

Article

Enhanced Photocatalytic Hydrogen Production of ZnIn_2S_4 by Using Surface-Engineered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene as a Cocatalyst

Mengdie Cai ^{*,†}, Xiaoqing Zha [†], Zhenzhen Zhuo, Jiaqi Bai, Qin Wang, Qin Cheng, Yuxue Wei and Song Sun ^{*,}

School of Chemistry and Chemical Engineering, Anhui University, Hefei 230601, China

* Correspondence: caimengdie1987@163.com (M.C.); suns@ustc.edu.cn (S.S.)

† These authors contributed equally to this work.

Abstract: Developing efficient and stable photocatalysts is crucial for photocatalytic hydrogen production. Cocatalyst loading is one of the effective strategies for improving photocatalytic efficiency. Here, $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T}_x = \text{F}, \text{OH}, \text{O}$) nanosheets have been adopted as promising cocatalysts for photocatalytic hydrogen production due to their metallic conductivity and unique 2D characterization. In particular, surface functionalized $\text{Ti}_3\text{C}_2(\text{OH})_x$ and $\text{Ti}_3\text{C}_2\text{O}_x$ cocatalysts were synthesized through the alkalization treatment with NaOH and a mild oxidation treatment of $\text{Ti}_3\text{C}_2\text{F}_x$, respectively. $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composites, which were fabricated by the in-situ growth of ZnIn_2S_4 nanosheets on the $\text{Ti}_3\text{C}_2\text{T}_x$ surface, exhibited the promoted photocatalytic performance, compared with the parent ZnIn_2S_4 . The enhanced photocatalytic performance can be further optimized through the surface functionalization of $\text{Ti}_3\text{C}_2\text{F}_x$. As a result, the optimized $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ composite with oxygen functionalized $\text{Ti}_3\text{C}_2\text{O}_x$ cocatalyst demonstrated excellent photocatalytic hydrogen evolution activity. The characterizations and density functional theory calculation suggested that O-terminated $\text{Ti}_3\text{C}_2\text{O}_x$ could effectively facilitate the transfer and separation of photogenerated electrons and holes due to the formation of a Schottky junction, with the largest difference in work function between ZnIn_2S_4 and $\text{Ti}_3\text{C}_2\text{O}_x$. This work paves the way for photocatalytic applications of MXene-based photocatalysts by tuning their surface termination groups.

Keywords: $\text{Ti}_3\text{C}_2\text{T}_x$ MXene; surface functionalization; work function; photocatalytic hydrogen production; cocatalyst



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1. Introduction

Hydrogen is regarded as an ideal energy with the advantages of a high energy capacity and zero pollutants. Among the various H_2 production strategies, solar-light-driven photocatalysis for H_2 production from water splitting is a promising route to alleviating the energy crisis [1–3]. Developing highly efficient photocatalysts is the key to realizing the industrialization of photocatalytic H_2 production. Regarding photocatalysts, ZnIn_2S_4 has attracted more attention in recent years because of its low toxicity, visible-light response, and considerable photostability [4,5]. However, the rapid recombination and tardy migration of the photogenerated electrons and holes restricts the photocatalytic H_2 production efficiency of bare ZnIn_2S_4 [6,7]. To address this issue, diverse approaches, including cocatalyst loading, vacancy engineering and heterojunction construction, have been systematically developed to improve the photocatalytic performance of ZnIn_2S_4 materials [8–10]. Among them, cocatalyst loading has been verified to be a feasible and efficient method to promote the photocatalytic efficiency by accelerating the separation and transfer of photogenerated charge carriers while simultaneously acting as active sites to facilitate the photocatalytic H_2 production reaction kinetics. The employment of noble metals (such as Pt, Au, Pd and Rh) as cocatalysts, has been proven to be highly efficient in improving the photocatalytic performance, but their high price largely limits their widespread application [11,12]. Therefore, it

is urgent to explore an inexpensive and efficient noble metal-free cocatalyst to replace Pt, Au, Pd and Rh to achieve large-scale photocatalytic H₂ production.

MXene, as an emerging family of 2D transition metal carbides/nitrides, has gained intensive scientific interest in photocatalysis, ascribed to its excellent metal conductivity, large specific surface area with abundant active sites and hydrophilicity [13–15]. The 2D planar structure of Ti₃C₂T_x MXene is beneficial to highly dispersing the host photocatalyst with a strong interfacial contact [16–18]. On the other hand, owing to its high conductivity and abundant exposed metal sites, Ti₃C₂T_x could act as a cocatalyst to facilitate the separation and migration of photogenerated charge carriers and lower the reaction energy barriers for accelerating the reaction kinetics. Therefore, Ti₃C₂T_x was widely used as a cocatalyst in photocatalytic H₂ production [18–20]. For instance, Zhao et al. [17] reported the construction of hierarchical 2D Bi₂MoO₆@Ti₃C₂T_x by in-situ growing Bi₂MoO₆ onto the surface of Ti₃C₂T_x nanosheets. Ti₃C₂T_x, as the cocatalyst, could not only suppress the agglomeration of Bi₂MoO₆ nanosheets and increase the reaction active sites, but also endow the photocatalyst with the Schottky junction. As a result, the Bi₂MoO₆@Ti₃C₂T_x exhibited enhanced photocatalytic activity. Zuo et al. [18] found that the ZnIn₂S₄-Ti₃C₂T_x-ZnIn₂S₄ sandwich-like hierarchical heterostructures exhibited a superior photocatalytic H₂ production performance due to the construction of the Schottky junction between ZnIn₂S₄ nanosheets and Ti₃C₂T_x. Ran et al. [19] reported that Ti₃C₂, as a potential cocatalyst, could efficiently improve the photocatalytic hydrogen production performance by forming the Schottky junction at the Ti₃C₂/CdS interface to facilitate the separation of the photogenerated electrons and holes. Meanwhile, they found that the Gibbs free energy for H adsorption (ΔG_{H^*}) of O-terminated Ti₃C₂ is close to zero. With the near-zero ΔG_{H^*} , the favorable Fermi level position and electrical conductivity, O-terminated Ti₃C₂ could serve as an alternative to noble metals in photocatalytic H₂ production. Liu et al. [20] utilized Ti₃C₂ nanosheets acting as the substrate and cocatalyst to synthesize a CdLa₂S₄/Ti₃C₂ photocatalyst, which could not only promote the dispersion of CdLa₂S₄, but also enhance the photogenerated charge carriers separation and transfer, leading to a significant enhancement in photocatalytic H₂ evolution. In most cases, Ti₃C₂ with a large work function could act as electron sink to facilitate the separation and transfer of the photogenerated charge carriers in photocatalytic H₂ production. In contrast, Peng et al. [21] proposed a dual-carrier-separation mechanism for photocatalytic H₂ evolution within Cu/TiO₂@Ti₃C₂T_x, where -OH-terminated Ti₃C₂T_x with a lower work function than TiO₂ served as the hole trap to accelerate the holes migration from TiO₂ to Ti₃C₂T_x. Obviously, the surface termination groups of Ti₃C₂T_x could arise tunable electronic properties (such as work function) to impact on the photocatalytic performance of the Ti₃C₂T_x-based photocatalysts.

Tailoring the surface termination groups of Ti₃C₂T_x could alter their work function, electronic and optoelectronic properties [22–24]. Recently, the theoretical calculations from Khazaei revealed that the work function of Ti₃C₂T_x was strongly dependent on the surface termination groups, and the work function of Ti₃C₂T_x could adjust in a wide range from 1.6 eV to 6.0 eV [24]. Jiang et al. [25] investigated the effect of the surface terminations of Ti₃C₂T_x on the electrocatalytic H₂ evolution. They found that O-terminated Ti₃C₂T_x nanosheets exhibited much higher H₂ evolution activity than other Ti₃C₂T_x, and the -O termination groups on the basal plane of Ti₃C₂ were the H₂ evolution reaction active sites. Especially, the -O termination groups could promote the adsorption of H and accelerate the H₂ evolution reaction. However, the insights into the effect of the surface termination groups in Ti₃C₂T_x MXene-based photocatalysts on the photocatalytic H₂ production are not established experimentally. Herein, we designed a series of Ti₃C₂T_x (T_x = F, OH, O) with different surface termination groups, and then the 2D ZnIn₂S₄ was in-situ grown on the surface of Ti₃C₂T_x using a facile hydrothermal synthesis method to synthesize ZnIn₂S₄/Ti₃C₂T_x composites. Specifically, the as-synthesized ZnIn₂S₄/Ti₃C₂O_x with the O-terminated Ti₃C₂T_x exhibited the superior photocatalytic H₂ production activity. When the content of Ti₃C₂O_x was 1.0 wt%, the ZnIn₂S₄/Ti₃C₂O_x presented the optimal photocatalytic H₂ production rate of 363 $\mu\text{mol g}^{-1} \text{h}^{-1}$. This work provides us with a

paradigm for the rational design of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene with tailored surface termination groups and the development of efficient MXene-based composites for photocatalytic applications.

2. Materials and Methods

2.1. Samples Preparation

2.1.1. Synthesis of $\text{Ti}_3\text{C}_2\text{F}_x$

Typically, 2 g LiF was added into 40 mL HCl aqueous solution (9 M) and stirred for 1 h until the LiF was completely dissolved. A total of 2 g of Ti_3AlC_2 powder was then added to the above solution and stirred for 0.5 h. The suspension was stirred at 53 °C for 41 h. Upon cooling, the mixture was centrifuged and washed with deionized water until the pH was close to 7. The product was dried at 60 °C under vacuum for 48 h.

2.1.2. Synthesis of Surface Functionalized $\text{Ti}_3\text{C}_2\text{T}_x$

In order to obtain the surface functionalized $\text{Ti}_3\text{C}_2\text{T}_x$, the pristine $\text{Ti}_3\text{C}_2\text{F}_x$ were treated with a different functionality-modification strategy. To achieve $\text{Ti}_3\text{C}_2(\text{OH})_x$ with $-\text{OH}$ rich termination groups, according to the previous literature [25], 0.2 g of the pristine $\text{Ti}_3\text{C}_2\text{F}_x$ was dispersed in 100 mL of 1 M NaOH aqueous solution in order to replace the $-\text{F}$ surface termination groups with $-\text{OH}$. After stirring for 2 h at room temperature, the product was centrifuged and washed with deionized water until the pH was close to 7. Then, the product was collected and dried at 60 °C under vacuum for 12 h. To obtain O-terminated $\text{Ti}_3\text{C}_2\text{O}_x$, the $\text{Ti}_3\text{C}_2\text{F}_x$ was calcined under 300 °C in Ar gas flow for 2 h.

2.1.3. Synthesis of ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$

Typically, 0.176 g $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, 0.041 g ZnCl_2 and 0.120 g thioacetamide (TAA) were added consecutively into 40 mL glycerol aqueous solution (20 vol%) and stirred for 0.5 h. The quantitative $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T}_x = \text{F}, \text{OH}, \text{O}$) (1.0 wt%) was added into the above solution. The mixed suspension was heated at 80 °C with stirring for 2 h. After centrifugation, the products were collected and dried at 60 °C for 12 h.

For comparison, the preparation of the pristine ZnIn_2S_4 was similar to that of $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ without the introduction of $\text{Ti}_3\text{C}_2\text{T}_x$.

2.2. Photocatalytic H_2 Production Experiments

The photocatalytic H_2 production tests were carried out in a Pyrex glass reaction (Beijing Perfectlight Labsolar-6A, Perfectlight Technology, Beijing, China) with a circulated cooling water system to maintain the temperature at 8 °C. A total of 100 mg of the photocatalyst was dispersed in 100 mL aqueous solution, containing 10 vol% triethanolamine (TEOA) as the sacrificial agent. Before irradiation under a Xe lamp (CEL-HXUV300, Perfectlight Technology, Beijing, China), the suspension was evacuated by the vacuum pump. The produced H_2 volume was analyzed using an on-line gas chromatograph (GC5190, TCD, A column, Ar carrier).

2.3. Characterization

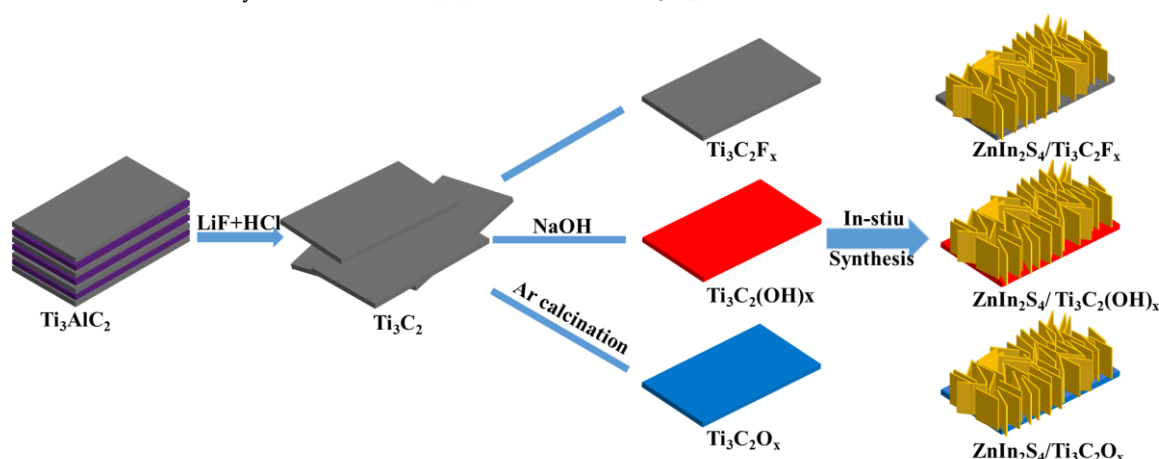
The powder X-ray diffraction (XRD) patterns of the prepared samples were collected using a Rigaku SmartLab (9 kW, Tokyo, Japan) diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418$ nm) operating at 40 kV and 4 mA. The morphological analysis of the samples were recorded with scanning electron microscopy (SEM) using a Regulus 8230 scanning electron microscope (Hitachi, Ltd., Tokyo, Japan) at an acceleration voltage of 5 kV. X-ray photoelectron spectroscopy (XPS) was carried out to investigate the surface chemical environment of the samples using an Escalab 250Xi X-ray photoelectron spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Measuring with an ultraviolet photoelectron spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) was performed with a -5 V bias voltage. The data were calibrated with a C1s spectrum of 284.6 eV. The Fourier transform spectrophotometer (Vertex80 + Hyperion2000, Bruker, Billerica, MA, USA) was employed to acquire IR spectra with the standard KBr disk method. Transmission electron

microscopy (TEM), high resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns of the samples were collected with a field-emission electron microscope (JEM-2100F, JEOL, Tokyo, Japan). UV-visible diffuse reflectance spectroscopy (UV-vis DRS) was recorded to study the optical absorption ability of photocatalysts with Hitachi U-4100 UV-visible spectrometer using a reference standard of BaSO₄. The photoluminescence (PL) spectra and time-resolved fluorescence spectra were conducted on an Edinburgh FLS 1000 spectrometer (Edinburgh Instruments Ltd., Livingston, UK) over an excitation wavelength of 375 nm. Electrochemistry impedance spectroscopy (EIS), Mott–Schottky analyses and transient photocurrent spectra were measured using a CHI660E analyzer (CH Instruments, Inc., Bee Cave, TX, USA) with a standard three-electrode system.

3. Results

3.1. Schematic Illustration of the Synthesis

The schematic illustration in Scheme 1 shows the synthesis process for the ZnIn₂S₄/Ti₃C₂T_x (T_x = F, OH, O) samples, which consists of three steps: the preparation of the Ti₃C₂ by the selective etching of Ti₃AlC₂, surface post-treatment (the alkalization treatment with NaOH and the mild oxidation treatment with Ar calcination) of Ti₃C₂F_x to replace the –F termination groups with –OH or –O groups and the in-situ hydrothermal synthesis of ZnIn₂S₄ on surface of Ti₃C₂T_x.



Scheme 1. Illustration for the formation of ZnIn₂S₄/Ti₃C₂T_x (T_x = F, OH, O) photocatalysts.

3.2. Samples Characterization

The X-ray diffraction (XRD) patterns of Ti₃AlC₂ and the as-prepared Ti₃C₂T_x (T_x = F, OH, O) samples in Figure S1 demonstrated a typical Ti₃AlC₂ and Ti₃C₂T_x MXene phase. No crystal structure variation was observed for the Ti₃C₂(OH)_x and Ti₃C₂O_x, indicating that the surface functionalization treatments just modulated the termination groups without changing the crystalline structure of Ti₃C₂F_x. The XRD pattern of Ti₃C₂O_x showed no peaks of TiO₂. Meanwhile, the morphology of the Ti₃C₂T_x nanosheets was maintained even after the alkalization and oxidation treatments (Figure S2).

To confirm the surface termination groups of the as-prepared Ti₃C₂T_x (T_x = F, OH, O) samples, we performed X-ray photoelectron spectroscopy (XPS), as shown in Figure 1a–c. Figure 1a showed the high-resolution XPS spectrum of F 1s, the binding energy at 685.8 eV was assigned to the Ti–F bond [26]. After the alkalization treatment and mild oxidation treatment of Ti₃C₂F_x, the Ti–F peak intensity in Ti₃C₂(OH)_x and Ti₃C₂O_x both significantly decreased, indicating that the surface functionalization treatments did not change its crystal structure, while the termination groups had modulated noticeably. The elemental composition result determined by XPS (Table S1) also confirmed the decrease of the –F termination groups. As seen from the Ti 2p XPS spectra in Figure 1b, more detailed structural variation could be obtained, four doublets were fitted for Ti 2p_{3/2} and Ti 2p_{1/2}, which indicated

that the Ti species in $\text{Ti}_3\text{C}_2\text{T}_x$ exhibited four kinds of chemical environment. The Ti $2p_{3/2}$ binding energies at approximately 455.1, 455.8, 456.9 and 459.1 eV could be assigned to C-Ti-C, C-Ti-OH, C-Ti-O and O-Ti-O bonds, respectively [23,27,28]. Obviously, compared to $\text{Ti}_3\text{C}_2\text{F}_x$, the intensity of the C-Ti-O peak for $\text{Ti}_3\text{C}_2\text{O}_x$ increased and the intensity of the C-Ti-OH peak for $\text{Ti}_3\text{C}_2(\text{OH})_x$ increased, which indicated that the -F terminations in the $\text{Ti}_3\text{C}_2\text{F}_x$ were replaced by -O and -OH after the oxidation treatment and alkalization treatment, respectively. The intensity of the O-Ti-O peak increased in $\text{Ti}_3\text{C}_2\text{O}_x$ and $\text{Ti}_3\text{C}_2(\text{OH})_x$, which was attributed to the surface oxidation with the transform C-Ti-C band to O-Ti-O. Furthermore, the O 1s XPS spectra (Figure 1c) exhibited Ti-O, Ti-OH and C-OH peaks at the binding energies of 530.1, 531.8 and 533.5 eV, respectively [29,30]. In particular, the peak at 531.8 eV demonstrated the highest proportion of -OH groups on the surface of $\text{Ti}_3\text{C}_2(\text{OH})_x$, while $\text{Ti}_3\text{C}_2\text{O}_x$ showed the highest concentration of Ti-O due to O-terminated surfaces. The XPS results showed the coexistence of Ti-F, Ti-OH and Ti-O bonds in all $\text{Ti}_3\text{C}_2\text{T}_x$ samples. It should be noted that the $\text{Ti}_3\text{C}_2\text{O}_x$, $\text{Ti}_3\text{C}_2(\text{OH})_x$ and $\text{Ti}_3\text{C}_2\text{F}_x$ represented a higher density of termination groups -F, -OH and -O on the surface, respectively. After the alkalization treatment, the Ti-F peak intensity significantly decreased while the Ti-OH peak intensity increased in $\text{Ti}_3\text{C}_2(\text{OH})_x$, implying the successful replacement of -F with -OH. Similarly, the -F groups in $\text{Ti}_3\text{C}_2\text{F}_x$ were successfully replaced by -O with the mild oxidation treatment to form the $\text{Ti}_3\text{C}_2\text{O}_x$.

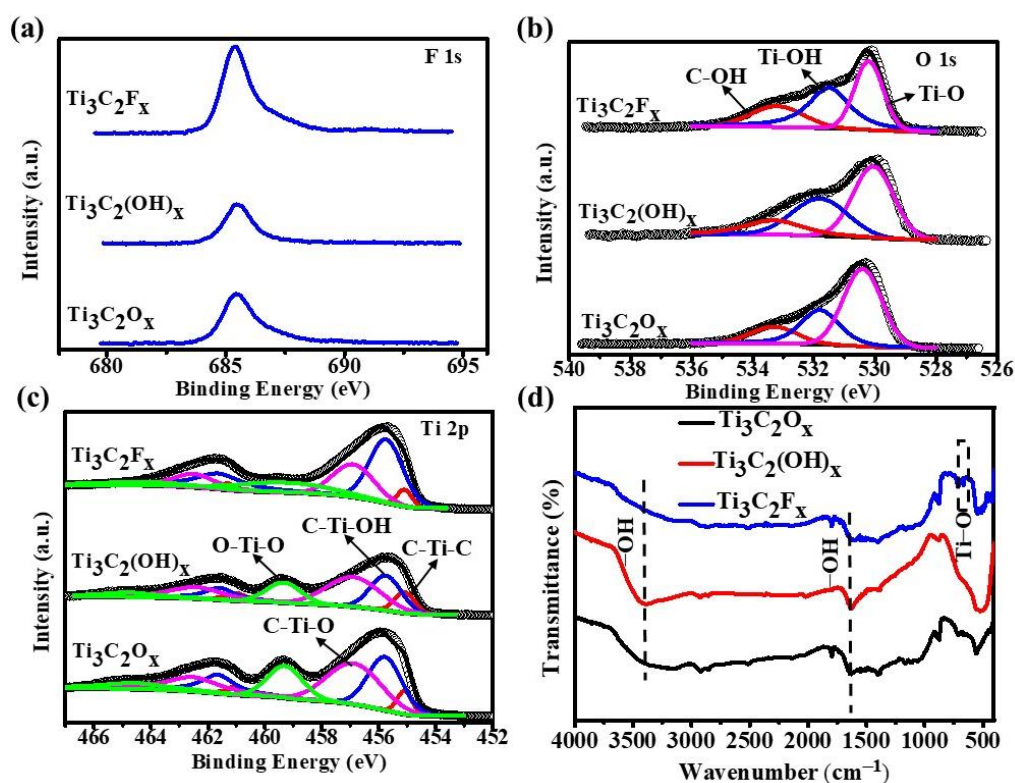


Figure 1. (a) F 1s XPS spectra, (b) Ti 2p XPS spectra, (c) O 1s XPS spectra and (d) FT-IR spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T}_x = \text{F}, \text{OH}, \text{O}$).

The surface termination groups of the $\text{Ti}_3\text{C}_2\text{T}_x$ samples were further analyzed using Fourier transform infrared spectroscopy (FTIR), as displayed in Figure 2d. The FTIR spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ samples showed two peaks at approximately 3430 and 1625 cm^{-1} , which assigned to the -OH band on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$. In addition, a peak at 657 cm^{-1} can be observed, which is attributed to the Ti-O band [31]. It is notable that $\text{Ti}_3\text{C}_2(\text{OH})_x$ showed the strongest -OH vibration intensity and that the $\text{Ti}_3\text{C}_2\text{O}_x$ exhibited a significantly increased Ti-O vibration, which was consistent with the XPS results. These results indicated

that the surface functionalized $\text{Ti}_3\text{C}_2(\text{OH})_x$ and $\text{Ti}_3\text{C}_2\text{O}_x$ were successfully synthesized with the alkalization treatment and mild oxidation treatment, respectively.

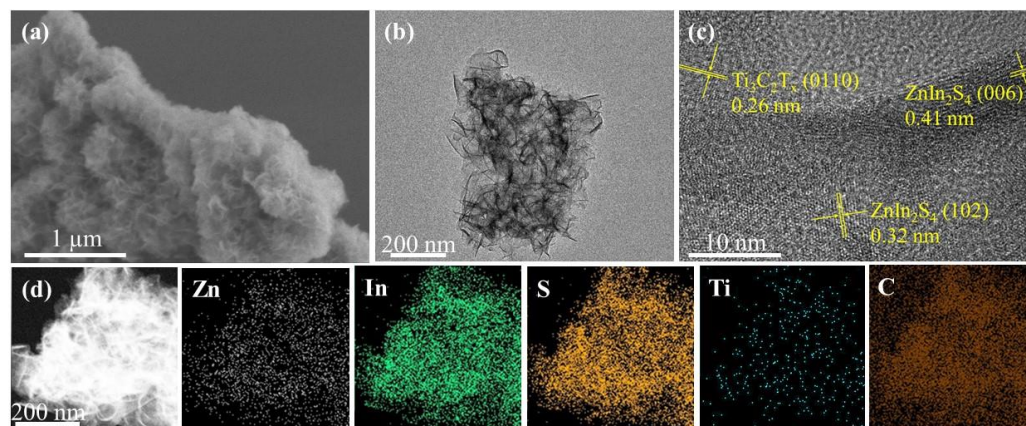


Figure 2. (a) SEM image, (b) TEM image, (c) HRTEM and (d) STEM image and corresponding EDX element mapping of Zn, In, S, Ti and C of $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$.

The $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T}_x = \text{F}, \text{OH}, \text{O}$) composites were obtained through the in-situ growth of ZnIn_2S_4 onto the surface of $\text{Ti}_3\text{C}_2\text{T}_x$. To acquire the crystallinity phase of the ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composites, the XRD analysis was introduced (Figure S3). It was found that all $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ samples presented similar diffraction peaks with ZnIn_2S_4 . The missing $\text{Ti}_3\text{C}_2\text{T}_x$ diffraction peaks could be ascribed to the low content and high dispersion of $\text{Ti}_3\text{C}_2\text{T}_x$ in the composites. The morphology of the ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ samples were investigated using scanning electron microscopy (SEM). The ZnIn_2S_4 presented a morphology of nanoflowers stacked with nanosheets (Figure S4). From the SEM image of $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ sample in Figure 3a, it can be seen that the ZnIn_2S_4 particles are uniformly dispersed and anchored onto the $\text{Ti}_3\text{C}_2\text{O}_x$ surface. The more detailed microstructure of the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ composite were further demonstrated using the transmission electron microscopy (TEM) technique. TEM observation confirmed such hierarchical $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ structure (Figure 2b). Furthermore, as shown in Figure 2c, the lattice distances of the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ photocatalyst were measured, and the lattice fringes spacing of 0.32 and 0.41 nm were corresponded to the (102) and (006) planes of ZnIn_2S_4 , while the lattice fringes spacing of 0.26 nm was assigned to the (0110) crystal plane of $\text{Ti}_3\text{C}_2\text{O}_x$. Moreover, there was an obvious interface contact observed between the ZnIn_2S_4 and the $\text{Ti}_3\text{C}_2\text{O}_x$, which could contribute to the faster transfer of the photogenerated charge. In addition, the corresponding EDX elemental mapping (Figure 2d) displayed that the Zn, In, S, Ti and C elements were uniformly distributed in the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ sample. The above results powerfully confirmed that the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ photocatalyst was successful constructed.

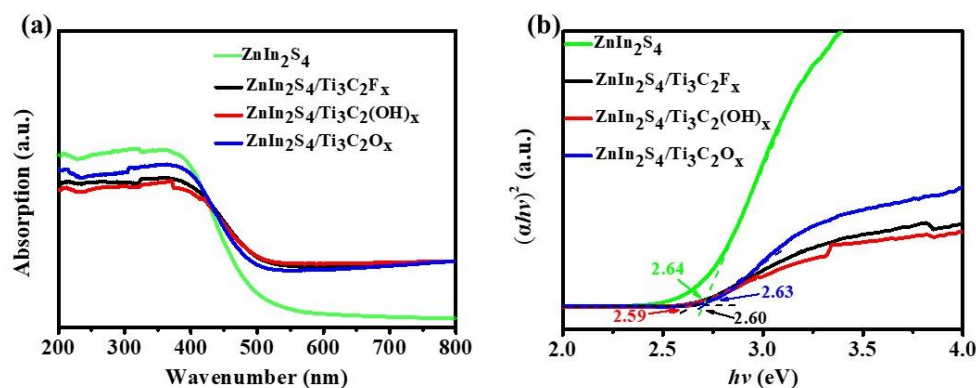


Figure 3. (a) UV-vis DRS spectra of ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$, and (b) Tauc's bandgap plot.

The optical properties of pristine ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{F}_x$ ($T = \text{F}, \text{OH}, \text{O}$) composites were analyzed using the UV-vis diffuse reflectance spectra (UV-vis DRS). As shown in Figure 3a, the pristine ZnIn_2S_4 showed an absorption edge at 560 nm, while the absorption edge of the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composites exhibited a slightly red shift with the introduction of $\text{Ti}_3\text{C}_2\text{T}_x$. Moreover, compared to that of ZnIn_2S_4 , the absorption intensities of the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composites increased in the whole visible light region, suggesting that the $\text{Ti}_3\text{C}_2\text{T}_x$ loading increased the visible light utilization efficiency of ZnIn_2S_4 . In addition, the UV-vis DRS spectra of ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composites were converted into Tauc's band gap plots (Figure 3b), the band gaps of ZnIn_2S_4 , $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{F}_x$, $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2(\text{OH})_x$ and $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ were measured to be 2.64 eV, 2.60 eV, 2.59 eV and 2.63 eV, respectively.

3.3. Photocatalytic H_2 Evolution Activity

The photocatalytic H_2 evolution activity of the as-obtained pure ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composites were evaluated under visible light irradiation using triethanolamine (TEOA) as a sacrificial reagent. It was well known that $\text{Ti}_3\text{C}_2\text{T}_x$ were not semiconductors and they could not generate electrons and holes upon light irradiation [32]. Therefore, $\text{Ti}_3\text{C}_2\text{T}_x$ had no photocatalytic H_2 evolution activity. In Figure 4a, the pure ZnIn_2S_4 exhibited the poor H_2 evolution rate of $253 \mu\text{mol h}^{-1} \text{g}^{-1}$. Inspiringly, after loading the $\text{Ti}_3\text{C}_2\text{T}_x$ cocatalysts, the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composites all exhibited the improved photocatalytic H_2 evolution activity, and the order of photocatalytic activity was $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x > \text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{F}_x > \text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2(\text{OH})_x > \text{ZnIn}_2\text{S}_4$. Furthermore, the photocatalytic H_2 evolution rate of the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ composites strongly depended on the amount of $\text{Ti}_3\text{C}_2\text{O}_x$. The $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ composite with 1.0 wt% $\text{Ti}_3\text{C}_2\text{O}_x$ achieved the optimal H_2 evolution rate of $363 \mu\text{mol h}^{-1} \text{g}^{-1}$ (Figure 4b). By further increasing the $\text{Ti}_3\text{C}_2\text{O}_x$ content, the H_2 evolution rate of the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ composite decreased, which could be due to the excessive amount of $\text{Ti}_3\text{C}_2\text{O}_x$ covering the active sites and hindering the light absorption of ZnIn_2S_4 [33]. The photocatalytic stability test of $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ for photocatalytic H_2 evolution was carried out for four consecutive cycles (Figure 4c). It can be seen that $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ maintained the photocatalytic H_2 evolution activity during the four consecutive cycles, indicating the excellent photostability of $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$.

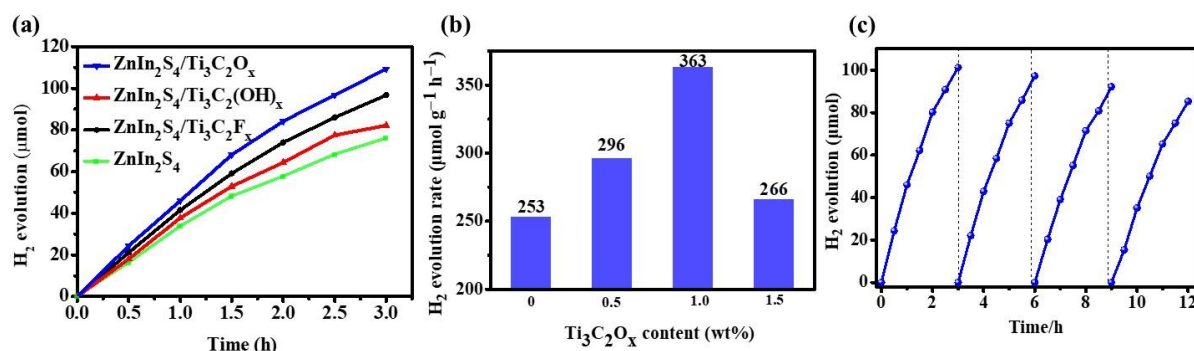


Figure 4. (a) Time course of photocatalytic H_2 evolution performance of ZnIn_2S_4 , and $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ samples, (b) comparison of the photocatalytic H_2 evolution rate of $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ samples with different $\text{Ti}_3\text{C}_2\text{O}_x$ contents and (c) recycling test of photocatalytic H_2 production over $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$.

3.4. The Mechanism of Enhanced Photocatalytic Activity

To shed light on the fundamental reasons for the enhanced photocatalytic performance of $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$, fluorescence property and photoelectrochemical measurements were employed. It is well known that the transfer efficiency of photogenerated electrons and holes was an important influencing factor for the photocatalytic performance. The photoluminescence (PL) spectrum was employed to illustrate the transfer efficiency of the photogenerated electrons and holes. Figure 5a showed the PL spectra of the ZnIn_2S_4 and

$\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composites measured at 375 nm. The order of the PL signal intensity at 565 nm was $\text{ZnIn}_2\text{S}_4 > \text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2(\text{OH})_x > \text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{F}_x > \text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$. The loading of $\text{Ti}_3\text{C}_2\text{T}_x$ lead to the decreased PL intensity of ZnIn_2S_4 , and the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ composite showed the lowest PL intensity, which indicated that the addition of the $\text{Ti}_3\text{C}_2\text{O}_x$ cocatalyst could effectively facilitate the transfer of the photogenerated electrons and hole on the ZnIn_2S_4 photocatalyst. The time-resolved photoluminescence (TRPL) spectra (Figure 5b) further certified this result. The calculated average fluorescence lifetime (Ave. τ) of $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ (0.594 ns) was significantly longer than that of ZnIn_2S_4 (0.167 ns), which demonstrated that the $\text{Ti}_3\text{C}_2\text{O}_x$ cocatalyst loading greatly reduced the recombination rate of the photogenerated electrons and holes on ZnIn_2S_4 . In addition, electrochemical impedance spectroscopy (EIS) and transient photocurrent response analyses were carried out to further investigate the separation and transfer ability of the photogenerated charge carriers. The EIS Nyquist plots were shown in Figure 5c and the arc radius on the EIS Nyquist plot of $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ was the smallest among these four samples, which indicated its lowest resistance for the charge carriers on the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ composite. This also confirmed that the $\text{Ti}_3\text{C}_2\text{O}_x$ cocatalyst enhanced the separation and transfer efficiency of the photogenerated electrons and holes of ZnIn_2S_4 . The transient photocurrent densities of the as-prepared samples were displayed in Figure 5d. Compared with that of the blank ZnIn_2S_4 , the photocurrent densities of the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ samples exhibited remarkable increases; in particular, $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ exhibited the highest photocurrent density, further confirming the excellent photogenerated carriers transfer and separation ability of $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$. All of these results proved that the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ exhibited the fastest transfer and separation ability of photogenerated electrons and holes, further resulting in the excellent photocatalytic H_2 production performance.

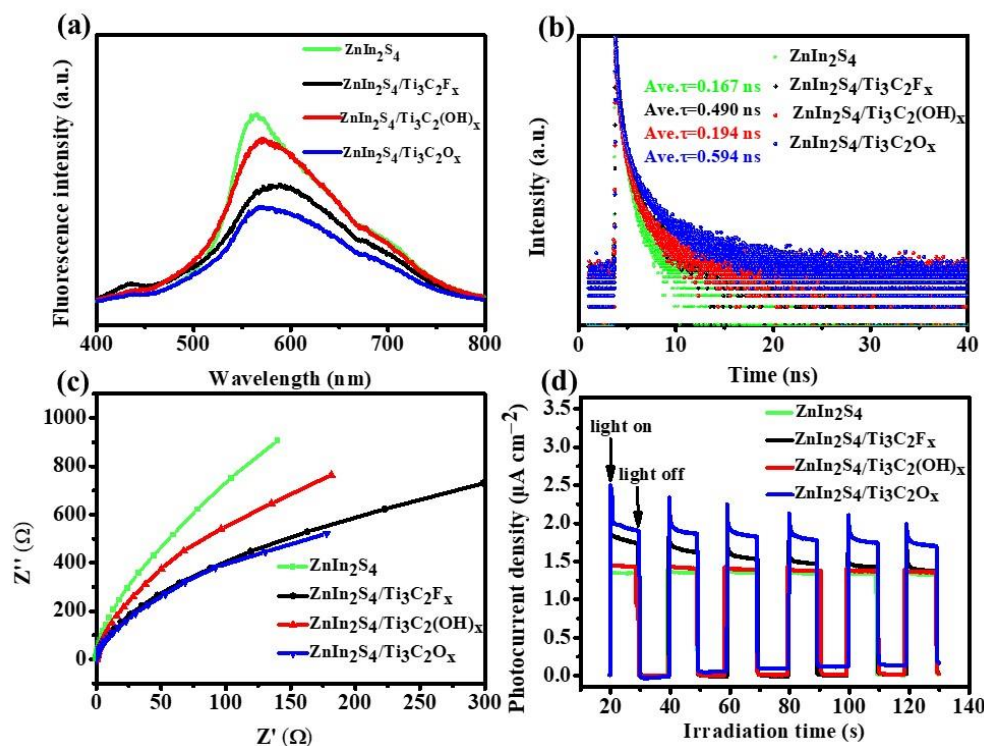


Figure 5. (a) PL spectra, (b) time-resolved PL spectra, (c) EIS Nyquist plots and (d) transient photocurrent responses of ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T}_x = \text{F}, \text{OH}, \text{O}$) samples.

In terms of the band theory, electron transfer behavior is closely related to the work functions of ZnIn_2S_4 and $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T}_x = \text{F}, \text{OH}, \text{O}$). In order to determine the work functions (Φ) of the ZnIn_2S_4 and $\text{Ti}_3\text{C}_2\text{T}_x$ samples, the ultraviolet photoelectron spectroscopy (UPS) technique was employed, as shown in Figure 6. The incident photon energy ($h\nu$) was 21.22 eV. As for ZnIn_2S_4 (Figure 6a), the secondary electron cutoff energy (E_{cutoff}) was

9.32 eV and the Fermi energy (E_{Fermi}) was 25.92 eV. The work function of ZnIn_2S_4 was calculated to be 3.33 eV using the formula: Work function (WF) = $h\nu + E_{\text{cutoff}} - E_{\text{Fermi}}$. Similarly, the work functions for $\text{Ti}_3\text{C}_2\text{F}_x$, $\text{Ti}_3\text{C}_2(\text{OH})_x$ and $\text{Ti}_3\text{C}_2\text{O}_x$ were calculated to be 4.22 eV, 3.73 eV and 4.57 eV, respectively (Figure 6b–d). Obviously, the work functions of the $\text{Ti}_3\text{C}_2\text{T}_x$ samples were all higher than that of ZnIn_2S_4 . Therefore, the photogenerated electrons could transfer from ZnIn_2S_4 to $\text{Ti}_3\text{C}_2\text{T}_x$. Meanwhile, the Schottky barrier could be formed at the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$ interface due to the difference in the work function and the band alignment between ZnIn_2S_4 and $\text{Ti}_3\text{C}_2\text{T}_x$, which could greatly accelerate the separation and transfer of the photogenerated electrons and holes [34]. The electrostatic potentials of $\text{Ti}_3\text{C}_2\text{F}_x$, $\text{Ti}_3\text{C}_2(\text{OH})_x$ and $\text{Ti}_3\text{C}_2\text{O}_x$ were obtained from a density functional theory (DFT), as shown in Figure S5. The order of work function values obtained from the DFT calculations was in accordance with that from the UPS characterization. Moreover, the difference in work function between ZnIn_2S_4 and $\text{Ti}_3\text{C}_2\text{T}_x$ was associated with the photogenerated electrons' transfer ability [35,36]. The largest difference in the work function between ZnIn_2S_4 and $\text{Ti}_3\text{C}_2\text{O}_x$ indicated that $\text{Ti}_3\text{C}_2\text{O}_x$ showed the strongest electron capture capability from ZnIn_2S_4 in the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ heterojunction, leading to the significantly high photocatalytic activity.

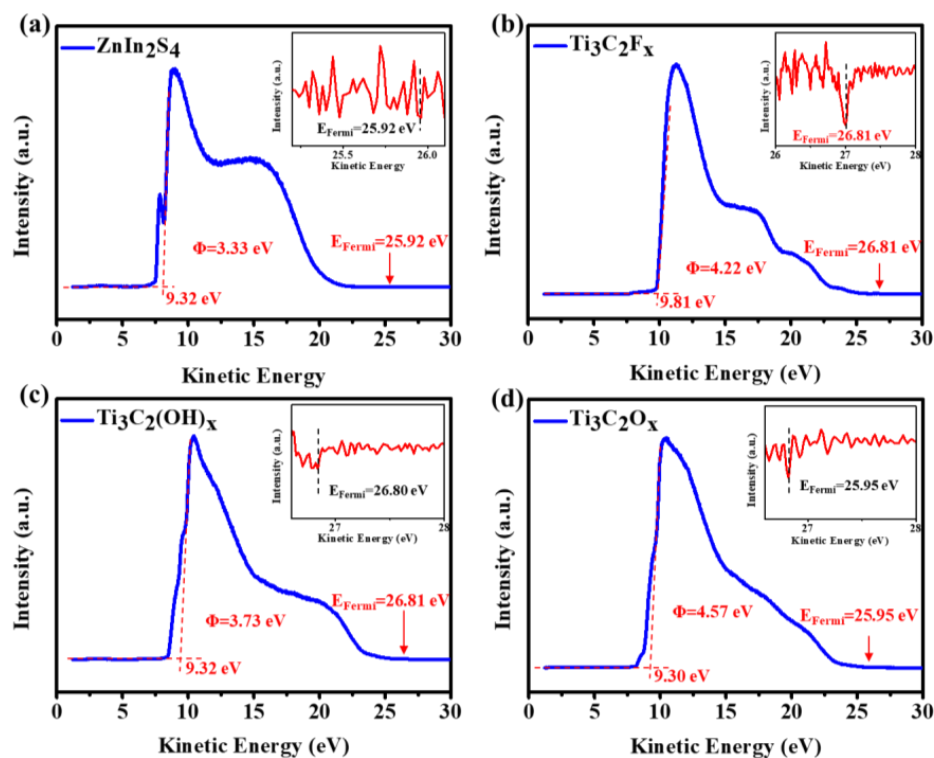


Figure 6. UPS spectrum of (a) ZnIn_2S_4 , (b) $\text{Ti}_3\text{C}_2\text{F}_x$, (c) $\text{Ti}_3\text{C}_2(\text{OH})_x$ and (d) $\text{Ti}_3\text{C}_2\text{O}_x$.

Based on the aforementioned results, a probable photocatalytic mechanism for $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ was proposed (Figure 7). The conduction band potential of the parent ZnIn_2S_4 was estimated by the Mott-Schottky method (Figure S6). Under visible light irradiation, the photogenerated electrons on the valence band (VB) of ZnIn_2S_4 were excited to the conduction band (CB). Because the work function of $\text{Ti}_3\text{C}_2\text{O}_x$ was higher than that of ZnIn_2S_4 , photogenerated electrons in the CB of ZnIn_2S_4 could quickly migrate to the surface of $\text{Ti}_3\text{C}_2\text{O}_x$ across the intimate interface, the Schottky junction formed between ZnIn_2S_4 and $\text{Ti}_3\text{C}_2\text{O}_x$ could further prevent the recombination of photogenerated electrons and holes in the $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$. Subsequently, the photogenerated electrons in $\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{O}_x$ were available to react with water to evaluate H_2 , while the holes on the VB of ZnIn_2S_4 are consumed by the sacrificial agent TEOA.

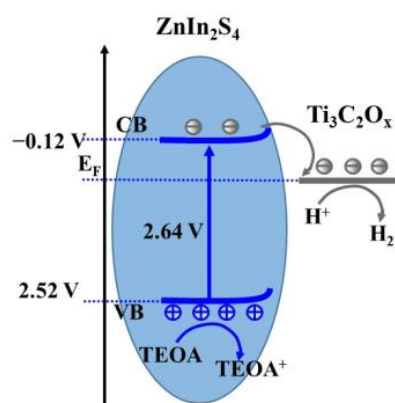


Figure 7. Schematic illustration for the photocatalytic H₂ evolution reaction over ZnIn₂S₄/Ti₃C₂O_x.

4. Conclusions

In summary, we have successfully designed and synthesized the surface functionalized Ti₃C₂(OH)_x and Ti₃C₂O_x using the surface post-treatments of Ti₃C₂F_x; then Ti₃C₂T_x (T_x = F, OH, O) were employed as the substrate and cocatalysts for the in-situ growth of ZnIn₂S₄ to obtain ZnIn₂S₄/Ti₃C₂T_x heterojunctions for photocatalytic H₂ production. Remarkably, the photocatalytic H₂ production activity of ZnIn₂S₄/Ti₃C₂T_x was greatly improved, compared to that of ZnIn₂S₄. Due to the differences in work function between ZnIn₂S₄ and Ti₃C₂T_x, the formation of the Schottky junction could effectively accelerate the separation and migration of photogenerated electrons and holes, and thus boost the photocatalytic H₂ evolution activity. In particular, among Ti₃C₂T_x (T_x = F, OH, O), the work function of Ti₃C₂O_x was the largest, and the Ti₃C₂O_x showed the strongest electron capture ability from ZnIn₂S₄. Experimental characterization analyses also demonstrated the rapid separation and transfer of photogenerated electrons and holes of ZnIn₂S₄/Ti₃C₂O_x. This work paves the way for photocatalytic applications of MXene-based photocatalysts by tuning their surface termination groups.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma16062168/s1>, Figure S1: XRD patterns of the Ti₃AlC₂ and the as-synthesized Ti₃C₂T_x (T_x = F, OH, O); Figure S2: SEM of (a) Ti₃C₂F_x, (b) Ti₃C₂(OH)_x and (c) Ti₃C₂O_x; Figure S3: XRD pattern of ZnIn₂S₄ and ZnIn₂S₄/Ti₃C₂T_x (T_x = F, OH, O); Figure S4: The SEM of ZnIn₂S₄; Figure S5: Electrostatic potentials of Ti₃C₂T_x (T_x = F, OH, O); Figure S6: Mott–Schottky diagram of ZnIn₂S₄; Table S1: the atomic ratio of Ti₃C₂T_x (T_x = F, OH, O) by XPS results [37,38].

Author Contributions: M.C.: Conceptualization, writing-review and editing and visualization; X.Z.: investigation and writing-original draft preparation; Z.Z.: methodology and Resources; J.B.: validation; Q.W.: data curation; Q.C.: data curation; funding acquisition; Y.W. and S.S.: project administration and funding acquisition. X.Z. contributed equally with M.C. All authors have read and agreed to the published version of the manuscript.

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