2D Ti $_3C_2$ as electron harvester anchors on 2D g-C $_3N_4$ to create boundary edge active sites for boosting photocatalytic performance

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2D Ti₃C₂ as electron harvester anchors on 2D g-C₃N₄ to create boundary edge active sites for boosting photocatalytic performance

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Graphical Abstract

Highlights

- 2D/2D Ti₃C₂/g-C₃N₄ heterojunctions are fabricated in the semi-closed system, which improve the photocatalytic activity and stability.
- 2D Ti₃C₂ serves as electron harvester to propel directed transfer of electrons from 2D g-C₃N₄ to 2D Ti₃C₂ and high-efficiency separation of charge carriers.
- The boundary edge active sites are created on 2D Ti₃C₂ structure unit, thus enhancing the photocatalytic performance.
- The photocatalytic reaction mechanism for H₂ production and degrading TH-HCl are revealed in detail.
- This work provides a significant reference for design, fabrication and mechanism insight of 2D/2D heterojunctions in the photocatalytic application.

Abstract

Control and insight into active sites and charge transport behaviors are challenging topics for fabricating heterojunction photocatalyst and investigating photocatalytic reaction mechanism. Herein, the 2D/2D Ti₃C₂/g-C₃N₄ heterojunctions are fabricated in the semi-closed system, in which the interaction at heterointerfaces is enhanced to improve the stability. Furthermore, 2D Ti₃C₂ not only serves as electron harvester to propel the directed transfer of photogenerated electrons from 2D g-C₃N₄ to 2D Ti₃C₂ and the high-efficiency separation of charge carriers, but also creates the boundary edge active sites on its surface, thus enhancing the photocatalytic performance. The photocatalytic reaction mechanism for H₂ production and degrading tetracycline hydrochloride (TH-HCl) are also revealed in detail, including identification of active sites, transport behaviors of charge carriers, generation of active species and intermediates, reaction ways, etc. This work provides a significant reference for the design, fabrication and mechanism insight of 2D/2D heterojunction materials in the photocatalytic application.

Keywords: 2D/2D Ti₃C₂/g-C₃N₄ heterojunction; Photocatalytic degradation of and H₂ production; Directed transfer of photogenerated electrons; Control of active sites; Photocatalytic reaction mechanism

1 Introduction

Two-dimensional (2D) semiconductor materials have brought about enormous attention in the last few decades for their superlative physicochemical characteristics. The atomically thin sheets in the crystal structure usually display covalent in-plane bonding and weak interlayer bonding, which endows 2D semiconductor materials with the unique electronic, optical and mechanical properties so that they exhibit prominent potential for catalysis, energy storage, adsorption, electron device and other technological applications [1, 2].

As a typical 2D semiconductor material, graphitic carbon nitride (g-C₃N₄) nanosheet has manifested the great potentials in the photocatalytic solar energy conversion and environmental purification, such as photocatalytic H₂ production, reduction of CO₂, degradation of pollutants in water, removal of volatile organic compounds and so on [3-10]. However, the major issue still to be addressed is how to accelerate charge transfer and improve the separation efficiency of photogenerated electron-hole pairs. As a consequence, a great deal of endeavors have been carried out to exploit the new strategies for enhancing photocatalytic activity of g-C₃N₄, such as doping metal/nonmetal elements [11, 12], loading noble metals [13], optimizing energy band structure [14], controlling micro-structure/morphology [15], modifying functional groups [16], fabricating semiconductor heterojunction [17], etc. These works have been made great advancements on the improvement of photocatalytic

activity of g-C₃N₄. It has been reported that fabricating the 2D/2D heterojunction is one of the effective strategies to suppress recombination of charge carriers and increase separation efficiency, which can be achieved by embellishing other 2D material on g-C₃N₄ nanosheets. As reported 2D/2D g-C₃N₄/graphdiyne heterojunction, it obviously improves the hole mobility of g-C₃N₄ and motivates separation of charge carriers [18]. In addition, by means of constructing 2D/2D heterojunction between oxygen-doped carbon nitride (OCN) and ultrathin CoAl-layered double hydroxide (CoAl-LDH), the formed strong electronic coupling effect on the heterostructure interface can induce photogenerated charge transfer from CoAl-LDH to OCN and make for the construction of an interfacial internal electric field between CoAl-LDH and OCN, thus improving the photocatalytic activity [19].

Recently, Ti₃C₂ as a member of the 2D MXene family materials has been extensively used for improving the photocatalytic activity of 2D photocatalysts via constructing 2D/2D heterojunction. For instance, Cao et al. report a 2D/2D heterojunction of ultrathin Ti₃C₂/Bi₂WO₆ nanosheets, which exhibits a short charge transport distance and a large contact interface, ensuring the outstanding bulk-to-surface and interfacial charge transfer abilities [20]. The recent researches reveal that 2D Ti₃C₂ served as a structure unit constructs composite heterojunctions with $g-C_3N_4$ nanosheet, which can distinctly improve the photocatalytic H₂ production and degradation activity owing its superior visible light harvest ability and metal-like nature [21, 22]. However, in these contributions, the obtained $Ti_3C_2/g-C_3N_4$ heterojunctions are usually prepared by simple low-temperature treated mechanical mixing of Ti₃C₂ and g-C₃N₄, which may result in decreasing stability and recyclability. Moreover, it also needs further discussions and investigations for the mechanism of photocatalytic H₂ production and organic pollutant degradation. As a result, we design a new preparation strategy that 2D/2D Ti₃C₂/g-C₃N₄ heterojunctions are fabricated by introducing 2D Ti₃C₂ into the thermal polymerization of g-C₃N₄ in the semi-closed system. On one hand, NH₃ released at the polymerization of g-C₃N₄ can make 2D Ti₃C₂ in a reductive atmosphere to avoid oxidization. On the other hand, the surface termination groups such as -O, -F and -OH on 2D Ti₃C₂ may be partly removed at

the high temperature [23], and so the generated surface dangling bonds not only take part in polymerization of $g-C_3N_4$ to enhance the interaction at the heterointerfaces between 2D Ti₃C₂ and 2D g-C₃N₄, improve the stability of heterostructure and accelerate the separation of charge carriers, but also serve as the active sites to promote photocatalytic reaction.

Therefore, in this work, we fabricate the 2D/2D Ti₃C₂/g-C₃N₄ heterojunctions by adding 2D Ti₃C₂ into urea raw material before performing thermal polymerization reaction in the semi-closed system. The enhanced interfacial interaction obviously improves the stability of heterostructure. Moreover, 2D Ti₃C₂ not only acts as electron harvester to induce the directed transfer of photogenerated electrons from 2D g-C₃N₄ to 2D Ti₃C₂ and increase the separation efficiency of charge carriers, but also creates the boundary edge active sites on its surface, which dramatically result in the enhanced photocatalytic performance for H₂ production and degrading tetracycline hydrochloride (TC-HCl).

2. Experimental section

2.1. Preparation of samples

Ti₃AlC₂ of 2 g was slowly whisked into 80 mL hydrofluoric acid (HF, \geq 40%) and stirred constantly at 60 °C for 24 h. Then the etched suspension was centrifuged and washed with distilled water and ethanol in turn. Finally, the obtained black 2D Ti₃C₂ powder was dried in vacuum at 80 °C for 4 h. Moreover, the correct amount of urea was firstly dried at 80 °C for 12 h in the oven. A certain amount of as-obtained Ti₃C₂ (0 g, 0.01 g, 0.02 g, 0.05 g and 0.1 g) were added in urea of 20 g, respectively. After grinding thoroughly, the obtained uniform mixtures were putted in an unsealed and covered crucible, subsequently annealed at 550 °C with a ramping rate of 2.5 °C min⁻¹ for 4 h. Finally, Ti₃C₂/g-C₃N₄-2, Ti₃C₂/g-C₃N₄-3 and Ti₃C₂/g-C₃N₄-4, respectively.

2.2. Characterization of samples

The phase compositions of samples were examined by X-ray diffraction (XRD) on SHIMADZU XRD-6100 diffractometer equipped a Cu Ka radiation source (λ =1.54178 A). The morphology of samples was observed by Hitachi JFM-7800F

scanning electronic microscopy (SEM). The micro- structure and morphology of samples were identified by JEOL-2100F transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The fourier transform infrared (FT-IR) spectra of samples were analysed by a Nicolet is 50 spectrometer using KBr as the dispersion medium. The X-ray photoelectron spectroscopy (XPS) was detected by Thermo ESCALAB 250X electron spectrometer with 150 W Al Ka radiations. UV-Vis diffuse reflectance spectroscopy (DRS) of samples was obtained on SHIMADZU UV-3600 Plus spectrophotometer using BaSO4 as the reflectance material. The steady-state photoluminescence (SS-PL) spectra and transient-state photoluminescence (TS-PL) decay curves were performed on a QuantaMasterTM 40 spectrofluorometer. The specific surface area and pore diameter distribution of the samples was measured by a nitrogen adsorption BET method on a TriStar II3020 analyzer. Total organic carbons (TOC) were detected by an Analytik Jena AG multi N/C 2100 analyzer. The active species were analyzed by electron spin resonance (ESR) using Bruker A300-10/12 Electron paramagnetic resonance spectrometer. The mass spectrometry (MS) was tested by hermo LXQ liquid chromatgraphy-ion trap mass spectrometry.

2.3. Photocatalytic experiments

The photocatalytic H₂ production was performed under the visible light provided by 300 W Xe arc lamp equipped with a cut-off filter ($\lambda > 420$ nm, 150 mW cm⁻²). Photocatalyst of 50 mg was dispersed in aqueous solution of 100 mL including 20 vol% triethanolamine (TEOA). Afterwards, a given mass of H₂PtCl₆·6H₂O (Pt of 3 wt%) was added in above solution as co-catalyst. The reaction system was degassed with Ar gas for 20 min to remove air before light on. The produced H₂ was detected on the gas chromatography GC-2030 with Ar as carrier gas. The apparent quantum efficiency (AQE) was detected under the same experiment conditions by changing cut-off filter to band-pass filters with 400 nm, 420 nm, 450 nm, 500 nm and 600 nm, respectively.

The photocatalytic degradations of tetracycline hydrochloride (TC-HCl) were performed under the visible light. First of all, as-prepared samples of 50 mg were

equably dispersed in the solution of TC-HCl (100 mL, 10 mg L⁻¹) with stirring for 30 min in the dark to reach adsorption-desorption equilibrium. After that, the suspension was irradiated with the visible light provided by a 250 W Xe arc lamp ($\lambda \ge 420$ nm). During given irradiation time intervals, the turbid liquid of 6 mL was removed and centrifuged (9000 rmp, 5 min). The absorbance of supernatant was measured on Agilent Cary 8454 UV-Vis spectrophotometer at the characteristic wavelength of 357 nm. Finally, the degradation efficiency of TC-HCl was calculated by Lambert-Beer law.

For the sake of investigating the active species produced in the photocatalytic process, three scavengers were added into the TC-HCl solution in which isopropanol (IPA), EDTA-2Na and vitamin C (VC) were served as the scavengers for trapping hydroxyl radicals (\cdot OH), holes (h⁺) and superoxide radical (\cdot O₂⁻), respectively.

2.4. Photoelectrochemical measurements

The transient photocurrent response and impedance spectra were detected on the VersaSTAT₃ electrochemical working station by using a standard three-electrode system contained 0.5 M Na₂SO₄ electrolyte. Pt plate and saturated Ag/AgCl electrode served as the counter electrode and reference electrode, respectively. The samples coated on ITO glass ($2 \times 2 \text{ cm}^2$) served as working electrodes.

3. Results and discussion

The structure and composition of as-prepared samples were investigated by XRD. As displayed in Fig. 1a, the MAX phase Ti₃AlC₂ sample possesses the intense diffraction peaks at 9.5°, 19.1°, 34.0°, 36.0°, 38.8°, 41.7°, 48.5°, 56.5°, 60.6°, which are attributed to the lattice planes of (002), (004), (100), (103), (104), (105), (107), (109) and (110), respectively [24, 25]. From the XRD pattern of Ti₃C₂ sample, the characteristic peak of (104) lattice planes of Ti₃AlC₂ disappears, and the diffraction peaks of (002) and (004) lattice planes take place obvious shift to the low angle direction, which indicates that the interlayer Al atoms in Ti₃AlC₂ are efficiently removed to transform into Ti₃C₂ [26]. In addition, the diffraction peaks at 8.9°, 18.2°, 27.8°, 35.9°, 41.7° and 60.5° originate from (002), (004), (006), (008), (010) and (110) lattice planes of Ti₃C₂ [27, 28]. Moreover, as shown in Fig. 1b, two

characteristic diffraction peaks at 13.2° and 27.4° are observed in the XRD pattern of single g-C₃N₄ sample, which correspond to (100) and (002) lattice planes of the tri-s-thiazine rings and the stacking of conjugated aromatic systems, respectively [29]. It is worth noting that two characteristic peaks of (008) and (010) of Ti₃C₂ are detected in the XRD pattern of Ti₃C₂/g-C₃N₄ sample, implying the formation of heterojunction between Ti₃C₂ and g-C₃N₄. Moreover, from FT-IR spectra (Fig. S1†), no absorption peaks of C–C and C–Ti bonds are produced in FT-IR spectra of Ti₃C₂ and Ti₃C₂/g-C₃N₄-3 samples, which may be because Ti₃C₂ exhibits the weak infrared absorption feature and has relative low content in Ti₃C₂/g-C₃N₄-3 sample [22]. FT-IR spectra of g-C₃N₄ and Ti₃C₂/g-C₃N₄-3 samples present the similar absorption features. The absorption peak at 810 cm⁻¹ is attributed to tri-s-triazine units in g-C₃N₄, and the several fingerprint peaks among 1200-1700 cm⁻¹ result from aromatics stretching modes of CN heterocycles, and the broad peaks between 3300 cm⁻¹ and 3500 cm⁻¹ originate from the vibration absorption of NH_x groups, respectively [17].



Fig. 1 XRD patterns of Ti₃AlC₂, Ti₃C₂, g-C₃N₄ and Ti₃C₂/g-C₃N₄₋₃ samples.

The morphologies of samples were further investigated by SEM and TEM techniques. As SEM image displayed in Fig. 2a, the MAX phase Ti₃AlC₂ raw material shows irregular block, but the obtained Ti₃C₂ presents the typical 2D nanosheet features after MAX phase Ti₃AlC₂ is etched by HF (Fig. 2b). In addition, comparing with SEM images of g-C₃N₄ (Fig. 2c) and Ti₃C₂/g-C₃N₄-3 (Fig. 2d) samples, they exhibit the similarly morphological features which show the macroscopical irregular bulk shape composed of 2D nanosheets. The 2D nanosheet structure of g-C₃N₄ is further revealed by TEM image in Fig. 2e. What is worth noting is that some 2D Ti₃C₂ nanosheets are distinctly loaded on the surface of 2D g-C₃N₄ nanosheets in TEM

images of Ti₃C₂/g-C₃N₄₋₃ sample (Fig. 2f-g), which demonstrates that the 2D/2D Ti₃C₂/g-C₃N₄ heterojunction is fabricated successfully, in favor of transfer and separation of charge carriers between 2D Ti₃C₂ and 2D g-C₃N₄ nanosheets to improve the photocatalytic activity. Furthermore, in order to determine the flow direction of photogenerated electrons and the positions of active sites, the Pt deposited Ti₃C₂/g-C₃N₄-3 sample are visually observed by TEM and HRTEM images after photocatalytic reaction. As TEM image shown in Fig. 2h, Pt nanoparticles are mainly deposited on the boundary edges of 2D Ti₃C₂ nanosheets, which indicates the photogenerated electrons should transfer from 2D g-C₃N₄ to 2D Ti₃C₂ and then migrate to the boundary edges of 2D Ti₃C₂ along the nanosheet planes inside 2D/2D Ti₃C₂/g-C₃N₄ heterojunction, suggesting the boundary edges of 2D Ti₃C₂ nanosheets can serve as active sites to take place the photocatalytic reaction. The results are further revealed by HRTEM image in Fig. 2i, where Pt nanoparticles are anchored on the boundary edge of 2D Ti₃C₂ nanosheet at the clear heterointerface between 2D Ti₃C₂ and 2D g-C₃N₄, and the interplanar crystal spacing of 0.23 nm corresponds to the (111) lattice planes of Pt. In addition, the EDS elemental mappings (Fig. 2j-m) of Ti₃C₂/g-C₃N₄-3 sample demonstrate the C, N and Ti elements all are detected and exhibit characteristic distribution, further implying the formation of 2D/2D Ti_3C_2/g - C_3N_4 hybrid.



Fig. 2. SEM images of Ti₃AlC₂ (a), Ti₃C₂ (b), g-C₃N₄ (c) and Ti₃C₂/g-C₃N₄-3 (d) samples; TEM images of g-C₃N₄ (e) and Ti₃C₂/g-C₃N₄-3 (f, g) samples; TEM (h) and HRTEM (i) images of Pt deposited Ti₃C₂/g-C₃N₄-3 sample; HAADR image (j) and EDS elemental mapping (k, l, j) of Ti₃C₂/g-C₃N₄-3 sample.

XPS measurements were carried out to inquire into the surface elemental compositions and chemical states of the samples. The survey XPS spectra in Fig. 3a present the distinct binding energy peaks of C, N and O elements, in which O element signal may be ascribed to the adsorbed H₂O and CO₂ molecules on the surface of samples. No detected Ti element signal in XPS spectrum of Ti_3C_2/g -C₃N₄-3 sample may be due to the low content Ti₃C₂ in the 2D/2D heterojunction. Moreover, the C 1s XPS spectrum of g-C₃N₄ sample (Fig. 3b) is grouped into three binding energy peaks at 284.6 eV, 286.3 eV and 288.0 eV, which originate from the hybridized sp² C in C=C, sp³ C in C-C(N) and sp² C in N-C=N, respectively [30]. The N 1s XPS spectra of g-C₃N₄ sample also can be fitted to three binding energy peaks at 398.5 eV, 399.8 eV and 400.9 eV (Fig. 3c), which correspond to sp² hybridized N in C-N=C of triazine rings, graphite N in N-C₃ and amino N in C-NH_x, respectively [30]. Furthermore, compared XPS spectra of Ti₃C₂/g-C₃N₄-3 with that of g-C₃N₄ sample, the binding energy peaks of sp² hybridized C in N-C=N and sp² hybridized N in

C-N=C all shift 0.1 eV to the low energy direction and locate at 287.9 eV and 398.4 eV, respectively, which confirms the strong interaction existed between 2D Ti₃C₂ and 2D g-C₃N₄ nanosheets, availing to accelerate the transfer and separation of charge carriers. Moreover, the Ti 2p XPS spectrum of Ti₃C₂/g-C₃N₄-3 sample in Fig. 3d shows four sets of typical $2p_{3/2}/2p_{1/2}$ spin-orbit coupling binding energy peaks at 454.6/460.6 eV, 455.4/462.1 eV, 456.5/463.3 eV, and 458.1/464.1 eV, which can be well ascribed to Ti-C, Ti²⁺, Ti³⁺ and Ti⁴⁺ states in Ti₃C₂, respectively [31], suggesting that the fabrication of 2D/2D Ti₃C₂/g-C₃N₄ heterojunction.



Fig. 3 XPS spectra of g-C₃N₄ and Ti₃C₂/g-C₃N₄-3 samples.

The photocatalytic activity of the fabricated 2D/2D Ti₃C₂/g-C₃N₄ heterojunction was firstly evaluated by H₂ production from water under the visible light ($\lambda > 420$ nm). As can be seen from H₂ production kinetic curves (Fig. 4a) and H₂ production rates (Fig. 4b), the single Ti₃C₂ sample displays the very weak photocatalytic activity and the single g-C₃N₄ sample only exhibits a relative low photocatalytic H₂ production rate of 12.5 µmol h⁻¹, respectively. However, the photocatalytic H₂ production activity is distinctly enhanced after forming 2D/2D heterojunction between 2D Ti₃C₂ and 2D g-C₃N₄, and the H₂ production rates increase and then decrease with increasing the content of Ti₃C₂. Especially the highest H₂ production rate rises to 26.7 µmol h⁻¹ over

the Ti₃C₂/g-C₃N₄-3 sample, which is about 2.13 times as high as that of single g-C₃N₄ sample (12.5 μ mol h⁻¹). Meanwhile, Fig. 4c demonstrates the apparent quantum efficiency (AQE) reaches up to 1.61% at 420 nm. Of particular note is that the Ti₃C₂/g-C₃N₄-3 sample displays the considerably high stability. As presented in Fig. 4d, the cycle experiments demonstrate the Ti₃C₂/g-C₃N₄-3 sample still maintains the stable H₂ production rate when withstanding 12 cycle runs with total 60 h, indicating that the 2D/2D Ti₃C₂/g-C₃N₄ heterojunction has the superior reusability and durability.



Fig. 4 H_2 production kinetic curves (a) and H_2 production rate (b) over different samples; wavelength dependent AQE (c) and cycle run kinetic curves (d) over Ti_3C_2/g -C₃N₄-3 sample.



Fig. 5 Dynamic curves (a), plots of $ln(C_0/C)$ versus time (b), rate constants (c) for degrading TC-HCl over different samples; absorbance variations of TC-HCl solution over Ti₃C₂/g-C₃N₄-3 sample (d).

Furthermore, the photocatalytic activity of the fabricated 2D/2D Ti₃C₂/g-C₃N₄ heterojunction was also evaluated by degradation of antibiotic TC-HCl under the visible light ($\lambda \ge 420$ nm). As shown in Fig. 5a, the photocatalytic activity of single Ti₃C₂ and g-C₃N₄ samples is comparatively low for removing TC-HCl, whereas that of the fabricated 2D/2D Ti₃C₂/g-C₃N₄ heterojunctions is improved overtly. The degradation activity of Ti₃C₂/g-C₃N₄ samples goes up and then down with increasing the content of Ti₃C₂, and the highest degradation rate of TH-HCl over the Ti₃C₂/g-C₃N₄-3 sample dramatically reaches up to 84.4% within 120 min which is far higher than that of single g-C₃N₄ sample (29.0%). Besides, the pseudo-fist-order model is used for the fitting of TC-HCl degradation reaction (Fig. 5b) [32], and the obtained degradation rate constants are shown in Fig. 5c. We note that the largest rate constant of degrading TC-HCl over the Ti₃C₂/g-C₃N₄-3 sample is 0.0141 min⁻¹, which runs up to about 5.04 times as high as than that of single g-C₃N₄-3 sample (0.0028 min⁻¹). Moreover, Fig. 5d shows the absorbance variations of TC-HCl solution over the Ti₃C₂/g-C₃N₄-3 sample during the degradation process, in which the characteristic

absorption peak of TC-HCl at 357 nm becomes weaker and weaker with prolonging reaction times, which indicates that the TC-HCl molecule may be destructed to be small molecules and ions [33].



Fig. 6 TOC removal rates of TC-HCl over $g-C_3N_4$ and $Ti_3C_2/g-C_3N_4-3$ samples (a), cycle degradation kinetic curves (b) and cycle degradation rates (c) of TC-HCl over $Ti_3C_2/g-C_3N_4-3$ sample; XRD patterns of $Ti_3C_2/g-C_3N_4-3$ sample before and after cycle reaction (d)

In order to further confirm the outstanding photocatalytic degradation performance of 2D/2D Ti₃C₂/g-C₃N₄ heterojunctions, the total organic carbon (TOC) of TC-HCl solution was analyzed after performing photocatalytic reaction of 120 min over the single g-C₃N₄ and Ti₃C₂/g-C₃N₄-3 samples. As shown in Fig. 6a, the TOC removal rate of TC-HCl over the Ti₃C₂-g-C₃N₄-3 sample is 79.0%, which runs up to about 3.48 times as high as that of the single g-C₃N₄ sample (22.7%), indicating that the most of TC-HCl molecules are mineralized into small molecules/ions. Moreover, the cycle degradation experiments of TC-HCl over the Ti₃C₂/g-C₃N₄-3 sample were also performed. As can be seen from cycle degradation kinetic curves (Fig. 6b) and cycle degradation rates (Fig. 6c) of TC-HCl, the Ti₃C₂/g-C₃N₄-3 sample can maintain continuously stable running through five cycle experiments, and the slight reduction

of degradation rate may result from the loss of photocatalyst in the cycle reaction process. In addition, the XRD pattern of the used Ti_3C_2/g -C₃N₄-3 sample has almost no changes compared with that of the fresh one (Fig. 6d), further indicating the fabricated 2D/2D Ti_3C_2/g -C₃N₄ heterojunction possesses the superior stability and reusability.



Fig. 7 UV-vis DRS (a), plots of $(ahv)^2$ versus hv (b), XPS valence band spectra (c) and Mott-Schottky plots (d, e, f) of g-C₃N₄, Ti₃C₂ and Ti₃C₂/g-C₃N₄-3 samples.

The photocatalytic performance is closely associated with the light absorption prosperity of photocatalysts which is usually investigated by UV-Vis DRS. As shown in Fig. 7a, the Ti₃C₂ sample obviously displays the broad absorption feature in the whole ultraviolet and visible regions, which has something to do with its dark color and metal-like nature [20, 22]. In addition, the absorption edge of g-C₃N₄ sample shows relative obvious red-shift and the light absorption over 500 nm is distinct enhanced after forming 2D/2D Ti₃C₂/g-C₃N₄ heterojunction, which is directly concerned with the modification effect of 2D Ti₃C₂ on the surface of 2D g-C₃N₄ nanosheets. The increased light absorption ability is more advantageous to the photocatalytic H₂ production and TC-HCl degradation reactions. Moreover, the band gap energy of g-C₃N₄ sample before and after forming 2D/2D Ti₃C₂/g-C₃N₄ heterojunction are calculated by Tauc formula ahv=A(hv- E_g)^{n/2} [34], where *v*, *a*, *h*, A, and E_g are light frequency, absorption coefficient, Planck constant, a constant and

band gap energy, respectively. It is well known that the value of n depends on the type of optical transition (n=1 for direct transition and n=4 for indirect transition) [34]. Therefore, on the basis of the direct band gap feature of g-C₃N₄ [34], the curves of $(\alpha hv)^2$ versus hv are carried out (Fig. 7b). The band gap values of g-C₃N₄ are 2.90 eV and 2.84 eV before and after modifying Ti₃C₂, respectively. In addition, the conduction band (CB) and valence band (VB) positions of semiconductor can be calculated by using empirical equations of $E_{VB}=X-E_e+0.5E_g$ and $E_{CB}=E_{VB}-E_g$, where ECB, X, Ee, Eg and EvB are CB value, the geometric average of absolute electronegativity of the constituent atoms (X=4.73 eV for g-C₃N₄), the energy of free electrons on the hydrogen scale (4.5 eV), the band gap and VB value of semiconductor, respectively [34]. Therefore, the values of CB and VB of original g-C₃N₄ are -1.22 eV and 1.68 eV, as well as those of g-C₃N₄ modified with Ti₃C₂ are -1.19 eV and 1.65 eV, respectively. The VB values are also identified via XPS valence band spectra of g-C₃N₄ and Ti₃C₂/g-C₃N₄₋₃ samples (Fig. 7c). In addition, the flat band potentials of Ti₃C₂, g-C₃N₄ and Ti₃C₂/g-C₃N₄-3 samples were also determined by means of electrochemical measurements [20-35]. As the Mott-Schottky plots shown in Fig. 7d-f, the Ti₃C₂, g-C₃N₄ and Ti₃C₂/g-C₃N₄-3 samples accord with the characteristics of n-type semiconductors owing to the positive slopes, whose the flat band potentials are measured to be -1.34 V, -0.94 V and -0.91 V, respectively.

The steady-state photoluminescence (SS-PL) spectra are usually applied to investigate the separation degree of photogenerated electron-hole pairs [36, 37]. In general, the weaker SS-PL intensity means the phocatalyst possesses less recombination rate of charge carriers. As SS-PL spectra shown in Fig. 8a, compared with single g-C₃N₄ sample, the Ti₃C₂/g-C₃N₄-3 sample exhibits the lower SS-PL intensity, suggesting that the recombination rate of photogenerated electrons and holes is reduced to promote interfacial charge transfer between 2D Ti₃C₂ and 2D g-C₃N₄ nanosheets. Besides, for the sake of exploring the dynamic electron migration process, the transient-state photoluminescence (TS-PL) decay curves are measured [38]. As displayed in Fig. 8b, the fluorescent lifetime (3.731 ns) of the Ti₃C₂/g-C₃N₄-3 sample is much shorter than that of single g-C₃N₄ sample (5.408 ns), implying the additional

nonradioactive decay channel may be opened through the electron transfer from 2D g-C₃N₄ to 2D Ti₃C₂ owing to the metal-like nature of Ti₃C₂, which can efficiently accelerate the separation of photogenerated charge carriers [20-22]. Furthermore, the migration and separation behaviors of charge carriers were also investigated by the photoelectrochemical experiments [39, 40]. Fig. 8c exhibits the transient photocurrent response curves of g-C₃N₄ and Ti₃C₂/g-C₃N₄-3 electrodes. It is obvious that both Ti₃C₂/g-C₃N₄-3 and g-C₃N₄ electrodes produce relatively longstanding and stable photocurrent responses under the visible light, and the photocurrent density of the former is much larger than that of the latter, which indicates that the Ti₃C₂/g-C₃N₄-3 sample observably improves the transfer and separation efficiency of photogenerated charge carriers. Meanwhile, the electrochemical impedance spectroscopy (EIS) is an effective method to reveal the electron transfer efficiency at the electrode [41, 42]. It is widely believed that the small EIS radius means the high mobility and separation of charge carriers. In Fig. 8d, the Ti_3C_2/g -C₃N₄-3 electrode displays a smaller ESI radius than the g-C₃N₄ electrode, demonstrating that the former possesses the lower interface resistance and the higher transfer ability, in favor of the separation of charge carriers. These results prove that 2D Ti₃C₂ in 2D/2D Ti₃C₂/g-C₃N₄ heterojunction serves as electron harvester to realize the high-efficiency separation of photogenerated charge carriers, thus enhancing the photocatalytic H₂ production and degradation performance. Besides, the specific surface areas and pore volumes of the Ti₃C₂/g-C₃N₄-3 sample are 64.53 m² g⁻¹ and 0.1918 cm³ g⁻¹, which all reach up to about 1.5 times as high as 43.19 m² g⁻¹ and 0.1281 cm³ g⁻¹ of the single g-C₃N₄, respectively, thus also availing to enhance the photocatalytic performance (Fig. S2⁺).



Fig. 8 SS-PL spectra (a), TS-PL decay curves (b), transient photocurrent responses (c) and Nyquist plots (d) of $g-C_3N_4$ and $Ti_3C_2/g-C_3N_4-3$ samples.

In order to clarify the photocatalytic degradation mechanism, the capture experiments were performed to analyze the active species during the photocatalytic degradation of THC-HCl. EDTA-2Na, VC and IPA are employed as the scavengers for hole (h⁺), superoxide radical ($\cdot O_2^-$) and hydroxyl radical ($\cdot OH$), respectively [43, 44]. As displayed in Fig. 9 (a-b), when EDTA-2Na and VC are added in the reaction system, the degradation reactions of TC-HCl are strongly suppressed and the degradation rates of TC-HCl are only 9.0% and 8.0% which is far less than that without adding capture agents (84.4%). The results reveals that h^+ and $\cdot O_2^-$ play the important roles in the degradation process. Furthermore, once IPA is used as the capture reagent, the degradation rate of TC-HCl still reaches to 48.4%, indicating that ·OH has the relative weak influence on the degradation of TC-HCl. Moreover, the above results can be further investigated by electron spin resonance (ESR) technique, which is used to detect $\cdot O_2^-$ and $\cdot OH$ generated during the degradation reaction process [45, 46]. Fig. 9c displays the DMPO-·O2⁻ ESR spectrum of Ti₃C₂/g-C₃N₄-3 sample, in which four sets of strong signals are produced when light on, suggesting that $\cdot O_2^-$ can be produced in large quantities during the degradation process. In

contrast, the DMPO⁻·OH ESR spectrum of Ti₃C₂/g-C₃N₄-3 sample (Fig. 9d) possess four groups of weak peaks when light on, indicating that a small amount of ·OH is produced in the photocatalytic degradation process. Grounded on the above results, we conclude that \cdot O₂⁻, h⁺ and \cdot OH all are the effective active species and \cdot O₂⁻ and h⁺ play the main roles for the photocatalytic degradation of TC-HCl.



Fig. 9 Kinetic curves (a) and degradation rates (b) of TC-HCl over Ti_3C_2/g -C₃N₄-3 sample with different scavengers, ESR spectra of DMPO⁻·O²⁻ (c) and DMPO⁻·OH (d) over g-C₃N₄ and Ti_3C_2/g -C₃N₄-3 samples

For probing into the degradation way of TC-HCl molecule, MS was used for analyzing the generated intermediate products in the photocatalytic degradation reaction [47, 48]. Fig. 10 shows the MS of TC-HCl solution over $Ti_3C_2/g-C_3N_{4-3}$ when the photocatalytic degradation reaction is performed for 0 min, 60 min and 120 min, respectively. According to the above MS analysis results, we present some possible intermediates in the degradation of TC-HCl (Fig. 11). Firstly, TC-HCl in the solution forms protonated tetracycline A (TC-H⁺, m/z=445) by losing Cl⁻ ions, and then tow unconjugated double bonds in rings are opened to produce B (m/z=481). Subsequently, the methyl breaks away from the tertiary amino group of B to form C (m/z=453). Then a series of continuous releasing -NH₃⁺ from C to D (m/z=453), -COH and -OH from D to E (m/z=453), -CH₃ from E to F (m/z=365) and -OH₂⁺ from F to G (m/z=349) take place. Finally undergoing the ring-opening reaction from G to H (m/z=305), losing –CH₃CHO group from H to I (m/z=261) and the ring-opening reaction from I to J (m/z=234), TC-HCl molecules are completely decomposed into CO_2 , H₂O, NH₄⁺, etc.



Fig. 10. MS of TC-HCl at degradation time of 0 min (a), 60 min (b) and 120 min (c) over Ti₃C₂/g-C₃N₄-3 sample.



Fig. 11. The possible intermediates and pathway of TC-HCl molecule at degradation reaction process over Ti₃C₂/g-C₃N₄-3 sample.

The possibly transferred and separated behaviors of charge carriers and photocatalytic reaction mechanism over the 2D/2D Ti₃C₂/g-C₃N₄ heterojunction are put forward. According to the flat band potential analyses, the Fermi levels of the g-C₃N₄ and Ti₃C₂ samples are measured to be -0.94 V and -1.34 V, respectively. However, after 2D/2D Ti₃C₂/g-C₃N₄ heterojunction is fabricated by modifying 2D Ti₃C₂ on the surface of 2D g-C₃N₄ nanosheets, the Fermi level changes to be -0.91 V owing to the intense interface interactions. Meanwhile, on the basis of results of UV-Vis DRS and XPS Valance spectra, the CB and VB positions of 2D g-C₃N₄ change from -1.22 eV and 1.68 eV to -1.19 eV and 1.65 eV, respectively. In consequence, as illustrated in Fig. 12, once the 2D/2D Ti₃C₂/g-C₃N₄ heterojunction is irradiated under the visible light, the photogenerated electrons and holes are produced on CB and VB of 2D g-C₃N₄ through the band gap transition, respectively. Thereafter, the photogenerated electrons are immediately collected by 2D Ti₃C₂ as electron harvester and then directionally assemble on the boundary edges of 2D Ti₃C₂, which certainly will accelerate transfer of charge carriers at the heterointerfaces between 2D Ti₃C₂ and 2D g-C₃N₄ to increase the separation efficiency and effective numbers of charge carriers dramatically, thus enhancing the photocatalytic performance. As far as the photocatalytic H₂ production reaction is concerned, the photogenerated electrons directionally transfer to Pt nanoparticles deposited at the boundary edge of 2D Ti₃C₂, and then reduce H⁺/H₂O to produce H₂. At the same time, the photogenerated holes can be consumed by sacrificial agent TEOA. For the photocatalytic degradation reaction of TC-HCl, the photogenerated electrons on the boundary edge of 2D Ti_3C_2 can reduce O_2 molecules in solution to produce O_2^- because the Fermi level of 2D Ti₃C₂ is more negative than the standard redox potential of O_2/O_2^- with -0.046 eV [49], as well as a handful of generated $\cdot O_2^-$ are further reduced to $\cdot OH$ by reacting with H⁺ because the holes cannot oxidize OH⁻ owing to the higher VB position (1.65 eV) of 2D g-C₃N₄ than the standard redox potential of OH^{-/}·OH (2.3 eV) [49]. Finally, the OH, holes and O_2^- active species stepwise oxidize TC-HCl to produce NH_4^+ , CO_2 , H₂O, etc.



Fig. 12 The transferred and separated behaviors of charge carriers and photocatalytic reaction mechanism over the 2D/2D Ti₃C₂/g-C₃N₄ heterojunction.

4. Conclusions

To sum up, the boundary edge active sites are created on 2D Ti₃C₂ decorated on 2D g-C₃N₄ nanosheets by means of fabricating the 2D/2D Ti₃C₂/g-C₃N₄ heterojunctions in the semi-closed system. Ti₃C₂ not only extends the visible light response range to increase the utilization rate of solar energy, but also can serve as electron harvester to realize the directional transfer of photogenerated electrons from 2D g-C₃N₄ to 2D Ti₃C₂ and promote the high-efficiency separation of charge carriers, thus dramatically boosting the photocatalytic performance. The optimal photocatalytic H₂ production rate reaches up to 26.7 μ mol h⁻¹ over the Ti₃C₂/g-C₃N₄-3 sample, which is about 2.13 times as high as that of single $g-C_3N_4$ sample (12.5 µmol h^{-1}). Meanwhile, the TOC removal rate of TC-HCl over the Ti₃C₂-g/C₃N₄-3 sample is 79.0%, which runs up to about 3.48 times as high as that of single g-C₃N₄ sample (22.7%), indicating that the most of TC-HCl molecules are mineralized into small molecules/ions. Furthermore, the cycle experiments demonstrate that the Ti₃C₂/g-C₃N₄-3 sample can maintain the stable H₂ production rate and TC-HCl degradation activity. All above results indicate the obtained 2D/2D Ti₃C₂/g-C₃N₄ heterojunctions have the superior activity, durability and reusability. This work affords a typical exemplification for the fabrication and insight into photocatalytic reaction mechanism of other new 2D/2D heterojunction materials.

Author Contributions Section

All authors contributed this work.

Acknowledgements

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Figure Captions

Fig. 1 XRD patterns of Ti₃AlC₂, Ti₃C₂, g-C₃N₄ and Ti₃C₂/g-C₃N₄₋₃ samples.

Fig. 2. SEM images of Ti_3AlC_2 (a), Ti_3C_2 (b), $g-C_3N_4$ (c) and $Ti_3C_2/g-C_3N_4-3$ (d) samples; TEM images of $g-C_3N_4$ (e) and $Ti_3C_2/g-C_3N_4-3$ (f, g) samples; TEM (h) and HRTEM (i) images of Pt deposited $Ti_3C_2/g-C_3N_4-3$ sample; HAADR image (j) and EDS elemental mapping (k, l, j) of $Ti_3C_2/g-C_3N_4-3$ sample.

Fig. 3 XPS spectra of g-C₃N₄ and Ti₃C₂/g-C₃N₄-3 samples.

Fig. 4 H_2 production kinetic curves (a) and H_2 production rate (b) over different samples; wavelength dependent AQE (c) and cycle run kinetic curves (d) over Ti₃C₂/g-C₃N₄-3 sample.

Fig. 5 Dynamic curves (a), plots of $ln(C_0/C)$ versus time (b), rate constants (c) for degrading TC-HCl over different samples; absorbance variations of TC-HCl solution over Ti₃C₂/g-C₃N₄-3 sample (d).

Fig. 6 TOC removal rates of TC-HCl over $g-C_3N_4$ and $Ti_3C_2/g-C_3N_4-3$ samples (a), cycle degradation kinetic curves (b) and cycle degradation rates (c) of TC-HCl over $Ti_3C_2/g-C_3N_4-3$ sample; XRD patterns of $Ti_3C_2/g-C_3N_4-3$ sample before and after cycle reaction (d)

Fig. 7 UV-vis DRS (a), plots of $(ahv)^2$ versus hv (b), XPS valence band spectra (c) and Mott-Schottky plots (d, e, f) of g-C₃N₄, Ti₃C₂ and Ti₃C₂/g-C₃N₄-3 samples.

Fig. 8 SS-PL spectra (a), TS-PL spectra (b), transient photocurrent responses (c) and Nyquist plots (d) of $g-C_3N_4$ and $Ti_3C_2/g-C_3N_4-3$ samples.

Fig. 9 Kinetic curves (a) and degradation rates (b) of TC-HCl over $Ti_3C_2/g-C_3N_4-3$ sample with different scavengers, ESR spectra of DMPO⁻·O²⁻ (c) and DMPO⁻·OH (d) over g-C_3N_4 and $Ti_3C_2/g-C_3N_4-3$ samples

Fig. 10. MS of TC-HCl at degradation time of 0 min (a), 60 min (b) and 120 min (c) over Ti₃C₂/g-C₃N₄-3 sample.

Fig. 11. The possible intermediates and pathway of TC-HCl molecule at degradation reaction process over Ti_3C_2/g -C₃N₄-3 sample.

Fig. 12 The transferred and separated behaviors of charge carriers and photocatalytic



reaction mechanism over the 2D/2D Ti₃C₂/g-C₃N₄ heterojunction.





Fig. 2. SEM images of Ti_3AlC_2 (a), Ti_3C_2 (b), $g-C_3N_4$ (c) and $Ti_3C_2/g-C_3N_4-3$ (d) samples; TEM images of $g-C_3N_4$ (e) and $Ti_3C_2/g-C_3N_4-3$ (f, g) samples; TEM (h) and HRTEM (i) images of Pt deposited $Ti_3C_2/g-C_3N_4-3$ sample; HAADR image (j) and



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 Ti_3C_2/g - C_3N_4 -3 sample.

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Fig. 6 TOC removal rates of TC-HCl over $g-C_3N_4$ and $Ti_3C_2/g-C_3N_4-3$ samples (a), cycle degradation kinetic curves (b) and cycle degradation rates (c) of TC-HCl over $Ti_3C_2/g-C_3N_4-3$ sample; XRD patterns of $Ti_3C_2/g-C_3N_4-3$ sample before and after



Fig. 7 UV-vis DRS (a), plots of $(ahv)^2$ versus hv (b), XPS valence band spectra (c) and Mott-Schottky plots (d, e, f) of g-C₃N₄, Ti₃C₂ and Ti₃C₂/g-C₃N₄-3 samples.



Fig. 8 SS-PL spectra (a), TS-PL spectra (b), transient photocurrent responses (c) and Nyquist plots (d) of $g-C_3N_4$ and $Ti_3C_2/g-C_3N_4-3$ samples.



Fig. 9 Kinetic curves (a) and degradation rates (b) of TC-HCl over Ti_3C_2/g -C₃N₄-3 sample with different scavengers, ESR spectra of DMPO⁻·O²⁻ (c) and DMPO⁻·OH (d) over g-C₃N₄ and Ti_3C_2/g -C₃N₄-3 samples



Fig. 10. MS of TC-HCl at degradation time of 0 min (a), 60 min (b) and 120 min (c) over Ti_3C_2/g -C₃N₄-3 sample.



Fig. 11. The possible intermediates and pathway of TC-HCl molecule at degradation reaction process over Ti_3C_2/g -C₃N₄-3 sample.



Fig. 12 The transferred and separated behaviors of charge carriers and photocatalytic reaction mechanism over the 2D/2D Ti₃C₂/g-C₃N₄ heterojunction.