Sulfur Vacancy and Ti$_3$C$_2$T$_x$ Cocatalyst Synergistically Boosting Interfacial Charge Transfer in 2D/2D Ti$_3$C$_2$T$_x$/ZnIn$_2$S$_4$ Heterostructure for Enhanced Photocatalytic Hydrogen Evolution

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Constructing an efficient photoelectron transfer channel to promote the charge carrier separation is a great challenge for enhancing photocatalytic hydrogen evolution from water. In this work, an ultrathin 2D/2D Ti$_3$C$_2$T$_x$/ZnIn$_2$S$_4$ heterostructure is rationally designed by coupling the ultrathin ZnIn$_2$S$_4$ with few-layered Ti$_3$C$_2$T$_x$ via the electrostatic self-assembly strategy. The 2D/2D Ti$_3$C$_2$T$_x$/ZnIn$_2$S$_4$ heterostructure possesses larger contact area and strong electronic interaction to promote the charge carrier transfer at the interface, and the sulfur vacancy on the ZnIn$_2$S$_4$ acting as the electron trap further enhances the separation of the photoinduced electrons and holes. As a consequence, the optimal 2D/2D Ti$_3$C$_2$T$_x$/ZnIn$_2$S$_4$ composite exhibits a high photocatalytic hydrogen evolution rate of 148.4 μmol h$^{-1}$, which is 3.6 times and 9.2 times higher than that of ZnIn$_2$S$_4$ nanosheet and flower-like ZnIn$_2$S$_4$, respectively. Moreover, the stability of the ZnIn$_2$S$_4$ is significantly improved after coupling with the few-layered Ti$_3$C$_2$T$_x$. The characterizations and density functional theory calculation demonstrate that the synergistic effect of the sulfur vacancy and Ti$_3$C$_2$T$_x$ cocatalyst can greatly promote the electrons transfer from ZnIn$_2$S$_4$ to Ti$_3$C$_2$T$_x$ and the separation of photogenerated charge carriers, thus enhancing the photocatalytic hydrogen evolution from water.

1. Introduction

Photocatalytic water splitting, which can directly convert the inexhaustible solar energy into clean and high-energy-density hydrogen, is regarded as one of the important ways to solve the global energy shortage and environmental pollution problem.[1] Over the past decades, the emergence of novel catalytic materials from particles to nanoscale has promoted the continuous development in photocatalytic water splitting.[2] However, due to the limitations of the electronic structure,[3] morphology,[4] energy band structure,[5] and surface chemical state,[6] the development of semiconductors with excellent efficiency of photocatalytic water splitting remains a challenge.[7] In recent years, ultrathin 2D materials have become promising catalysts for photocatalytic hydrogen reaction due to their advantages of more exposed active sites[8] and shorter electron migration distance.[9] Among them, nontoxic hexagonal ZnIn$_2$S$_4$, due to its narrow bandgap and the S–Zn–S–In–S–In–S-type lamellar stack structure, has attracted great attention in the family of 2D photocatalyst.[10] However, most of the reported ZnIn$_2$S$_4$ was prepared by hydrothermal or solvothermal methods, leading to lamellar cross-linking and agglomeration, and the active sites cannot fully contact water molecules, such as the classic marigold structure.[11] Yang et al. reported that the preparation of highly dispersed ZnIn$_2$S$_4$ colloidal solution by the refluxing and stripping methods
shortened the carrier transport path and effectively inhibited the recombination of electrons and holes. The light absorption capacity of 2D ZnIn$_2$S$_4$ nanosheets, the excitation, migration, and the recombination of photogenerated electron holes in 2D ZnIn$_2$S$_4$ can be controlled by lattice and outer valence electrons in the nanoscale. Therefore, it is beneficial to improve the photocatalytic performance of ZnIn$_2$S$_4$ by accurately regulating the electronic structure by overcoming the van der Waals force between nanosheets.

Introducing sulfur (S) vacancy into the lattice of ultrathin 2D semiconductors is an effective strategy to tune their electronic structure. The vacancy affects the intrinsic bandgap value of semiconductors and induces the generation of intermediate energy levels to increase the charge carrier concentration and captures electrons to promote photogenerated carrier separation. Recently, Cao et al. reported that the direction of photogenerated electron transfer could be controlled by adjusting the vacancy type of CdS. Gao et al. grew S-vacancy ZnS vertically on the Zn-In-LDH surface, which stimulated the synergistic effect of vacancy and 2D interface and improved the performance of photocatalytic hydrogen production. However, due to the instability and the limited number of vacancies, 2D semiconductor photocatalysts are still faced with the significant recombination of the photogenerated electrons and holes. The introduction of effective cocatalysts to 2D photocatalyst is an effective means to optimize the electron transport path and promote the transfer and separation of photoinduced charge carriers.

Since the first reported MXene in 2011, 2D MXenes material has demonstrated excellent performance in the fields of supercapacitor, lithium-ion battery, catalysis, electromagnetic shielding, and other fields. Due to the excellent conductivity, high hydrophilicity, and large ultrathin 2D interface, a large number of active sites on the surface, and a superior Fermi level position, MXenes are widely used as cocatalyst in the field of photocatalytic water splitting. For example, the Ti$_3$C$_2$ MXene was demonstrated as a potential cocatalyst to replace the rare precious metal Pt, the apparent quantum efficiency of Ti$_3$C$_2$/CdS at 420 nm under visible light reached 40.1% when with Ti$_3$C$_2$ as the cocatalyst. Moreover, Xie et al. found that Ti$_3$C$_2$T$_x$ wondrously delayed the photocorrosion of sulfide by photogenerated holes through the adsorption of spillage metal ions. In recent years, the in situ growth of the photocatalysts on the 2D interface of Ti$_3$C$_2$ has been widely used for the design of photocatalytic heterosystem. For example, ZnIn$_2$S$_4$ nanosheets were in situ grown on the surface of Ti$_3$C$_2$ to improve photocatalytic H$_2$ evolution performance. However, the analogous vertical contact between the edges of ZnIn$_2$S$_4$ layer and the Ti$_3$C$_2$ plane results in a long carrier transfer path, which is not beneficial for the rapid transfer and separation of the electrons and holes, and the S vacancy on the ZnIn$_2$S$_4$ surface was not taken into account. To further improve the transfer rate of the photoinduced electrons, the rational design of 2D/2D MXene-based heterostructure with close contact interface and multiaactive sites opens up an effective strategy for the construction of efficient photocatalyst for hydrogen production.

Herein, ultrathin 2D ZnIn$_2$S$_4$ nanosheet containing S vacancy was prepared, and the 2D ZnIn$_2$S$_4$ was combined with the few-layered Ti$_3$C$_2$T$_x$ nanosheet by electrostatic self-assembly to synthesize the tightly contacted 2D/2D Ti$_3$C$_2$T$_x$/ZnIn$_2$S$_4$ composite, which was used as the efficient photocatalyst for photocatalytic hydrogen evolution. The S vacancy acted as electron traps on the 2D ZnIn$_2$S$_4$ surface, and the few-layered Ti$_3$C$_2$T$_x$ with larger work function can quickly capture the photogenerated electrons on the 2D ZnIn$_2$S$_4$ nanosheet, which greatly promotes the electron transfer and the separation of photogenerated charge carriers. As a result, the 2D/2D Ti$_3$C$_2$T$_x$/ZnIn$_2$S$_4$ showed a superior photocatalytic hydrogen evolution performance, due to the compact 2D/2D heterointerfaces and the synergistic effect of the S vacancy and the Ti$_3$C$_2$T$_x$ cocatalyst.

2. Results and Discussion

2.1. Synthesis, Structure, and Morphology

Figure 1A illustrates the synthetic route of layered ZnIn$_2$S$_4$ (labeled as L-ZnIn$_2$S$_4$), ZnIn$_2$S$_4$ nanosheet (labeled as N-ZnIn$_2$S$_4$), few-layered Ti$_3$C$_2$T$_x$, and Ti$_3$C$_2$T$_x$/N-ZnIn$_2$S$_4$ (labeled as TC/N-ZIS) composites. The TC/N-ZIS with different amounts of Ti$_3$C$_2T_x$ were denoted as 1-TC/N-ZIS, 2-TC/N-ZIS, 3-TC/N-ZIS, 4-TC/N-ZIS, 5-TC/N-ZIS, 6-TC/N-ZIS, and 8-TC/N-ZIS, respectively. The ZnIn$_2$S$_4$ nanoflower (labeled as F-ZnIn$_2$S$_4$) sample was simply synthesized by a hydrothermal method (Figure S1, Supporting Information). Compared to the synthesis condition of F-ZnIn$_2$S$_4$, the L-ZnIn$_2$S$_4$ was obtained by adding additional trisodium citrate dihydrate to the reaction solution before hydrothermal reaction. In this way, ZnIn$_2$S$_4$ was grown in layers along the plane direction. Therefore, N-ZnIn$_2$S$_4$ with rich S vacancy can be simply prepared by treating the L-ZnIn$_2$S$_4$ with ultrasonication self-exfoliation due to the weak Van der Waals force between the ZnIn$_2$S$_4$ layers. The multilayer Ti$_3$C$_2$T$_x$ was prepared by etching the Ti$_3$C$_2$T$_x$ with HCl/LiF solution as the etchant, and the few-layered Ti$_3$C$_2$T$_x$ can be obtained by exfoliating the multilayer Ti$_3$C$_2$T$_x$ with ultrasonication. Subsequently, the TC/N-ZIS was obtained by coupling the N-ZnIn$_2$S$_4$ with the few-layered Ti$_3$C$_2$T$_x$ nanosheet through the electrostatic self-assembly strategy with the assistance of the NH$_3$−.

From the SEM images of F-ZnIn$_2$S$_4$ sample (Figure S2A,D Supporting Information), F-ZnIn$_2$S$_4$ showed a tightly packed marigold-like morphology, which in accordance with the reported results. However, the L-ZnIn$_2$S$_4$ exhibited the lamellar structure (Figure S2B,E Supporting Information). The Ti$_3$AlC$_2$ also showed the lamellar structure (Figure S2C, Supporting Information), and the multilayer Ti$_3$C$_2$T$_x$ obtained by etching the Ti$_3$C$_2$T$_x$ displayed the accordion-like morphology (Figure S2F, Supporting Information).

The L-ZnIn$_2$S$_4$ can be completely exfoliated into light yellow N-ZnIn$_2$S$_4$ colloidal solution by short-time ultrasonic treatment in the absence of any intercalator or surfactant species (Figure S3, Supporting Information), while the F-ZnIn$_2$S$_4$ cannot be completely dispersed in the solution under ultrasonic treatment for 3 h and will precipitate after standing for 1 h (Figure S4, Supporting Information). To figure out the reason why the N-ZnIn$_2$S$_4$ can stably exist in the solution, the zeta potential of N-ZnIn$_2$S$_4$ colloidal solution was measured (Figure S5, Supporting Information). The high negative charge value of −39.8 mV of the N-ZnIn$_2$S$_4$ colloidal solution indicated that there was a strong repulsive force between the N-ZnIn$_2$S$_4$ nanosheets, which accounts for the stability of the N-ZnIn$_2$S$_4$ colloidal solution.
In addition, with the –OH, –O, and –F functional groups on the surface of Ti3C2Tx, the zeta potential of few-layered Ti3C2Tx colloidal solution was measured to be −31.8 mV. Therefore, the Ti3C2Tx nanosheets were electronegative and exhibited excellent dispersity in water.\textsuperscript{[35]} Due to the electronegative surface of the Ti3C2T and the N-ZnIn2S4, a green and transparent mixed Ti3C2Tx/N-ZnIn2S4 colloidal solution can be formed when 1.36 mL Ti3C2Tx colloidal solution (1.5 mg mL\textsuperscript{−1}) was added to 50 mL N-ZnIn2S4 colloidal solution (2.0 mg mL\textsuperscript{−1}), and the zeta potential was changed to −39.4 mV. Moreover, with the increased amount of Ti3C2Tx colloidal solution from 1.36 to 5.80 mL, the zeta potential of the mixed Ti3C2Tx/N-ZnIn2S4 colloidal solution increased from −39.8 to −36.2 mV. Hence, when the NH\textsubscript{4}⁺ was induced to the mixed Ti3C2Tx/N-ZnIn2S4 colloidal solution by gradually adding NH\textsubscript{4}HCO\textsubscript{3} solution, the Ti3C2Tx and the N-ZnIn2S4 were drawntogether and formed the 2D/2D Ti3C2Tx/N-ZnIn2S4 composite (Figure S6, Supporting Information). Notably, the NH\textsubscript{4}⁺ here acted as a binder to attract the N-ZnIn2S4 nanosheet and the Ti3C2Tx to contact with each other and form a compact heterostructure at the Ti3C2Tx/N-ZnIn2S4 interfaces.

The crystal structure of all samples was analyzed by X-ray diffraction (XRD), as can be seen in the XRD pattern of Ti3C2Tx (Figure 1B), the main peak for the (104) plane of Ti3C2AlC2 disappeared, indicating that Al was removed from the Ti3C2AlC2 and formed the Ti3C2T MXene. Moreover, the peaks located at 7.7° (002), 16.6° (004), and 60.7° (110) further demonstrated the successful formation of the Ti3C2T MXene.\textsuperscript{[36,37]} Figure 1C shows that the diffraction peaks at 22.3°, 27.5°, 30.5°, 47.3°, 52.5°, and 55.7° were well consistent with the (006), (102), (104), (110), (116), and (022) planes of ZnIn2S4, indicating that the F-ZnIn2S4, L-ZnIn2S4, and N-ZnIn2S4 were successfully prepared and in the hexagonal phase structures (JCPDS No. 65–2023).\textsuperscript{[38]} It was worth noting that the peaks of F-ZnIn2S4 were sharper than those of L-ZnIn2S4 and N-ZnIn2S4. It can be obviously observed from the SEM images of F-ZnIn2S4 (Figure S2A, Supporting Information), L-ZnIn2S4 (Figure S2B, Supporting Information), and N-ZnIn2S4 (Figure 2B) that the F-ZnIn2S4 shows the shape of large flower-like particle while the L-ZnIn2S4 was made up of the layer-by-layer stacked small flakes. Therefore, the sharper XRD peaks of F-ZnIn2S4 may be attributed to the larger crystalline grain size of F-ZnIn2S4 than that of the L-ZnIn2S4 and N-ZnIn2S4.\textsuperscript{[39]} Figure 1D shows the XRD pattern of a series of x-TCN-ZIS composites, which can be observed that the diffraction peaks of the x-TC/N-ZIS composites were similar to those of N-ZnIn2S4. However, the diffraction peaks at (002) shifted to the lower degree relative to N-ZnIn2S4, which can be ascribed to the increased layer spacing of N-ZnIn2S4 and the dispersion of N-ZnIn2S4 attached to the Ti3C2T surface.\textsuperscript{[40]} Due to the low content of Ti3C2T and its high dispersion, the diffraction peaks of the Ti3C2T cannot be observed.

The N\textsubscript{2} adsorption–desorption isotherms of F-ZnIn2S4, L-ZnIn2S4, N-ZnIn2S4, Ti3C2T, and 4-TCN-ZIS samples were shown in Figure S7A (Supporting Information). It can be seen...
that the N-ZnIn$_2$S$_4$ nanosheets were in line with the H4 hysteresis loop\cite{41}, indicating that there were narrow fissure pores between the N-ZnIn$_2$S$_4$ nanosheets. Moreover, the Brunauer–Emmett–Teller (BET) specific surface area of N-ZnIn$_2$S$_4$ was 123.82 m$^2$ g$^{-1}$, which was 1.56 times than that of F-ZnIn$_2$S$_4$ and 2.12 times than that of L-ZnIn$_2$S$_4$, respectively (Table S1, Supporting Information), indicating the successful exfoliation of L-ZnIn$_2$S$_4$. After N-ZnIn$_2$S$_4$ was coupled with Ti$_3$C$_2$T$_x$ to form the TC/N-ZIS composite, the BET specific surface area was slightly reduced compared with N-ZnIn$_2$S$_4$ (Figure S7 and Table S1, Supporting Information), but was slightly increased relative to Ti$_3$C$_2$T$_x$ powder (48.09 m$^2$ g$^{-1}$), which can be attributed to the formation of the compact interface between the Ti$_3$C$_2$T$_x$ and the N-ZnIn$_2$S$_4$.

The morphology and the thickness of the Ti$_3$C$_2$T$_x$, N-ZnIn$_2$S$_4$, and 4-TC/N-ZIS were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements. The SEM images of the Ti$_3$C$_2$T$_x$ powder showed that the Ti$_3$C$_2$T$_x$ is in the 2D nanosheet structure, and no agglomeration or restacking phenomena can be observed (Figure S8A, Supporting Information; Figure 2A). In addition, the Ti$_3$C$_2$T$_x$ showed highly dispersed large flakes and slight wrinkles on the surface and edge, which might be ascribed to the surface energy change of the MXene after inducing NH$_4^+$.\cite{42} Figure S8B (Supporting Information) and Figure 2B and show that the N-ZnIn$_2$S$_4$ was in a curly and fluffy foam shape, which was composed of multiple small flakes with a size of 200–500 nm. Moreover, there were gaps between these small N-ZnIn$_2$S$_4$ flakes, which was beneficial to the redispersion of the N-ZnIn$_2$S$_4$ in water. From the AFM images of the Ti$_3$C$_2$T$_x$ and the N-ZnIn$_2$S$_4$, it can be observed that the size of the N-ZnIn$_2$S$_4$ nanosheet is smaller than that of the Ti$_3$C$_2$T$_x$ (Figure 2E,H). The height profiles (Figure 2F,I) corresponding to the white line in the AFM images showed that the thickness of Ti$_3$C$_2$T$_x$ and N-ZnIn$_2$S$_4$ were less than 2.76 and 3.65 nm, respectively, indicating the ultrathin nature of Ti$_3$C$_2$T$_x$ and N-ZnIn$_2$S$_4$ nanosheets.

As shown in Figure 2C, after the integration of the Ti$_3$C$_2$T$_x$ with the ultrathin N-ZnIn$_2$S$_4$ flakes, it can be observed that the N-ZnIn$_2$S$_4$ flakes were highly dispersed and immobilized on the 2D few-layered Ti$_3$C$_2$T$_x$, indicating the successful formation of 2D/2D TC/N-ZIS heterostructure. In addition, the TC/N-ZIS composite showed the 2D structure, which is beneficial to the charge carriers transfer from the interior of the TC/N-ZIS photocatalyst to the surface, and initiate the photocatalytic reaction. The energy-dispersive spectroscopy (EDS) element mapping (Figure S9, Supporting Information) of the 4-TC/N-ZIS sample demonstrated the existent of the Zn, In, S, Ti, and C, and these elements were uniformly distributed in the 2D/2D 4-TC/N-ZIS composite, which further confirmed the successful coupling of Ti$_3$C$_2$T$_x$ with N-ZnIn$_2$S$_4$. Additionally, the EDS spectrum displayed that the atomic ratio of the Zn, In, and S in the 4-TC/N-ZIS heterostructure was 1:1.77:3.19 (Figure S10 and Table S2, Supporting Information). The SEM images of the other TC/N-ZIS composites with different content of Ti$_3$C$_2$T$_x$ can also be found in Figure S11 (Supporting Information).

The morphology and microstructure of the samples were further investigated by high resolution transmission electron microscopy (HRTEM), as shown in Figure 3. The clean lamellar distribution of Ti$_3$C$_2$T$_x$ colloid on the copper grid indicated the

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Figure 2. SEM images of A) Ti$_3$C$_2$T$_x$, B) N-ZnIn$_2$S$_4$, and C) 4-TC/N-ZIS composite, the photographs of the Tyndall effect of the D) Ti$_3$C$_2$T$_x$ and G) N-ZnIn$_2$S$_4$ colloidal solution, AFM and height profile of E,F) few-layered Ti$_3$C$_2$T$_x$ and H,I) N-ZnIn$_2$S$_4$. 

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successfull exfoliation (Figure S12, Supporting Information). As shown in the TEM images of the Ti₃C₂Tₓ (Figure 3A), the ultrathin nature and some wrinkles of the few-layered Ti₃C₂Tₓ can be observed obviously, which was consistent with the SEM results. Moreover, Figure 3B shows cross-sections of the edge of the exfoliated Ti₃C₂Tₓ nanosheets, and the space between the Ti₃C₂Tₓ flakes was measured to be 1.32 nm. Figure 3C shows the ultrathin nanosheet structure of N-ZnIn₂S₄, which was consistent with the results of SEM and AFM. However, the F-ZnIn₂S₄ sample displayed the tightly packed marigold morphology, indicating the severe agglomeration of the ZnIn₂S₄ nanosheets (Figure S13, Supporting Information). In Figure 3D, the fringe spacing of 0.32 and 0.29 nm corresponded to (102) and (104) planes of hexagonal ZnIn₂S₄, respectively. In addition, apparent shadow regions in the lattice fringe were clearly observed in the purple circles, indicating the presence of S vacancies in N-ZnIn₂S₄.

The TEM images of the 4-TC/N-ZIS composite showed that the ultrathin structure was maintained after the N-ZnIn₂S₄ flakes were immobilized on the surface of the few-layered Ti₃C₂Tₓ (Figure 3E,F), indicating the successfully constructing of the 2D/2D compact interface between the N-ZnIn₂S₄ and the Ti₃C₂Tₓ nanosheet. As shown in Figure 4G, the lattice fringes spacing of 0.41 and 0.32 nm were in good agreement with the (006) and (102) planes of ZnIn₂S₄, respectively, while the lattice fringes spacing of 0.26 nm corresponding to the (0110) plane of Ti₃C₂Tₓ.

Moreover, an obvious interface was observed between the N-ZnIn₂S₄ and the Ti₃C₂Tₓ flakes, further demonstrating the existence of the close interfacial contact between these two ultrathin nanosheets. Notably, the vacancies still exist in the 4-TC/N-ZIS composite shown in the purple circles in Figure 3G. In Figure 3H, the selected area electron diffraction (SAED) showed the existence of the (002), (108), and (100) plane of ZnIn₂S₄ and the (0110) plane of Ti₃C₂Tₓ, respectively, indicating the successful coupling of the ZnIn₂S₄ and the Ti₃C₂Tₓ again. In addition, the element mapping corresponding to HAADF-STEM images displayed that the Zn, In, S, Ti, and C elements were distributed uniformly in the ultrathin 4-TC/N-ZIS sample. Based on the above results, it can be concluded that the 2D/2D ZnIn₂S₄/Ti₃C₂Tₓ heterostructure was successfully formed.

**2.2. Surface Chemical State, Vacancy, and Electronic Structure**

Raman spectra, ESR spectra, and XPS were carried out to investigate the surface chemical states, vacancies, and electronic structures of the photocatalysts. The Raman spectra of the F-ZnIn₂S₄ and N-ZnIn₂S₄ (Figure S14, Supporting Information) showed peaks at 247.4, 297.4, and 344.2 cm⁻¹, corresponding to the longitudinal optical mode (LO₁) and transverse optical mode (TO) of ZnIn₂S₄, respectively.
From the Raman spectra of Ti$_3$C$_2$T$_x$, the peaks at 387.1 and 622.4 cm$^{-1}$ corresponded to the A$_{1g}$ signal of the –OH, –O, and –F groups on the surface of Ti$_3$C$_2$T$_x$ (Figure 4A), and the absence of Ti-Al vibration further indicated the success of etching.\[45\] Notably, the obvious signals at 1349 and 1470 cm$^{-1}$ corresponded to D and G bands of graphitized carbon generated during the etching process, which was consistent with the previous report.\[37\] Interestingly, the graphitized carbon can act as the electron trap to capture photogenerated electrons, which is also beneficial to the separation of electron and holes.\[32,46\] Moreover, the derivative graphitized carbon is closely connected to the Ti$_3$C$_2$T$_x$, therefore, the carbon species seems to function as an electron channel between the Ti$_3$C$_2$T$_x$ and N-ZnIn$_2$S$_4$ for accelerating the electron migration. The Raman spectra of x-TC/N-ZIS showed the vibration peaks of Ti$_3$C$_2$T$_x$ and N-ZnIn$_2$S$_4$, indicating the coexistence of Ti$_3$C$_2$T$_x$ and N-ZnIn$_2$S$_4$ in the x-TC/N-ZIS composite. Compared to N-ZnIn$_2$S$_4$, the TO$_2$ vibration signals of all x-TC/N-ZIS redshift to the higher wavenumber. Moreover, the $I_D/I_G$ value (Table S3, Supporting Information) of all the x-TC/N-ZIS composite increased compared with that of Ti$_3$C$_2$T$_x$ which indicated a slight damage to the graphitized carbon during the synthetic process. The above results demonstrated strong
interaction and enhanced charge transfer between the Ti₃C₂Tₓ and the N-ZnIn₂S₄.[147]

The Fourier transform infrared spectroscopy (FT-IR) (Figure S15A, Supporting Information) showed three peaks at 3401, 1615, and 1396 cm⁻¹ for F-ZnIn₂S₄, L-ZnIn₂S₄, and N-ZnIn₂S₄, which corresponded to the absorbed water and hydroxyl groups on the surface. In addition, a peak at 1109 cm⁻¹ can be observed, which corresponded to the C-O bond generated during the hydrothermal process.[48] As can be seen in Figure S15B (Supporting Information), the FT-IR spectra of the x-TC/N-ZIS showed similar peaks with that of the N-ZnIn₂S₄, indicated that the functional groups were not removed after the coupling of N-ZnIn₂S₄ with Ti₃C₂Tₓ. Notably, the hydroxyl groups retained on the surface endow the x-TC/N-ZIS composite with excellent hydrophilicity and thus facilitate photocatalytic water splitting.

To shed light on the sulfur vacancy on ZnIn₂S₄, the F-ZnIn₂S₄, N-ZnIn₂S₄, and 4-TC/N-ZIS were investigated by electron spin-resonance (ESR) spectroscopy. As shown in Figure 4B, F-ZnIn₂S₄, N-ZnIn₂S₄, and 4-TC/N-ZIS all appeared obvious signal at g = 2.004, indicated the existence of S vacancy.[19] In general, the enhancement of the ESR signal indicated the existence of more electron capture center.[19] Therefore, as the S vacancies acted as the electron-trapped center, the stronger ESR signal of N-ZnIn₂S₄ may be attributed to more S vacancies in N-ZnIn₂S₄ than that of F-ZnIn₂S₄. More importantly, the 4-TC/N-ZIS sample showed stronger signal at g = 2.004 than that of N-ZnIn₂S₄. As a consequence, higher signal at g = 2.004 indicated more electron capture center was formed in the 4-TC/N-ZIS sample. Based on the previous report,[13b,50] the sulfur vacancy in N-ZnIn₂S₄ was demonstrated as the electron trap to capture the photogenerated electrons, thus prolonging the charge carrier lifetime and enhancing the photocatalytic hydrogen production rate. Moreover, the S vacancy in N-ZnIn₂S₄ acted as an electron trap and enriched electrons at the S vacancy was demonstrated by using ESR and density functional theory (DFT) in the work of Zhang et al. and Wang et al.[16,19] Consequently, the formation of S vacancy in N-ZnIn₂S₄ is conducive to the separation of the photoinduced electrons and holes, and thus enhance the photocatalytic H₂ evolution performance.

X-ray photoelectron spectroscopy (XPS) was performed to further demonstrate the existence of sulfur vacancies and the interaction of ZnIn₂S₄ and Ti₃C₂Tₓ in heterostructures.[51] The XPS survey spectra corresponding to the F-ZnIn₂S₄, N-ZnIn₂S₄, Ti₃C₂Tₓ, and 4-TC/ZIS were shown in Figure S16 (Supporting Information). The binding energy of Zn 2p in F-ZnIn₂S₄ (Figure 4C) was located at 1022.07 and 1045.12 eV compared to that of N-ZnIn₂S₄. The high-resolution XPS spectra of the Zn 2p in N-ZnIn₂S₄ showed that the binding energy of Zn 2p₁/₂ and Zn 2p₃/₂ negatively shifted to 1021.93 and 1044.98 eV compared to that of F-ZnIn₂S₄. Similarly, the binding energy of In 3d₁/₂ (444.90 eV) and In 3d₃/₂ (452.45 eV) in N-ZnIn₂S₄ was also negatively shifted compared with that of F-ZnIn₂S₄. The high-resolution XPS spectra of the Zn 2p in N-ZnIn₂S₄ showed that the binding energy of Zn 2p₁/₂ and Zn 2p₃/₂ negatively shifted to 1021.93 and 1044.98 eV compared to that of F-ZnIn₂S₄. Similarly, the binding energy of In 3d₁/₂ (444.90 eV) and In 3d₃/₂ (452.45 eV) in N-ZnIn₂S₄ was also negatively shifted compared with that of F-ZnIn₂S₄. In addition, the Zn 2p binding energy of S 2p₁/₂ (161.54 eV) and S 2p₃/₂ (162.75 eV) in N-ZnIn₂S₄ negatively shifted compared to that of F-ZnIn₂S₄. Consequently, the formation of S vacancies, which resulted in the reduction of coordination number of sulfur atoms and the decrease of the electron cloud density around them.[13b,19]

Interestingly, after 2D/2D contact with Ti₃C₂Tₓ the binding energy of Zn 2p₁/₂ (1022.06 eV), Zn 2p₃/₂ (1045.11 eV), In 3d₁/₂ (445.00 eV), In 3d₃/₂ (452.55 eV), S 2p₁/₂ (161.60 eV), and S 2p₃/₂ (162.81 eV) positively shifted to the higher value than that of N-ZnIn₂S₄ (Figure 4C-E), indicated the decreased density of outer electrons, which demonstrated that the electrons transferred from the N-ZnIn₂S₄ to Ti₃C₂Tₓ.[51]

The high-resolution XPS spectra of C 1s (Figure 4F) showed the binding energy at 285.13 (461.85), 285.09 (462.04), 284.76 (463.27), and 284.16 eV (464.39 eV) correspond to the C–Ti, C₂Tₓ, C–O, and Ti–O in 4-TC/C₂Tₓ, respectively.[29] However, due to the small amount of Ti₃C₂Tₓ, only weak Ti 2p peaks can be observed in the XPS spectra of Ti 2p in 4-TC/C₂Tₓ (Supporting Information). In the process of assembly, N-ZnIn₂S₄ nanosheet with small size will cover the surface of Ti₃C₂Tₓ, which further leading to the weak signal of the Ti. In order to obtain stronger Ti signal, the XPS spectra was carried out after the 4-TC/ZIS sample was etched by Ar ion at different of 5, 10, and 15 nm (Figure S18, Supporting Information). However, the results showed that the Ti signal is still low due to the low content of the Ti₃C₂Tₓ.

2.3. Band Structure and Photocatalytic Hydrogen Evolution Performance

The light-harvesting capability of the photocatalyst was investigated by UV–vis diffuse reflectance spectrum (UV–vis DRS). As shown in Figure 5A, F-ZnIn₂S₄, L-ZnIn₂S₄, and N-ZnIn₂S₄ show obvious absorption of visible light, and the intrinsic absorption edge of the L-ZnIn₂S₄ displayed a clear blue shift compared with that of F-ZnIn₂S₄. Moreover, after the L-ZnIn₂S₄ was exfoliated to ultrathin N-ZnIn₂S₄, the intrinsic absorption edge was further shifted to lower wavelength, which was due to the well-known quantum size effect.[55] In addition, based on the (F(Rₚₜₜ)hν)²/² versus photon-energy plots (inset in Figure 5A), the band gap of the F-ZnIn₂S₄, L-ZnIn₂S₄, and N-ZnIn₂S₄ was measured to be 2.31, 2.39, and 2.44 eV, respectively. Interestingly, the TC/N-ZIS composites exhibited enhanced significant light absorption compared to N-ZnIn₂S₄. In addition, with the increase of Ti₃C₂Tₓ from 1 to 8 wt%, the light absorption intensity of the TC/N-ZIS composites gradually increased in the region of 250–800 nm, which was attributed to full-spectrum absorption of dark Ti₃C₂Tₓ (Figure S19, Supporting Information). In order to accurately obtain the band structure of N-ZnIn₂S₄, the energy of the valance band position relative to Fermi level of N-ZnIn₂S₄ was measured to 1.82 eV by the ultraviolet photoelectron spectrometer (UPS) (Figure S20, Supporting Information). The spectrum was calibrated using Ag
Figure 5. Ultraviolet–visible diffuse reflectance spectra of A) F-ZnIn$_2$S$_4$, L-ZnIn$_2$S$_4$, N-ZnIn$_2$S$_4$ (the insets are the digital photographs of F-ZnIn$_2$S$_4$, L-ZnIn$_2$S$_4$, and N-ZnIn$_2$S$_4$, and the corresponding band gap values calculated by the Kubelka–Munk method), and B) x-TC/N-ZIS ($x = 1, 2, 3, 4, 5, 6,$ and $8$, the insets are the colors of the samples with different Ti$_3$C$_2$T$_x$ content), C) energy band alignment (vs NHE, pH = 0) of N-ZnIn$_2$S$_4$, D) time course of photocatalytic H$_2$ production performance, E) the photocatalytic H$_2$ production rate of Ti$_3$C$_2$T$_x$, F-ZnIn$_2$S$_4$, L-ZnIn$_2$S$_4$, N-ZnIn$_2$S$_4$, and x-TC/N-ZIS samples, F) photocatalytic H$_2$ production rate over N-ZnIn$_2$S$_4$, N-ZnIn$_2$S$_4$/3%Pt, 3-TC/N-ZIS, N-ZnIn$_2$S$_4$/4%Pt, 4-TC/N-ZIS, and 4-TC/N-ZIS/3%Pt, H) photocatalytic H$_2$ production rate over L-ZnIn$_2$S$_4$ and x-TC/I-ZIS ($x = 2, 4,$ and $6$), G) the apparent quantum efficiency (AQE) of 4-TC/N-ZIS at different wavelength, and I) cyclic experiments of H$_2$ production over F-ZnIn$_2$S$_4$, N-ZnIn$_2$S$_4$, and 4-TC/N-ZIS.

standard samples (Figure S21, Supporting Information). Moreover, due to the Fermi level of the semiconductor close to the flat band potential, we obtained Mott–Schottky plot at the frequency of 0.5, 1.0, and 1.5 kHz (Figure S22, Supporting Information) and the value of the flat band potential was converted by Equation (1)\textsuperscript{[56]}

\[ E_{(NHE)} = E_{(Ag/AgCl)} + E' + 0.059pH \] (1)

where $E'_{(Ag/AgCl)} = 0.197$ V. The flat-band potentials of F-ZnIn$_2$S$_4$, L-ZnIn$_2$S$_4$, and N-ZnIn$_2$S$_4$ were calculated to be $-0.15$, $-0.21$, and $-0.2$ V versus NHE (pH = 0), respectively, which met the reduction potential requirement for reducing H$^+$ to hydrogen. Besides, the positive value of the slope of the Mott–Schottky plot represents that the three semiconductors were the n-type semiconductor.\textsuperscript{[57]} Thus, combined with the above measured results, the band structure of N-ZnIn$_2$S$_4$ can be calculated and summarized in Figure 5C, and the CB, VB, and Fermi level positions of N-ZnIn$_2$S$_4$ are located at $-0.82$, $1.62$, and $-0.2$ V versus NHE (pH = 0), respectively.

The photocatalytic hydrogen production performance of the photocatalyst was investigated under visible light ($\lambda \geq 400$ nm) irradiation with triethanolamine (TEOA) as the hole scavenging agent. As shown in Figure 5D,E, the hydrogen production...
rate of N-ZnIn$_2$S$_4$ (40.7 μmol h$^{-1}$) was 1.8 times and 2.5 times higher than that of 1-ZnIn$_2$S$_4$ (23.0 μmol h$^{-1}$) and F-ZnIn$_2$S$_4$ (16.1 μmol h$^{-1}$), respectively, due to the ultrathin 2D structure of the N-ZnIn$_2$S$_4$ and the existence of S vacancy on the surface. The hydrogen production rate of the TC/N-ZIS composites was improved with Ti$_x$C$_{1-x}$T$_c$ as the cocatalyst, and the 4-TC/N-ZIS sample exhibited the optimal hydrogen production rate of 148.4 μmol h$^{-1}$, which is 3.6 times and 9.2 times higher than that of N-ZnIn$_2$S$_4$ and F-ZnIn$_2$S$_4$, respectively. However, when the content of Ti$_x$C$_{1-x}$T$_c$ was increased and higher than 4 wt%, the hydrogen production rate of TC/N-ZIS composites decreased gradually, which can be attributed to the coverage of active sites on the N-ZnIn$_2$S$_4$ caused by excessive Ti$_x$C$_{1-x}$T$_c$. In order to investigate the effect of specific surface area on the photocatalytic hydrogen evolution performance, we calculated the hydrogen production rate per surface area of the samples (Table S4, Supporting Information). It can be observed that the hydrogen production rate per surface area of the 4-TC/N-ZIS sample reached 71.17 μmol h$^{-1}$ m$^{-2}$, which is 4.3 times and 7.1 times higher than that of the N-ZnIn$_2$S$_4$ (16.48 μmol h$^{-1}$ m$^{-2}$) and F-ZnIn$_2$S$_4$ (10.06 μmol h$^{-1}$ m$^{-2}$). The results further demonstrated that the enhanced photocatalytic hydrogen evolution performance was attributed to the fast interfacial charge transfer at the compact 2D/2D heterointerfaces between the ZnIn$_2$S$_4$ and Ti$_x$C$_{1-x}$T$_c$, and the sulfur vacancy on the N-ZnIn$_2$S$_4$ further enhanced the separation of the photoinduced electrons and holes.

As a contrast, F-ZnIn$_2$S$_4$ was coupled with Ti$_x$C$_{1-x}$T$_c$ to form the 4-TC/F-ZIS, it can be observed from the SEM images of 4-TC/F-ZIS that 2D Ti$_x$C$_{1-x}$T$_c$ covered on the surface of F-ZnIn$_2$S$_4$ flower sphere (Figure S23, Supporting Information). However, most of the F-ZnIn$_2$S$_4$ surface was not contacted with the 2D Ti$_x$C$_{1-x}$T$_c$ due to the spherical shape F-ZnIn$_2$S$_4$, and the F-ZnIn$_2$S$_4$ can only vertically contacted with the 2D Ti$_x$C$_{1-x}$T$_c$ instead of the formation of 2D/2D interface. In this case, the hydrogen evolution rate (39.2 μmol h$^{-1}$) of 4-TC/F-ZIS showed only 2.4 times higher than that (16.0 μmol h$^{-1}$) of F-ZnIn$_2$S$_4$ (Figure S24, Supporting Information). These results indicated that the construction of 2D/2D interface was crucial to shortening the electron transport path between ZnIn$_2$S$_4$ and Ti$_x$C$_{1-x}$T$_c$ and enhanced the separation efficiency of photogenerated electrons and holes. To compare the Ti$_x$C$_{1-x}$T$_c$ with noble metal as the cocatalyst, N-ZnIn$_2$S$_4$ was also loaded with Pt metal and their photocatalytic hydrogen evolution performance was investigated. After the loading with 3% Pt (N-ZnIn$_2$S$_4$/3%Pt), the photocatalytic hydrogen evolution rate (115.6 μmol h$^{-1}$) of N-ZnIn$_2$S$_4$/3%Pt was 2.8 times higher than that of N-ZnIn$_2$S$_4$ (40.7 μmol h$^{-1}$). And the 3-TC/N-ZIS showed comparative hydrogen evolution rate (116.9 μmol h$^{-1}$) to that of N-ZnIn$_2$S$_4$/3%Pt. Notably, the hydrogen production rate of 4-TC/N-ZIS was 2.2 times higher than that of the N-ZnIn$_2$S$_4$/4%Pt, which demonstrated that 2D Ti$_x$C$_{1-x}$T$_c$ was an efficient cocatalyst for promoting photocatalytic hydrogen production (Figure 5F). Interestingly, after loading with 3% Pt on 4-TC/N-ZIS, the hydrogen production rate reached 384.6 μmol h$^{-1}$ on account of the synergistic effect between Ti$_x$C$_{1-x}$T$_c$ and Pt.

In addition, the x-TC/I-ZIS composites were also prepared by in situ growth of ZnIn$_2$S$_4$ on the Ti$_x$C$_{1-x}$T$_c$ surface and used for the photocatalytic hydrogen evolution. From the XRD pattern (Figure S25, Supporting Information) and the SEM images (Figure S26, Supporting Information) of the x-TC/I-ZIS composites, it can be observed that the x-TC/I-ZIS was successfully prepared and the surface of the Ti$_x$C$_{1-x}$T$_c$ surface was covered by ZnIn$_2$S$_4$. As shown in Figure 8D, the hydrogen evolution rate of 2-TC/I-ZIS, 4-TC/I-ZIS, and 6-TC/I-ZIS was only 1.2, 1.3, and 1.2 times higher than that of I-ZIS (13.2 μmol h$^{-1}$), which might be ascribed to the reason that the most active sites on the Ti$_x$C$_{1-x}$T$_c$ surface were covered by ZnIn$_2$S$_4$, leading to the decreased photocatalytic hydrogen evolution rate compared to that of 4-TC/N-ZIS. The apparent quantum efficiency (AQE) of 4-TC/N-ZIS at different wavelengths was investigated, and their relationship with the optical absorption properties of 4-TC/N-ZIS was shown in Figure 8E. The AQE of the 4-TC/N-ZIS at 380, 400, 420, and 450 nm were 16.75%, 12.84%, 5.62%, and 2.61%, respectively. In addition, the AQE of the N-ZnIn$_2$S$_4$/3%Pt at 400 nm reached 28.61%. Notably, the AQE of 4-TC/N-ZIS was in direct proportion to the light absorption intensity as shown in Figure 8H, indicating that the absorption capacity of photons is one of the important factors determining hydrogen production efficiency. It is worth mentioning that the 4-TC/N-ZIS composite represents better photocatalytic hydrogen production performance compared with some reported ZnIn$_2$S$_4$-based photocatalysts under visible light (Table S5, Supporting Information).

The stability test was carried out to evaluate the cycling stability of the F-ZnIn$_2$S$_4$, N-ZnIn$_2$S$_4$, and 4-TC/N-ZIS, the results were shown in Figure 8I. Obviously, the hydrogen production of F-ZnIn$_2$S$_4$ and N-ZnIn$_2$S$_4$ decreased by 96.4% and 98.1%, respectively after five cycles. To explore the reasons for the instability of the N-ZnIn$_2$S$_4$, the N-ZnIn$_2$S$_4$ sample after reaction was analyzed by XPS. From the high-resolution XPS spectrum of N-ZnIn$_2$S$_4$, the valence states of Zn and In did not change, indicating that they were not reduced during the reaction. However, in addition to S$^-$, the element S appeared in the elemental phase of S$^0$ (Figure S27, Supporting Information), which indicated that the photooxidation corrosion of N-ZnIn$_2$S$_4$ occurred during the reaction. Notably, the hydrogen production of the 4-TC/N-ZIS sample decreased only by 15.6% after 5 cycles, indicating the enhanced stability of the 4-TC/N-ZIS. XRD pattern and Raman spectra displayed that the crystal structure of the 4-TC/N-ZIS did not change before and after reaction (Figure S28, Supporting Information). The high-resolution XPS spectrum of the used 4-TC/N-ZIS sample showed that the chemical composition of the 4-TC/N-ZIS composites did not change after reaction (Figure S29, Supporting Information). In addition, the SEM image (Figure S30, Supporting Information) showed that the 4-TC/N-ZIS still possessed the nanosheet structure, and the contact interface between N-ZnIn$_2$S$_4$ and Ti$_x$C$_{1-x}$T$_c$ can still be observed from the HRTEM image (Figure S31, Supporting Information), indicating the high stability of the 2D/2D TC/N-ZIS heterointerface. Moreover, according to the previous research, the absorption effect of Ti$_x$C$_{1-x}$T$_c$ on dissolved ions might restrain the photocorrosion reaction of ZnIn$_2$S$_4$. The above results indicated that the main reasons for the decrease of the activity of the 4-TC/N-ZIS sample may be as follows. First, during the photocatalytic reaction process, the agglomeration of photocatalyst is inevitable, which will occlude the active sites of the photocatalysts. Second, the mechanical force caused by the stirring can give rise to the slight microstructure collapse of 4-TC/N-ZIS, which is harmful to stability of the 2D/2D Ti$_x$C$_{1-x}$T$_c$/ZnIn$_2$S$_4$ interface and the separation of the photogenerated electrons and holes. Thirdly, although
a great deal of the photogenerated holes generated by ZnIn$_2$S$_4$ in the reaction process were consumed by the sacrificial agent, there may still some holes react with $S^{2−}$ to form the $S^{0}$, leading to partial decomposition of the ZnIn$_2$S$_4$. Therefore, the decrease of photocatalytic activity might be due to combined result of the above-mentioned factors.

2.4. Charge Separation and Transfer

To further reveal the synergistic effect of sulfur vacancy and Ti$_3$C$_2$T$_x$ on the separation efficiency of electron–hole pairs on N-ZnIn$_2$S$_4$, photoelectrochemical measurement were carried out. From the solid state photoluminescence (PL) spectra in Figure S32A (Supporting Information), compared with F-ZnIn$_2$S$_4$, the significant decreased fluorescence signal at about 476 nm of ultrathin N-ZnIn$_2$S$_4$ indicated that the recombination of photogenerated electrons and holes was greatly restrained. More importantly, the fluorescence peak signals of TC/N-ZIS were further decreased compared to that of N-ZnIn$_2$S$_4$ (Figure S32B, Supporting Information), demonstrating the positive effect of Ti$_3$C$_2$T$_x$ for effectively suppress the charge carrier recombination. In order to further understand the electron transfer mechanism in the ZnIn$_2$S$_4$ and TC/N-ZIS composites, the carrier dynamics of the photocatalysts were further detected by time-resolved fluorescence decay spectroscopy (TRPL) (Figure 6A), and the average fluorescence lifetime ($\tau_A$) was calculated by Equation (2)\textsuperscript{[12,60]}

$$\tau_A = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$$

where $\tau_1$ is generated by the nonradiative recombination of charge carriers in the defect states of ZnIn$_2$S$_4$, and $\tau_2$ is caused by the recombination of free excitons,\textsuperscript{[12]} $A_1$ and $A_2$ correspond to the amplitudes respectively. The calculated average lifetime ($\tau_A = 6.26$ ns) of the N-ZnIn$_2$S$_4$ was longer than that of F-ZnIn$_2$S$_4$ ($\tau_A = 5.75$ ns) indicated that the S vacancy can reduce the photogenerated charge carriers recombination by capturing electrons and serving as their host.\textsuperscript{[13b]} Of course, compared with F-ZnIn$_2$S$_4$, the ultrathin structure of N-ZnIn$_2$S$_4$ shortens the carrier transmission distance and reduces its recombination rate in the migration process. Notably, the calculated average lifetime of 4-TC/N-ZIS ($\tau_A = 4.47$ ns) was shorter than that of N-ZnIn$_2$S$_4$, which was due to reason that the photoinduced electrons on N-ZnIn$_2$S$_4$ could rapidly transfer to the Ti$_3$C$_2$T$_x$ via the 2D/2D interface. In addition, the 4-TC/N-ZIS composites displayed the shortest lifetime relative to 2-TC/N-ZIS, 6-TC/N-ZIS, and 8-TC/N-ZIS (Figure S33, Supporting Information). The above results of charge carrier migration dynamics indicated that the synergistic effect of the Ti$_3$C$_2$T$_x$ and S vacancy greatly improved the separation of the photogenerated electrons and holes.
which is beneficial to enhance the photocatalytic hydrogen production performance.\textsuperscript{[19]}

In addition, from the EIS Nyquist plots shown in Figure 6B, the arc radius of \( x \)-TC/N-ZIS (\( x = 2, 4, 6, \) and 8) was smaller than those of N-ZnIn\(_2\)S\(_4\), F-ZnIn\(_2\)S\(_4\), and L-ZnIn\(_2\)S\(_4\), indicating the better charge transfer efficiency of the \( x \)-TC/N-ZIS due to the 2D/2D interface between the few-layered Ti\(_3\)C\(_2\)T\(_x\) and N-ZnIn\(_2\)S\(_4\). Notably, the minimal arc radius of Ti\(_3\)C\(_2\)T\(_x\) was attributed to its excellent electrical conductivity, which is conducive to the electron transport (Figure S34, Supporting Information).

Moreover, it should be noted that a higher photogenerated current suggests a more efficient separation of photogenerated electron–hole pairs. Higher photocurrent density as shown in Figure 6C indicates again N-ZnIn\(_2\)S\(_4\) has better photogenerated carrier separation ability than F-ZnIn\(_2\)S\(_4\). The 4-TC/N-ZIS possessed the highest photocurrent density, further demonstrating the efficient charge carrier transfer and separation on the 4-TC/N-ZIS composite. Surface photovoltage measurement (SPV) measurement was carried out to investigate the surface charge carrier transfer on the 4-TC/N-ZIS composite.\textsuperscript{[61]}

As shown in Figure 6D, an obvious positive signal of N-ZnIn\(_2\)S\(_4\) in the range of 300–450 nm can be observed, indicated that the N-ZnIn\(_2\)S\(_4\) was a n-type semiconductor, which was consistent with the results of Mott–Schottky.\textsuperscript{[62]} No signal could be detected for the Ti\(_3\)C\(_2\)T\(_x\) sample, indicated that the metallic Ti\(_3\)C\(_2\)T\(_x\) did not exhibit photoexcitation property. Compared with N-ZnIn\(_2\)S\(_4\) (10.8 mV), the stronger peak signal (14.1 mV) of 4-TC/N-ZIS indicating that more photogenerated electrons were transferred to the 4-TC/N-ZIS surface, thus forming a stronger surface-to-bulk electric field based on favorable electron transfer capability of Ti\(_3\)C\(_2\)T\(_x\). The above results of photoelectrochemical characterizations confirmed the excellent separation of electron–hole pairs on the 4-TC/N-ZIS composite, which is beneficial to the photocatalytic hydrogen evolution from water.

\section*{2.5. Theoretical Calculation}

DFT calculations were used to reveal the charge migration on the 2D/2D Ti\(_3\)C\(_2\)T\(_x\)/N-ZnIn\(_2\)S\(_4\) heterojunction interface. Due to the O-terminated Ti\(_3\)C\(_2\)T\(_x\) with a low content of –OH and –F terminal groups can be obtained by the LiF/HCl etching method,\textsuperscript{[63]} to get closer to reality, we reckon without –OH and –F terminal groups and used the Ti\(_3\)C\(_2\)O\(_2\) slab for the DFT calculation. As shown in Figure 7A–C, the work functions of Ti\(_3\)C\(_2\)O\(_2\), N-ZnIn\(_2\)S\(_4\), and ZnIn\(_2\)S\(_4\) with S vacancy were calculated to be 5.34, 4.20, and 3.74 eV, respectively, which indicates that the electrons on the ZnIn\(_2\)S\(_4\) and ZnIn\(_2\)S\(_4\) with S vacancy can transfer to the Ti\(_3\)C\(_2\)O\(_2\) due to the higher work function of the Ti\(_3\)C\(_2\)O\(_2\).

The charge carriers transfer pathway of the Ti\(_3\)C\(_2\)O\(_2\)/ZnIn\(_2\)S\(_4\) interfaces was demonstrated by the result of the electron density difference as depicted in Figure 7D. Strikingly, the electrons on the ZnIn\(_2\)S\(_4\) were transferred to the Ti\(_3\)C\(_2\)O\(_2\), corroborating the strong electron coupling effect between the Ti\(_3\)C\(_2\)O\(_2\) and ZnIn\(_2\)S\(_4\). Figure 7E plots the planar-averaged charge density difference along the Z direction to directly display the change...
of charge density. Evidently, the electrons mainly transfer from the ZnIn$_2$S$_4$ to Ti$_3$C$_2$O$_2$, which is consistent with the XPS results.

Moreover, after a S vacancy was removed on the ZnIn$_2$S$_4$ surface, more electrons can transfer from the ZnIn$_2$S$_4$ to Ti$_3$C$_2$O$_2$ (Figure 7F,G), indicated that the surface S vacancy on the ZnIn$_2$S$_4$ surface can further facilitate the electron migration and enhance the separation of the photogenerated electrons and holes. Notably, according to the distribution of partial charge density near the edge of the conduction band (Figure 7H) and valence band (Figure 7I) of ZnIn$_2$S$_4$, the conduction band minimum (CBM) was located at the In–S atomic layer, and the valence band maximum (VBM) was located at the Zn–S atomic layer. For the 2D/2D Ti$_3$C$_2$O$_2$/ZnIn$_2$S$_4$ heterojunction, the Ti$_3$C$_2$O$_2$ surface is in contact with the In-S terminated surface of ZnIn$_2$S$_4$, i.e., the Ti$_3$C$_2$O$_2$ is close to the CBM of the ZnIn$_2$S$_4$, which further accelerated the photogenerated electron transfer from ZnIn$_2$S$_4$ to Ti$_3$C$_2$O$_2$ and greatly benefited the separation of the photogenerated electrons and holes.

### 2.6. Possible Photocatalytic Mechanism

Electron paramagnetic resonance (EPR) can effectively capture free radicals to determine the active groups produced during the photocatalytic reaction. Superoxide radical (O$_2^-$) and hydroxyl radical (OH) signals were detected by using DMPO as the spin marker in aqueous and methanol solutions, respectively. Figure 8A,B displays that there were no O$_2^-$ and OH signals for both N-ZnIn$_2$S$_4$ and 4-TC/N-ZIS in the dark. After 10 min irradiation under the Xenon lamp with a 400 nm cutoff filter, the 4-TC/N-ZIS sample showed a stronger quadruplex O$_2^-$ peak signal than that of N-ZnIn$_2$S$_4$ with the intensity ratio of 1:2:2:1, indicating more O$_2^-$ can be generated in the 4-TC/N-ZIS composite.
Similarly, a higher quadruplex -OH peak than that of N-ZnIn$_2$S$_4$ with the intensity ratio of 1:1:1:1 indicated that more -OH can be excited in the 4/2/5/14/Zn-ZIS composite under the visible light irradiation. Since superoxide ($\cdot$O$_2^-$) and hydroxyl ($\cdot$OH) radicals are produced by holes and photogenerated electrons, respectively, the higher signal of 4/2/5/14/Zn-ZIS indicated superior separation of charge carriers. As a consequence, the 4/2/5/14/Zn-ZIS composite exhibited better photocatalytic hydrogen evolution performance than that of the N-ZnIn$_2$S$_4$.

In addition, in order to further understand the electron transfer behavior between the Ti$_x$C$_2$T$_x$ and N-ZnIn$_x$S$_x$ in the TC/N-ZIS composites, the energy level structures of Ti$_x$C$_2$T$_x$ and N-ZnIn$_x$S$_x$ were discussed based on the vacuum energy level. UPS was used to determine the electronic structures of Ti$_x$C$_2$T$_x$ and N-ZnIn$_x$S$_x$ and calibrated by Ag standard sample, and a bias voltage of $-5\ E$ was used for all measurements (Figure S25, Supporting Information). The work function ($\Phi$) of the photocatalyst was calculated according to Equation (3) and (4)[64]

$$\Phi = h\nu + W$$  
(3)

$$W = E_{\text{cutoff}} - E_{\text{Fermi}}$$  
(4)

where $h\nu$, $W$, $E_{\text{cutoff}}$, and $E_{\text{Fermi}}$ are the incident photon energy, the width of the UPS spectrum, the kinetic energy of cutoff edge, and Fermi edge, respectively.

As shown in Figure 8C,D, the work functions of N-ZnIn$_2$S$_4$ and Ti$_x$C$_2$T$_x$ were calculated to be 2.91 and 4.07 $eV$, respectively. Therefore, the positions of the corresponding Fermi energy level of the N-ZnIn$_x$S$_x$ and Ti$_x$C$_2$T$_x$ relative to the vacuum energy level were $-2.91$ and $-4.07\ eV$, respectively. It is worth noting that the work functions of N-ZnIn$_2$S$_4$ (2.91 $eV$) and Ti$_x$C$_2$T$_x$ (4.07 $eV$) obtained from the UPS spectrum are different from the calculated work functions of ZnIn$_2$S$_4$ with S vacancy (3.74 $eV$) and Ti$_x$C$_2$O$_3$ (5.34 $eV$) based on the DFT. The discrepancy can be ascribed to the complex surface structures of the N-ZnIn$_2$S$_4$ and Ti$_x$C$_2$T$_x$. For example, there are some groups, such as $-\text{OH}$, $-\text{F}$, $-\text{O}$, on the surface of Ti$_x$C$_2$T$_x$. For simplicity, we used ZnIn$_2$S$_4$ (001) and Ti$_x$C$_2$O$_3$ (001) for the DFT calculation, which can also help us to better understand the nature of the material. However, for the sake of rigor, we used the experimental value obtained from the UPS spectrum as the standard to determine the position of energy level.

As a result, under light irradiation, the electrons excited on N-ZnIn$_x$S$_x$ will transfer to Ti$_x$C$_2$T$_x$ when the 2D/2D interface was formed between the N-ZnIn$_x$S$_x$ and Ti$_x$C$_2$T$_x$, which was consistent with the results of XPS. According to the previous UPS valence band spectrum of N-ZnIn$_x$S$_x$ (Figure S20, Supporting Information), the position of VB ($E_{\text{VB}}$ vs Fermi level) of N-ZnIn$_x$S$_x$ was $-1.82\ eV$, which was $-4.73\ eV$ relative to the vacuum level. Since the band gap value ($E_g$) of N-ZnIn$_x$S$_x$ was 2.44 $eV$ based on the UV–vis DRS, and according to the equation of $E_{\text{CB}} = E_{\text{VB}} - E_g$[53], the CB position of the N-ZnIn$_x$S$_x$ relative to the vacuum energy level was $-2.29\ eV$. In this case, the Fermi energy level ($E_F$) of N-ZnIn$_x$S$_x$ was closer to its CB, which in line with the characteristics of n-type semiconductor and was consistent with the Mott–Schottky and SPV results. According to the above results, the positions of the energy level of N-ZnIn$_x$S$_x$ and Ti$_x$C$_2$T$_x$ relative to the vacuum level before and after the contact of N-ZnIn$_x$S$_x$ with Ti$_x$C$_2$T$_x$ was shown in Figure 8E. Specifically, after the N-ZnIn$_x$S$_x$ was combined with the Ti$_x$C$_2$T$_x$, to form the 2D/2D Ti$_x$C$_2$T$_x$/N-ZnIn$_x$S$_x$ interface, the photogenerated electrons generated on the CB of N-ZnIn$_x$S$_x$ will transfer to Ti$_x$C$_2$T$_x$ due to the smaller work function of N-ZnIn$_x$S$_x$. Although the contact interface between N-ZnIn$_x$S$_x$ and Ti$_x$C$_2$T$_x$ is only a few hundred nanometers, electrons can still accumulate on the Ti$_x$C$_2$T$_x$ side and lead to the positive charge of N-ZnIn$_x$S$_x$ side. Therefore, a space charge layer at the interface can be formed while this space charge layer may be extremely thin. Notably, the S vacancies inside N-ZnIn$_x$S$_x$ can act as efficient electron trap to suppress the recombination of photogenerated electron–hole pairs,[136] which promotes the accumulation of electrons on the surface S vacancies of N-ZnIn$_x$S$_x$ nanosheets. Moreover, due to the electron harvesting effect of Ti$_x$C$_2$T$_x$, the recombination of the electrons and holes will be greatly reduced. In the meantime, the CB and VB of N-ZnIn$_x$S$_x$ near the 2D/2D Ti$_x$C$_2$T$_x$/N-ZnIn$_x$S$_x$ interface are bent “upward” to form the Schottky junction. Although the existence of potential Schottky barrier will increase the difficulty of electron transfer to a certain extent, the photogenerated electrons on N-ZnIn$_x$S$_x$ are able to cross the barrier and transfer to Ti$_x$C$_2$T$_x$. Moreover, the formed Schottky barrier could restrain the backflow of electrons from Ti$_x$C$_2$T$_x$ to N-ZnIn$_x$S$_x$ and boost the separation of photogenerated electrons and holes, which will greatly enhance photocatalytic hydrogen evolution performance.

Based on the photocatalytic experiments, characterization analysis, and the DFT calculation, the mechanism of charge transfer and photocatalytic hydrogen production over 2D/2D Ti$_x$C$_2$T$_x$/N-ZnIn$_x$S$_x$ composites was proposed (Figure 8F). Under light irradiation, the electrons excited from the VB of the N-ZnIn$_x$S$_x$ to CB, and the photogenerated electrons migrate to the Ti$_x$C$_2$T$_x$, spontaneously. The 2D/2D Ti$_x$C$_2$T$_x$/N-ZnIn$_x$S$_x$ heterointerfaces provide wide and shortest paths for the transfer of charge carriers, thus restraining the recombination of photoinduced electrons and holes. The Ti$_x$C$_2$T$_x$ serves as the electron acceptor and active sites to promote hydrogen evolution from the water. Simultaneously, the photogenerated holes on the VB of the ZnIn$_2$S$_4$ nanosheet were scavenged by sacrificial agents. Note-worthy, the sulfur vacancies in ZnIn$_2$S$_4$ act as electron traps further facilitate charge carrier transfer at the 2D/2D interface and enhance the separation of the photoinduced electron–hole pairs, which was verified by the characterization analysis and DFT calculation. Moreover, the formation of the Schottky barrier between the N-ZnIn$_x$S$_x$ and Ti$_x$C$_2$T$_x$ intimate contact interface can inhibit the backflow of electrons from the Ti$_x$C$_2$T$_x$ to N-ZnIn$_x$S$_x$, further suppressing the recombination of the photoinduced electrons and holes.[65] In short, benefiting from the synergistic effect of the 2D/2D interface, S vacancy, and Ti$_x$C$_2$T$_x$ cocatalyst, the separated photoinduced electrons and holes, the photocatalytic hydrogen evolution performance of the N-ZnIn$_x$S$_x$ was greatly enhanced.

3. Conclusion

In summary, the 2D/2D Ti$_x$C$_2$T$_x$/N-ZnIn$_x$S$_x$ composites were successfully synthesized by coupling ultrathin N-ZnIn$_x$S$_x$ with few-layered Ti$_x$C$_2$T$_x$. The unique 2D/2D compact interface of the Ti$_x$C$_2$T$_x$/N-ZnIn$_x$S$_x$ composites provided the broad and short electron transfer paths, which significantly enhanced the
transfer and separation of photoinduced charge carriers. The S vacancies in the ultrathin N-ZnIn2S4 can serve as an electron trap, which facilitate the separation of charge carriers and greatly accelerated electrons transferred from the N-ZnIn2S4 surface to Ti3C2T.x. In addition, the formation of the Schottky barrier at the 2D/2D Ti3C2T.x/N-ZnIn2S4 interface inhibited the backflow of electrons from the Ti3C2T.x to N-ZnIn2S4, further enhanced the separation of the photoinduced electron–hole pairs. Experimental characterization analysis and DFT calculations demonstrated that the rapid transfer and separation of photoexcited charge carriers is attributed to the strong interaction between the 2D/2D Ti3C2T.x/N-ZnIn2S4 intimate interface and the S-vacancy on the ZnIn2S4. The optimal 4-TC/N-ZIS composite exhibited a high photocatalytic hydrogen evolution rate of 148.4 μmol h−1, which is 3.6 times and 9.2 times higher than that of the N-ZnIn2S4 and Ti3C2T.x/N-ZnIn2S4, respectively. This work revealed the intrinsic principle of the enhanced photocatalytic performance of 2D/2D Ti3C2T.x/N-ZnIn2S4 composites and provides a new way for the construction of highly efficient photocatalysts with 2D/2D heterostructure.

4. Experimental Section

4.1. Synthesis of ZnIn2S4 Nanoflower

F-ZnIn2S4 was synthesized by the hydrothermal method. Specifically, 1 mmol ZnCl2 and 2 mmol InCl3·4H2O were dissolved in 60 mL deionized (DI) water by ultrasound. After stirring for 30 min, 8 mmol thiourea was added to the solution, and kept stirring for 1 h. The mixed solution was transferred into a 100 mL Teflon-lined autoclave and heated at 180 °C for 3 h. After naturally cooling to room temperature, yellowish precipitate was collected and washed with DI water and anhydrous ethanol 4 times respectively by centrifugation to obtain a yellow ZnIn2S4 precipitate. Subsequently, then the nanoflower ZnIn2S4 powder was obtained by freeze-drying the yellow precipitate, and was denoted as F-ZnIn2S4.

4.2. Synthesis of Layered ZnIn2S4

Typically, 1 mmol ZnCl2, 2 mmol InCl3·4H2O, and 0.9 g trisodium citrate dihydrate were dissolved in 60 mL DI water. After stirring for 30 min, a transparent solution was obtained. The subsequent process was the same as that for the synthesis of F-ZnIn2S4 nanoflower, and the obtained layered ZnIn2S4 was denoted as L-ZnIn2S4.

4.3. Synthesis of Sulfur Vacancy-Rich ZnIn2S4 Nanosheet

Sulfur vacancy-rich ultrathin ZnIn2S4 was prepared by exfoliating the layered ZnIn2S4. Briefly, the washed and undried layered ZnIn2S4 was dispersed into 150 mL DI water, and exfoliated by ultrasonic treatment for 40 min at 5 °C in a high-power ultrasonic machine with circulating cooling water. After that, the transparent solution was centrifuged at 7000 rpm to obtain the sulfur vacancy-rich ultrathin ZnIn2S4 supernatant. The ZnIn2S4 colloidal solution with a concentration of 2 mg mL−1. The sulfur vacancy-rich ultrathin ZnIn2S4 nanosheets were obtained by freeze-drying, which was denoted as N-ZnIn2S4.

4.4. Synthesis of Few-Layered Ti3C2T.x

Few-layered Ti3C2T.x nanosheets were synthesized by a modified reported method.[36] Typically, 3.2 g LiF and 40 mL of 9 M HCl was added to a 100 mL Teflon vessel and stirred for 20 min to dissolve the LiF completely. Subsequently, 2.0 g Ti3AlC2 powder (Foshan XinXi Technology Co. Ltd, 99.5%, 400 mesh) was slowly added into the above mixed solution and stirred at 40 °C for 48 h. After that, a black suspension was obtained and was centrifugally washed with DI water at 8500 rpm multiple times until the pH is greater than 6. Then, the precipitate after washing was dispersed in 200 mL DI water, and was treated by ultrasonic treatment for 2 h in the Ar atmosphere at 5 °C. Whereafter, a black colloidal solution was obtained and centrifuged at 6000 rpm for 30 min, then the few-layered Ti3C2T.x colloidal solution with a concentration of 1.5 mg mL−1 was collected.

4.5. Synthesis of 2D/2D Ti3C2T.x/N-ZnIn2S4

To prepare the 2D/2D Ti3C2T.x/N-ZnIn2S4 with different amounts of the Ti3C2T.x, different volumes of few-layered Ti3C2T.x colloidal solution (1.5 mg mL−1) were added to 50 mL of N-ZnIn2S4 colloid (2.0 mg mL−1) and sonicated at 5 °C in the Ar atmosphere for 5 min. Then, 10 mL of 1 M NH4HCO3 solution was gradually added to the above mixed solution under stirring conditions, and kept stirring for 2 h and sonicate in the Ar atmosphere for 10 min. After standing at 5 °C for 1 h, the flocculent precipitate can be formed and sunk to the bottom of the beaker. After separating the supernatant, the flocculent precipitate was dried by vacuum freeze drying. Before illumination, the colloidal solution was transferred into a 275 mL quartz reactor. Typically, 20 mg photocatalyst was dispersed in a mixed solution containing 10 mL TEOA and 40 mL DI water by ultrasonic treatment for 30 min. Before illumination, the photocatalytic reaction system was degassed with ultrahigh pure argon gas for 30 min. The light source was a 300 W Xenon lamp (CEL-HFX300, Beijing China Education Au-light Co., Ltd.) equipped with a 400 nm cutoff filter. In addition, the suspension solution was stirred during the photocatalytic hydrogen evolution reaction, and the temperature of the reactor was kept at 25 °C by circulating cooling water. The hydrogen was quantitatively detected by a gas chromatography (GC-2018, SHIMADZU) equipped with a 5 Å molecular sieve column, a TCD detector, and with Ar as the carrier gas. The experimental details and the calculation method for the apparent quantum efficiency (AQE) are supplemented in the Supporting Information.

4.6. Photocatalytic Hydrogen Evolution

The photocatalytic water splitting performance of the photocatalyst was tested in a 275 mL quartz reactor. Typically, 20 mg photocatalyst was dispersed in a mixed solution containing 10 mL TEOA and 40 mL DI water by ultrasonic treatment for 30 min. Before illumination, the photocatalytic reaction system was degassed with ultrahigh pure argon gas for 30 min. The light source was a 300 W Xenon lamp (CEL-HFX300, Beijing China Education Au-light Co., Ltd.) equipped with a 400 nm cutoff filter. In addition, the suspension solution was stirred during the photocatalytic hydrogen evolution reaction, and the temperature of the reactor was kept at 25 °C by circulating cooling water. The hydrogen was quantitatively detected by a gas chromatography (GC-2018, SHIMADZU) equipped with a 5 Å molecular sieve column, a TCD detector, and with Ar as the carrier gas. The experimental details and the calculation method for the apparent quantum efficiency (AQE) are supplemented in the Supporting Information.

4.7. Characterization

The characterization methods and DFT calculation are supplemented in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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