Construction of Bronze TiO$_2$/Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$ Ternary Composite Photocatalyst toward High Photocatalytic Performance

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Abstract: Research has demonstrated that the formation of composites of titanium dioxide (TiO$_2$) with silver phosphate (Ag$_3$PO$_4$) through the construction of heterojunctions can expand its light absorption range and suppress the recombination of photogenerated electron–hole pairs, thereby improving the photocatalytic performance. However, this method offers only limited performance improvements, and the composite photocatalysts are costly due to the expensive Ag$_3$PO$_4$. In this study, Ti$_3$C$_2$ MXene, which has good hydrophilicity and excellent electrical conductivity, is first used to form Schottky junction composites with bronze TiO$_2$ (TiO$_2$(B)) via electrostatic self-assembly. Then, Ag$_3$PO$_4$ quantum dots were further formed on the surface of the TiO$_2$(B)/Ti$_3$C$_2$ MXene by in situ self-growth, and Ag$_3$PO$_4$ formed heterojunctions and Schottky junctions with TiO$_2$(B) and Ti$_3$C$_2$ MXene, respectively. Finally, a ternary composite photocatalyst TiO$_2$(B)/Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$ was jointly constructed by these functional junctions. Under the synergistic effect of these functional junctions, the mobility and fast separation performance of photogenerated electron–hole pairs of the composite photocatalyst were significantly improved, the recombination of photogenerated electron–hole pairs was effectively suppressed, and the light absorption performance was enhanced. As a result, the composite photocatalyst exhibited excellent photocatalytic performances.

Keywords: ternary composite photocatalyst; heterojunction; photocatalytic degradation; bronze TiO$_2$; Ti$_3$C$_2$ MXene

1. Introduction

The titanium dioxide (TiO$_2$) photocatalyst has been widely studied as a safe, inexpensive, and environmentally friendly photocatalyst. However, it does not exhibit high photocatalytic performances since it is only active for ultraviolet (UV) light due to its wide forbidden band gap and because the photogenerated electron–hole pairs easily recombine [1–4]. Previous studies have demonstrated that the compositing of TiO$_2$ and silver phosphate (Ag$_3$PO$_4$) via the construction of heterojunctions can expand its light absorption range and suppress the recombination of photogenerated electron–hole pairs, thereby improving the photocatalytic performance. However, such a performance improvement is limited, and the composite catalysts are costly due to the expensive Ag$_3$PO$_4$ [5–8]. Ti$_3$C$_2$ MXene is a new two-dimensional material with good hydrophilicity and excellent electrical conductivity. It can be used as a co-catalyst with other semiconductors to form Schottky junctions, which can not only effectively expand the light absorption range but also
promote the rapid separation of photogenerated electron–hole pairs, thus enhancing the photocatalytic performances of the composite photocatalysts [9–12].

To obtain high-performance and low-cost photocatalysts, TiO$_2$(B)/Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$ ternary composite photocatalysts were constructed in this study. First, a TiO$_2$(B)/Ti$_3$C$_2$ MXene composite was constructed by electrostatic self-assembly of strip-like TiO$_2$(B) and lamellar Ti$_3$C$_2$ MXene, and then Ag$_3$PO$_4$ quantum dots were formed on the surface of the TiO$_2$(B)/Ti$_3$C$_2$ MXene by in situ growth, thereby forming the TiO$_2$/Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$ ternary composite photocatalyst. The composite photocatalyst exhibited excellent photocatalytic performances, which first increased and then decreased with the increase in the content of the co-catalyst Ti$_3$C$_2$ MXene. The composite photocatalyst reached the best performance when the content of Ti$_3$C$_2$ MXene was 20% of the mass of TiO$_2$(B). Compared with the common TiO$_2$ phases (anatase, brookite, and rutile), bronze TiO$_2$ has a good electrical conductivity and a loose, porous structure, which facilitates the rapid migration of carriers and the formation of reaction sites in heterojunction photocatalysts, ultimately enhancing the performances of composite photocatalysts. Therefore, bronze TiO$_2$ was used in this study as a component of the composite photocatalyst [13–16].

2. Results and Discussion

As shown in Figure 1a, the standard PDF cards of Ag$_3$PO$_4$, TiO$_2$(B), and Ti$_3$AlC$_2$ were JCPDS#06-0505, JCPDS#35-0088, and JCPDS#015-3266, respectively. The diffraction pattern of the Ti$_3$C$_2$ MXene demonstrated that, after HF etching, the strongest diffraction peak of Ti$_3$AlC$_2$ was at 2θ = 28.99°, corresponding to the (104) crystal plane disappearing, while the diffraction peaks at 2θ = 9.52° and 19.12° corresponding to the (002) and (004) crystal planes, respectively, were enhanced, and their positions shifted towards smaller diffraction angles. Referring to the literature [17–20], the characteristics of the above diffraction peaks indicated that the Al atomic layer of Ti$_3$AlC$_2$ was successfully removed via etching to obtain the Ti$_3$C$_2$ MXene in this study. A comparison of the XRD (X-ray diffraction) patterns of the TiO$_2$(B)/20%Ti$_3$C$_2$, Ti$_3$C$_2$ MXene, and TiO$_2$(B) revealed that the diffraction peaks of the TiO$_2$(B)/20%Ti$_3$C$_2$ spectrum were mainly those of TiO$_2$(B), which appeared weakly and were only observed at 2θ = 9.14°, corresponding to the (002) crystal plane of the Ti$_3$C$_2$ MXene. In addition, compared with that of the TiO$_2$(B), the half-peak width of the diffraction peak of the TiO$_2$(B)/20%Ti$_3$C$_2$ spectrum increased, which may have been due to the low content of the Ti$_3$C$_2$ MXene and the relatively weak diffraction peaks. Figure 1b shows that the diffraction pattern of the ternary composite was mainly composed of diffraction peaks corresponding to Ag$_3$PO$_4$, while those corresponding to the Ti$_3$C$_2$ MXene and TiO$_2$(B) were not observed, which was mainly because Ag$_3$PO$_4$ had good crystallinity and exhibited strong diffraction compared to the Ti$_3$C$_2$ MXene and TiO$_2$(B).
Figure 1. (a) XRD diffraction patterns of Ag$_3$PO$_4$, TiO$_2$(B), Ti$_3$AlC$_2$, Ti$_3$C$_2$ and TiO$_2$(B)/20%Ti$_3$C$_2$; (b) XRD diffraction patterns of TTA-2.5, TTA-5, TTA-10, TTA-20 and TTA-30.

Figure 2a shows the SEM (scanning electron microscope) image of the Ti$_3$C$_2$ MXene prepared from Ti$_3$AlC$_2$. Since the Al atomic layer in the Ti$_3$AlC$_2$ was removed by etching, the Ti$_3$C$_2$ MXene had an accordion-like morphology, which is typical of Ti$_3$C$_2$ MXene. Figure 2b shows the SEM image of the experimentally prepared bronze TiO$_2$, which had a strip-like morphology. Figure 2c shows the SEM image of the TiO$_2$(B)/Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$ ternary composite, showing that the Ti$_3$C$_2$ MXene was closely combined with the TiO$_2$(B), with a large number of fine Ag$_3$PO$_4$ particles distributed on their surfaces, which are shown more clearly in the TEM (Transmission Electron Microscope) images in Figure 2d,f. Figure 2e,g show the HRTEM (High Resolution Transmission Electron Microscope) images, from which we can observe the lattices of Ag$_3$PO$_4$ (211), bronze TiO$_2$ (110), and Ti$_3$C$_2$ (105) as well as heterojunctions formed in the overlapping regions of these lattices. Figure 2h shows the mapping diagram of the elements in the composite, revealing that the composite contained five elements (Ti, O, Ag, P, and C), the distributions of which were consistent with the above phase and morphological analysis.
Figure 2. (a) SEM of Ti$_3$C$_2$ MXene; (b) SEM of TiO$_2$(B); (c) SEM of TiO$_2$(B)/20%Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$; (d,f) TEM of TiO$_2$(B)/20%Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$; (e,g) HRTEM of TiO$_2$(B)/20%Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$; (h) mapping and HAADF (high angle annular dark field image) of samples.

Figure 3a shows the degradation curves of the samples. The photocatalytic performance of the TiO$_2$(B)/Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$ composite was significantly higher than those of the TiO$_2$(B), Ag$_3$PO$_4$ and TiO$_2$(B)/20%Ti$_3$C$_2$ MXene and is significantly higher than that of photocatalyst P$_{25}$ sold in the market. The photocatalytic performance of the TiO$_2$(B)/Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$ composite first increased with the increase in the content of the Ti$_3$C$_2$ MXene and reached the highest value when the content was increased to 20%, beyond which further increases and lowered the photocatalytic performance of the composite instead. Figure 3b shows a linear fit of the degradation kinetics of the sam-
amples. According to the Langmuir–Hinshelwood model, the degradation reaction can be considered to be a first-order reaction at low RhB concentrations, and thus, the fitting of the degradation kinetics can be simplified to a linear case. The degradation reaction in this experiment satisfied the apparent first-order reaction rate equation \( \ln(C/C_0) = -k \cdot t \), where \( k \) is the apparent first-order reaction rate constant. Thus, \( \ln(C/C_0) \) is a function of the irradiation time \( t \). The \( k \) values of the TiO\(_2\)(B), TiO\(_2\)(B)/20\%Ti\(_3\)C\(_2\) MXene, Ag\(_3\)PO\(_4\) and P\(_{25}\) were low, with values of 0.008, 0.011, 0.085 and 0.04 min\(^{-1}\), respectively, while the \( k \) value corresponding to TTA(TiO\(_2\)(B)/Ti\(_3\)C\(_2\) MXene/Ag\(_3\)PO\(_4\)) was significantly higher, which gradually increased from \( k_{TTA-2.5} = 0.182 \) min\(^{-1}\) to the maximum \( k_{TTA-20} = 0.345 \) min\(^{-1}\) and then decreased to \( k_{TTA-30} = 0.241 \) min\(^{-1}\).

Figure 3. (a) Photocatalytic degradation curves; (b) linear fittings of degrading kinetics under different catalytic conditions.

Figure 4 shows the UV-Vis absorption spectra of the samples. Compared with TiO\(_2\)(B), the visible light absorption capacity was clearly improved after forming a composite of TiO\(_2\)(B) and Ti\(_3\)C\(_2\) MXene, and the light absorption performance of sample TTA-20 obtained by further incorporating Ag\(_3\)PO\(_4\) was even higher. The band gaps of the Ti\(_3\)C\(_2\), TiO\(_2\)(B), TiO\(_2\)(B)/20\%Ti\(_3\)C\(_2\) MXene, and TTA-20 were calculated to be 1.67, 3.14, 3.23, and 3.32 eV, respectively, based on the Tauc plot. These results confirmed the band gap reduction by the formation of the composite, which is an important reason for the improved light absorption performances of the composite materials.
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Figure 4. (a) Ultraviolet-visible (UV-Vis) absorption spectra and (b) band gaps of samples.
As shown in Figure 5, the fluorescence emission spectra as well as the transient photocurrent response and electrochemical impedance Nyquist plots of the samples were obtained to analyze the influence of the formation of composites on the recombination and migration of photogenerated electron–hole pairs in the samples. Figure 5a shows that the fluorescence of the TiO₂(B)/20%Ti₃C₂ MXene was significantly weaker than that of the TiO₂(B), and the fluorescence of TTA-20 (TiO₂(B)/20%Ti₃C₂ MXene/Ag₃PO₄) was the weakest. This was because the highly conductive Ti₃C₂ MXene was composited with TiO₂(B) to form Schottky junctions on the contact surface, which caused the fast migration of photogenerated electrons to the Ti₃C₂ MXene, achieving rapid separation of photogenerated electron–hole pairs and suppressing the recombination. By forming the Ti₃C₂ MXene and TiO₂(B) composite, Ag₃PO₄ quantum dots were introduced on the surfaces of the Ti₃C₂ MXene and TiO₂(B) by in situ self-growth, the Ag₃PO₄ and Ti₃C₂ MXene formed Schottky junctions, and the Ag₃PO₄ and TiO₂(B) formed heterojunctions. These junctions created a synergistic effect with the Schottky junctions formed by the Ti₃C₂ MXene and TiO₂(B), further promoting the rapid migration and separation of photogenerated electrons and greatly suppressing the recombination of photogenerated electron–hole pairs. Figure 5b shows the transient photocurrent responses of the samples. The photocurrents of the samples were enhanced by compositing. The photocurrent of TTA-20 was the strongest, followed by those of the TiO₂(B)/20%Ti₃C₂ MXene, Ag₃PO₄, and TiO₂(B), in that order. The photocurrent enhancement pattern was consistent with the fluorescence weakening pattern, and the photocurrent enhancement also indicated that the recombination of photogenerated electron–hole pairs was effectively suppressed. Thus, Figure 5b further confirms the results and analysis of Figure 5a. Figure 5c shows the Nyquist plot of the electrochemical impedances of the samples. In general, the smaller the curvature radius of the curve is, the greater the electron mobility of the sample is. The mobility was significantly enhanced by forming the composite. The electron mobility of TTA-20 was the largest, followed by that of the TiO₂(B)/20%Ti₃C₂ MXene, and both were larger than those of the TiO₂(B) and Ag₃PO₄.
The following reagents were used: Rhodamine B (RhB, C_{28}H_{31}ClN_{2}O_{3}) (Solarbio, Beijing, China); titanium aluminum carbide (Ti_{3}AlC_{2}) (Xianfeng Nanomaterials, Nanjing, China); disodium hydrogen phosphate 12-water (Na_{2}HPO_{4}·12H_{2}O, Jinshan Chemical Reagent, Chengdu, China); silver nitrate (AgNO_{3}) (Sinopharm Chemical Reagent, Shanghai, China); and sodium hydroxide (NaOH), hydrofluoric acid (HF), and nano-TiO_{2} (Aladdin Industrial, Shanghai, China). The deionized (DI) water used for the experiments was prepared in our laboratory. All reagents were of analytical grade and were used without further purification.

Ti_{3}C_{2} MXene was prepared from Ti_{3}AlC_{2} by HF etching as follows. An appropriate amount of 40% (mass fraction) Ti_{3}AlC_{2} was slowly added to the HF acid solution at a ratio of 1 g/20 mL and stirred at room temperature for 24 h. The prepared product was separated by centrifugation at 4000 rpm and rinsed repeatedly with DI water to near neutrality.

The preparation of TiO_{2}(B) was as follows. A 10 M NaOH aqueous solution was prepared. Then, raw TiO_{2} was added, stirred well, poured into a hydrothermal reactor, and heated up to 200 °C in a blast drying oven and held for 24 h. Next, the reaction product was removed, rinsed with a large amount of DI water to near neutrality, soaked with 0.1 M
dilute hydrochloric acid for 72 h, rinsed again with a large amount of DI water to near neutrality, dried at 60 °C for 10 h, and finally calcined in a muffle furnace at 500 °C for 2 h to obtain TiO$_2$(B).

The TiO$_2$(B)/Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$ ternary composite was prepared as follows. About 100 mg of TiO$_2$(B) and 20 mg of Ti$_3$C$_2$ MXene were added to DI water and sonicated for 4 h to allow the formation of a composite of TiO$_2$(B) and Ti$_3$C$_2$ MXene by electrostatic self-assembly, which was followed by drying in a vacuum drying oven to obtain the TiO$_2$(B)/20%Ti$_3$C$_2$ MXene composite. Na$_2$HPO$_4$·12H$_2$O and TiO$_2$(B)/20%Ti$_3$C$_2$ MXene were added to DI water at a molar ratio of 0.8:1 (note that the number of moles of TiO$_2$(B)/20%Ti$_3$C$_2$ MXene was the sum of the numbers of moles of the two components) and mixed well. A solution was prepared using AgNO$_3$ in a molar ratio of 3:1 with Na$_2$HPO$_4$·12H$_2$O, and then the solution was slowly added dropwise using a syringe to the mixture of Na$_2$HPO$_4$·12H$_2$O and TiO$_2$(B)/20%Ti$_3$C$_2$ MXene. The mixture was stirred continuously to form Ag$_3$PO$_4$ quantum dots on the surface of the TiO$_2$(B)/20%Ti$_3$C$_2$ MXene via in situ self-growth. The product was rinsed with DI water and dried in the vacuum drying oven to obtain TiO$_2$(B)/20%Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$, which was labeled as TTA-20. The preparation flow chart is shown in Figure 6. Using the same method, TiO$_2$(B)/2.5%Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$, TiO$_2$(B)/5%Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$, TiO$_2$(B)/10%Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$, and TiO$_2$(B)/30%Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$ were prepared and labeled as TTA-2.5, TTA-5, TTA-10, and TTA-30, respectively.

![Figure 6. Preparation flow chart of TiO$_2$(B)/Ti$_3$C$_2$ MXene/Ag$_3$PO$_4$ ternary composite.](image)

3.2. Analytical Tests

An X-ray powder diffraction (XRD, BRUCKER D8 ADVANCE, Bruker, Bremen, Germany) was used to test and analyze the phases of the samples using the following test parameters: Cu target, wide-angle diffraction, scan range of 5°–70°, scan rate of 10°/min, test wavelength of 1.5406 Å, tube voltage of 40 kV, and tube current of 40 mA. Field-emission scanning electron microscopy (FE-SEM, Gemini SEM 300, Zeiss, Oberkochen, Germany) was used to characterize the morphologies and structures of the samples at an operating voltage of 3 kV. Field-emission transmission electron microscopy (FEI Talos F200X, FEI, Hillsboro, OR, USA), with a maximum magnification of 1.1 million times and a limit resolution of 0.12 nm, was used to observe and analyze the morphologies and structures of the samples at an operating voltage of 200 kV. An ultraviolet–visible (UV-Vis) spectrophotometer (UV-3600, Shimadzu company, Kyoto, Japan), with a test range of 200–2500 nm, was used to test the photocatalytic degradation of RhB and obtain the UV-Vis absorption spectra of the samples. An electrochemical workstation (CHI-7600E, Shanghai
Chenhua Instrument, Shanghai, China) was used to test the photocurrents and impedances of the samples.

Two liters of 20 mg/L RhB solution were prepared, and 100 mL was taken for each experiment, added to 20 mg of the sample, and sonicated for 30 min. Then, this mixture was placed under a light source with an intensity of 600 W/m² (at the liquid surface) in a solar simulator (Solar-500Q, Newbit, Beijing, China) to start the photocatalytic degradation experiment, which lasted for 60 min. During the experiment, 5 mL of liquid was taken from the mixture every 10 min and subjected to centrifugation at 10,000 rpm for 10 min. After centrifugation, the supernatant was taken and its absorbance \( A_n \) was measured by the UV-Vis spectrophotometer. There was a direct proportionality relation between the solution concentration \( C_n \) and \( A_n \), \( C_n/C_0 = A_n/A_0 \), where \( C_0 \) was the concentration of 20 mg/L of the RhB solution, and \( A_0 \) was the absorbance of the 20 mg/L RhB solution.

4. Conclusions

In this study, the TiO\(_2\)(B)/Ti\(_3\)C\(_2\) MXene Schottky junction composite was first prepared by electrostatic self-assembly, and then Ag\(_3\)PO\(_4\) quantum dots were generated on the surface of the TiO\(_2\)(B)/Ti\(_3\)C\(_2\) MXene by in situ self-growth, thereby forming Ag\(_3\)PO\(_4\)/TiO\(_2\)(B) heterojunctions and Ag\(_3\)PO\(_4\)/Ti\(_3\)C\(_2\) MXene Schottky junctions. Through the successful construction and synergy of these functional junctions (As shown in Figure 7), the light absorption capacity of the composite photocatalyst was greatly enhanced, and the recombination of photogenerated electron–hole pairs was effectively suppressed, thus substantially improving the photocatalytic degradation performance of the composite photocatalyst. It was further found that the photocatalytic performance of the TiO\(_2\)(B)/Ti\(_3\)C\(_2\) MXene/Ag\(_3\)PO\(_4\) composite increased with the increase in the Ti\(_3\)C\(_2\) MXene content, and it reached the maximum when the Ti\(_3\)C\(_2\) MXene content increased to 20%, beyond which the photocatalytic performance of the composite decreased as the Ti\(_3\)C\(_2\) MXene content continued to increase.

![Figure 7. Mechanism of enhanced photocatalytic properties.](image-url)

Author Contributions: Conceptualization, methodology, S.W. and Y.C.; software, Y.L. (Yong Li); validation, Y.L. (Yong Li) and Y.L. (Yanfang Liu); formal analysis, Y.L. (Yong Li) and M.Z.; investigation, Y.L. (Yong Li), Y.L. (Yanfang Liu) and M.Z.; resources, S.W. and Y.C.; data curation, S.W.; writing—original draft preparation, Y.L. (Yong Li), M.Z. and X.L.; writing—review and editing, Y.L. (Yong Li), M.Z. and Y.L. (Yanfang Liu); visualization, Q.Z. (Qinghua Zhao) and Q.Z. (Qianyu Zhou); project administration, Y.L. (Yong Li); funding acquisition, Y.L. (Yong Li) and S.W. All authors have read and agreed to the published version of the manuscript.

Funding: The National Natural Science Foundation of China (Grant No.: 52062045), Central Government Funds for Local Scientific and Technological Development (Grant No.: XZ202101YD0019C...

5. Li, Y.; Liu, Y.; Zhang, M.; Zhou, Q.; Li, X.; Chen, T.; Wang, S. Preparation of Ag$_{19}$.


17. Li, Z.; Huang, W.; Liu, J.; Lv, K.; Li, Q. Embedding CdS@Au into Ultrathin Ti$_3$–xC$_2$Ty to Build Dual Schottky Barriers for Photocatalytic H$_2$ Production. ACS. Catal. 2021, 11, 8510–8520. [CrossRef]


19. Chen, Y.; Li, X.; Cai, G.; Li, M.; Tang, D. In situ formation of (0 0 1)TiO$_2$/Ti$_3$C$_2$ heterojunctions for enhanced photoelectrochemical detection of dopamine. Electrochem. Commun. 2021, 125, 106987. [CrossRef]