Ag$_3$PO$_4$-Deposited TiO$_2$@Ti$_3$C$_2$ Petals for Highly Efficient Photodecomposition of Various Organic Dyes under Solar Light

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Abstract: Two-dimensional Ti$_3$C$_2$ MXenes can be used to fabricate hierarchical TiO$_2$ nanostructures that are potential photocatalysts. In this study, the photodecomposition of organic dyes under solar light was investigated using flower-like TiO$_2$@Ti$_3$C$_2$, deposited using narrow bandgap Ag$_3$PO$_4$. The surface morphology, crystalline structure, surface states, and optical bandgap properties were determined using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), nitrogen adsorption analysis, and UV-Vis diffuse reflectance spectroscopy (UV-DRS). Overall, Ag$_3$PO$_4$-deposited TiO$_2$@Ti$_3$C$_2$, referred to as Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$, demonstrated the best photocatalytic performance among the as-prepared samples, including TiO$_2$@Ti$_3$C$_2$, pristine Ag$_3$PO$_4$, and Ag$_3$PO$_4$/TiO$_2$ P25. Organic dyes, such as rhodamine B (RhB), methylene blue (MB), crystal violet (CV), and methylene orange (MO), were efficiently degraded by Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$. The significant enhancement of photocatalysis by solar light irradiation was attributed to the efficient deposition of Ag$_3$PO$_4$ nanoparticles on flower-like TiO$_2$@Ti$_3$C$_2$ with the efficient separation of photogenerated e-/h+ pairs, high surface area, and extended visible-light absorption. Additionally, the small size of Ag$_3$PO$_4$ deposition (ca. 4–10 nm diameter) reduces the distance between the core and the surface of the composite, which inhibits the recombination of photogenerated charge carriers. Free radical trapping tests were performed, and a photocatalytic mechanism was proposed to explain the synergistic photocatalysis of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ under solar light.

Keywords: Ti$_3$C$_2$ MXene; Ag$_3$PO$_4$; photocatalyst; organic dyes; solar light; Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$

1. Introduction

Globally, as industrialization and urbanization accelerate, the demand for food and consumer goods (clothing, electronics, furniture, vehicles, etc.) increases. Unsustainable resource use and inefficient waste management, however, contribute to environmental problems, which have become a source of concern [1–3]. Numerous harmful pollutants endanger the environment and human health, such as heavy metal ions, toxic gases, and organic dye [4,5]. The majority of organic dyes found in wastewater originate from various industrial waste streams, including paint, dyeing clothing, bleaching paper, synthesizing rubber, and processing plastic, thereby, resulting in water pollution.

Organic dyes at high concentrations (5–1500 mg/L) cause significant environmental and organismal toxicity, including carcinogenic, mutagenic, and teratogenic effects [6–8]. Owing to their low removal capacity, conventional biological processes used to remove dyes, such as flocculation, filtration, precipitation, and coagulation, have gradually become obsolete [9,10]. In comparison, heterogeneous photocatalysts used in advanced oxidation processes are considered promising alternatives for the removal of a wide variety of organic pollutants with a highly efficient degradation rate [11].

Titania (TiO$_2$) is the most widely used and recognized photocatalytic material in environmental remediation owing to its superior photocatalytic performance, non-toxicity, and stability [12–14]. However, pure TiO$_2$ has a low quantum efficiency and a large
bandgap, limiting its application (i.e., electrons can be triggered only under UV light). In addition, the rapid recombination of photogenerated electron–hole pairs reduces its degradation efficiency [15]. Recently, several strategies have been proposed to solve these problems by fabricating TiO\(_2\) derived from Ti\(_3\)C\(_2\) [16].

Despite the absence of noble metal deposition (Au, Ag, Pt, RuO\(_2\), etc.), the flower-shaped TiO\(_2@\)Ti\(_3\)C\(_2\) composite exhibits significantly enhanced photocatalytic activity [4,17]. Recent work has been published on the synthesis of TiO\(_2@\)Ti\(_3\)C\(_2\) nanoflowers from the MAX phase (Ti\(_3\)AlC\(_2\)) [4,16,17]. They demonstrated that the presence of Ti\(_3\)C\(_2\) in the TiO\(_2\) structure eliminates electron–hole pair recombination, maximizes charging transfer, and expands the light absorption area to use visible light. Under solar light irradiation, the degradation efficiencies of RhB were 97% within 40 min and 95% within 60 min. Therefore, flower-shaped TiO\(_2@\)Ti\(_3\)C\(_2\) is a highly promising photocatalyst [4,16,17].

Silver-based semiconductor photocatalysts have been widely used due to their high efficiency as visible-light-driven photocatalysts [18]. Among silver-based photocatalysts, trisilver phosphate (Ag\(_3\)PO\(_4\)) with a narrow bandgap (2.36 eV) has attracted the photocatalytic field’s attention due to its high oxidation capacity and ability to remove pollutants under visible light illumination [18–21]. Nevertheless, Ag\(_3\)PO\(_4\) continues to fall short of meeting the demand for large-scale industrial applications, primarily due to its low reuse rates, as it suffers greatly from severe photocorrosion [22,23].

This is due to the intrinsic fast charge recombination, self-corrosion, and photocorrosion of silver or silver oxides in the absence of a sacrificial reagent. Therefore, the key strategy is to prevent its photocorrosion in practical applications. In this regard, heterostructure photocatalysts composed of Ag\(_3\)PO\(_4\) and TiO\(_2\) semiconductors have attracted attention over the years due to their increased photocatalytic efficiency, increased stability, and lower noble metal consumption [20]. To our knowledge, no research on the combination of Ag\(_3\)PO\(_4\) and Ti\(_3\)C\(_2\)-derived TiO\(_2\) has been conducted.

Herein, an Ag\(_3\)PO\(_4\)-deposited TiO\(_2@\)Ti\(_3\)C\(_2\) composite, Ag\(_3\)PO\(_4@\)TiO\(_2@\)Ti\(_3\)C\(_2\), was developed as a highly efficient visible photocatalyst. Flower-like TiO\(_2\) was initially synthesized from Ti\(_3\)C\(_2\) MXenes through three consecutive steps of hydrothermal oxidation, ion exchange, and heating processes [4,16,17]. Thereafter, using an in-situ precipitation method, Ag\(_3\)PO\(_4\) nanoparticles (NPs) were deposited on flower-like TiO\(_2@\)Ti\(_3\)C\(_2\). It is conceivable that the presence of metal-like Ti\(_3\)C\(_2\) in the TiO\(_2@\)Ti\(_3\)C\(_2\) composite acts as an “electron sink”, facilitating the highly efficient photodegradation of organic dyes.

In addition, the flower-like morphology has a high surface area and an efficient deposition of Ag\(_3\)PO\(_4\) on TiO\(_2@\)Ti\(_3\)C\(_2\) petals, which effectively separates electron–hole pairs and improves the solar light harvesting capability. Ag\(_3\)PO\(_4\)-deposited TiO\(_2@\)Ti\(_3\)C\(_2\) exhibited significant photocatalytic performance in the photodecomposition of a variety of organic dyes (including RhB, MB, CV, and MO).

2. Materials and Methods

2.1. Chemical and Materials

Titanium carbide powder (Ti\(_3\)C\(_2\) MXenes) was provided by Invisible Co. Ltd., Seoul, Korea. Sodium hydroxide (NaOH) was purchased from Daejung Chemicals & Metals Co., Ltd., Siheung, Korea. Silver nitrate (AgNO\(_3\), 99.9%) was obtained from Duksan Pure Chemicals Co., Ltd., Ansan, Korea. Hydrogen peroxide (H\(_2\)O\(_2\), 30%), hydrochloric acid (HCl), ethyl alcohol (C\(_2\)H\(_5\)OH), sodium phosphate (Na\(_3\)PO\(_4\)), methylene blue (MB), rhodamine B (RhB), methylene orange (MO), and crystal violet (CV) were purchased from Sigma-Aldrich, Munich, Germany. All chemicals were used directly, without any further treatment.

2.2. Preparation of TiO\(_2@\)Ti\(_3\)C\(_2\) Heterostructure

The procedure for fabricating flower-like TiO\(_2@\)Ti\(_3\)C\(_2\) was previously described by Vu Thi Quyen et al. [17]. First, 100 mg of Ti\(_3\)C\(_2\) MXene was added and vigorously stirred for 15 min with a solution of 2 M NaOH (80 mL) and 30 wt% H\(_2\)O\(_2\) (8 mL). Second, the hydrothermal reaction was performed by transferring the mixture into two 50 mL autoclave...
systems at 140 °C for 15 h. The dispersion was then allowed to cool naturally to room temperature, and the samples were washed with deionized (DI) water and ethanol several times before being dried in an oven at 60 °C for 12 h. The dried sample was soaked in a 0.05 M HCl solution (500 mL) for 12 h to ensure ion exchange. After heating the sample in a furnace at 500 °C for 5 h, the TiO$_2$@Ti$_3$C$_2$ composite was obtained. The formation of TiO$_2$ is presented by the following equations:

\begin{align*}
2\text{H}_2\text{O}_2 & \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \\
\text{Ti}_3\text{C}_2 + 5\text{O}_2 & \rightarrow 3\text{TiO}_2 + 2\text{CO}_2 \\
3\text{TiO}_2 + 2\text{NaOH} & \rightarrow \text{Na}_2\text{Ti}_3\text{O}_7 + \text{H}_2\text{O} \\
\text{Na}_2\text{Ti}_3\text{O}_7 + \text{HCl} & \rightarrow \text{H}_2\text{Ti}_3\text{O}_7 + 2\text{NaCl} \\
\text{H}_2\text{Ti}_3\text{O}_7 & \rightarrow 3\text{TiO}_2 + \text{H}_2\text{O}
\end{align*}

2.3. Preparation of Ag$_3$PO$_4$ Particles

To prepare Ag$_3$PO$_4$ particles, a simple method was followed. To generate Ag$_3$PO$_4$, 0.1 M Na$_3$PO$_4$ (8 mL) was added dropwise to 0.1 M AgNO$_3$ solution (24 mL) and stirred for 5 h in the dark. To remove redundant ions, the precipitate was centrifuged and washed with deionized water. The purified sample was dried overnight at 60 °C to obtain the Ag$_3$PO$_4$ powder.

2.4. Preparation of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$

Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ composites were prepared by adding various amounts of AgNO$_3$ (x) and Na$_3$PO$_4$ (y) solutions with a ratio of x:y = 3:1. First, 0.05 g TiO$_2$@Ti$_3$C$_2$ was added to 0.1 M AgNO$_3$ solutions. The mixed solutions were vigorously stirred and sonicated for 10 min. Thereafter, 0.1 M Na$_3$PO$_4$ was gradually dropped into the solution and stirred for 5 h to form Ag$_3$PO$_4$. To avoid photocorrosion, the reaction was conducted in the dark. The resulting powder products were washed, centrifuged with DI water, and dried at 60 °C to obtain Ag$_3$PO$_4$. To avoid photocorrosion, the reaction was conducted in the dark. The samples were kept in the dark throughout the preparation process to avoid photocorrosion. In comparison with sample A4, Ag$_3$PO$_4$/TiO$_2$ P25 was also prepared under the same conditions.

The fabrication procedure for the composites is depicted in Scheme 1. First, Ti$_3$C$_2$ MXene was subjected to hydrothermal oxidation, ion exchange, and heat treatment steps, transforming its accordion-like structure into a flower shape. Thereafter, Ag$_3$PO$_4$ NPs containing varying amounts of Ag$_3$PO$_4$ were deposited by in-situ precipitation on the flower-like structure to form the Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ composites. Photodegradation tests were conducted under solar-driven light.

2.5. Photocatalysis of Dye Degradation

A Xe lamp (1000 W) was used as an artificial solar light source with a light intensity of 1000 mW/cm$^2$. Under simulated solar light, the photocatalytic activities of the as-prepared samples were evaluated for the photodecomposition of RhB dye. Typically, 10 mg of each sample was added to 20 mL of an aqueous solution containing RhB (9 mg/L). Prior to light irradiation, the adsorption experiments of Ag$_3$PO$_4$, TiO$_2$, and Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ were performed by stirring the solutions in the dark for 15 min to improve dispersion and adsorption–desorption equilibrium. Thereafter, the solution was exposed to solar light. Following that, an aliquot of each sample (1 mL) was removed and centrifuged at the indicated intervals to obtain the supernatant for UV-vis spectrophotometer evaluation.

The degradation efficiency of the dye materials can be described by the following equation: degradation percentage (%) = C$_0$ – C$_t$ / C$_0$ × 100. To determine the rate constant
of RhB degradation, the degradation kinetics were assumed to follow the pseudo-first order model [21,24]:

$$-\ln \frac{C}{C_0} = kt$$

where $C_0$ and $C_t$ denote the initial concentration of RhB and a specific concentration of RhB after exposure to light for $t$ minutes, respectively. Here, “$k$” is the pseudo-first-order rate constant calculated from the linear slope of $\ln(C_0/C)$ versus $t$ (time). 10 mg/L concentration of MB, MO, and CV were used for photodegradation with the same procedure. The absorbance changes for each dye were determined using a UV-Vis spectrometer at different wavelengths, RhB (554 nm), MB (664–665 nm), MO (464 nm), and CV (590 nm).

![Scheme 1](image)

**Scheme 1.** Schematic indicating the fabrication processes, beginning with multilayer Ti$_3$C$_2$ MXene and ending with the formation of Ag$_3$PO$_4$-deposited flower-shaped TiO$_2$@Ti$_3$C$_2$.

### 2.6. Characterization

The X-ray diffraction (XRD) patterns of the samples were determined using a Rigaku Smartlab X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.544 \text{ Å}$) (Rigaku Corporation, Tokyo, Japan). The morphologies and microstructures of the samples were investigated using a Hitachi S-4700 field emission scanning electron microscope (FE-SEM) (Hitachi Ltd., Tokyo, Japan) and FEI Tecnai transmission electron microscopy (TEM) (FEI, Hillsboro, OR, United States). XPS measurements were conducted using an X-ray photoelectron spectrometer (XPS, Multilab 2000, Thermo Scientific, Waltham, MA, United States). The surface area, pore size, and pore volume were measured using an N$_2$ adsorption–desorption apparatus (ASAP 2020, Micromeritics Instrument Corp, Norcross, GA, USA). Optical properties of the samples were determined using a Jasco V770 UV-Vis diffuse reflectance spectrophotometer (Jasco Inc., Easton, MD, USA).

### 3. Results and Discussion

#### 3.1. XRD Analysis

The diffraction patterns of the TiO$_2$@Ti$_3$C$_2$, Ag$_3$PO$_4$, and A4 samples are shown in Figure 1a. The XRD data of Ag$_3$PO$_4$ revealed sharp and narrow dominant peaks at 33.3° (210) and 36.6° (211), which corresponded to the body-centered crystal structure and high crystallinity (JCPDS no. 06-0505) [25]. Furthermore, TiO$_2$@Ti$_3$C$_2$ exhibited a distinct peak at $2\theta = 25.3^\circ$, indicating the high crystallinity of the anatase phase with other weaker peaks
at 37.8°, 53.9°, 55.34°, and 62.6° (JCPDS card No. 21-1272) [21]. A small peak at 48.5° confirmed the presence of Ti$_3$C$_2$ in the sample [4,16,17].

**Figure 1.** XRD patterns of as-prepared samples: (a) TiO$_2$@Ti$_3$C$_2$, Ag$_3$PO$_4$, and optimized A4 sample. (b) Additional XRD patterns of A1, A2, A3, and A5 samples, including A4.

In the case of the composites, Figure 1b shows the diffraction patterns of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (samples A3, A4, and A5), which clearly display both Ag$_3$PO$_4$ crystal and TiO$_2$ anatase phase peaks, confirming that the composites were composed of Ag$_3$PO$_4$ and TiO$_2$. The diffraction peaks of TiO$_2$ in the heterostructure composite are weaker than those of Ag$_3$PO$_4$ owing to the lower crystallinity of TiO$_2$. However, samples A1 and A2 containing a lower concentration of Ag$_3$PO$_4$ mostly exhibit peaks of TiO$_2$ anatase at = 25.3° (JCPDS card No. 21-1272), instead of Ag$_3$PO$_4$ peaks due to self-corrosion [22].

### 3.2. Morphology Analysis by SEM, TEM

The accordion-like shape of Ti$_3$C$_2$ is shown in the SEM image in Figure 2a. After oxidation, ion exchange, and heat treatment, accordion-shape Ti$_3$C$_2$ transforms into TiO$_2$@Ti$_3$C$_2$ with a flower shape (Figure 2b). Figure 2c depicts pure Ag$_3$PO$_4$ NPs with an irregular shape and a diameter of ca. 300–500 nm [19]. The SEM image in Figure 2d shows aggregated Ag$_3$PO$_4$-deposited TiO$_2$@Ti$_3$C$_2$ that retains its flower-like shape. To overcome certain limitations of SEM analysis, which focuses on the surface morphology of samples, TEM and HRTEM images were used to clarify the transmission morphology and crystalline structure of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (sample A4). According to the EDX spectrum (Figure S1), the main elements present in the sample are carbon, oxygen, titanium, silver, and phosphorous. C, O, and Ti were obtained from TiO$_2$@Ti$_3$C$_2$, with a portion of the O derived from Ag$_3$PO$_4$. It can be demonstrated that Ag$_3$PO$_4$ is coated on the surface of TiO$_2$@Ti$_3$C$_2$.

**Figure 3a** shows a typical TEM image of the flower-shaped TiO$_2$@Ti$_3$C$_2$ with some petal fragments and large agglomerated Ag$_3$PO$_4$ on it. However, the higher magnification images in Figure 3b,c demonstrate that the dominant Ag$_3$PO$_4$ NPs were formed and deposited on each TiO$_2$@Ti$_3$C$_2$ nanorod. Positively charged silver ions were attracted to the surface of negatively charged TiO$_2$, and the reaction between Ag$^+$ and PO$_4^{3−}$ occurred immediately upon the addition of Na$_3$PO$_4$ solution, resulting in the deposition of Ag$_3$PO$_4$ NPs on TiO$_2$@Ti$_3$C$_2$ rods [26]. The TEM images show that precipitating Ag$_3$PO$_4$ using TiO$_2$@Ti$_3$C$_2$ nanorods as a template can reduce particle aggregation owing to the high specific surface area of the nanorods, which affects Ag$_3$PO$_4$ nucleation and reduces the diameter to around 4–10 nm.
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**Figure 2.** SEM images of (a) Ti$_3$C$_2$, (b) TiO$_2$@Ti$_3$C$_2$, (c) Ag$_3$PO$_4$, and (d) Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (A4) samples.

Figure 3a shows a typical TEM image of the flower-shaped TiO$_2$@Ti$_3$C$_2$ with some petal fragments and large agglomerated Ag$_3$PO$_4$ on it. However, the higher magnification images in Figure 3b,c demonstrate that the dominant Ag$_3$PO$_4$ NPs were formed and deposited on each TiO$_2$@Ti$_3$C$_2$ nanorod. Positively charged silver ions were attracted to the surface of negatively charged TiO$_2$, and the reaction between Ag$^+$ and PO$_4^{3-}$ occurred immediately upon the addition of Na$_3$PO$_4$ solution, resulting in the deposition of Ag$_3$PO$_4$ NPs on TiO$_2$@Ti$_3$C$_2$ rods [26]. The TEM images show that precipitating Ag$_3$PO$_4$ using TiO$_2$@Ti$_3$C$_2$ nanorods as a template can reduce particle aggregation owing to the high specific surface area of the nanorods, which affects Ag$_3$PO$_4$ nucleation and reduces the diameter to around 4–10 nm.

Additionally, the Ag$_3$PO$_4$ nanoparticles were relatively stable and did not detach during sonication as part of the TEM preparation process, whereas the agglomerated Ag$_3$PO$_4$ fragments moved and changed position during real-time TEM measurements. Figure 3c,d show the high-resolution TEM (HR-TEM) images of the Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ composite. TiO$_2$@Ti$_3$C$_2$ (101) has lattice fringes with an interplanar spacing of 0.35 nm, while cubic Ag$_3$PO$_4$ (210) has an interplanar spacing of 0.26 nm (Figure 3d). A SAED image further demonstrates the clear formation and polycrystallinity of these materials, which is shown in Figure S2. These TEM images can assist in resolving the initial ambiguity regarding the morphology of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ shown in the SEM images.

**Figure 3.** (a–c) TEM images of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (sample A4) viewed under different magnifications. (d) HR-TEM lattice image of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$. 

Figure 4 depicts the scanning TEM (STEM) image of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ with elemental mapping. The high-angle annular dark-field (HAADF) STEM image of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ shows areas with different contrasts, with the brighter regions representing Ag$_3$PO$_4$ particles and the darker regions representing TiO$_2$@Ti$_3$C$_2$ rods. The elemental mapping analysis displays C, O, P, K, and Ag elements from an arbitrary area. In detail, the Ti signal is primarily associated with the backbone of TiO$_2$@Ti$_3$C$_2$, whereas the P and Ag signals are associated with the large agglomerated Ag$_3$PO$_4$ fragments on top of the flower and Ag$_3$PO$_4$ NPs decorated alongside the petals. Additionally, the O signals are distributed uniformly throughout the composite. The elemental mapping results provide more comprehensive and clear observations of the elemental distribution across the whole composite, corresponding to the SEM and HR-TEM above.
Additionally, the Ag₃PO₄ nanoparticles were relatively stable and did not detach during sonication as part of the TEM preparation process, whereas the agglomerated Ag₃PO₄ fragments moved and changed position during real-time TEM measurements. Figure 3c,d show the high-resolution TEM (HR-TEM) images of the Ag₃PO₄/TiO₂@Ti₃C₂ composite. TiO₂@Ti₃C₂ (101) has lattice fringes with an interplanar spacing of 0.35 nm, while cubic Ag₃PO₄ (210) has an interplanar spacing of 0.26 nm (Figure 3d). A SAED image further demonstrates the clear formation and polycrystallinity of these materials, which is shown in Figure S2. These TEM images can assist in resolving the initial ambiguity regarding the morphology of Ag₃PO₄/TiO₂@Ti₃C₂ shown in the SEM images.

Figure 4 depicts the scanning TEM (STEM) image of Ag₃PO₄/TiO₂@Ti₃C₂ with elemental mapping. The high-angle annular dark-field (HAADF) STEM image of Ag₃PO₄/TiO₂@Ti₃C₂ shows areas with different contrasts, with the brighter regions representing Ag₃PO₄ particles and the darker regions representing TiO₂@Ti₃C₂ rods. The elemental mapping analysis displays C, O, P, K, and Ag elements from an arbitrary area. In detail, the Ti signal is primarily associated with the backbone of TiO₂@Ti₃C₂, whereas the P and Ag signals are associated with the large agglomerated Ag₃PO₄ fragments on top of the flower and Ag₃PO₄ NPs decorated alongside the petals. Additionally, the O signals are distributed uniformly throughout the composite. The elemental mapping results provide more comprehensive and clear observations of the elemental distribution across the whole composite, corresponding to the SEM and HR-TEM above.

3.3. XPS Results

To characterize the chemical compositions and elemental states of the as-prepared samples, XPS measurements were conducted. The survey spectra of Ti₃C₂ MXene, TiO₂@Ti₃C₂ flowers, and Ag₃PO₄/TiO₂@Ti₃C₂ illustrate the characteristic elemental peaks at approximately 532.35, 455.16, and 284.96 eV allocated to O 1s, Ti 2p, and C 1s, respectively (Figure S3). The weak peak of F 1s at 685.1 eV in Ti₃C₂, indicates that some fluoride was left over from the synthesis process [17].

The TiO₂@Ti₃C₂ heterostructure exhibits a much stronger O 1s peak intensity when compared to Ti₃C₂, indicating the existence of an appreciable amount of oxide in the heterostructure due to the oxidation process and the formation of TiO₂ [4]. In the spectra
results of composite Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$, the peaks of P 2p and Ag 3d represent Ag$_3$PO$_4$ in the composite. Generally, Ag 3d peaks have a higher intensity than Ti 2p, suggesting that many silver elements or their compounds are present on the surface of the solid sample, decorating the TiO$_2$@Ti$_3$C$_2$ flower shape. This result is consistent with the SEM and TEM images discussed previously.

Figure 5 demonstrates the Ti 2p, C 1s, and O 1s high-resolution XPS spectra of Ti$_3$C$_2$, TiO$_2$@Ti$_3$C$_2$, and Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (sample A4). The Ti-C peak at 454.26 eV in Ti 2p spectra indicates the presence of Ti$_3$C$_2$; however, there is no Ti-C peak in TiO$_2$@Ti$_3$C$_2$ [27,28]. Additionally, the intensification of the Ti-O peak (Ti$^{4+}$) at 458.83 eV indicates the formation of TiO$_2$ in the flower-shaped TiO$_2$@Ti$_3$C$_2$. The Ti-C bond is absent in TiO$_2$@Ti$_3$C$_2$ in the high-resolution C 1s; however, C=C/C=H, C=O, and O=C=O bonds exist at approximately 284.88, 286.40, and 288.72 eV, respectively [28–30]. Owing to the use of TiO$_2$@Ti$_3$C$_2$ as a template for precipitate Ag$_3$PO$_4$, the Ti 2p and C 1s spectra of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (sample A4) are similar to those of TiO$_2$@Ti$_3$C$_2$.

Nevertheless, the differences in O 1s XPS spectra among the three samples were unavoidable owing to the changing environment in which oxygen was present. Ti$_3$C$_2$ exhibited a distinct peak attributed to C-Ti-OH linkage at 530.72 and 532.59 eV, whereas the others showed the strongest Ti-O peak at 529.60 eV. Furthermore, Ti$_3$C$_2$ MXene also exhibited F 1s spectra (Figure S4a), which could be ascribed to residual fluorine after the etching steps. The Ag 3d and P 1s spectra of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (sample A4) are presented in Figure S4b,c.
The binding energies of 366.83 and 372.91 eV assigned to Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$, respectively, indicate that Ag$^+$ is dominated in the composites. The deconvoluted Ag 3d peaks are slightly shifted toward lower binding energy, and the FHMW is also wider. This is attributed to self-corrosion after exposure to the environment for a period of time [22]. The peak of the P 2p spectra located at 131.82 eV corresponds to P$^{5+}$ in the PO$_4$$^{3-}$ [31].

3.4. Surface Area and Optical Analysis

The N$_2$ adsorption–desorption isotherms and the corresponding BET surface areas, pore volumes, and pore sizes of TiO$_2$@Ti$_3$C$_2$, Ag$_3$PO$_4$/P25, and Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ are shown in Figure 6a and Table 1. Based on the isotherm curves, all samples belong to type IV, and the pore size indicates that they are mesopores [4]. As can be seen, the TiO$_2$@Ti$_3$C$_2$ flowers have the highest BET surface area (53 m$^2$g$^{-1}$). After the deposition of Ag$_3$PO$_4$, the surface area and pore volume of the Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ sample (40 m$^2$g$^{-1}$) decreased slightly but remained higher than that of Ag$_3$PO$_4$/TiO$_2$ P25 (27 m$^2$g$^{-1}$). This high surface area enables photocatalytic reactions to occur.

Figure 6. (a) BET surface area plot of TiO$_2$@Ti$_3$C$_2$, Ag$_3$PO$_4$/P25, and Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$; (b) UV-Vis DRS spectra of the as-prepared samples, including pristine TiO$_2$ P25, TiO$_2$@Ti$_3$C$_2$, pure Ag$_3$PO$_4$, and Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (sample A4).

Table 1. Specific surface area, pore volume, and pore size distribution of TiO$_2$@Ti$_3$C$_2$, Ag$_3$PO$_4$/TiO$_2$ P25, and Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (sample A4).

| Sample                  | BET Surface Area (m$^2$g$^{-1}$) | Pore Volume (cm$^3$g$^{-1}$) | Pore Size (nm) |
|-------------------------|----------------------------------|------------------------------|----------------|
| TiO$_2$@Ti$_3$C$_2$     | 53                               | 0.309                        | 21.91          |
| Ag$_3$PO$_4$/TiO$_2$ P25| 27                               | 0.202                        | 31.04          |
| Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (A4) | 40 | 0.156 | 20.12 |

The light-harvesting capability is important for evaluating photocatalytic activity as demonstrated by UV-Vis absorption spectra in Figure 6b. Owing to its metallic properties, Ti$_3$C$_2$ MXene exhibits a nearly horizontal spectrum over the entire wavelength range. The sequential transformations of MXene (metallic material) to the TiO$_2$@Ti$_3$C$_2$ heterostructure (semiconductor material) throughout the processes resulted in the gradual development of the TiO$_2$@Ti$_3$C$_2$ absorption peak [4,16,17]. Its light absorption is improved compared with that of the commercial TiO$_2$ P25.

It can be seen that the decoration of Ag$_3$PO$_4$ on the flower-shaped TiO$_2$@Ti$_3$C$_2$ extends the optical absorption by the combination of Ag$_3$PO$_4$ and TiO$_2$@Ti$_3$C$_2$. Due to the high surface area of the 3D nanoflower structure, the harvested and scattered light
is omnidirectional. In this case, the forward and backward light results in constructive interference, which can extend the photon lifetime and improve the absorbance [16]. These findings further confirm that the Ag$_3$PO$_4$-deposited TiO$_2$@Ti$_3$C$_2$ composite can enhance the light-harvesting ability, making it a promising photocatalyst under visible illumination.

3.5. Photocatalytic Performance

3.5.1. The Effects of Ag$_3$PO$_4$ Content on the Photodegradation of Rhodamine B

Figure 7a illustrates the photocatalytic degradation of RhB (9 mg L$^{-1}$) using Ag$_3$PO$_4$, TiO$_2$ and Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ composites (samples A1, A2, A3, A4, and A5) at a concentration of 0.5 g L$^{-1}$ under solar light irradiation. Overall, the composite exhibited effective photodegradation reaction under solar light irradiation in a short period of time, with sample A4 displaying significant enhanced photocatalytic performance by demonstrating 97% RhB degradation within 12 min.

As samples A1 and A2 contain less Ag$_3$PO$_4$ and may be susceptible to self-corrosion and photocorrosion, as discussed in the XRD diffractogram, these samples took 20 min to partially degrade 28.9% and 59.9% RhB, respectively. Although sample A5 contains more Ag$_3$PO$_4$ than sample A4, there was no significant difference in the photocatalytic activities between samples A5 and A4. When comparing degradation performances within 20 min, pure Ag$_3$PO$_4$ had a degradation efficiency of 95% and Ag$_3$PO$_4$/TiO$_2$ P25 86%. The lower photocatalytic performance of Ag$_3$PO$_4$/TiO$_2$ P25 is most likely due to self-corrosion in the composite after prolonged storage [22].

Figure 7b shows the calculated rate constant (k) values of 0.017, 0.046, 0.161, 0.289, and 0.278; 0.095 min$^{-1}$; and 0.0093 min$^{-1}$ for samples A1–A5, Ag$_3$PO$_4$, Ag$_3$PO$_4$/TiO$_2$ P25, and flower-like TiO$_2$@Ti$_3$C$_2$, respectively. These results indicate that, among the as-prepared samples, sample A4 exhibited the greatest photocatalysis performance. These results indicate that combining TiO$_2$ derived from MXene with Ag$_3$PO$_4$ can significantly improve its photocatalytic performance when exposed to solar illumination.

3.5.2. Photodegradation of Other Organic Dyes

The three dyes, MB, CV, and MO (10 mg L$^{-1}$, 0.5 g L$^{-1}$) were also photodegraded under solar light irradiation. The adsorption and photocatalytic performance of sample A4 over time for the three organic dyes are shown in Figures 8b and S5. The results indicate that the composite is effective in adsorbing cationic dyes (MB and CV) but has no effect on anionic dye concentration (MO) after 15 min in the dark. It can be attributed to the composite’s surface, which is anionic and negatively charged in the aqueous solution, which enables it to readily attract and adsorb cationic dyes in comparison to its anionic dye
counterpart [32]. These results aid in the cationic dyes’ molecules more easily reaching the surface of materials, leading to higher degradation performance in MB and CV compared to MO. After 6 min, the photocatalyst degraded 94.4% of MB, nearly 99.2% CV in 14 min, and 92.4% MO after 40 min. The pseudo-first-order rate constants for MB, CV, and MO were calculated to be 0.489, 0.279, and 0.073 min\(^{-1}\), respectively.

**Figure 8.** (a) Photocatalytic results of Ag\(_3\)PO\(_4\)/TiO\(_2\)@Ti\(_3\)C\(_2\) (sample A4) and (b) the corresponding rate constants for organic dyes.

Compared with TiO\(_2\)@Ti\(_3\)C\(_2\), pristine Ag\(_3\)PO\(_4\), and Ag\(_3\)PO\(_4\)/TiO\(_2\) P25, the Ag\(_3\)PO\(_4\)/TiO\(_2\)@Ti\(_3\)C\(_2\) composite exhibited superior photocatalytic activity. Recent publications on photocatalytic materials indicate the possibility of a highly promising photocatalyst for flower shaped TiO\(_2\)@Ti\(_3\)C\(_2\) with a high surface area. Combining TiO\(_2\)@Ti\(_3\)C\(_2\) with Ag\(_3\)PO\(_4\) results in synergetic photodegradation of various dyes. The flower-like structure of TiO\(_2\) derived from Ti\(_3\)C\(_2\) can improve its light-harvesting ability, and its high specific surface area allows the solvent to approach the reactive sites more easily.

Additionally, Ag\(_3\)PO\(_4\) in the composites can shorten the diffusion paths for photoexcited carriers, thereby, inhibiting the recombination of electron–hole pairs [4,25]. The photocatalytic activity of the optimized sample was compared to that of other reported similar photocatalysts. As demonstrated in Table 2, the Ag\(_3\)PO\(_4\)/TiO\(_2\)@Ti\(_3\)C\(_2\) composite (sample A4) can degrade a variety of pollutants, including both cationic and anionic dyes, in a relatively short period of time, as compared to the state-of-the-art works listed in Table 2.

### 3.6. Scavenger Trapping and Recycling Tests of RhB Degradation

To ascertain the main active species in the photocatalytic reactions, scavenger trapping tests were conducted on RhB photodegradation over the Ag\(_3\)PO\(_4\)/TiO\(_2\)@Ti\(_3\)C\(_2\) composite (sample A4). The three types of scavengers were tert-butanol (a quencher of \(\bullet\)OH), Na\(_2\)EDTA (a quencher of \(h^+\)), and p-benzoquinone (p-BQ, a quencher of \(\bullet\)O\(_2^−\)). The dye solution containing a specified amount of catalyst was added to 2 mL of trapping agent (0.01 M), stirred for 15 min in the dark, and exposed to solar light for 20 min. As shown in Figure 9a, the addition of tert-butanol had no effect on the photocatalytic performance, thereby, indicating that free \(\bullet\)OH radicals were not the dominant oxidizing species. The presence of Na\(_2\)EDTA and p-BQ, however, decreased the degradation efficiency to 4.76% and 21.7%, respectively. From these results, it can be concluded that \(h^+\) and \(\bullet\)O\(_2^−\) radicals play a critical role in the photodecomposition of RhB.
Table 2. A comparison of the photocatalytic efficiency of TiO$_2$@Ti$_3$C$_2$ and Ag$_3$PO$_4$-based photocatalysts developed for dye degradation.

| Pollutant | Pollutant conc. | Photocatalyst | Decoration Ag$_3$PO$_4$ Method | Ag$_3$PO$_4$ Diameter | Dosage (g L$^{-1}$) | Irradiation Time (min) | Efficiency (%) | Light Source | Source [Ref.] |
|-----------|----------------|---------------|-------------------------------|-----------------------|-------------------|------------------------|----------------|-------------|----------------|
| RhB       | 9 ppm          | Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ | In situ precipitation | 4-10 nm | 0.5 | 12 | 97 | Solar light | Current study |
| MO        | 10 ppm         | Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ | In situ precipitation | 300-500 nm | 0.5 | 15 | 90 | Visible light | [4] |
| MB        | 10 ppm         | Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ | In situ precipitation | 100-400 nm | 0.5 | 10 | 98 | Visible light | [17] |
| CV        | 10 ppm         | Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ | In situ precipitation | 100-400 nm | 0.5 | 4 | 98.1 | Visible light | [25] |
| RhB       | 20 µm          | Safflower-shaped TiO$_2$/Ti$_3$C$_2$ | - | - | 0.8 | 60 | 95 | Visible light | [4] |
| RhB       | 10 ppm         | TiO$_2$/Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ nanoflower | - | - | 0.43 | 40 | 97 | Visible light | [17] |
| RhB       | 0.02 mM        | Ag$_3$PO$_4$/TiO$_2$ | In situ precipitation | 300-360 nm | 0.4 | 10 (Vis) | -100 | Visible light | [20] |
| MO, phenol | 0.06 mM       | Ag$_3$PO$_4$/TiO$_2$ | In situ precipitation | 300-360 nm | 0.4 | 10 (Vis) | -100 | Visible light | [19] |
| RhB       | 10 ppm         | Ag$_3$PO$_4$/TiO$_2$ NFs | In situ precipitation | 100-400 nm | 0.5 | 6 | 98 | Visible light | [35] |
| RhB, MB, pesticides | 6 ppm, 8 ppm | Ag$_3$PO$_4$/TiO$_2$ | One pot | 100-400 nm | 0.5 | 6 | 98.1 | Visible light | [33] |
| MB        | 20 ppm         | Ag$_3$PO$_4$/m-TiO$_2$ | In situ precipitation | ~4 nm | 0.5 | 28 | 100 | Visible light | [35] |
| MB        | 10 mM          | Ag$_3$PO$_4$/TiO$_2$ nanosheet film | Impregnating-deposition process | 100-300 nm | - | 70 | 98.1 | Visible light | [34] |
| MB        | 10 ppm         | Ag$_3$PO$_4$/TiO$_2$-CNFs | Hydrothermal | 20-32 nm | 0.5 | 10 | 100 | Visible light | [35] |
| MB        | 10 ppm         | Ag$_3$PO$_4$/TiO$_2$ NFs | Hydrothermal | - | 0.4 | 15 | 100 | Visible light | [36] |
| RhB       | 10 ppm         | CFC/TiO$_2$/Ag$_3$PO$_4$ | Hydrothermal | 20-100 nm | - | 100 | 98.4 | Visible light | [37] |
| MO        | 20 ppm         | Ag$_3$PO$_4$/TiO$_2$-CO | Ion exchange | 250-600 nm | 1 | 120 | 80 | Solar light | [38] |
| RhB       | 10 ppm         | Ag$_3$PO$_4$/TiO$_2$ | Hydrothermal and ultrasonication | 0.1-1.5 µm | 1 | 25 | 100 | Solar light | [31] |

Figure 9. (a) Effects of scavengers on the RhB photodecomposition. (b) The stability of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (A4) after three consecutive recycling runs.

Along with the photocatalytic efficiency, stability evaluations of photocatalysts are necessary for practical use. Figure 9b shows the RhB degradation efficiency of sample A4 over three consecutive recycling runs. The degradation efficiency was significantly reduced after repeated exposure to solar light, indicating that the photocatalyst was not stable and rapidly deteriorated due to the photocorrosion of Ag$_3$PO$_4$ NPs [22]. In the first run, a degradation efficiency of 97% was obtained in 12 min, whereas the degradation efficiencies of RhB were approximately 74% and 39% after the second and third runs, respectively. After a few recycling tests under solar light, the photocorrosion of the catalyst resulted in a low photodecomposition rate by forming an uncontrolled amount of Ag$^+$, which can agglomerate and hinder the photocatalytic ability [31].
3.7. Proposed Photocatalytic Mechanism

Based on the obtained scavenger trapping and recycling results, the photocatalytic mechanism of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ is schematically shown in Figure 10. Under solar illumination, electrons from the valence band (VB) of Ag$_3$PO$_4$ could be excited to its conduction band (CB), resulting in the formation of holes in the valence band (VB). Since the $E_{VB}$ of TiO$_2$ is more negative than that of Ag$_3$PO$_4$, holes from Ag$_3$PO$_4$ also transferred to TiO$_2$ and directly degraded RhB, which was absorbed on the surface of TiO$_2$ during the oxidization process [25,31]. According to literature, the conduction potential of Ag$_3$PO$_4$ is higher than the activation energy of single-electron oxygen, preventing photogenerated electrons from being captured by dissolved oxygen.

![Figure 10. A schematic illustration of the proposed photocatalytic mechanism of Ag$_3$PO$_4$/TiO$_2$@Ti$_3$C$_2$ (A4) exposed to solar light.](image)

Instead, a small amount of Ag is formed as a result of photocorrosion [31]. Electrons and holes in Ag could also be excited by light energy, with electrons migrating to the CB of TiO$_2$, while the remaining holes could be recombined with photoexcited electrons in Ag$_3$PO$_4$ CB, thereby, partially preventing further corrosion [31]. Furthermore, some electrons were transferred from TiO$_2$ and Ag$_3$PO$_4$ to Ti$_3$C$_2$ MXene, resulting in band bending and the formation of a Schottky junction as well as a uniform Fermi level [4,17,39]. The photo-reduction reaction occurring on the surface of Ti$_3$C$_2$ and the TiO$_2$ conduction band generated $•$O$_2^-$ radicals, which are required for effective RhB decomposition. The production of $•$O$_2^-$ and h$^+$ could easily degrade a variety of dyes, including RhB, MB, CV, and MO, under solar light. The proposed mechanism is consistent with scavenger trapping experiments and is formulated as follows:

1. **Photo-oxidation reaction:**
   
   Ag$_3$PO$_4$ + hv $\rightarrow$ Ag$_3$PO$_4$ (h$^+$ + e$^-$)

   ![Photo-oxidation reaction](image)
Ag₃PO₄ (h⁺) + TiO₂ → Ag₃PO₄ + TiO₂ (h⁺)
TiO₂ (h⁺) + RhB → By-products + CO₂ + H₂O

2. Photo-reduction reaction:
   - Photoexcited electrons and separation of e⁻/h⁺:
     Ag⁺ + Ag₃PO₄ (e⁻) → Ag + Ag₃PO₄
     Ag + hv → Ag (h⁺ + e⁻)
   - Transfer routes and formation of O₂•⁻:
     Ag₃PO₄ (e⁻) + Ag (h⁺) → Ag₃PO₄ + Ag
     Ag (e⁻) + TiO₂ → Ag + TiO₂ (e⁻)
     TiO₂ (e⁻) + Ti₃C₂ → TiO₂ + Ti₃C₂ (e⁻)
     Ag₃PO₄ (e⁻) + Ti₃C₂ → Ag₃PO₄ + Ti₃C₂ (e⁻)
     Ti₃C₂ (e⁻) + O₂ → Ti₃C₂ + O₂•⁻
     TiO₂ (e⁻) + O₂ → TiO₂ + O₂•⁻
   - Degradation of pollutants:
     O₂•⁻ + RhB → By-products + CO₂ + H₂O

Based on this proposed mechanism, the stability of the composite did not significantly improve. This might be due to a longer electron transfer distance between TiO₂ and Ti₃C₂ than between Ag₃PO₄ and Ti₃C₂. Second, an unknown amount of Ti₃C₂ on the surface and/or insufficient interfacial contact between Ag₃PO₄ and Ti₃C₂ might lower the composite’s stability. Both reasons could not prevent the rapid formation of Ag, reducing the stability and photocatalytic performance of the composite.

4. Conclusions

This study successfully synthesized Ag₃PO₄/TiO₂@Ti₃C₂ composites by precipitating Ag₃PO₄ NPs on the surface of TiO₂@Ti₃C₂ flowers. Some characterization methods were conducted to investigate the surface morphology, structural composition, surface area, and optical properties of Ag₃PO₄/TiO₂@Ti₃C₂. The characteristics of Ag₃PO₄-deposited TiO₂@Ti₃C₂ endow superior photocatalytic activities in the comparison with TiO₂@Ti₃C₂, pristine Ag₃PO₄, and Ag₃PO₄/TiO₂ P25, particularly sample A4. This composite exhibited excellent photocatalytic performance for various organic dyes (degraded 97% RhB, 94% MB, 99% CV, and 92% MO) within a short period of time when exposed to solar light irradiation.

The high photocatalytic activity of the composite was due to the high surface area of TiO₂@Ti₃C₂ with small Ag₃PO₄ particles (4–10 nm) that can easily reach dye molecules. The e⁻/h⁺ transfer throughout the composite system also contributes to increased charging transfer, expanded light absorption wavelength, and decreased electron–hole pair recombination, which gives synergistic effects for photocatalytic activity. Based on the scavenger trapping and recycling test results, the mechanism was proposed.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/nano12142464/s1, Figure S1: EDS patterns of Ag₃PO₄/TiO₂@Ti₃C₂ (sample A4); the inset image shows a SEM image of the sample, Figure S2: SAED image of Ag₃PO₄/TiO₂@Ti₃C₂ (sample A4) taken of an arbitrary area, Figure S3: XPS survey spectra of Ti₃C₂, TiO₂@Ti₃C₂, and Ag₃PO₄/TiO₂@Ti₃C₂, Figure S4: (a) F 1s high-resolution XPS spectra of Ti₃C₂, and (b–c) Ag 3d and P 1s high-resolution XPS spectra of Ag₃PO₄/TiO₂@Ti₃C₂ (sample A4), Figure S5: Photodegradation absorption spectra of (a) Methylene Blue, (b) Crystal Violet, and (c) Methylene Orange under solar light.

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