalytic performance, but most studies use common anatase phase TiO₂ [16–19], and monoclinic (space group C2/m) TiO₂(B) has rarely been studied, while TiO₂(B) has better electrical conductivity, a sparse porous structure, and stronger photogenerated hole oxidation, and these properties make it possible for TiO₂(B) to obtain stronger photocatalytic performance by compounding [20–23]. In this study, Na₂Ti₃O₇ nanobelts were successfully prepared via hydrothermal methods and further used as a precursor for ion exchange with H⁺ in 0.1 M dilute HCl to obtain TiO₂ hydrate, which was dried and calcined to obtain TiO₂(B) nanobelts. Throughout the preparation process, the morphology of the Na₂Ti₃O₇ nanobelts was maintained. Na₂Ti₃O₇ had good adsorption properties, as did TiO₂(B) with the same morphology, which was beneficial to its absorption of sunlight and photocatalytic degradation performance. Finally, Ag₃PO₄ nanoparticles were generated on the surface of the TiO₂(B) nanobelts via a simple in situ method, thereby successfully constructing Ag₃PO₄/TiO₂(B) heterojunctions, which substantially enhanced the photocatalytic degradation performance of TiO₂(B).

2. Results and Discussion

Figure 1a,b present SEM (Scanning Electron Microscope) images of Na₂Ti₃O₇ and the TiO₂(B) nanobelt, respectively, which show that they had the same morphology and were both belt-like. Therefore, TiO₂(B) prepared from Na₂Ti₃O₇ using the experimental method in this study was able to well-maintain the morphology of Na₂Ti₃O₇. Figure 1c shows EDS (Energy-Dispersive X-Ray Spectroscopy Spectra) of Na₂Ti₃O₇; Na, O, and Ti appear in the spectra, which verifies the chemical composition of the prepared product. Figure 1d shows EDS spectra of TiO₂(B); O and Ti appear in the spectra, which verifies the chemical composition of the prepared product. Figure 1e shows XRD (X-Ray Diffraction) patterns of TiO₂, the analysis of which revealed that the TiO₂(B) nanobelts prepared in this experiment did not belong to the rutile, anatase, or brookite phases common to TiO₂ in nature, but they did belong to a monoclinic crystal system (space group C2/m).

Figure 2a presents TEM (Transmission Electron Microscopy) diffraction patterns of the TiO₂(B) nanobelts, and Figure 2b shows the diffraction spots of crystal planes (0 2 0), (0 2 0), (6 0 3), and (6 0 3) as calculated using the crystal structure data measured via XRD. Comparing the two images revealed that the measured and theoretically calculated results were in good agreement. In addition, the regular lattice pattern of the diffraction spots also indicated a high crystallinity of the prepared TiO₂ nanobelts. This is also confirmed by Figure 2d, which clearly shows a uniform distribution of TiO₂ grains. Figure 2c shows that the (0 2 0) crystal planes were uniformly arranged with a measured crystal plane spacing of 0.188 nm, which agreed very well with that measured via XRD. The above TEM test analysis further confirmed that the crystal structure of the TiO₂(B) nanobelts did not belong to the rutile, anatase, or brookite phases of TiO₂ that are common in nature but was a new phase of TiO₂ that is not commonly found in nature.
Figure 1. (a) SEM image of Na$_2$TiO$_7$ nanobelt; (b) SEM image of TiO$_2$ nanobelt; (c,d) EDS spectra of TiO$_2$ and Na$_2$Ti$_3$O$_7$ nanobelt; (e) XRD patterns of TiO$_2$. EDS, energy-dispersive X-ray spectroscopy.

Figure 2. Cont.
Figure 2. (a,b) Diffraction patterns of TiO$_2$(B) nanobelt; (c,d) HRTEM (High-Resolution Transmission Electron Microscopy) images of TiO$_2$(B) nanobelt.

Figure 3 shows XRD patterns of the samples. The phases of the TiO$_2$(B) nanobelts and prepared Ag$_3$PO$_4$ are analyzed in the left panel of Figure 3, with the standard powder diffraction file (PDF) cards PDF#06-0505 and PDF#46-1237, corresponding to Ag$_3$PO$_4$ and TiO$_2$(B), respectively. It can be clearly seen from the diffraction patterns that the crystallinity of Ag$_3$PO$_4$ was significantly better than that of the TiO$_2$(B) nanobelts, and the diffraction peaks of Ag$_3$PO$_4$ corresponded very well to the standard PDF card. The right panel of Figure 3 shows XRD diffraction patterns of the composites of Ag$_3$PO$_4$ and TiO$_2$(B) with different molar ratios. There were very obvious diffraction peaks of Ag$_3$PO$_4$ in the composites, and the relative intensity of the peaks did not change significantly with the increase in the molar ratio of Ag$_3$PO$_4$. Among the diffraction peaks of TiO$_2$(B), only the strongest diffraction peak, corresponding to the (110) plane, was weakly reflected in the composite, and it weakened with the increase in the molar ratio of Ag$_3$PO$_4$.

Figure 3. (a) XRD patterns of Ag$_3$PO$_4$ and TiO$_2$(B); (b) XRD patterns of Ag$_3$PO$_4$/TiO$_2$(B) with different molar ratios.
Figure 4 shows SEM and mapping images of the Ag$_3$PO$_4$/TiO$_2$(B) composite, where Figure 4a shows a SEM image when the molar ratio of Ag$_3$PO$_4$ to TiO$_2$ was 0.4:1, and Figure 4b shows the SEM image when the molar ratio increased to 1.5:1. The Ag$_3$PO$_4$ particles were clearly attached to the surface of belt-like TiO$_2$(B), and the number of Ag$_3$PO$_4$ particles increased as the molar ratio of Ag$_3$PO$_4$ increased. EDS mapping (Figure 4c–f) showed that the sample contained Ti, O, Ag, and P elements, which were uniformly distributed in the area where the composite was located, indicating that the composite contained Ag$_3$PO$_4$ and TiO$_2$(B), and the two were distributed relatively uniformly.

The left panel of Figure 5 shows the photocatalytic degradation curves of RhB solution by Ag$_3$PO$_4$/TiO$_2$(B) composites with different molar ratios. It can be seen that the TiO$_2$(B) nanobelts degraded RhB slowly, and the degradation rate was less than 20% after 30 min of degradation. After combining with Ag$_3$PO$_4$, the photocatalytic degradation of RhB by the composite product was improved, particularly when increasing the molar ratio of Ag$_3$PO$_4$. When the molar ratio of Ag$_3$PO$_4$ to TiO$_2$(B) increased to 1.5:1, within 30 min, the composite photocatalyst achieved nearly 100% degradation of RhB, and the photocatalytic performance increased by nearly five times, which was much higher than the photocatalytic degradation performance of commercial P$_{25}$. The right panel of Figure 5 shows actual photographs of the color change of RhB solution due to photocatalytic degradation by Ag$_3$PO$_4$/TiO$_2$(B) composites with different molar ratios. These photographs visually demonstrate the rapid enhancement of the photocatalytic performance of the composite with the increase in the molar ratio of Ag$_3$PO$_4$. The Ag$_3$PO$_4$/TiO$_2$(B) composite was obtained on the surface of the TiO$_2$(B) nanobelts through the in situ growth of Ag$_3$PO$_4$. 

Figure 4. (a,b) SEM images of Ag$_3$PO$_4$/TiO$_2$ composite; (c) The SEM image corresponding to map; (d) Map of Ti; (e) Map of O; (f) Map of Ag; (g) Map of P.
crystal grains. Compared with that of the TiO$_2$(B) nanobelts, the photocatalytic performance of the composite increased rapidly with the increase in the molar ratio of Ag$_3$PO$_4$. When the molar ratio of Ag$_3$PO$_4$ to TiO$_2$(B) reached 1.5:1, the photocatalytic performance of the composite far exceeded (was nearly five times) that of the pure TiO$_2$(B) nanobelt. We believe that the enhancement of the photocatalytic ability of the composite was, first, due to the introduction of Ag$_3$PO$_4$, which greatly expanded the absorption range of the material within the solar spectrum and enhanced the absorption of visible light [24–26] and, second, because of the construction of heterojunctions, which promoted the separation of photogenerated electron–hole pairs and inhibited their recombination [27–29]. In addition, it can be seen from the mapping results that the two substances constructed heterojunctions that were highly uniformly distributed, which gave full play to their role in the composite.

Figure 5. Photocatalytic degradation curves and images of Ag$_3$PO$_4$/TiO$_2$ composite.

Figure 6 shows the absorbance curves of the samples against a continuous spectrum. This test investigated the variation curves of absorbance of the TiO$_2$(B) nanobelts and Ag$_3$PO$_4$ in the visible region (wavelength > 400 nm). It was obvious that the light-absorption ability of Ag$_3$PO$_4$ was significantly higher than that of the TiO$_2$(B) nanobelts in the visible region. After the TiO$_2$(B) nanobelts and Ag$_3$PO$_4$ formed a composite, its visible-light-absorption ability was enhanced to some extent compared with that of the TiO$_2$(B) nanobelts, indicating that the introduction of Ag$_3$PO$_4$ enhanced the visible light absorption ability of the composite.

Figure 6. Continuous spectra of absorbance of synthesized samples.
To investigate the recombination and migration of photogenerated electrons before and after the combination of Ag$_3$PO$_4$ and TiO$_2$(B), we tested their PL (photoluminescence) spectra and photocurrent curves, respectively, as shown in Figure 7. As can be clearly seen from the PL spectrum in the left panel of Figure 7, the peaks of the PL lines of the TiO$_2$(B) nanobelts were the strongest, while the peaks of the PL lines of the composite decreased rapidly with the increase in the molar ratio of the added Ag$_3$PO$_4$. Stronger fluorescence reflects an easier recombination of the photogenerated electron–hole pairs of the substance, making it difficult for the photogenerated electron–hole pairs to migrate to the surface of the catalyst to participate in the photocatalytic redox reaction, which is not conducive to the performance of photocatalysis [30–32]. The right panel of Figure 7 shows the photocurrent curves of the samples. The photocurrents of pure TiO$_2$(B) nanobelts and Ag$_3$PO$_4$ nanoparticles were the lowest. In comparison, the photocurrent of Ag$_3$PO$_4$/TiO$_2$(B) composite was enhanced and increased continuously with the increase in the molar ratio of Ag$_3$PO$_4$, reaching a maximum when the molar ratio of Ag$_3$PO$_4$ was increased to 1.5:1. These two sets of curves well explained the underlying reason for the variation pattern of photocatalytic performance in Figure 5 and also indirectly proved that Ag$_3$PO$_4$ nanoparticles grown on the surface of TiO$_2$(B) nanobelts through our simple in situ method indeed successfully constructed a Ag$_3$PO$_4$/TiO$_2$(B) heterojunction composite, effectively promoting the separation of photogenerated charges and thereby enhancing the photocatalytic performance of the composite catalyst.

![Figure 7. PL and photocurrent spectra of synthesized samples.](image)

3. Materials and Experiment

3.1. Materials

Regarding the chemicals used in the experiment, NaOH and nano-TiO$_2$ were purchased from Aladdin Industries, Inc. (Shanghai, China), Na$_2$HPO$_4$·12H$_2$O from Chengdu Jinshan Chemical Reagent Co., Ltd. (Chengdu, China), AgNO$_3$ from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and Rhodamine B (RhB, C$_{28}$H$_{31}$ClN$_2$O$_3$) from Beijing Solarbio Technology Co., Ltd. (Beijing, China). All the reagents were analytically pure and used without further purification.

3.2. Preparation of TiO$_2$(B) Nanobelt, Ag$_3$PO$_4$, and Ag$_3$PO$_4$/TiO$_2$(B)

Nano-TiO$_2$ (1 g) was added to 100 mL of 10 M NaOH aqueous solution, stirred evenly, poured into a 150 mL hydrothermal reactor, heated to 200 °C, and held for 24 h before cooling naturally. Then, the reaction product was taken out of the reactor and rinsed with a large amount of deionized (DI) water to a nearly neutral pH, which was followed by vacuum filtration and drying to obtain the Na$_2$Ti$_5$O$_7$ nanobelts. After that, Na$_2$Ti$_5$O$_7$ was soaked in 0.1 M dilute HCl for 72 h to allow ion exchange between H$^+$ and Na$^+$ in Na$_2$Ti$_5$O$_7$ to obtain TiO$_2$·xH$_2$O, which was rinsed with a large amount of DI water until the pH of the
solution was nearly neutral, vacuum filtered, dried at 60 °C in a blast drying oven, calcined at 500 °C in a muffle furnace with a heating rate of 1 °C/min for 2 h, and cooled naturally to obtain the TiO$_2$(B) nanobelts. To prepare Ag$_3$PO$_4$/TiO$_2$(B), 100 mg of the prepared TiO$_2$(B) nanobelts was weighed first, and corresponding masses of Ag$_3$PO$_4$ were calculated according to molar ratios of (1:0.4), (1:0.8), and (1:1.5), respectively, as were the corresponding masses of AgNO$_3$ and Na$_2$HPO$_4$·12H$_2$O required for the preparation of Ag$_3$PO$_4$. Then, 100 mg of the TiO$_2$ nanobelts and the corresponding mass of Na$_2$HPO$_4$·12H$_2$O were added into 100 mL of DI water, which was followed by ultrasonication for 30 min. Next, the corresponding mass of AgNO$_3$ was dissolved in 50 mL of DI water and then slowly added into the sonicated mixture with constant stirring. Finally, the mixture was vacuum-filtrated and dried to obtain composites with different molar ratios, which were labeled as Ag$_3$PO$_4$/TiO$_2$(B) (0.4:1), Ag$_3$PO$_4$/TiO$_2$(B) (0.8:1), and Ag$_3$PO$_4$/TiO$_2$(B) (1.5:1). Ag$_3$PO$_4$ was directly obtained by mixing a certain proportion of AgNO$_3$ and Na$_2$HPO$_4$·12H$_2$O solution, which was followed by vacuum filtration and drying.

3.3. Analysis and Testing

Field emission scanning electron microscopy (FE-SEM, Gemini SEM 300, Manufactured by Zeiss, Oberkochen, Germany) and field emission transmission electron microscopy (FE-TEM, FEI Talos F200X, Manufactured by FEI, Hillsboro, OR, USA) were used to observe and analyze the morphology of the samples as well as test and analyze the elemental composition and distribution of the samples. FE-TEM (FEI Talos F200X, Manufactured by FEI, USA) and X-ray powder diffractometry (XRD, Bruker D8 Advance, Manufactured by Bruker, Bremen, Germany) were used to test and analyze the crystal structure and phase of the samples. A fluorescence spectrometer (PL FLS 1000/FS5, Manufactured by Edinburgh, UK) was used to test the fluorescence emission spectra of the samples. An electrochemical workstation (CHI-760E, Manufactured by Chenhua, Shanghai, China) was used to test the photocurrent of the samples. A UV-Vis spectrophotometer (UV-1200, Manufactured by Macy, Shanghai, China) was used to test and analyze changes in photocatalytic degradation performance, as well as obtain absorbance curves of the samples for RhB. In addition, a muffle furnace (KSL-1700X, Manufactured by Kejing, Hefei, China), a blast drying oven (DHG-9246A, Manufactured by Kejing, Hefei, China), and a benchtop high-speed centrifuge (LC-LX-H185C, Manufactured by Lichen, Shanghai, China) were also used to prepare the experimental materials.

3.4. Photocatalytic Performance Test

Each sample (20 mg) was added to 100 mL of 20 mg/L RhB solution and sonicated for 30 min. The mixture was placed under a light source simulated by a solar simulator (Solar-500Q, Manufactured by Newbit, Beijing, China), with the intensity of the light source adjusted to obtain a light intensity of 600 W/m$^2$ at the liquid surface. Approximately 6 mL of the experimental liquid was taken every 10 min and placed into the centrifuge for 10 min at 10,000 r/min. The supernatant was taken and tested by the UV-Vis spectrophotometer for absorbance $A_n$ (n = experimental serial number, with 1 for the first sample taken). Since the absorbance is proportional to the concentration of the solution ($C_n$), then there is a solution concentration ratio $C_n/C_0 = A_n/A_0$ ($A_0 =$ absorbance of the 20 mg/L of RhB solution, $C_0 =$ concentration of the 20 mg/L of RhB solution). The absorbance of each sample was measured at 10-min intervals for 60 min according to the above method, and the corresponding degradation rates were calculated to plot the photocatalytic degradation curve.

4. Conclusions

In this study, Na$_2$Ti$_3$O$_7$ nanobelts were successfully prepared via the hydrothermal method, and then, TiO$_2$·xH$_2$O was obtained via ion exchange, which was followed by calcinating TiO$_2$·xH$_2$O in a muffle furnace at 500 °C for 2 h to obtain TiO$_2$(B) nanobelts. The belt-like morphology of Na$_2$Ti$_3$O$_7$ was maintained throughout the preparation process,
which made the TiO$_2$(B) have good adsorption performance and enhanced the photocatalytic performance of the TiO$_2$(B) photocatalyst. Using AgNO$_3$ and Na$_2$HPO$_4$·12H$_2$O as reactants, Ag$_3$PO$_4$ nanoparticles were generated on the surface of the TiO$_2$(B) nanobelts by a simple in situ method, thereby successfully preparing Ag$_3$PO$_4$/TiO$_2$(B) heterojunction composites. The pure TiO$_2$(B) nanobelts degraded the simulated pollutant RhB slowly, with a degradation rate lower than 20% after 30 min of degradation. By combining the TiO$_2$(B) nanobelts with Ag$_3$PO$_4$, the performance of the composite photocatalyst was rapidly improved with the increase in the molar ratio of Ag$_3$PO$_4$, and the composite was able to degrade nearly 100% of RhB in 30 min when the molar ratio of Ag$_3$PO$_4$ to TiO$_2$ was increased to 1.5:1. The improvement of the photocatalytic performance of the Ag$_3$PO$_4$/TiO$_2$(B) composite was mainly attributed to the successful construction of heterojunctions between Ag$_3$PO$_4$ and TiO$_2$(B), thereby greatly inhibiting the recombination of photogenerated electron–hole pairs and enhancing the light quantum yield of the photocatalyst. In addition, the introduction of Ag$_3$PO$_4$ in the composite successfully extended the light absorption range of the photocatalyst into the visible region, thus improving the utilization of simulated sunlight. Based on the above two reasons, the photocatalytic performance of the Ag$_3$PO$_4$/TiO$_2$(B) composite was significantly improved.

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