Facile Preparation of Highly Active CO₂ Reduction (001)TiO₂/Ti₃C₂Tx Photocatalyst from Ti₃AlC₂ with Less Fluorine

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Abstract: To date, (001)TiO₂/Ti₃C₂Tx hybridized photocatalyst is usually prepared through the complicated treatment of Ti₃AlC₂ in the presence of corrosive fluorine with a molar ratio of nF:nTi of more than 20. To reduce the use of corrosive fluorine, herein, exploiting beyond the conventional method, we report a facile synthetic method for (001)TiO₂/Ti₃C₂Tx, elaborately using HF as both an etchant for Al elimination and a morphology control agent for the growth of (001)TiO₂ nanosheets, with a sharply diminished use of fluorine (nF:nTi = 4:1) and simplified operation procedures. After optimization, the resulting (001)TiO₂/Ti₃C₂Tx heterojunction exhibited markedly high photocatalytic activity with the CO₂ reduction rate of 13.45 μmol g⁻¹ h⁻¹, which even surpasses that of P25 (10.95 μmol g⁻¹ h⁻¹), while the photoelectron selectivity to CH₄ is approaching 92.84%. The superior photoactivity is interpreted as the fact that Ti₃C₂Tx with a lower work function induces photoinduced hole transfer and suppresses the charge recombination, thus facilitating the CO₂ multi-electron reduction. This study provides a novel and simple synthesis for (001)TiO₂/Ti₃C₂Tx towards sustainable energy transformations.

Keywords: MXenes; Ti₃C₂; (001) TiO₂; photocatalysis; CO₂ reduction

1. Introduction

TiO₂ is an extremely attractive candidate for photocatalysis, given the multiple advantages of low price, chemical durability, and ecological friendliness [1,2]. However, realistic applications of TiO₂ are restricted due to the rapid recombination of photogenerated electron–hole pairs. Therefore, numerous methods have been developed with the focus on the promotion of photoinduced charge transfer, such as loading co-catalyst [3,4], morphology modulation [5], and the construction of heterojunction [6–8]. Thereinto, loading co-catalyst on TiO₂ has hitherto been a satisfactory choice for improving its photoactivity and stability by accelerating the separation efficiency of photogenerated carriers. Nevertheless, the widespread utilization of noble-metal cocatalysts, such as Au and Pt, remains challenging for both high cost and scarcity. Hence, there is a considerable incentive to exploit cost-effective noble-metal-free cocatalysts for the enhancement of the TiO₂ photocatalytic performance.

MXenes, a new family of two-dimensional layered transition metal carbides, nitrides, or carbonitrides, possess a structural formula of Mₙ₊₁XₙTv, where M refers to the early transition metal, X stands for carbon and/or nitrogen, T represents the surface functional groups (-O, -OH, -F), and n ranges from 1 to 3. Along with a mushrooming in the study of MXenes, up to now, more than 40 MXenes have been synthesized by selectively etching the metal layer from the precursor MAX phases [9]. Moreover, various syntheses for
different-dimension MXenes (e.g., quantum nanodots, nanorods, and nanosheets) have been reported [10]. Among all the MXenes, Ti3C2 is one of the most representative and prevalently studied materials in the field of photocatalysis, especially as a co-catalyst, because of the following reasons: (i) Its intrinsically metallic conductivity assures the efficient separation and transfer of photogenerated charge carriers from semiconductors [11–14]. (ii) The appropriate work function allows it to construct Schottky heterojunction with most semiconductors to alter their photoelectric properties [15,16]. As reported in previous work [17], Ti3C2T x can be coupled with (Ti, C) co-doped BiOBr to manipulate the carrier flow direction and achieve specific redox reactions via the elaborated Schottky heterojunction. (iii) The enormous surface functional groups favor the enhanced reactant adsorption capability [18].

In recent years, MXene-based materials receive considerable attention in photo/electrocatalysis. Amrillah et al. provided an insightful discussion on a series of syntheses for MXene-based and MXene-derived catalysts, including alcoholysis, hydrothermal treatment, and calcination process [10]. Typically, Ti3C2 is an ideal platform for the in situ growth of TiO2 to prepare TiO2-Ti3C2 composite materials by partial oxidation. TiO2-Ti3C2 heterojunctions prepared by such in situ methods have intimate interfacial contact, which is conducive to the interface transfer of photoinduced electrons. To optimize the photocatalytic performance of TiO2/Ti3C2 catalysts, morphology engineering of TiO2 (originated from partial oxidized Ti3C2) embedded in Ti3C2 has aroused the interest of material chemists [19]. In this way, plenty of TiO2 nanostructures, including nanoparticles, nanoflowers, nanocrystals, and nanosheets, have been derived from Ti3C2 MXene [16,20–22]. Among them, (001)TiO2 nanosheets stand out because they offer an excellent photoactivity that renders the TiO2/Ti3C2 heterojunction system attractive for many applications (photocatalytic environmental purification [16,22], photoelectrochemical detection [23], artificial photosynthesis of chemical fuels [24]).

To date, most of the synthesis methods for (001)TiO2/Ti3C2 have been carried out using at least two steps: (i) the raw material Ti3AlC2 was etched for Al layer elimination with HF, followed by washing to remove HF, and the Ti3C2 was finally obtained by drying; (ii) afterward, an additional fluorine source (e.g., NaBF3) is added to regulate the in situ growth of (001)TiO2 nanosheets on Ti3C2 by hydrothermal process [16,22]. For step (i), theoretically, to etch the Al layer of 1 mol Ti3AlC2, 3 mol HF is needed according to the reaction equation [25]: Ti3AlC2 + 3HF → Ti3C2 + AlF3 + 3/2H2. However, in those cases, the molar ratio of HF to Ti3AlC2 (nHF:nTi3AlC2) is normally larger than 50:1, which is much more than the actual required amount. In fact, according to the study of Alhabeb et al., fewer HF (nHF:nTi3AlC2 = 10:1) is enough to remove the Al layer of Ti3AlC2 [26]. It is well known that the large use of harmful HF is not environmentally friendly, thereby reducing the use of HF, meanwhile ensuring the elimination of the Al layer is rather significant. For step (ii), NaBF4 is used as the shape-directing agent of (001)TiO2 nanosheets. Additionally, its fluorine ion (F−) plays an essential role in preparing (001)TiO2 nanosheets, since F− can combine with Ti atom to reduce the surface energy of (001) facet, resulting in the preferential growth of high-energy (001) facets during the growth process of TiO2 crystal [27]. While many efforts have been devoted to fabricating (001)TiO2/Ti3C2, some of the key challenges are still present that need to be addressed, especially the large usage of corrosive HF and the complexity of the operation.

Herein, a facile one-step hydrothermal method of (001)TiO2/Ti3C2T x composite was developed, as schematically illustrated in Figure 1. In this case, HF was delicately used as both an etchant for Al layer elimination of Ti3AlC2 and a morphology control agent providing F− for the controlled growth of (001)TiO2 nanosheets. In sharp contrast to traditional methods, we let the HF used in the etching process continue to participate in the hydrothermal reaction, rather than washing it off, so as to improve the utilization rate of HF and reduce its discharge. As a result, (i) the usage of HF is dramatically reduced; the molar ratio of F to Ti in the pristine materials of HF and Ti3AlC2 (nF:nTi) decreased from 21:1 to 4:1 as compared to the traditional synthesis method [16]. (ii) This work also simplifies the opera-
tion procedures, avoiding a series of processes, including washing, drying, and the addition of an extra morphology control agent. For detailed distinction, the experiment conditions and molar ratio (nF:nTi) for synthesizing (001)TiO$_2$/Ti$_3$C$_2$Tx are summarized in Table S1. The optimized (001)TiO$_2$/Ti$_3$C$_2$Tx exhibited superior photocatalytic CO$_2$ reduction activity, which was better than that of commercial P25 TiO$_2$. It also showed remarkable selectivity for CH$_4$ production. The reason for the extraordinary photocatalytic performances may be the fact that Ti$_3$C$_2$Tx with a lower work function induces the photogenerated hole transfer and suppresses the charge recombination, facilitating the CO$_2$ multi-electron reduction.

Figure 1. Schematic illustration of the synthesis procedure for (001)TiO$_2$/Ti$_3$C$_2$Tx composite photocatalysts.

2. Results and Discussion

The phase structure of the sample was analyzed using X-ray diffraction (XRD) spectroscopy. As shown in Figure 2a, the diffraction peak of Ti$_3$AlC$_2$ MAX is consistent with that reported in the literature [12]. In comparison to Ti$_3$AlC$_2$, the HF etching process causes the (104) diffraction peak at 39° to disappear in Ti$_3$C$_2$Tx, as well as the (002) and (004) diffraction peaks to shift towards lower angles, which are indications of Al layer elimination and increased layer spacing in the Ti$_3$C$_2$Tx structure [28], as likewise evidenced by the observation of SEM images for both Ti$_3$AlC$_2$ and Ti$_3$C$_2$Tx (Figure S2). For conciseness, the TiO$_2$/Ti$_3$C$_2$Tx samples prepared by hydrothermal method are hereafter named TT-x, where x refers to the added volume (unit: mL) of the HF. All of the TiO$_2$/Ti$_3$C$_2$Tx samples are well indexed to the peaks of both Ti$_3$AlC$_2$ and anatase phase TiO$_2$ (JCPDS No. 21-1272), indicating that TiO$_2$/Ti$_3$C$_2$Tx heterojunctions were successfully prepared (Figure 2a). However, there remains a faint (104) diffraction peak of Al at 39° for the TT-2 sample, which is mainly since the amount of HF added during the preparation was too small to etch the Al layer of Ti$_3$AlC$_2$ completely. When the amount of HF added was greater than 3 mL, the peak of Al fully disappeared in the corresponding position of the sample. Notably, the intensity of the diffraction peaks of TiO$_2$ decreased with the increasing HF addition higher than 5 mL. This is mainly because the excessive amount of HF will further etch the TiO$_2$ nanosheets and make them less crystalline. Among them, the crystallinity of TiO$_2$ in the TiO$_2$/Ti$_3$C$_2$Tx composites prepared by the HF addition in the range of 3 mL to 5 mL was better.
In addition to XRD, Raman spectra were used to reveal the constituents of the as-prepared samples, yielding similar results. As shown in Figure 2b, Ti$_3$AlC$_2$ contains several characteristic bands that appeared at ca. 169, 268, 411, and 598 cm$^{-1}$, which are associated with the $\omega$1, $\omega$2, $\omega$3, and $\omega$4 Raman-active phonon vibration modes, respectively, while the two peaks between 1000 and 1800 cm$^{-1}$ (D and G band) are referred to the stretching vibrations of graphitic carbon [12,22]. For the other two samples, the Ti$_3$C$_2$Tx sample showed the expected Raman vibrational modes [15,29]. Compared to the Ti$_3$C$_2$Tx sample, the TT-5 sample displayed an ascending Raman signal at 150 cm$^{-1}$ ($E_g$), together with three other peaks at 393 cm$^{-1}$ ($B_{1g}$), 507 cm$^{-1}$ ($A_{1g}$), 630 cm$^{-1}$ ($E_g$), which are originated from anatase (001)TiO$_2$ [12,30]. Besides, the D- and G-modes peaks of Ti$_3$C$_2$Tx were also observed clearly in TT-5. Reasonably, both XRD and Raman results confirm the transformation of Ti$_3$C$_2$Tx to TiO$_2$ during hydrothermal treatment.

Another direct piece of evidence for the successful preparation of TiO$_2$/Ti$_3$C$_2$Tx is provided by the morphology and microstructure observation via field emission scanning electron microscopy (FESEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). The most striking feature of the typical heterojunction is the existence of TiO$_2$ nanosheets embedded in Ti$_3$C$_2$Tx that are deliberately created using a fluorine source (HF) under the hydrothermal process. This characteristic is directly observed with FESEM (Figure 2c), showing square TiO$_2$ nanosheets with a thickness of 130 nm embedded in the layered Ti$_3$C$_2$Tx. The TEM image (Figure 2d) of TiO$_2$/Ti$_3$C$_2$Tx...
displays several square thin nanosheets on a substrate, and its partially enlarged image (Figure 2e) shows the obvious lattice spacing of 0.235 nm, which is identified for the TiO$_2$ (001) plane. Usually, the growth rate of crystals is exponentially related to the surface energy [31]. During the growth of TiO$_2$ nuclei, the (001) planes with high surface energy (0.90 J/m$^2$) decrease rapidly, and the TiO$_2$ nanocrystals evolve spontaneously into a truncated bipyramidal structure dominated by stable (101) facets because of their low surface energy (0.44 J/m$^2$) [32]. It is worth noting that modifying the surface adsorption species of the crystal can change the surface energy, exposing specific highly active facets of the crystal. F is a species with the affinity for Ti atoms so that it can bind Ti atoms and reduce the surface energy of the (001) facets, making them more stable than the (101) facets during the anatase TiO$_2$ crystal growth process [27,33]. Therefore, in our case, the absorbed F atom functioned as a capping agent to modify the surface energy of (001) facets of TiO$_2$, resulting in exceptional stabilization. Furthermore, the elemental distribution in the composite was visualized by STEM-energy-dispersive X-ray spectroscopy (EDS) mapping analysis (Figure 2f). By focusing on an area containing square sheets with lying and standing positions, it is clearly revealed that the distributions of Ti atoms and O atoms are perfectly coincided with the square region, verifying the formation of TiO$_2$ nanosheet structure. Therefore, it can be concluded that the (001)TiO$_2$/Ti$_3$C$_2$Tx has been successfully prepared.

As evidenced above, after HF pretreatment and hydrothermal process for precursor Ti$_3$AlC$_2$, the Al layer has been removed and the TiO$_2$/Ti$_3$C$_2$Tx heterojunction was formed. To further confirm the changes in the surface composition of the prepared samples Ti$_3$AlC$_2$, TT-5, and TT-5-u (the sample pretreated with 5 mL HF but without hydrothermal treatment) at different stages in synthesis, XPS measurements were carried out. As a consequence of the Al layer removal, Al 2s and 2p peaks in Ti$_3$AlC$_2$ disappeared in TT-5 and TT-5-u, which can be observed via the XPS survey spectra (Figure S3). The comparison of the high-resolution Ti 2p spectrum between TT-5 and TT-5-u is shown in Figure 3a,d. For TT-5, the Ti 2p spectrum can be fitted by seven components located at 454.8, 456.3, 456.5, 459.4, 461.3, 462.6, and 465.0 eV, which are attributed to Ti-C (454.8 eV and 461.3 eV), Ti-X (456.3 eV) (substoichiometric TiCx (x < 1) or titanium oxycarbides), Ti$^{3+}$ (456.5 eV and 462.6 eV), and TiO$_2$ (459.4 eV and 465.0 eV) [12,16,22]. In comparison to TT-5-u, the TT-5 sample shows two more peaks of TiO$_2$ (459.4 eV and 465.0 eV) and the fade of the other Ti species, demonstrating the gradual transformation from Ti$_3$C$_2$Tx to TiO$_2$. Furthermore, the C 1s spectrum (Figure 3b) of TT-5 exhibited several distinct peaks at 288.8, 286.4, and 281.9 eV, corresponding to C-F, C-O, and C-Ti-O, respectively [16,22,34]. Apparently, C-F is derived from HF; Ti-C and C-C originate from Ti$_3$C$_2$Tx and adventitious carbon, respectively. It is noteworthy that the TT-5 showed a new C-Ti-O peak at 282.5 eV as compared with TT-5-u (Figure 3e), demonstrating that the TiO$_2$/Ti$_3$C$_2$Tx heterojunction is linked by a C-Ti-O bond. The O 1s spectrum of TT-5-u is fitted by two components located at 532.18 and 530.0 eV (Figure 3f), which are corresponding to Ti-OH, Ti-O [35]. After hydrothermal treatment, the Ti-O intensity of TT-5 significantly increased as compared to Ti-OH (Figure 3c), which suggests the existence of TiO$_2$. The XPS results verify the successful preparation of the TiO$_2$/Ti$_3$C$_2$Tx heterojunction, which is well consistent with the results of XRD, Raman, and EDS analyses.
The photocatalytic activity of the samples was evaluated by photocatalytic CO$_2$ reduction in a gas-solid reaction system under simulated solar light. Mild conditions were kept without using any photosensitizer or organic sacrificial reagents. Methane (CH$_4$) and carbon monoxide (CO) are generated as the predominant products via the two-electron and eight-electron reduction processes, respectively (Figure 4a). Ti$_3$C$_2$Tx with metallic properties is generally not photocatalytically active [28]. However, a weak CO$_2$ photoreduction activity of Ti$_3$C$_2$Tx was detected here, resulting from the TiO$_2$ (partial oxidation Ti$_3$C$_2$Tx) during storage or light exposure. As for the other samples, the photoactivity showed a trend to increase and then decline as the increasing addition of HF. From TT-2 to TT-5, the photoactivity gradually enhanced due to the increase in (001)TiO$_2$ nanosheets (Figure S5 and Table S2), TT-5 shows larger surface area to increase and then decline as the increasing addition of HF. From TT-2 to TT-5, the photoactivity showed a trend to increase and then decline as the increasing addition of HF. From TT-2 to TT-5, the photoactivity gradually enhanced due to the increase in (001)TiO$_2$ nanosheets (Figure S5 and Table S2), TT-5 shows larger surface area and more micropores (<2 nm) as compared to TT-2, which may favor the adsorption of CO$_2$ gas molecules. However, following adding excessive HF, the TiO$_2$ may further be etched (as shown in Figure S4), resulting in a decrease in the photoactivity for TT-6 and TT-8. The results suggest that there is an optimum amount (5 mL) of HF in the synthesis of TiO$_2$/Ti$_3$C$_2$Tx for achieving high photocatalytic CO$_2$ reduction rates. Among all the samples, TT-5 exhibited the best CO$_2$ photoreduction rate of 13.45 µmol g$^{-1}$ h$^{-1}$ (10.28 µmol g$^{-1}$ h$^{-1}$ for CH$_4$ and 3.17 µmol g$^{-1}$ h$^{-1}$ for CO), which was higher than that of P25 TiO$_2$ (10.95 µmol g$^{-1}$ h$^{-1}$). Note that methane was not detected for commercial P25, while TT-5 was up to 92.84% methanogenic selectivity (Figure 4b). As reported previously, the existence of Ti$_3$C$_2$ favors the selectivity for photocatalytic CO$_2$–CH$_4$ conversion [36,37]. Combining the reported studies and above experimental results, the reason for the extraordinary selectivity for CH$_4$ production could be interpreted as Ti$_3$C$_2$ with lower work function induces the photogenerated hole transfer and suppresses the charge recombination, facilitating the CO$_2$ multi-electron reduction.

Figure 3. High-resolution XPS spectra for Ti 2p (a,d), C 1s (b,e) and O 1s (c,f) of TT-5 (a–c) and TT-5-u (d–f).
A series of control experiments were conducted to reveal the source of reduction products; the results are shown in Figure S6. The product concentration is below the limit of detection when the experiments were carried out in the absence of catalyst or irradiation or in Ar, proving that the detectable CO and CH$_4$ were derived from photocatalytic CO$_2$ reduction over (001)TiO$_2$/Ti$_3$C$_2$Tx. To further disclose the origin of the products, an isotopically labeled $^{13}$CO$_2$ experiment was performed. As shown in Figure 4c,d, the strong signals were observed at $m/z =$ 17 and = 29, which were attributed to $^{13}$CH$_4$ and $^{13}$CO, respectively. This result further confirms that the reduction products indeed originate from the CO$_2$ photoreduction rather than from the impurity or the sample.

With efforts to acquire an in-depth understanding of the reaction intermediates in CO$_2$ photoreduction for TT-5, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed (Figure 5). Obviously, various peaks can be observed during the photocatalytic reaction that corresponds to the formation of carbonate species, in which CO$_3^{2-}$ and HCO$_3^-$ are generated from CO$_2$ and -OH [38]. The peaks at 1868, 1844, 1828, 1792, 1698, 1684, 1576, and 1558 cm$^{-1}$ were attributed to HCOO [12,28,39], while the band for COOH$^*$ was located at 1569 cm$^{-1}$ [40]; they might serve as possible intermediates for CO production. Furthermore, the peaks at 1772, 1750, 1716, 1457, and 1419 cm$^{-1}$ belong to HCHO [12,28,41], and the peak at 1734 cm$^{-1}$ originates from CH$_3$O [41], both of which are important intermediate species for the production of CH$_4$. Notably, the signal of CH$_4$ was undetectable on DRIFT spectra, as it is a non-polar molecule. Therefore, the CO$_2$ photoconversion process could be deduced as follows: CO$_2$ molecules are firstly adsorbed on the surface of the TT-5 sample and reacted with H$^+$ dissociated from H$_2$O to form COOH (CO$_2^*$ + e$^-$ + H$^+$ → COOH$^*$). Then, COOH$^*$ transformed to CO$^*$ by a protonation process (COOH$^*$ + e$^-$ + H$^+$ → CO$^*$ + H$_2$O) [40,42]. One part of the adsorbed CO$^*$ is released to form gaseous CO (CO$^*$ → CO); more importantly, the other part of CO$^*$ continues to participate in the reduction reaction to form HCHO$^*$ and CH$_3$O$^*$ (CO$^*$ + 2e$^-$ + 2H$^+$ →...
HCHO*; HCHO* + e− + H+ → CH₃O*). Eventually, the CH₄ production could be achieved
by the further protonation of CH₃O* (CH₃O* + 3e− + 3H+ → CH₄↑ + H₂O) [43].

![Figure 5](image_url)

**Figure 5.** In situ DRIFTs spectra of photocatalytic CO₂ reduction on TT-5.

Furthermore, considering that the separation and migration of photoinduced electron-
hole pairs play an important role in achieving the enhancement of photocatalytic efficiency,
the transient photocurrent response test was performed. As shown in Figure 6a, the anode
photocurrent increases during irradiation and declines without irradiation. It can clearly be
seen that TT-5 exhibited improved photocurrent responses compared with other samples,
suggesting the efficient separation of the charge carriers in the composites of TT-5. Notably,
the rapid decay characteristic of P25 could be assigned to fast electron–hole recombination
kinetics due to the absence of Ti₃C₂Tx with high conductivity [12,44]. For the others,
their photocurrent is relatively stable, because the presence of Ti₃C₂Tx slows down
the recombination rate of photogenerated carriers, which is beneficial for the multi-electron
reduction of CO₂ (CO₂ + 8H⁺ + 8e− → CH₄↑ + 2H₂O).

In an effort to better understand the pathway of interfacial charge transfer between
(001)TiO₂ nanosheets (synthesized according to our previous report [45]) and Ti₃C₂Tx, the
work functions (W_sample) of them were studied via Kelvin probe using a gold mesh as the
reference. Specifically, the W_sample is calculated by Equation (1) [46]:

\[
W_{\text{sample}} = W_{\text{probe}} + e \cdot CPD_{\text{sample}}
\]

where CPD_sample is the contact potential difference (CPD) of the given sample, which was
measured by the Kelvin probe; W_probe represents the work function of the gold mesh
(≈4.25 eV); and e is the electronic charge. Based on the probed CPD results (Figure 6b), the
W of (001)TiO₂ nanosheets and Ti₃C₂Tx are calculated to be 4.66 and 4.42 eV, respectively
(Figure 6c). Accordingly, the Fermi levels (E_f) of the samples are determined via the
conversion formulas (Equations (2)–(4)) [28], as shown below:

\[
E_{f,\text{vac}} = E_{\text{vac}} - W_{\text{sample}}
\]

\[E_{f}(\text{vs.SHE, pH0}) = -4.5 \text{ V} - E_{f,\text{vac}}\] (3)

\[E_{f}(\text{vs.SHE, pH7}) = E_{f}(\text{vs.SHE, pH0}) - 0.059 \text{ pH}\] (4)

where the E_f,vac represents the Fermi levels of the samples at the vacuum level, and E_vac is
the energy of a stationary electron at the vacuum level (regarded as 0 eV). Thus, the E_f of
Ti₃C₂Tx and TiO₂ are calculated to be −0.49 and −0.25 eV (vs. SHE at pH = 7), respectively.
Obviously, the Fermi energy level of Ti₃C₂Tx is more negative than that of (001)TiO₂
nanosheets (i.e., the work function of Ti₃C₂Tx is lower than that of (001)TiO₂), and thus
the photogenerated holes rather than electrons of TiO₂ nanosheets are trapped by Ti₃C₂Tx.
Based on the above experimental results, we inferred the mechanism of (001) TiO\textsubscript{2}/Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} for photocatalytic CO\textsubscript{2} reduction (Figure 6d). Under illumination, the electrons on the valence band of (001)TiO\textsubscript{2} nanosheets are excited to the conduction band, and these photoelectrons gathered on the conduction band react with the adsorbed CO\textsubscript{2} to generate CH\textsubscript{4} and CO via the photocatalytic process. Because of the differences in work function for (001)TiO\textsubscript{2} nanosheets and Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} with metallic properties, a Schottky barrier could be formed at the interface of (001)TiO\textsubscript{2} and Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} [16,22], which would promote the holes rather than electrons transfer to Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, while enabling the accumulation of electrons on TiO\textsubscript{2}. Undoubtedly, this is favorable for the efficiently multi-electron CO\textsubscript{2} photoreaction.

### 3. Experimental Procedures

#### 3.1. Chemicals

All the chemicals were of analytic grade and used as received. Deionized (DI) water used in this research was from local sources. Ti\textsubscript{3}AlC\textsubscript{2} powder was supplied by 11 Technology Co., Ltd. (Changchun, China). Hydrofluoric acid (HF), sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), and sodium bicarbonate (NaHCO\textsubscript{3}) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

#### 3.2. Sample Preparation

Preparation of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}: Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} was prepared by an HF-etching method. In detail, 1 g Ti\textsubscript{3}AlC\textsubscript{2} powder was slowly put into the aqueous HF solution (40 wt\%) under magnetic stirring for 24 h to eliminate the Al layer. Then, the black suspension was filtered and washed with distilled water until the pH of the filtrate was about 7. After drying at 60 ℃ under vacuum for 12 h, the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} powder was obtained.

Preparation of (001) TiO\textsubscript{2}/Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}: (001) TiO\textsubscript{2}/Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} composite photocatalysts were synthesized by a one-step hydrothermal method. Typically, 2 g Ti\textsubscript{3}AlC\textsubscript{2} powder was slowly...
added to HF solution (5 mL, 40 wt%) and kept agitating at room temperature for 24 h in order to remove the Al layer. Then, distilled water was directly added to the above suspensions to a total volume of 120 mL. After sonicating for 10 min, the homogeneous mixture was sealed into a 200 mL Teflon-lined autoclave with a stainless steel jacket for a hydrothermal process at 180 °C for 12 h, in which HF was delicately used as both an etchant for Ti3AlC2 and a morphology control agent for the growth of (001)TiO2 nanosheets on Ti3C2Tx. After natural cooling, the precipitate was collected by filtration, washed thoroughly with distilled water until the pH of the filtrate turned to 7, and dried at 60 °C. Subsequently, the (001)TiO2/Ti3C2Tx was obtained and labeled as TT-5 (5 mL HF) for short.

Similarly, a serial of composites was synthesized by varying the usage of HF under other identical conditions, and the acquired samples were named TT-x (x = 2, 3, 4, 5, 6, and 8), where x represents the usage (unit: mL) of HF. To study the transformation process of Ti3AlC2 to (001)TiO2/Ti3C2Tx, samples pretreated with 5 mL HF but without hydrothermal process were collected and labeled TT-5-u.

3.3. Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on an X-ray diffractometer (D8 ADVANCE Bruker, Karlsruhe, Germany) with Cu Kα radiation at a scan rate of 0.02° s⁻¹. Raman spectra were collected through a Raman spectroscopy (DXR2 XI, Thermo Fisher, Waltham, MA, USA) with an excitation wavelength of 633 nm. The morphology and microstructure of the samples were analyzed using a field emission scanning electron microscope (FESEM, SU8010 Hitachi, Tokyo, Japan) and high-angle annular dark-field transmission electron microscopy (HAADF-STEM, Talos F200S, Thermo Scientific, Waltham, MA, USA), respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG Multilab 2000 XPS system (Thermo VG Scientific, London, UK) to obtain information related to the surface chemical state and composition of the sample. All the spectra were calibrated to the C 1 s peak at 284.8 eV. The UV–vis diffuse reflectance spectra (DRS) were obtained with a UV–vis spectrophotometer (UV2600, Shimadzu, Kyoto, Japan) using BaSO4 as the reference standard. The Brunauer–Emmett–Teller (BET) surface area and pore size distribution data of the samples were analyzed using a nitrogen adsorption apparatus (ASAP-2020, Micromeritics, Norcross, GA, USA). The samples were degassed at 175 °C for 4 h before N2 adsorption measurement. A Kelvin probe apparatus (Instytut Fotonowy, Cracow, Poland) with a sensitivity of 1 mV was utilized to determine the contact potential difference (CPD) of the samples with a gold mesh Kelvin probe as the reference. Surface work function (W) was monitored using an LED lamp as a light source in conjunction with a monochromator. In situ FTIR spectra were measured on a Bruker Tensor II FTIR spectrometer (Bruker, Karlsruhe, Germany).

3.4. Electrochemical Measurements

Electrochemical characterization for transient photocurrent responses (TPR) was conducted on an electrochemical analyzer (CHI 760e, CH Instruments, Shanghai, China). Pt wire, Ag/AgCl (saturated KCl), and 0.4 M Na2SO4 solution were functioned as the counter electrode, reference electrode, and electrolyte, respectively. For the working electrode, 30 mg of catalyst was ground in 1 mL water/absolute ethanol mixed solvent (v/v = 1/1) and 30 µL of Nafion solution to make a slurry, which was coated onto indium tin oxide (ITO) conductive glass with an exposed area of 1 cm² after ultrasonic dispersion. A 365 nm LED (3 W, Shenzhen Lamplic, Shenzhen, China) was used as the light source.

3.5. Photocatalytic CO2 Reduction and Isotope-Labeling Measurement

The photocatalytic CO2 reduction of the samples was conducted in a glass automatic online gas analysis system (Labsolar-6A, Beijing, China) (Figure S1a). The light source was a 300 W xenon lamp (PLS-SXE300+, Beijing, China). The photocatalytic activity test was carried out in three main steps: coating catalyst, in situ CO2 production, and the occurrence of the CO2 photocatalytic reduction. (1) Coating catalyst: 30 mg of the photocatalyst was
dispersed in 15 mL distilled water to form a suspension, which was then transferred to a petri dish (φ = 60 mm). After drying, the catalyst film was deposited on the bottom of the dishes. (2) In situ CO₂ generation: 2.1 g of NaHCO₃ powder was placed on the bottom of a homemade double-neck reactor, and the coated dish in (1) was supported in the reactor using a quartz tripod (Figure S1b). Before illumination, the photocatalytic system was vacuumed to exclude the air. Finally, 7 mL of H₂SO₄ (2 M) was injected into the reactor to react with NaHCO₃ for generating CO₂ and H₂O vapor within the reactor. (3) CO₂ photoreduction (Figure S1c): After adsorption equilibrium, a 300 W xenon lamp (PLS-SXE300+, Perfect Light) was used as the light source to initiate the photocatalytic reaction. The concentration of the CO₂ reduction products was analyzed by gas chromatography (GC-2014, Shimazu, Kyoto, Japan) with FID and TCD detectors. For determining the carbon source of the reduction products, ¹³CO₂ isotope labeling experiment was carried out under the same conditions as the above-mentioned CO₂ reduction test, except for the substitute of NaH¹³CO₃ using NaH¹³CO₃ (SHANGHAI ZZBIO Co., Ltd., Shanghai, China). The gas products were verified by a mass spectrometer (MS, HPR-20, Hiden Analytical, Warrington, UK). The electron selectivity for CH₄ production during the photocatalytic CO₂ reduction process is evaluated using the following equation [47]: CH₄ selectivity (%) = [(8n(CH₄)) / [(8n(CH₄) + 2n(CO))] × 100, CO selectivity (%) = [(2n(CO)) / [(8n(CH₄) + 2n(CO))] × 100, where n(CH₄) and n(CO) denote the number of moles of CH₄ and CO₂, respectively.

4. Conclusions

In summary, a facile one-step hydrothermal approach of (001)TiO₂/Ti₃C₂Tx composites was developed, where HF was delicately used as both an etchant for Ti₃AlC₂ and a morphology control agent for TiO₂ nanosheets. This method simultaneously addressed the issues of the large usage of HF and complex operation procedure. Furthermore, by tailoring the HF amount within a narrow range, the morphology of TiO₂ nanosheets could be purposefully manipulated. The optimized sample (TT-5) shows a superior photoactivity with a CO₂ reduction rate of 13.45 µmol g⁻¹ h⁻¹, as well as a CH₄ production selectivity of 92.84%. The excellent photocatalytic performance is mainly since purposeful spatial isolation of photogenerated charge carriers induced by Ti₃C₂Tx dramatically improves the electron density of TiO₂, thereby facilitating the CO₂ multi-electron reduction of (001)TiO₂/Ti₃C₂Tx heterojunction. This work may provide an easy and novel approach to fabricating highly efficient MXene-derived composites for sustainable energy conversion.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12070785/s1, Figure S1: Photocatalytic CO₂ reduction device (a), in situ CO₂ production (b), CO₂ photoreduction reaction (c); Figure S2: SEM image of Ti₃AlC₂ (a) and Ti₃C₂ (b), showing that the morphology of bulk Ti₃AlC₂ changed to accordion-like Ti₃C₂Tx as a consequence of the eliminated Al layer via HF etching; Figure S3: X-ray photoelectron spectroscopy (XPS) survey spectra (a) and high-resolution XPS spectra of Al 2p (b) of Ti₃AlC₂, TT-5-u and TT5; Figure S4: SEM images of TiO₂/Ti₃C₂Tx samples prepared with different usage of HF; Figure S5: Nitrogen adsorption/desorption isotherms and the corresponding pore-size distribution curves (inset) of the TT-2, TT-5 and TT-8 samples; Figure S6: The control experiments of photocatalytic CO₂ reduction performance over TT-5 under altered conditions; Table S1: Synthesis conditions of (001)TiO₂/Ti₃C₂Tx composites; Table S2: BET surface area and the corresponding pore volume and pore size of samples [48–51].

Author Contributions: Conceptualization, K.L. (Kangle Lv); methodology, K.L. (Kangle Lv); formal analysis, J.L., K.L. (Kaining Li), Q.T., Q.L. and K.L. (Kangle Lv); investigation, J.L. and K.L. (Kaining Li); resources, K.L. (Kangle Lv); data curation, J.L. and K.L. (Kaining Li); writing—original draft preparation, J.L. and K.L. (Kailing Li); Visualization, C.W.; writing—review and editing, Q.L., J.F. and K.L. (Kangle Lv); supervision, project administration and funding acquisition, K.L. (Kangle Lv). All authors have read and agreed to the published version of the manuscript.
Funding: This work was supported by the National Natural Science Foundation of China (51672312, 21972171 and 52073263) and the Fundamental Research Funds for the Central Universities, South-Central Minzu University (CZP22001).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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