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Review

MXenes as noble-metal-alternative co-catalysts in photocatalysis

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ABSTRACT

Photocatalysis has become a focal point in research as a clean and sustainable technology with the potential to solve environmental problems and energy crises. The loading of noble-metal co-catalysts can substantially improve the photocatalytic efficiency of semiconductors. Because the high cost and scarcity of noble metals markedly limit their large-scale applications, finding a noble-metal-alternative co-catalyst is crucial. MXene, a novel 2D transition metal material, has attracted considerable attention as a promising substitute for noble metal co-catalysts owing to its cost-efficiency, unique 2D layered structure, and excellent electrical, optical, and thermodynamic properties. This review focuses on the latest advancements in research on MXenes as co-catalysts in relatively popular photocatalytic applications (hydrogen production, CO₂ reduction, nitrogen fixation, and organic pollutant oxidation). The synthesis methods and photocatalytic mechanisms of MXenes as co-catalysts are also summarized according to the type of MXene-based material. Finally, the crucial opportunities and challenges in the prospective development of MXene-based photocatalysts are outlined. We emphasize that modern techniques should be used to demonstrate the effects of MXenes on photocatalysis and that the photocatalytic activity of MXene-based photocatalysts can be further improved using defective engineering and recent phenomena such as the localized surface plasmon resonance effect and single-atom catalysis.

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1. Introduction

With the development of human industrialization, the excessive use of limited fossil fuel resources will lead to energy shortages, environmental contamination, and abnormal cli-

matic variations [1,2]. It is, therefore, necessary to develop an environmentally friendly and sustainable technology to address these problems. Among the diverse advanced technologies, photocatalysis is regarded as one of the cleanest technologies and one that exhibits great potential in various areas of

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application, such as H₂O splitting [3–5], CO₂ reduction [6,7], and the oxidation of organic pollutants [8]. As a rule, a photocatalytic reaction includes three processes: (1) light harvest by photocatalysts to generate photoexcited carriers, (2) carrier isolation and transfer to the surface of the photocatalyst, and (3) carrier-induced surface redox reactions. The photocatalytic activity is determined by these three processes. Most conventional photocatalysts, such as TiO₂, ZnIn₂S₄, and g-C₃N₄, demonstrate poor photocatalytic efficiency because their photo-triggered electron-hole pairs rapidly recombine [9–11]. Loading co-catalysts can effectively improve the efficiency of carrier separation. The co-catalyst can not only act as an electron sink to enhance the charge separation ability but can also provide abundant active sites [12–14]. Many noble metals, such as Pt [15], Ag [16], and Au [17], have been considered as efficient co-catalysts for photocatalytic reactions. However, the application of precious metal co-catalysts is limited by their high price and scarcity. Thus, there is an urgent need for designing high efficiency, low cost noble-metal-alternative co-catalysts.

A neotype of 2D hierarchical transition metal carbides, nitrides, or carbonitrides (MXenes) has been synthesized by selective etching of the A-element of 3D ternary compounds (known as MAX phases). M denotes an early transition metal element, such as Sc, Ti, and V; A is one of the elements of IIIA and IVA; and X stands for the C/N element [18]. The formula for MXenes is M_{n+1}X_n or M_{n+1}X_nT_x (T represents surface functional groups such as -O, -F, and -OH), and n ranges from 1 to 3, which determines the number of atomic layers in the unit cell [19,20].

Figure 1 illustrates some typical structured MXenes (M₂XT_x, M₃X₂T_x, and M₄X₃T_x), in which the top row shows structures of mono-M MXenes that cover the X elements [21]. For the solid solution phase, two kinds of M transition metals are randomly distributed in the MXenes (see the second row in Fig. 1). Ordered double-M MXenes are shown in the third row, where single or double layers of one M metal are sandwiched between layers of another M metal [22]. Although other 2D carbon-based materials such as graphene and graphdiyne have been developed for various fields [23–28], their simple chemistry limits their use. However, MXenes with complex, layered structures that contain at least two elements may offer new properties because they provide numerous compositional var-

Fig. 1. Typical structures of MXenes (M₂XT_x, M₃X₂T_x, and M₄X₃T_x) and compositions (mono-M MXenes and double-M MXenes), where M is an early transition metal and X is C and/or N (with the C element as an example) [21].

iables that can be fine-tuned to achieve specific properties [22,29]. Owing to their conductivity, unique structure, and adjustable band structure, MXenes have been considered to be valuable materials for various applications, for instance, energy storage [30–34], biosensors [35,36], and catalysis [21,37,38].

Although MXenes have immense potential in the domain of photocatalysis, they cannot be directly used as photocatalysts because they are essentially not semiconductors [39]. Computational studies have predicted that some M_{n+1}X_nT_x carbides/nitrides can be used as semiconductors by altering their surface functional groups. Unfortunately, those have not been experimentally synthesized [40]. Most studies show that MXenes have been successfully developed as co-catalysts for the multiplication of photocatalytic behavior [41–45]. A majority of the recently published review papers on MXenes mainly focused on synthesis, properties, and potential applications in energy-related fields [18,20,46–51]. Because few reviews exist on MXenes as co-catalysts for photocatalytic applications, this study aims to offer a critical overview of the latest advancements in using MXene as a co-catalyst in photocatalysis, which includes photocatalytic H₂ evolution, photocatalytic CO₂ reduction, photocatalytic N₂ fixation, and photocatalytic oxidation of organic pollutants. The synthesis and photocatalytic mechanism of MXenes as co-catalysts are also summarized in this review. In the last section, an outlook for future research directions is proposed from the current challenges.

2. General method for the synthesis of MXenes

The MXenes reported to date have been obtained by selectively etching the A element from the MAX phase in the presence of hydrofluoric acid (HF) [29], HF-forming etchants (fluorides and HCl) [52,53], or molten fluorides (KF, NaF or LiF at 550 °C) [54], as shown in the first step in Fig. 2. This process can be realized because HF-based etchants have high selectivity and can break metallic M-A bonds, which are more fragile than M-X bonds. To obtain mono- or fewer-layered MXenes, the multilayered MXenes are peeled by manual or mechanical agitation (final step in Fig. 2). In addition, an intercalation stage can be optionally used for enhanced MXene exfoliation, and some substances, such as dimethyl sulfoxide [55], tetrabutylammonium hydroxide [56], NH₄HF₂ [57], and urea [58], have been verified as effective intercalators.

HF-mediated wet etching is the most frequently used method to synthesize MXenes. Naguib *et al.* [29] pioneered the etching of the parent Ti₃AlC₂ (MAX) with a HF solution, and multilayered MXenes were successfully exfoliated via ultrasonication in a methanol solution. Generally, the chemical reactions for the synthesis of M_{n+1}X_nT_x (MXene) by HF etching are described as in Eqs. 1–3 [20].

The Al layer in the MAX phase can react with HF to generate AlF₃ and H₂ gas, resulting in the exfoliation of the MXene layer (Eq. 1). Furthermore, the multilayered MXene is formed with O, OH, F terminations, or more likely, a combination of all species

Fig. 2. Schematic diagram illustrating the synthesis of MXenes [51].

(Eq. 2 and Eq. 3). As surface terminations can affect the physicochemical properties of MXenes, it is especially important to elucidate their functions [37]. To avoid the use of toxic and concentrated HF solutions, Ghidui *et al.* [52] revealed a safer and high-yield route of $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene) synthesis by etching Ti_3AlC_2 (MAX) with the mixed solution of LiF and HCl. The etching conditions, such as the LiF and HCl content, have certain impacts on the quality of MXene. For example, Shahzad *et al.* [59] developed a minimally intensive layer delamination (MILD) method to isolate the larger single $\text{Ti}_3\text{C}_2\text{T}_x$ flakes by fine-tuning the content of LiF and HCl. This method is conducive to cation intercalation in the etching process, where manual shaking (no sonication) was used and resulted in larger and less defective single flakes of MXene [50]. In general, different MXene applications require different preparation methods. HF etching is recommended for smaller, more defective flakes. For better conductivity and larger sheets, the MILD method is recommended. Urbankowski *et al.* [54] first reported the synthesis of nitride MXene (Ti_4N_3) by heating Ti_4AlN_3 in the presence of molten fluorides (KF, NaF or LiF) at 550 °C. During the heating treatment procedure, some fluorine-containing by-products were generated. Therefore, it is necessary to use H_2SO_4 to remove these impurities. Finally, few-layered and monolayered flakes were obtained by adding tetrabutylammonium hydroxide under ultrasonic conditions. This molten fluoride salt method is a breakthrough in the preparation of MXenes.

3. Synthesis of hybridized photocatalysts with MXenes as co-catalysts

Growing attention has been paid to the intellectual engineering and synthesis of MXenes as co-catalysts in photocatalytic applications, achieving desirable results. Consequently, it is of immense importance to summarize the synthesis method of MXenes as photocatalytic co-catalysts. At present, there are three main synthesis methods: mechanical mixing, self-assembly, and *in-situ* oxidation.

3.1. Mechanical mixing

Mechanical mixing is a relatively simple method for synthesizing composite catalysts; this method has the advantages of saving energy, a low cost, and convenience. The processes of grinding of the solid powders and mixing of the substances in solution were both used to deposit MXenes on the surface of

the photocatalysts. According to Sun *et al.* [60], Ti_3C_2 was successfully deposited on the surface of a g- C_3N_4 photocatalyst via simple mechanical grinding of the mixed g- C_3N_4 and Ti_3C_2 (MXene) powders, and the calcined g- $\text{C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composite exhibited improved carrier separation efficiency and enhanced photocatalytic H_2 production performance. Ye *et al.* [61] demonstrated that Ti_3C_2 with surficial alkalinization can memorably improve the performance of P25 for photocatalytic CO_2 reduction, where the $\text{Ti}_3\text{C}_2\text{-OH}$ and P25 were mixed in water by magnetic stirring. Such excellent photocatalytic performance is attributed to the superior conductivity, CO_2 adsorption, and activation potential of $\text{Ti}_3\text{C}_2\text{-OH}$.

3.2. Self-assembly

Compared to the composites obtained by the mechanical mixing method, the samples obtained by self-assembly have more intimate contact and more uniform dispersion. Su *et al.* [3] prepared 2D/2D patterned $\text{Ti}_3\text{C}_2/\text{g-}\text{C}_3\text{N}_4$ hybrids by electrostatic self-assembly and manifested 2D MXene as an efficient co-catalyst for photocatalytic reactions. Because the protonated g- C_3N_4 is positively charged and the MXene surface is negatively charged, the electrostatic induced sticking (self-assembly) between Ti_3C_2 and g- C_3N_4 causes the formation of a $\text{Ti}_3\text{C}_2/\text{g-}\text{C}_3\text{N}_4$ 2D/2D patterned heterojunction. Similarly, $\text{Ag}_3\text{PO}_4/\text{Ti}_3\text{C}_2$ [41], TiO_2 nanofibers/ Ti_3C_2 [62], $\text{CdS}/\text{Ti}_3\text{C}_2\text{T}_x$ [63], and a series of MXene-based composite photocatalysts can be synthesized by this method.

3.3. In-situ oxidation

In contrast with the above methods, a hybridized photocatalyst containing MXene can be obtained by direct *in-situ* oxidation of MXenes. As the formed metal oxide (MO) is chemically bonded with MXenes, the strong and intimate contact endows the hybrid with unique optical and electronic properties. Peng *et al.* [64] synthesized a compound of Ti_3C_2 and TiO_2 uncovering {001} facets via a partially hydrothermal oxidation of Ti_3C_2 . Su *et al.* [45] prepared $\text{Nb}_2\text{O}_5/\text{C}/\text{Nb}_2\text{C}$ nanocomposites via single-step CO_2 oxidation of Nb_2CT_x . They found that the oxidation time of Nb_2CT_x plays an important role in the optical and photocatalytic properties of the $\text{Nb}_2\text{O}_5/\text{C}/\text{Nb}_2\text{C}$ hybrid, and the sample with an oxidation time of 1 h has the highest hydrogen evolution rate (HER), which is four fold higher than that of pure Nb_2O_5 . The products of MXene oxidation by this method are generally MO/MXene or MO/MXene/C (mostly amorphous carbon), in which C and MXene can be used as co-catalysts in photocatalytic reactions [39]. However, this method can only be used when the MO is a semiconductor.

4. Photocatalytic mechanism for MXenes as co-catalysts

For most semiconductor photocatalysts, the photo-generated carriers could rapidly recombine to release heat and luminous energy, leading to a low photocatalysis performance [65–69]. Loading co-catalysts is considered an available tactic to advance the performance and efficiency of photocata-

lysts (Fig. 3). Coupling MXenes with semiconductor photocatalysts is beneficial in the application of photocatalysis because the 2D layered substrate of MXenes can provide abundant adsorption sites and strong metal conductivity [61,70]. It has been well documented that MXene-based nanocomposites exhibit better stability and reproducibility [13,71].

Because of the different Fermi energy levels of MXenes and the host catalysts, the photo-aroused electrons will migrate from the conduction band (CB) of the main catalyst to the MXenes with strong conductivity [72]. With the accumulation of negative photo-generated electrons on the MXenes, the CB and valence band (VB) of the main catalyst will bend upward, forming a Schottky barrier. In addition, the Schottky barrier will impede the electron transfer back to the main catalyst from the MXenes and promote the fast shuttle of electrons [13]. The electrons accumulated on MXenes can react with H^+ to produce hydrogen or reduce CO_2 to CH_4 , CO , CH_3OH , etc.; likewise, the holes can be used for decontaminating the organic pollutants [73].

The Schottky barrier between the MXenes and the main catalyst can inhibit the recombination of photo-generated carriers and promote the process of photocatalysis. Of course, the interface between the main catalyst and MXenes needs strong and intimate contact, which has a synergistic effect with the Schottky section to improve the photocatalytic efficiency.

5. Application of MXene-based composites in photocatalysis

5.1. Photocatalytic hydrogen evolution

The development of sustainable society requires progress toward clean technology and likewise triggers the enthusiasm of researchers for renewable energy exploration [25,74,75]. H_2 , which has a high energy density of 140 MJ kg^{-1} , produces only water during combustion; thus, it is considered to be the cleanest product that can meet future fuel demands [76–80]. H_2 production driven by sunlight can function as an intriguing strategy to eliminate energy crises and environmental problems. However, large-scale solar H_2 production requires efficient and stable co-catalysts. Recently, MXene has emerged as a co-catalyst in the field of photocatalysis. MXene can work as an ambitious and cost-effective alternative to H_2 production that uses noble metal co-catalysts.

In 2016, Ran *et al.* [81] fabricated a composite material consisting of Ti_3C_2 nanoparticles and CdS with preminent reactivity, which can act as one kind of noble-metal-free photocatalyst

Fig. 3. Scheme illustrating the photocatalytic mechanism of MXene-based photocatalysts [73].

for visible-light-motivated H_2 generation. The CdS/ Ti_3C_2 composite photocatalyst (Fig. 4A and 4B) was prepared using a hydrothermal strategy. Through optimization of the loading amount of Ti_3C_2 co-catalyst, the 2.5 wt% CdS/ Ti_3C_2 composite showed the highest photocatalytic H_2 evolution rate ($14,342 \mu\text{mol h}^{-1} \text{g}^{-1}$). It had an apparent quantum efficiency (AQE) of 40.1% @ 420 nm when lactic acid was used as the sacrificial reagent, identifying the noble-metal-free metal-sulfide photocatalyst with the highest activity (Fig. 4C). The highly efficient separation of electron-hole pairs and the rapid H_2 production on the abundant -O terminations presenting on Ti_3C_2 nanoparticles (NPs) is the reason for the distinctive photocatalytic behavior of CdS/ Ti_3C_2 . This study indicated that MXenes can serve as alternatives to precious metals in solar water splitting.

Despite MXene being an effective co-catalyst for H_2 evolution, the co-catalytic performance is restrained by weak contact with the main catalyst. Recently, Yang *et al.* [82] showed that the physical interaction between CdS NPs and layered $Ti_3C_2T_x$ can be strengthened by O_2 - N_2 -plasma treating $Ti_3C_2T_x$. They successfully prepared plasma-modified $Ti_3C_2T_x$ /CdS hybrids via a mild solvothermal method. By optimizing the content of $Ti_3C_2T_x$ /CdS of 1.0 wt%, the highest H_2 -production rate ($825 \mu\text{mol h}^{-1} \text{g}^{-1}$) was achieved using visible light alongside lactic acid as sacrificial reagent, which had an AQE of 10.2% @ 450 nm. As described in Figs. 4D–E, the CB potential of CdS NPs is more negative than the E_f of $Ti_3C_2T_x$, which enabled the electrons to migrate from CdS to $Ti_3C_2T_x$.

Generally, the excellent H_2 evolution performance could be attributed to the oxygen-containing group on the $Ti_3C_2T_x$ surface and the intimate contact between CdS NPs and Ti_3C_2 . The former is good for capturing H_2O/H^+ , while the latter is feasible for inhibiting the electron-hole recombination. Some metal sulfides undergo easy photo-corrosion during the photocatalytic reaction; therefore, it is significant to improve the stability of these metal sulfide photocatalysts. Xu *et al.* [63] provided a new mechanistic insight into $Ti_3C_2T_x$ *in-situ* confine Cd^{2+} ions to avoid their leaching and achieved desirable results.

Fig. 4. HRTEM (A) and SEM (B) images of CdS/ Ti_3C_2 composite (CT2.5). Comparison of the photocatalytic H_2 production rate [81], the band structure (D), and the proposed photocatalytic mechanism of CdS/ $Ti_3C_2T_x$ (E) [82].

Although the HER performance of CdS can be greatly improved via employing MXene as a co-catalyst; Cd is an environmentally hostile contaminant. Wang *et al.* [13] prepared some titania composites with 2D transition metal carbides through a hydrothermal method. Through optimization of the content of a $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composite, a fourfold enhancement could be achieved in the photocatalytic HER with 5 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ as co-catalyst compared to that of pure rutile TiO_2 (Fig. 5A). They likewise offered a deeper understanding of the mechanism of other MXenes (Nb_2CT_x and Ti_2CT_x) as co-catalysts with TiO_2 . Those photocatalysts also showed increased photocatalytic H_2 evolution activity because photo-excited electrons can transfer to metal carbides (M_xC_y) from CB, and the formed Schottky barrier between metal carbides and TiO_2 can impede electrons from returning to semiconductor species (Fig. 5B). The study suggested that MXenes be used as an effective co-catalyst to support TiO_2 for solar H_2 generation.

It is well known that the intimate contact between a co-catalyst and the main catalyst is of immense importance, as it can provide more highways for photo-generated electron transfer. Using F-termination Ti_3C_2 as a precursor, Xiang *et al.* [83] reported the fabrication of TiO_2 by *in-situ* growth on MXene, where the remaining Ti_3C_2 could be employed as a co-catalyst to promote photocatalytic activity by capturing photo-generated electrons from TiO_2 because of the sinking nature of its electrons and the suitable Fermi level. Furthermore, Tian *et al.* [84] synthesized a 2D/2D/2D heterojunction of a Ti_3C_2 MXene/ MoS_2 nanosheet/ TiO_2 nanosheet through a two-step hydrothermal method (Fig. 5C) for water splitting to

Fig. 5. Effect of $\text{Ti}_3\text{C}_2\text{T}_x$ loading amount on photocatalytic H_2 production over $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites (A), the formation of Schottky barrier at the MXene/ TiO_2 interface (B) [13], schematic illustration of the preparation of $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{MoS}_2$ composites (C), effect of MoS_2 loading amount on the photocatalytic H_2 production of $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{MoS}_2$ hybridized photocatalyst (D), and the recyclability of the $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{MoS}_2$ -15% photocatalyst (E) [84].

produce H_2 , and the heterojunction showed remarkable enhancement and excellent stability in photocatalytic reactions (Fig. 5D and Fig. 5E). The reason for the improvement of photocatalytic H_2 production ability is that the TiO_2 nanosheet grows on MXene *in situ*, which is more favorable for electron transport. Simultaneously, the dual co-catalysts also promoted the separation of photo-generated carriers to some extent.

As a polymeric semiconductor photocatalyst, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) with a bandgap of 2.7 eV exhibits photocatalytic H_2 generation performance with the irradiation of visible light [60,77]. In 2017, Shao *et al.* [85] reported an innovative material containing 2D Ti_2C MXene and $\text{g-C}_3\text{N}_4$, and it was found that a 0.4 wt% $\text{Ti}_2\text{C}/\text{g-C}_3\text{N}_4$ heterostructure composite possessed the highest H_2 evolution rate ($47.5 \mu\text{mol h}^{-1}$), which is 14.4 fold higher than that of individual $\text{g-C}_3\text{N}_4$ and even transcends Pt-loading $\text{g-C}_3\text{N}_4$. In addition, the prepared $\text{Ti}_2\text{C}/\text{g-C}_3\text{N}_4$ exerts good durability and repeatability. The excellent performance can be ascribed to the intimate combination of $\text{g-C}_3\text{N}_4$ and Ti_2C MXene, which accelerated the photo-induced carrier segregation and delivery to metallic Ti_2C , leading to charge accumulation. Afterward, these accumulated electrons cause the negative shift of Fermi energy level that is beneficial to H_2 production (Fig. 6A). Similar findings were also reported by Su *et al.* [3] in further research on 2D/2D $\text{Ti}_3\text{C}_2/\text{g-C}_3\text{N}_4$ hybrids, in which the optimized $\text{Ti}_3\text{C}_2/\text{g-C}_3\text{N}_4$ photocatalyst exhibited a 10 fold higher HER performance ($72.3 \mu\text{mol h}^{-1} \text{g}^{-1}$) than that of pure $\text{g-C}_3\text{N}_4$.

Recently, Tian *et al.* [86] obtained $\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2$ MXene quantum dots (QDs) using a self-assembly method. The Ti_3C_2 MXene QDs showed better performance than Pt as a co-catalyst in elevating the photocatalytic HER with a $\text{g-C}_3\text{N}_4$ nanosheet (Fig. 6B and Fig. 6C). The results of the study demonstrated that low-dimensional MXenes material can be employed to enlarge the specific surface area and afford more active sites.

Fig. 6. The mechanism of photocatalytic H_2 evolution on $\text{Ti}_2\text{C}/\text{g-C}_3\text{N}_4$, E_f and E_f' refer to the Fermi levels of $\text{g-C}_3\text{N}_4$ before and after attaining equilibrium, severally (A) [85], the photocatalytic H_2 production curves (B), and the corresponding H_2 evolution rate (C) [86].

Table 1Summary of the photocatalytic CO₂ reduction over MXene-based photocatalysts.

Catalyst	Weight (mg)	MXene	Light Source	System	Production	Ref.
TiO ₂ /Ti ₃ C ₂	50	Ti ₃ C ₂	Xe lamp (300 W)	CO ₂ <i>in-situ</i> generated by NaHCO ₃ and HCl (200 ml Pyrex reactor)	4.4 μmol/g/h (CH ₄)	[91]
Bi ₂ WO ₆ /Ti ₃ C ₂	100	2 wt% Ti ₃ C ₂	Xe lamp	CO ₂ <i>in-situ</i> generated by NaHCO ₃ and H ₂ SO ₄ (200 ml Pyrex reactor)	1.78 μmol/g/h (CH ₄) 0.44 μmol/g/h (CH ₃ OH)	[43]
TiO ₂ (P25)/Ti ₃ C ₂ -OH	50	5 wt% Ti ₃ C ₂ -OH	Xe lamp (300 W)	Closed circulation system (70 kPa of CO ₂)	16.61 μmol/g/h (CH ₄) 11.74 μmol/g/h (CO)	[61]
CeO ₂ /Ti ₃ C ₂	50	5 wt% Ti ₃ C ₂	Xe lamp	CO ₂ <i>in-situ</i> generated by NaHCO ₃ and HCl (200 ml Pyrex reactor)	26.1 μmol/m ² /h (CO)	[72]
Ti ₃ C ₂ QDs/Cu ₂ O/Cu	—	Ti ₃ C ₂ QDs	Xe lamp (300 W)	High purity CO ₂ gas (100 ml quartz bottle)	153.38 ppm/cm ² (CH ₃ OH)	[42]
CsPbBr ₃ /MXene	—	Ti ₃ C ₂ NSs	Xe-lamp (300 W, λ > 420 nm)	Photocatalyst in ethyl acetate	14.64 μmol/g/h (CH ₄) 32.15 μmol/g/h (CO)	[92]

5.2. Photocatalytic CO₂ reduction

With the development of human industrialization, the consumption of fossil energy produces considerable CO₂, which increases the greenhouse effect [87,88]. Conversion of CO₂ into high value-added fuels has become a major scientific challenge, because it can solve both the energy problem and the environmental crisis. Although CO₂ is an essential element of C1 in the chemical industry, its stable molecular structure hinders its application in industrial production. Photocatalytic CO₂ reduction (artificial photosynthesis) has been considered as an ideal way to solve this challenge and obtain clean fuel using solar light. Recent studies show that MXene can also perform as an attractive co-catalyst for photocatalytic CO₂ reduction (Table 1).

Ye *et al.* [61] attested the distinctly enhanced performance of P25 in CO₂ photo-reduction by exploiting Ti₃C₂ MXene as a precious-metal-free co-catalyst. The introduction of Ti₃C₂-OH (surface alkalization) with P25 could dramatically enhance the photocatalytic CO₂RR with the production rate of CO (11.74 μmol h⁻¹ g⁻¹) and CH₄ (16.61 μmol h⁻¹ g⁻¹), which are approximately 3 and 277 fold higher, respectively, than those of pure P25 (Fig. 7A). According to the density functional theory (DFT) results (Fig. 7B), the adsorption energy of CO₂ on Ti₃C₂-F was -0.13 eV, which is much higher than that of CO₂ on Ti₃C₂-OH (-0.44 eV). Therefore, CO₂ could be adsorbed on Ti₃C₂-OH more easily than Ti₃C₂-F. This study suggested that the superior conductivity and CO₂ adsorption and activation capacity of Ti₃C₂-OH contributed to the enhancement of photocatalytic CO₂ reduction. Compared to other carbon-based materials such as graphene and graphdiyne [89,90], MXene-based compounds exhibit superior selectivity in photocatalytic CO₂ reduction to CH₄ [61,91].

Decreasing the size and the number of layers of MXene is conducive to reducing the carrier transfer distance and providing a large interface contact area. Cao *et al.* [43] successfully prepared a novel 2D/2D heterojunction of ultrathin Ti₃C₂ MXene/BiWO₆ nanosheets (Fig. 7C-E), and they found that a 5 wt% Ti₃C₂/BiWO₆ hybrid presented the highest CO₂ photo-reduction reactivity in general and had a total yield of CH₄

and CH₃OH that was 4.6 fold higher than that prepared on pure Bi₂WO₆ ultrathin nanosheets. This work not only presented a novel 2D/2D heterojunction photocatalyst but also proved that Ti₃C₂ can qualify as a high-efficiency co-catalyst in the photocatalytic reduction of CO₂. Furthermore, Chen *et al.* [42] expanded the dimension of MXene materials to zero and coupled it with 1D Cu₂O nanowires on Cu mesh through a facile self-assembly method. The methanol production from the photocatalytic CO₂RR from Ti₃C₂ QDs/Cu₂O nanowires (NWs)/Cu heterojunction was 8.25 and 2.15 fold higher than that of Cu₂O NWs/Cu and Ti₃C₂ nanosheets/Cu₂O NWs/Cu, respectively

Fig. 7. Comparison of the gas evolution rates of CO and CH₄ over P25, 5Pt/P25, 5 wt% Ti₃C₂-OH/P25, and 5 wt% Ti₃C₂@OH/P25 under Xe lamp irradiation (A); side view of the adsorption models of CO₂ on 2*2*1 Ti₃C₂-F and 2*2*1 Ti₃C₂-OH supercells (B) [61]; FESEM (C); AFM (D) images and height cutaway view (E) of ultrathin Ti₃C₂ MXene/BiWO₆ [43]; evolution rate of methanol as a function of irradiation time (F); and the proposed energy level diagram of Ti₃C₂ QDs/Cu₂O NWs/Cu and Ti₃C₂ sheets/Cu₂O NWs/Cu photocatalysts (G) [42].

(Fig. 7F). Based on theoretical and experimental results, the Ti_3C_2 QDs can facilitate the activity and stability of CO_2 photo-reduction over Cu_2O nanowires by enhancing electron transport, carrier density, and light absorption, as well as by improving carrier separation. As illustrated in Fig. 7G, under simulated sunlight, photo-motivated electrons transmit from the VB to the CB of Cu_2O . Because Ti_3C_2 QDs have high conductivity and their Fermi energy level is lower than the CB potential of Cu_2O , photo-generated electrons tend to transfer to Ti_3C_2 QDs for accumulation rather than recombination. The Fermi energy level of Ti_3C_2 QDs is negative to the redox potential of CO_2 to methanol; therefore, the accumulated electrons contribute to the enhancement of CO_2 reduction to methanol. Compared to the more positive Fermi energy level of the Ti_3C_2 sheet (0.71 V vs NHE, pH = 7) [91], Ti_3C_2 QDs are more favorable for catalyzing the reaction.

5.3. Photocatalytic nitrogen fixation

Nitrogen, the most abundant gas in the atmosphere, plays a crucial role in preserving life on earth. Currently, ammonia (NH_3) is the necessary raw material for the large-scale production of numerous chemical products, especially fertilizers. Atmospheric N_2 is the cornerstone of ammonia synthesis, but it is difficult use because of its stable nonpolar energetic $\text{N}\equiv\text{N}$ triple bond [93]. Undeniably, the Haber-Bosch process is a landmark in the utilization of N_2 , as it converts atmospheric N_2 and H_2 into NH_3 at a high temperature and pressure [94]. Nevertheless, the traditional synthetic ammonia process requires extremely harsh conditions and causes extensive energy consumption. Therefore, synthesizing NH_3 via the photocatalytic reduction of N_2 under mild conditions is of great significance. MXene, as a rising co-catalyst, has been used for photocatalytic N_2 fixation.

MXene demonstrates excellent performance in photocatalytic N_2 fixation. For instance, Qin *et al.* [95] reported a Z-scheme heterojunction ($\text{AgInS}_2/\text{MXene}$) based on 0D AgInS_2 nanoparticles and 2D MXene (Ti_3C_2) nanosheets for photocatalytic N_2 reduction under ambient conditions. Originating from the unique sheet-structure of Ti_3C_2 and formation of a Z-scheme heterojunction, the $\text{AgInS}_2/\text{MXene}$ heterojunction exhibits excellent interfacial charge transfer properties. The obtained composite with 30% AgInS_2 shows the highest N_2 fixation activity with an ammonia yield of $38.8 \mu\text{mol g}^{-1}\text{h}^{-1}$ under visible light. DFT simulations were also used to investigate N_2 adsorption modes on the surface of Ti_3C_2 (001) three different ways (Figs. 8A–C). The optimal adsorption configuration is of N_2 in a dinuclear end-on bound structure in which one of the N atoms binds with a Ti–Ti tripolymer and the other binds with Ti–Ti dimers (Fig. 8C). In this case, the adsorption energy (E_{ad}) of N_2 molecules would be as large as -5.20 eV . Through these advantageous properties, MXene may provide an accessible kinetic pathway for highly efficient N_2 fixation. The electron transfer behaviors between Ti_3C_2 and N_2 were investigated through the charge density difference (Figs. 8D and 8E). As the *d*-orbital electrons on vicinal Ti atom are injected into the absorbed nitrogen molecule, the triple bond of N_2 will be weak-

Fig. 8. Three models for the adsorption of N_2 molecules on Ti_3C_2 (001) surface (A–C). The charge density difference of the N_2 -adsorbed Ti_3C_2 (001) surface: side view (D) and top view (E). The red and yellow isosurfaces represent the charge accumulation and depletion in the space, respectively [95].

ened, to some extent, by an increased bond length (from $1.0975 \text{ \AA}$ in free N_2 to $1.334 \text{ \AA}$), which is conducive to the N_2 reduction.

Recently, Hao *et al.* developed a RuO_2 -loaded TiO_2 -MXene hybrid via a hydrothermal method for nitrogen photocatalytic fixation [96]. The results suggest that MXene (Ti_3C_2) with metallic conductivity provides an efficient transport pathway for photo-generated electrons. In addition, molecular N_2 can easily adsorb on the surface of MXenes with high exothermic energy. In contrast, Wang *et al.* [97] reported a new microporous MIL-100(Fe)/ Ti_3C_2 MXene composite with enhanced photocatalytic oxidation of nitrogen. The optimized MIL-100(Fe)/ Ti_3C_2 composite loaded with 15% Ti_3C_2 delivered the largest visible photocatalytic efficiency of 57.92%, which is three fold higher than MIL-100(Fe). Benefiting from the black body effect of Ti_3C_2 MXene, an enhanced light-harvesting ability and photothermal effect were achieved. This work serves as an example that Ti_3C_2 MXene can be regarded as a significant material for application in the photocatalytic nitrogen fixation field.

Although DFT theoretical calculations confirm that MXene is a potential catalyst for nitrogen reduction [37], studies on MXene-based materials in photocatalytic nitrogen fixation are relatively rare. Thus, more attention should be paid to experimental and theoretical research in this field.

5.4. Photocatalytic oxidation of organic pollutant

MXenes have been widely used as co-catalysts in the photocatalytic removal of organic pollutants (Table 2) because of their peculiar layered framework and superior electrical characteristics. Numerous environmental pollutants, which include organic dyes, antibiotics, and volatile organic compounds (VOCs), have been reported as having been removed by MXene-based photocatalysts [41,98,99].

Although the photocatalytic degradation of MB and AB80 dye over $\text{Ti}_3\text{C}_2\text{T}_x$ was accelerated under UV irradiation, the photocatalytic degradation ability of dyes using MXene alone is not evident [40]. In most cases, MXene is used as a co-catalyst in photocatalysis. Peng *et al.* [64] synthesized a composite of 2D Ti_3C_2 and TiO_2 exposing {001} facets via the hydrothermal oxidation of Ti_3C_2 assisted by NaBF_4 (Fig. 9A). Here, Ti_3C_2 can not

Table 2

Summary of photocatalytic oxidation of organic pollutants on MXene-based photocatalysts.

Catalyst	Weight (mg)	MXene	Light source	Pollutant	Degradation rate or rate constant	Effect of MXene	Ref.
BiOBr/Ti ₃ C ₂ MXene	50	Ti ₃ C ₂	300-W Xe lamp (420 nm filter)	100 mL RhB aqueous solution (20 mg/L)	89.3% (TOC)	Improved light absorption range and accelerated the separation of photo-induced carriers.	[102]
(001)TiO ₂ /Ti ₃ C ₂	10	Ti ₃ C ₂	300-W mercury lamp	200 mL MO aqueous solution (20 mg/L)	97.4% (50 min)	Acting as a reservoir of holes.	[64]
In ₂ S ₃ /TiO ₂ @Ti ₃ C ₂ T _x	60	Ti ₃ C ₂ T _x	300-W Xenon lamp (420 nm filter)	100 mL MO solution (20 mg/L)	92.1% (1 h)	Type-II heterojunction and Schottky junction prolonging electron lifetime.	[101]
TiO ₂ /Ti ₃ C ₂	100	Ti ₃ C ₂	175-W mercury lamp	100 mL MO (20 mg/L)	98% (30 min)	Efficient electron-hole separation	[103]
TiO ₂ @Ti ₃ C ₂ /g-C ₃ N ₄	100	Ti ₃ C ₂	300-W Xe lamp (400 nm filters)	100 mL aniline (20 mg/L); 100 mL RhB (10 mg/L)	74.6% (aniline); 99.9% (RhB)	Excellent supporter of migrating electrons.	[104]
α-Fe ₂ O ₃ /Ti ₃ C ₂	20	Ti ₃ C ₂	500 W Xe lamp (420 nm filter)	100 mL RhB (10 mg/L)	98% (2 h)	Anchoring α-Fe ₂ O ₃ and enhancing light absorption.	[100]
Ceria/Ti ₃ C ₂	50	Ti ₃ C ₂	500-W Hg lamp	50 ml RhB solution (20 mg/L)	75% (1.5 h)	Improving the utilization of optical energy.	[105]
Bi ₂ WO ₆ /Ti ₃ C ₂	20	Ti ₃ C ₂	300-W xenon lamp (400 nm filter)	5 μL HCHO 5 μL CH ₃ COCH ₃ was injected into the reactor and vaporized	CO ₂ production: 72.8 μmol/g/h (HCHO) 85.3 μmol/g/h (CH ₃ COCH ₃)	Increasing VOC adsorption and trapping photo-induced electrons.	[99]
TiO ₂ /Ti ₃ C ₂ T _x	10	Ti ₃ C ₂ T _x	UV or Solar light simulator	10 ml Carbamazepine (5 mg/L) MO dye	98.67% (UV) 55.83% (Solar light) 0.094 min ⁻¹	Affecting the degradation mechanism and reaction route.	[106]
Ag ₃ PO ₄ /Ti ₃ C ₂	20	Ti ₃ C ₂	300 W Xe lamp (420 nm filter)	2,4-dinitrophenol, tetracycline hydrochloride, Thiamphenicol, chloramphenicol	0.005 min ⁻¹ 0.32 min ⁻¹ 0.0042 min ⁻¹ 0.025 min ⁻¹	Electron sink to facilitate the separation of carriers, and a built-in electric field to inhibit the photo-corrosion of Ag ₃ PO ₄ .	[41]

only provide the Ti source to produce high energy TiO₂ nanosheets, but it also serves as the sink for photo-generated holes through the hole trapping performed by the Schottky junction, resulting in a highly efficient separation efficiency of photocarriers (Figs. 9B and Fig. 9C). Quenching experiments showed that hydroxyl radicals are the main reactive oxygen species (ROs) responsible for the degradation of MO dye (Fig. 9D). In addition, the prepared {001} TiO₂/Ti₃C₂ MXene exhibited excellent stability in photocatalysis (Fig. 9E).

In addition to TiO₂, 2D α-Fe₂O₃ is also employed to coat materials with Ti₃C₂. In 2018, Zhang *et al.* [100] reported an α-Fe₂O₃/Ti₃C₂ MXene composite using a simple ultrasonic assisted assembly strategy. The UV-vis DRS spectra demonstrated that the visible light absorption of α-Fe₂O₃/Ti₃C₂ is markedly red-shifted, and the increased absorption in the visible light region is due to the interaction between Ti₃C₂ and α-Fe₂O₃. The α-Fe₂O₃/Ti₃C₂ composite photocatalyst shows enhanced photocatalytic activity towards RhB degradation and excellent recycling stability under visible light irradiation. Overall, the high degradation rate was mainly attributed to the synergistic effects of strong visible light absorption and excellent charge separation efficiency. This study showed that Ti₃C₂ can be employed as an ideal substrate for anchoring other semiconductor photocatalysts.

Aside from constructing a binary heterojunction, novel ternary quasi-core-shell structured In₂S₃/TiO₂@Ti₃C₂T_x MXene composites have also been synthesized, and these showed outstanding photocatalytic performance towards the degradation of methyl orange dye [101]. The double heterojunction (type-

II heterojunction and Schottky junction) was constructed in the composite, making it beneficial in prolonging the lifetime of carriers and the generation of free radicals. In addition, the catalytic performance of MXenes can be steered by doping, morphology, or composition modifications.

Along with dyes, some drugs, such as tetracycline hydrochloride, thiamphenicol, and chloramphenicol have been proven capable of photocatalytic degradation by Ag₃PO₄/Ti₃C₂ MXene [41]. Research has discovered that Ti₃C₂ can dramatically boost photocatalytic performance and repeatability even more than graphene oxide in this system. Huang *et al.* [99] showed that Ti₃C₂ MXene nanoparticles can be electrostatically adsorbed on the surface of Bi₂WO₆ for the efficient removal of VOCs. The optimized Bi₂WO₆/Ti₃C₂ catalyst revealed 2- and 6.6-fold higher reactivity in the photocatalytic degradation of HCHO and CH₃COCH₃ when compared with pristine Bi₂WO₆ (Fig. 9F). Notably, such excellent catalytic performance could be attributed to the favorable adsorption of VOCs and the superior photo-generated carrier separation efficiency of Ti₃C₂ MXene.

6. Summary and outlook

In this review, we summarized the recent progress of semiconductor photocatalysis using MXenes as co-catalysts and discussed the synthesis and possible mechanisms of MXene-based photocatalysts, indicating the following:

(1) The introduction of MXenes has been shown to improve the reactivity of semiconductor photocatalysis during wa-

Fig. 9. SEM image of exposing {001} TiO₂/Ti₃C₂ MXene (A), charge-transfer path of {001} TiO₂/Ti₃C₂ MXene (B), schematic band alignments and charge flows at {001} TiO₂/Ti₃C₂ MXene interface (C), effects of scavengers on the degradation of MO with {001}TiO₂/Ti₃C₂ under UV light irradiation (D), stability test for {001} TiO₂/Ti₃C₂ toward MO degradation (E) [64], and histogram of CO₂ production rate in photocatalytic oxidation of HCHO and CH₃COCH₃ over Bi₂WO₆ under the irradiation of visible light (F) [99].

ter-splitting to produce hydrogen. It can also increase the reduction of CO₂ in producing solar fuels as well as increase nitrogen fixation and the oxidation of organic pollutants, which has the potential to solve environmental problems and the energy crisis.

(2) MXenes exhibit promising potential as cost-effective and noble-metal-free co-catalysts, as indicated by their electronic conductivity as well as the theoretical calculations for Gibbs free energy for their photocatalytic application.

(3) MXenes have a unique two-dimensional layered structure, which can provide abundant sites for the adsorption and activation of targets.

(4) MXenes can function as electron sinks to accelerate the migration of photo-generated electrons while inhibiting photo-generated carrier recombination, thereby promoting the process of photocatalytic reaction. Currently, although significant advancements have been made in the study of MXenes as photocatalytic co-catalysts, there are still many problems that need to be solved.

(5) Although MXene-based catalysts exhibit higher photo-reactivity than noble-metal-based photocatalysts, the photocatalytic applications have thus far mainly been focused on hydrogen production, CO₂ reduction, and the degradation of organic pollutants in water. There are few studies related to air purification (degradation of gaseous pollutants), ammonia synthesis, and overall water splitting. Therefore, these subjects need more careful studies to be performed.

(6) Most importantly, some similar mechanisms were presented that explain the enhanced reactivity of MXene-based photocatalysts. However, the effects of MXenes are still under debate. Some researchers have suggested that it is graphene quantum dots—derived from Ti₃C₂ rather than 2D Ti₃C₂—that act as the real co-catalyst for La₂Ti₂O₇/Ti₃C₂ composites during photocatalytic reactions [107]. With the development of modern instruments, we can apply some *in-situ* techniques such as *in-situ* DRIFTS to unveil the effects of MXenes as co-catalysts on photocatalysis.

(7) The majority of MXene preparation mainly relies on etching the A-layer of MAX using toxic HF or HF alternatives. The wastewater produced during the etching process has high toxicity and is strongly corrosive, which is harmful to the environment. Therefore, developing a safe and environmentally friendly MXene synthesis process is highly urgent.

(8) Although some theoretical results show that MXenes with functional groups can be applied as semiconductor photocatalysts, this has not yet been proven in experiments. Therefore, additional thorough explorations should be performed in this regard. Currently, MXenes are mainly used as co-catalysts and could be engineered for photoelectric performance by modifying their surface chemistries or the assignments of the surface groups related to the M atoms [40]. Understanding the specific functions of these terminated functional groups is necessary in the next stage of research toward improving the photocatalytic performance of MXene-based photocatalysts.

(9) Some updated techniques could be introduced to further improve the photocatalytic activity of MXene-based photocatalysts, such as the localized surface plasmon resonance effect [1,108,109], defective engineering [110,111], and single-atom catalysis [112,113]. These approaches can be used to improve light harvesting ability, stimulate the separation of photo-generated charge carriers, and provide unique active sites, which can further enhance the photoreactivity of MXene-based photocatalysts.

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Graphical Abstract

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MXenes as noble-metal-alternative co-catalysts in photocatalysis

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This mini-review presents recent achievements in research on MXenes as co-photocatalysts in H₂ production, CO₂ reduction, N₂ fixation, and organic degradation. The structures, synthesis, and mechanisms of MXenes as co-photocatalysts are also summarized and discussed.

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非贵金属助催化剂MXene在光催化领域应用的研究进展

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摘要: 环境友好型半导体光催化是当前最具前景的光催化技术之一, 它不仅能够将太阳能转化为化学能以解决能源危机, 还可以将污染物降解矿化从而解决环境问题。但是, 传统的半导体光催化剂受限于光利用率低、光生载流子复合率高、稳定性较差等几个方面, 无法达到理想的光催化效果。在半导体光催化剂上负载助催化剂是提升光催化效率的有效策略之一。负载助催化剂能够增强光生电荷在半导体与助催化剂界面间的传输, 提供额外的催化活性位点, 增强光捕获能力, 因而被广泛应用于光催化剂的改性。目前广泛使用的贵金属助催化剂包括Au, Ag, Pt, Ru等, 虽然这些贵金属助催化剂性能优异, 但是它们存在储量少和成本高的问题, 严重影响其规模化应用。因此, 开展高效且成本低廉的非贵金属助催化剂的研究非常必要。近来, 一种新型二维过渡金属材料(MXene)因其具有独特的二维层状结构、优异的导电性能、出色的光学和热力学性质而成为催化领域的研究热点。

本文综述了有关非贵金属助催化剂MXene在光催化领域的最新研究进展, 内容包括: (1)MXene材料的体相与表面结构特性; (2)薄层MXene的制备方法, 例如氢氟酸刻蚀法、氢氟酸替代物刻蚀法以及熔融氟盐刻蚀法; (3)MXene基复合光催化剂的合成及改性策略, 包括机械混合、自组装、原位氧化等; (4)MXene辅助增强光催化活性机理。论文还重点介绍了MXene作为助催化剂在光催化领域中的应用, 包括光催化分解水产氢、光催化CO₂还原、光催化固氮以及有机污染物的光催化降解。最后, 论文分析了MXene基异质结光催化剂存在的问题与面临的挑战, 并对MXene助催化剂的未来发展进行了展望。主要观点包括: (1)关于光催化分解水、空气净化、合成氨领域的研究较少, 需要进一步开展; (2)MXene基异质结光催化剂的反应机理仍存在争议, 需采用现代化仪器设备(包括原位表征技术)对其进行更为深入的探究; (3)目前, 大多数MXene材料的制备都是通过强腐蚀性的氢氟酸或氢氟酸替代物刻蚀, 开发环境友好且高效的MXene制备方法迫在眉睫; (4)阐明MXene表面终端基团的作用有助于提升MXene基复合光催化剂的性能; (5)引入新的改性策略如局域表面等离子体共振效应(LSPR)、缺陷调控、单原子催化(SAC)等来提高MXene基光催化剂的催化性能, 是未来MXene基复合催化剂的发展方向。

关键词: 二维过渡金属材料; 光催化降解; 产氢; 二氧化碳还原; 固氮

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