



Article Rice Crust-Like ZnO/Ti₃C₂T_x MXene Hybrid Structures for Improved Photocatalytic Activity

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Abstract: Novel two-dimensional ZnO/Ti₃C₂T_x hybrid photocatalysts with modified surface areas were prepared using a simple calcination technique. The microstructures, crystalline features, and bonding states of the ZnO structure-covered $Ti_3C_2T_x$ MXenes were closely characterized using various tools. The photoluminescence intensity of the hybrid photocatalyst was greatly reduced compared to the pristine ZnO, while its Brunauer-Emmett-Teller (BET) surface area increased by more than 100 times. Under solar light illumination, the photocatalytic degradation efficiency of the hybrid photocatalyst for organic pollutants (MO, RhB) appeared to be three-fold larger as compared to pristine ZnO. The superb photocatalytic performance of the photocatalyst was attributed to several factors, such as ideal band alignment, Schottky barrier formation, and large surface area. Moreover, the ZnO/Ti₃C₂T_x hybrid photocatalyst showed excellent cycling stability. These results suggest that the novel hybrid structure may be a potential candidate for removing organic pollutants in wastewater.

Keywords: Ti₃C₂T_x MXene; hybrid structures; ZnO; organic pollutants; photocatalysts

1. Introduction

In recent decades, a growing number of people have become concerned with harmful gas emissions from industry and organic pollutants in wastewater, most of which have detrimental effects on human health and the environment [1–3]. According to the literature, rhodamine B (RhB) and methyl orange (MO) are popularly used as colorants in textiles, paper, food products, fiber dyeing, and printing [4]. Owing to their widespread applications, both chemicals have been released to the environment via wastewater [5]. Some dyes can be extremely toxic and mutagenic, which is the leading cause of esthetic pollution, carcinogenicity, and neurotoxicity for animals, human health, and aquatic life [5]. For instance, repeated exposure to toxic organic dyes can raise heart palpitations, skin irritation, shock, and quadriplegia even at low concentrations [6–8]. These dyes limit valuable downstream uses such as drinking water, photosynthetic activity, and irrigation. In particular, the presence of a small number of dyes in solution is highly visible. The natural deterioration of these dyes in wastewater is very difficult and takes a long time with complicated processes [9,10].

With rapid progress in nanoscience and nanotechnology, photocatalysts that utilize light-assisted catalytic reactions have played a crucial role in removing these toxic pollutants [11,12]. In particular, the removal of organic contaminants in wastewater has been both promising and challenging. To improve the photocatalytic performance, a variety of oxide semiconductors such as ZnO, g-C₃N₄, CdS, and TiO₂ have been extensively investigated based on their chemical stability, wide bandgap, and cost-effectiveness [12–17]. However, these oxide semiconductors suffered from photo corrosion and high carrier recombination rates [18–20].

A novel class of two-dimensional (2D) materials, MXenes, has been explored for diverse applications, including aqueous supercapacitors, water filtration, photoelectrochemical water splitting,

electromagnetic interference shielding, and Li ion batteries, due to their unique structure and properties [16,21,22]. Conventionally, MXenes are synthesized using an HF etching technique from MAX phase and non-MAX phase precursors, where A is in group A of the periodic table (mostly IIIA or IVA) [23]. Therefore, MXenes have the chemical formula of $M_{n+1}X_nT_x$ with n = 1, 2, or 3, where M is an early transition metal (typically, Ti, Mo, Cr, and V), X stands for carbon or nitrogen, and T_x denotes the surface functional group (-F, -OH, and =O). The subscript x describes the coverage of termination groups [24]. In 2011, the first reported MXene, Ti₃C₂T_x, was synthesized by Gogotsi and colleagues by selectively etching Al layers of the Ti₃AlC₂ MAX phase [25]. To date, around 55 different MXenes have been discovered, and dozens have been theoretically predicted via the removal of the A-layer from their parent MAX phases [26]. The selective etching of the A element is accomplished typically using two kinds of etchants: (i) non-HF-forming and (ii) HF-forming etchants. With rising HF concentration, strong M-A bonds in the MAX phase are broken and the AlF₃ phase is produced as a byproduct following the chemical reaction below [27]:

$$M_{n+1}AlX_n + 3HF \rightarrow M_{n+1}X_n + AlF_3 + 3/2H_2$$
⁽¹⁾

Among matters in the MXene family, $Ti_3C_2T_x$ has been most highlighted thanks to its unique and novel etching technique and detailed theoretical works on its electrochemical and physical properties [28–30]. Since $Ti_3C_2T_x$ MXene basically shows a metallic property, coupling with other semiconductors is in demand for photocatalytic applications [31,32]. For example, Qiao et al. demonstrated that the photocatalytic activity of $Ti_3C_2T_x$ MXene could be improved when merged with CdS [32]. Recently, Zhu and co-workers synthesized Ti_3C_2 -Bi/BiOCl by a facile solvothermal technique and found notably enhanced photocatalytic performance in degrading ciprofloxacin [33].

In this work, rice crust-like ZnO was successfully grafted onto $Ti_3C_2T_x$ MXene using a simple calcination technique for enhanced photocatalytic dye decomposition efficiency. At room temperature, the photocatalytic performance of an optimized ZnO/Ti₃C₂T_x hybrid structure was three times higher than that of pure ZnO under solar light illumination. In addition, its excellent recyclability was also demonstrated. The elaborate hybrid design and simple synthesis routine may extend the breadth of applications of $Ti_3C_2T_x$ -based hybrid materials for high-performance photocatalysts. The ZnO/Ti₃C₂T_x hybrid photocatalyst is non-toxic, chemically stable, and its synthesis routine developed in this work can be scaled up to the large-scale manufacturing because the synthetic scheme is simple. Considering its demonstrated performance and facile manufacturability together, the ZnO/Ti₃C₂T_x photocatalyst may be a practical choice for removing toxic dyes in water treatment plants.

2. Results and Discussion

2.1. Crystal Structures and Morphologies

Figure 1 illustrates X-ray diffraction (XRD) patterns of pure ZnO, $Ti_3AlC_2 MAX$, $Ti_3C_2T_x MX$ ene, and the ZnO/ $Ti_3C_2T_x$ hybrid structure. After HF etching, the main diffraction peaks become weaker and broader, and the major (002) peak of the $Ti_3AlC_2 MAX$ phase is shifted to lower 2θ angles (blue pattern). Interestingly, the intense (104) peak of Ti_3AlC_2 appearing at $2\theta = 39.19^{\circ}$ disappears after etching. All of these indicate that Al layers were appropriately removed from their parent MAX phase, creating $Ti_3C_2T_x MX$ ene, and are in good agreement with previous reports [24,25]. The XRD pattern of ZnO reveals it has a hexagonal wurtzite structure of the well-crystallized ZnO (JCPDS card No. 0036-1451) [34]. A ZnO/ $Ti_3C_2T_x$ hybrid structure displays mixed peaks coming from both the ZnO microstructure and $Ti_3C_2T_x MX$ ene, which signals the successful formation of the hybrid structure. Small TiO₂ peaks, which are assigned to low-index planes (JCPDS card No. 21-1272), indicate that this

byproduct may be generated during the formation of the hybrid structure. The d-spacings of major planes were calculated using Bragg's law [35]:

$$d = \frac{n\lambda}{2\sin\theta} \tag{2}$$

where *d* is the interplanar spacing, n is a positive integer, λ is the X-ray wavelength, and θ is the angle of incidence. For instance, the *d*-spacing of the ZnO (101) plane was calculated to be ~0.25 nm, which agrees well with the value from HR-TEM measurements.



Figure 1. XRD patterns of the Ti_3AlC_2 MAX phase, $Ti_3C_2T_x$ MXene, pure ZnO, and ZnO/ $Ti_3C_2T_x$ hybrid structure.

Figure 2 shows scanning electron microscopy (SEM) images of the Ti_3AlC_2 MAX phase, $Ti_3C_2T_x$ MXene, pure ZnO, and ZnO/ $Ti_3C_2T_x$ hybrid structure. The characteristic laminate structure of the Ti_3AlC_2 MAX phase is found in Figure 2a. A clear multilayer structure like an accordion is developed after HF etching, revealing the successful transformation to $Ti_3C_2T_x$ MXene (Figure 2b). In Figure 2c, ZnO, which was prepared at standard calcination conditions, shows hexagonal pyramid or truncated hexagonal pyramid microstructures. The pyramid sizes range from 30 to 50 µm. Once hybridization is completed, numerous ZnO structures resembling rice crust are coated on the $Ti_3C_2T_x$ surface (Figure 2d). The diameters of the ZnO structures are in the range of 250–500 nm. Interestingly, the rice crust-like ZnO structure is distinct from that of pristine ZnO.



Figure 2. SEM images of (**a**) $Ti_3AlC_2 MAX$ phase, (**b**) $Ti_3C_2T_x MX$ ene, (**c**) pure ZnO, and (**d**) ZnO/ $Ti_3C_2T_x$ hybrid structure. The insets show low-magnification SEM images.

The HR-TEM images and corresponding FFT/SAED patterns further support the formation of the hybrid structure, as shown in Figure 3. Discrete, color-contrasting, and highly crystalline regions of ZnO and $Ti_3C_2T_x$ are observed along with the sharp interfaces between them (Figure 3a,b). The measured interplanar distance of 0.25 nm, which corresponds to the (101) plane of ZnO, is identical with the value calculated from the XRD pattern (Figure 3b). The SAED pattern in Figure 3d shows a combination of diffraction rings and hexagonal diffraction spots, which are ascribed to highly crystalline ZnO and $Ti_3C_2T_x$, respectively [36,37]. The high crystallinity and sharp interface are considered important rate-determining factors for charge generation, mostly in the ZnO part, and for charge transfer across the ZnO-Ti₃C₂T_x boundary.

2.2. Bonding States

Figure 4 exhibits the full and focused X-ray photoelectron spectroscopy (XPS) spectra of pure $Ti_3C_2T_x$ MXene and the rice crust-like ZnO/ $Ti_3C_2T_x$ hybrid structure. For both of them, several primary peaks are observed at the binding energies of 682.57, 529.17, 459.25, and 285.19 eV, which are assigned to F 1d, O 1d, Ti 2p, and C 1s, respectively (Figure 4a). This represents that both materials include $Ti_3C_2T_x$ Mxene, and the MXene is terminated with –F and =O/–OH [38]. In contrast, the two main peaks of Zn $2p_{1/2}$ and Zn $2p_{3/2}$ are only found for the ZnO/ $Ti_3C_2T_x$ hybrid structure. Those peaks appear at 1043.16 and 1020.9 eV, indicating the presence of Zn^{2+} in the hybrid structure (Figure 4b) [39]. Furthermore, three O 1s peaks appear at 530.98, 529.57, and 528.48 eV for the hybrid structure, which correspond to the Zn–O, Ti–O–Zn, and Ti–O–Ti bonds, respectively (Figure 4c). The two higher-energy peaks come from ZnO, while the lowest-energy peak arises from TiO_x on the surface of MXene. The slight shift of the Ti–O–Ti peak to the lower energy compared to pure MXene may be caused by oxygen vacancies [40]. On the other hand, a C–Ti–Ox peak is observed at 530.58 eV for pure $Ti_3C_2T_x$ MXene without Zn–O and Ti–O–Zn peaks. The Ti 2p and C 1s spectra for the hybrid structure represent the presence of the $Ti_3C_2T_x$ phase (Figure 4d,e). In more detail, the Ti 2p

peaks are deconvoluted into two majority groups: Ti atoms linked to termination groups (OH and/or O)–Ti²⁺–C; (OH and/or O)–Ti–C; F–Ti–C), and Ti atoms linked to O (Zn–O–Ti and TiO₂), which may be a consequence of surface oxidation [41,42]. Analyzing subpeaks, the (OH and/or O)–Ti²⁺–C and Zn–O–Ti peaks are strong, whereas a TiO₂ peak is weak. And the sharp peak position of Ti $2p_{3/2}$ at 456.9 eV is higher than that of pure Ti₃C₂T_x MXene (453.2 eV). These indicate that the Ti₃C₂T_x MXene is hybridized with ZnO on its surface and the TiO₂ is a minor phase. Moreover, the C 1s peaks are fit into two groups. The majority peak at 283.5 eV, which corresponds to C–Ti–T_x, is slightly shifted to higher energy compared to that of pure Ti₃C₂T_x MXene (283.3 eV). This slight shift can be ascribed to defects in the Ti–C layers caused by the hybridization procedure. On the other hand, the remaining peak corresponds to C–C. The appearance of this C–C peak may be due to the selective dissolution of Ti at high temperatures, which leads to graphitic C–C [42,43]. All these results are indicative of the formation of the ZnO/Ti₃C₂T_x hybrid structure. In addition, it is estimated from the XPS spectra in Figure 4d that only 1.3 at% of Ti atoms belong to TiO₂. This supports that the TiO₂ is a minor phase.



Figure 3. (a,b) HR-TEM images, (c) FFT pattern, and (d) SAED pattern of a $ZnO/Ti_3C_2T_x$ hybrid structure.



Figure 4. (a) Full XPS spectra of pure $Ti_3C_2T_x$ MXene and the ZnO/ $Ti_3C_2T_x$ hybrid structure. Focused XPS spectra of (b) Zn 2p, (c) O 1s, (d) Ti 2p, and (e) C 1s for the hybrid structure are shown. O 1s spectrum for pure MXene is also displayed in (c) for comparison.

2.3. Optical Properties, Specific Surface Area, and Thermal Decomposition

Figure 5a displays the UV-Vis absorption spectra of the as-synthesized products. Pristine ZnO shows a UV absorption peak around 268–380 nm, which is a characteristic peak of pure ZnO. Unlike pure $Ti_3C_2T_x$ MXene, which just displays a straight line without a meaningful absorption peak, clear absorption peaks are observed for $ZnO/Ti_3C_2T_x$ hybrid structures in the visible region. Here, three kinds of hybrid structures were prepared by modulating the relative weight ratios of $Ti_3C_2T_x$ to ZnO in the synthesis process (see "Section 3" for more detail). The bandgap energies are calculated at ~1.6 eV for all hybrid structures, which is narrower than that of pure ZnO, presumably due to the presence of metallic $Ti_3C_2T_x$ MXene, as shown in Figure S1. Figure 5b shows the room temperature PL spectra (with λ_{ex} = 270 nm) of the as-synthesized photocatalysts. It is well known that lower PL intensity represents a retarded electron-hole recombination rate, leading to enhanced photocatalytic performance. It is found that pure ZnO displays a big visible emission band centered at 542 nm. On the other hand, the PL intensities of hybrid structures are remarkably reduced from the value of pristine ZnO, which is attributed to the efficient separation of photogenerated electron and hole pairs via the Schottky junction. It is discernible that the PL intensity of ZnO/Ti₃C₂T_x-2 is weakest, indicating that the electron-hole recombination is suppressed most and carrier lifetime becomes longest for this hybrid structure. From these results, it is expected that the hybrid structures outperform pure ZnO in photocatalytic activity.



Figure 5. (a) UV-Vis absorption spectra, (b) PL spectra, and (c) N_2 adsorption/desorption isotherms of as-synthesized samples.

The specific surface areas of as-synthesized samples were estimated by Brunauer-Emmett-Teller (BET) measurements. As shown in Figure 5c, $Ti_3C_2T_x$ MXene shows a type III/IV isotherm, indicative of a mesoporous material [44]. It is observed that the surface area of pristine ZnO substantially increases when it is hybridized with $Ti_3C_2T_x$ MXene. The estimated specific surface areas are 0.01 and 2.48 m²g⁻¹ for pure ZnO and ZnO/Ti₃C₂T_x-2 hybrid structure, respectively. This significant increase in specific surface area is also beneficial for enhanced photocatalytic activity. For a better understanding of the three photocatalysts, their major physical parameters are summarized in Table 1.

 Table 1. Summary of major physical parameters for three different materials.

Photocatalyst	Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Estimated Bandgap (eV)	Sheet Resistance (M Ω sq ⁻¹)
ZnO	0.01	$1.6 imes 10^{-4}$	3.3	23.94
ZnO/Ti ₃ C ₂ T _x	2.48	0.018	1.6	18.05
Ti ₃ C ₂ T _x MXene	9.19	0.037		0.95

Furthermore, thermogravimetric analysis (TGA) was conducted to examine the thermal decomposition of the ZnO/Ti₃C₂T_x hybrid structure. Figure S2 exhibits the TGA curves of pure Ti₃C₂T_x MXene and ZnO/Ti₃C₂T_x hybrid structure tested over a temperature range of room temperature to 800 °C. The Ti₃C₂T_x MXene shows three weight-changing stages (Figure S2a). A weight loss (6.51%) in the temperature range of 24–235 °C is attributed to the removal of water that was adsorbed on the surface of Ti₃C₂T_x. Then, in the second temperature range of 235–418 °C, the sample weight increases by 3.19%, which is caused by the oxidation of the MXene. At the last stage, the Ti₃C₂T_x MXene is decomposed, starting from 418 °C. In contrast, the ZnO/Ti₃C₂T_x hybrid structure reveals two weight-changing stages (Figure S2b). In the first stage of 24–400 °C, the moisture is released from the sample. Then, the hybrid structure undergoes thermal decomposition in the second stage, starting from ~420 °C. The decomposition-initiating temperature, which is almost the same as that of pure Ti₃C₂T_x MXene, shows that the major component of the hybrid structure is Ti₃C₂T_x MXene. The weight loss (1.97%) greatly reduced from the value (5.17%) of Ti₃C₂T_x MXene is ascribed to the enhanced thermal stability of the hybrid structure, which is enabled by the MXene-covering effect of surface ZnO structures.

2.4. Photocatalytic Activities

Figure 6 shows time-dependent dye degradation trends under light illumination using pure ZnO and $ZnO/Ti_3C_2T_x$ hybrid structures as photocatalysts. Two types of dyes (MO, RhB) were used as probe dyes. The real-time dye concentration (C) in Figure 6a,b was converted from the absorbance peak intensity at the characteristic wavelength of each dye: 463 nm for MO and 553 nm for RhB (Figure 6c,d). The real-time dye concentration relative to its initial concentration (C_0) represents the time-dependent dye degradation efficiency. From Figure 6a,b, the photolysis of MO and RhB appears to be negligible, revealing that the dyes are hardly degraded without the photocatalyst (pink curves). When a photocatalyst is introduced into the dye solutions, the light absorbance decreases and, correspondingly, the dye degradation efficiency increases as a function of irradiation time. Apparently, the dye degradation efficiencies of $ZnO/Ti_3C_2T_x$ hybrid structures are far higher than that of pristine ZnO. For example, the pure ZnO degrades 49% of MO in 50 min and 51% of RhB in 70 min. In contrast, the $ZnO/Ti_3C_2T_x$ hybrid structures turn out to degrade more than 60% of the dyes within the first 10 min of irradiation. To fully decompose MO and RhB, irradiation times of 50 min and 70 min are necessary, respectively (see the almost flat absorption curves and transparent solutions in Figure 6c,d). For the best hybrid structure, the MO and RhB degradation efficiencies are estimated to be 99.7% (in 50 min) and 99.8% (in 70 min), respectively. Moreover, the ¹H nuclear magnetic resonance (NMR) spectra of MO in D₂O were analyzed and compared before and after light illumination, as shown in Figure S3. Before light illumination, the ¹H NMR spectrum of MO shows a spiky singlet at δ^{1} H = 2.99 ppm, which corresponds to aliphatic protons, and several signals over the δ^1 H range of 6.75–8.00 ppm, which represent the existence of aromatic protons [45,46]. After 50 min of photocatalytic treatment, the proton spectra in the aromatic and aliphatic regions disappear, and only a peak for small aliphatic hydrocarbons is found. These prove the actual degradation of MO molecules induced by light illumination.



Figure 6. C/C_0 vs. irradiation time curves for the photocatalytic degradation of (**a**) MO and (**b**) RhB, using pure ZnO and ZnO/Ti₃C₂T_x hybrid structures as photocatalysts. Blank represents the spontaneous decomposition of MO and RhB without photocatalyst. The time-dependent UV-Vis absorption spectra of (**c**) MO and (**d**) RhB obtained from the ZnO/Ti₃C₂T_x-2 hybrid structure are shown.

In Table 2, we compare the dye degradation performance of our hybrid photocatalyst with previous reports. Here, times for individual photocatalysts to fully degrade RhB are compared. It is obvious that our novel $ZnO/Ti_3C_2T_x$ hybrid photocatalyst shows better photocatalytic performance.

Report	Photocatalyst	Light Source	RhB Solution	Degradation Time
Zhang et al. [47]	Fe ₂ O ₃ /ZnFe ₂ O ₄ /Ti ₃ C ₂	visible light	100 mL (20.8 μM)	150 min
Cui et al. [48]	Bi ₂ WO ₆ /Nb ₂ CT _x	visible light	100 mL (31.3 μM)	100 min
This work	ZnO/Ti ₃ C ₂ T _x	visible light	50 mL (20 μM)	70 min

 Table 2. Comparison of photocatalytic performance of various photocatalysts.

To evaluate the recyclability of the $ZnO/Ti_3C_2T_x$ hybrid photocatalyst, cyclic photocatalytic tests were also performed. In the cyclic tests, the photocatalyst just undergone through a photodegradation cycle was collected from the photoreactor, washed with DI water several times, and dried in an oven at 60 °C for the next cycle. From Figure 7a,b, no significant change in photocatalytic dye degradation is found. Furthermore, XRD measurements were conducted before and after cyclic tests to check any possible deterioration of crystal quality. Figure 7c exhibits that the crystalline phase and quality of the hybrid structure are well maintained even after recycling five times. These results prove the excellent recyclability and photostability of the hybrid nanostructure.



Figure 7. Recyclability of the $ZnO/Ti_3C_2T_x$ -2 photocatalyst for photocatalytic degradation of (**a**) RhB and (**b**) MO. (**c**) XRD patterns of the hybrid photocatalyst before and after the cyclic photodegradation tests of RhB.

A proposed mechanism for the enhanced photocatalytic performance of the ZnO/Ti₃C₂T_x hybrid structure is schematically illustrated in Figure 8. The improved photocatalytic performance may be ascribed to the creation of a Schottky junction, which can prevent the recombination of photogenerated electron-hole pairs, as evidenced by PL measurements [32,49]. There are two reasons for this phenomenon: (1) the Fermi level of Ti₃C₂T_x MXene is lower than the conduction band (CB) edge of ZnO, and (2) the work function of ZnO is higher than that of Ti₃C₂T_x. When the light illuminates the ZnO/Ti₃C₂T_x hybrid structure, optically excited electrons quickly move from the CB of ZnO to Ti₃C₂T_x, and the Schottky barrier hinders their return [50,51]. These generated electrons are likely to attack O₂ molecules, resulting in superoxide anion radicals ($^{\circ}O_{2}^{-}$). At the same time, holes generated in the valence band (VB) of ZnO are apt to interact with H₂O or OH⁻ ions, producing $^{\circ}OH$ radicals.

Afterward, organic micropollutants can be decomposed into several products via the reaction with $^{\circ}OH$ and $^{\circ}O_2^{-}$ active radicals. The whole photodegradation process can be briefly given as follows [16,51]:

$$ZnO + h\nu \rightarrow ZnO (e_{CB}^{-} + h_{VB}^{+})$$
(3)

$$\text{Fi}_{3}\text{C}_{2}\text{T}_{x} + \text{ZnO}(\text{e}_{\text{CB}^{-}} + \text{h}_{\text{VB}^{+}}) \rightarrow \text{Ti}_{3}\text{C}_{2}\text{T}_{x}(\text{e}^{-}) + \text{ZnO}(\text{h}_{\text{VB}^{+}})$$
(4)

$$Ti_3C_2T_x (e^-) + O_2 \rightarrow {}^{\bullet}O_2^- + Ti_3C_2T_x$$
 (5)

$$ZnO(h_{VB}^{+}) + OH^{-} \rightarrow ^{\bullet}OH$$
 (6)

 O_2^- or $^{\bullet}OH + \text{organic dyes} \rightarrow ^{\bullet}R$ (intermediates) \rightarrow reaction products + CO_2 , H_2O , O_2 (7)



Figure 8. Proposed mechanism for the improved photocatalytic performance of the $ZnO/Ti_3C_2T_x$ hybrid structure.

3. Materials and Methods

3.1. Materials and Chemicals

 Ti_3AlC_2 powder with a size of ~400 mesh was supplied from 11 Technology Co., Ltd. (Changchun, China). Zinc nitrate hexahydrate (Zn(NO₃)₂ 6H₂O), MO (C₁₄H₁₄N₃NaO₃S), RhB (C₂₈H₃₁ClN₂O₃), and deuterium oxide (D₂O) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Hydrofluoric acid (HF, 48–51%) was purchased from Fisher Scientific (Fair Lawn, NJ, USA). Ethyl alcohol

 (C_2H_5OH) was bought from Daejung Chem (Siheung, South Korea). All chemicals were used as supplied without further treatment.

3.2. Preparation of $ZnO/Ti_3C_2T_x$ Hybrid Structures

 $Ti_3C_2T_x$ MXene was synthesized by selectively etching Al layers of the parent Ti_3AlC_2 MAX phase powder, employing the improved Gogotsi's method [25]. Typically, a 1.0 g of Ti_3AlC_2 powder was slowly immersed into 28 mL of HF under stirring at 250 rpm, and the mixed solution was further stirred in an oil bath at 50 °C. After 24 h of reaction, the precipitate was collected and washed ten times with DI water until the pH value of suspension fell to ~7. Then, the obtained suspension was dried overnight in an oven at 60 °C for further experiments.

ZnO/Ti₃C₂T_x hybrid structures were prepared by a simple calcination technique, as schematically presented in Figure 9. Briefly, varying amounts (10, 20, 30 mg) of the pre-synthesized Ti₃C₂T_x MXene powders were well dispersed in 5 mL of Zn²⁺ solution (1.34 M). Then, the mixed solution was dried in the oven to evaporate the solvent, leaving behind a powder. At the next step, the left powder was placed in a crucible and calcined for 4 h at 550 °C with a heating rate of 5 °C/min in an ambient atmosphere. Finally, the obtained products were cooled to room temperature and named as ZnO/Ti₃C₂T_x-1 (10 mg), ZnO/Ti₃C₂T_x-2 (20 mg), and ZnO/Ti₃C₂T_x-3 (30 mg), respectively. Moreover, the pure ZnO was synthesized for comparison in the same conditions without Ti₃C₂T_x MXene.



Figure 9. Schematic illustration of the synthesis process of ZnO/Ti₃C₂T_x hybrid structures.

3.3. Characterizations

The XRD patterns of thus-synthesized samples were measured using an X-ray diffractometer (Rigaku, SmartLab, Tokyo, Japan) with 3 kW Cu K_{α} radiation. Their morphologies and detailed structures were examined using SEM (Hitachi, S-4700, Tokyo, Japan) and transmission electron microscopy (TEM, Tecnai, G2 F30 S-TWIN, Hillsboro, OR, USA). The optical properties of these samples were analyzed using photoluminescence spectroscopy (PL, Cary Eclipse, Santa Clara, CA, USA) and UV-Vis spectrophotometry (UV-Vis, Cary 50 Bio, Santa Clara, CA, USA). The bonding states of selected samples were examined using XPS (K-alpha thermo electron, Thermo Fisher Scientific, Boston, MA, USA). Thermogravimetric analysis (TGA, SDT Q600 V20.9) was conducted in an ambient

atmosphere from room temperature to 800 °C. The ¹H NMR spectroscopy was analyzed on MO in D₂O solvent using a Bruker spectrometer (Billerica, MA, USA) with the operating frequency of 400 MHz. Furthermore, the porosity and specific surface area were analyzed from N₂ adsorption-desorption isotherms obtained by a BET analyzer (BEL JAPAN Inc., Osaka, Japan).

3.4. Photocatalytic Dye Degradation Tests

The photocatalytic degradation properties of MO and RhB in water under solar light were evaluated to study the photocatalytic activities of pristine ZnO and ZnO/Ti₃C₂T_x hybrid structures. A xenon lamp (300 W) was used as a solar simulation source (MAX-350). For this test, 30 mg of the photocatalyst was well dispersed in 50 mL of dye solutions (20 μ M) and stirred in a dark environment to enable adsorption-desorption equilibrium at room temperature. Then, these mixture solutions were illuminated by a xenon lamp over varying time spans (0–70 min). Time-dependent dye degradation was recorded from UV-Vis absorption spectrum every 10 min at ambient temperature. The photodegradation efficiency was calculated using the following formula:

% degradation =
$$(1 - C_0/C_t) \times 100$$
 (8)

where C₀ and C_t are the initial concentration and real-time concentration of a dye, respectively.

4. Conclusions

In summary, $ZnO/Ti_3C_2T_x$ hybrid structures with rice crust-like morphologies were synthesized by a simple calcination technique. In the hybrid structures, ZnO microstructures were coated on the surface of $Ti_3C_2T_x$ MXene, maintaining high crystal quality and sharp interfaces. Unlike the pristine MXene, the hybrid structures showed clear light absorption peaks, and their PL intensities were greatly reduced from the value of pure ZnO. The ZnO/Ti₃C₂T_x hybrid structures revealed superb photocatalytic degradation performance for organic dyes (MO, RhB). They degraded those dyes three times faster than pristine ZnO under solar light illumination. In addition, the hybrid photocatalysts showed excellent recyclability. A plausible mechanism for the enhanced photocatalytic activity was also suggested. The synthesis routine and experimental results in this work may widen the application areas of MXene-based hybrid structures for photocatalytic pollutant treatment.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/10/1140/s1, Figure S1: Tauc plots for pure ZnO and ZnO/Ti₃C₂T_x-2 hybrid structure, Figure S2: TGA curves for pure Ti₃C₂T_x MXene and ZnO/Ti₃C₂T_x-2 hybrid structure, Figure S3: ¹H NMR spectra of MO in D₂O before and after 50 min of light irradiation.

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