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#### Short communication

# 2D/2D MXene/g- $C_3N_4$ for photocatalytic selective oxidation of 5-hydroxymethylfurfural into 2,5-formylfuran



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A R T I C L E I N F O	A B S T R A C T
<i>Keywords:</i> Photocatalysis Nanocomposite G-C <sub>3</sub> N <sub>4</sub> MXene Selective oxidation	The selective oxidation of 5-hydroxyfurfural (HMF) into the corresponding aldehyde is one of the key reactions in the production of chemical products. Here, we prepared the MXene/g- $C_3N_4$ composite (MX/CN) for photo- catalytic selective oxidation of HMF into 2,5-diformylfuran (DFF). At the mild reaction conditions, both DFF selectivity and yield can reach up to $\geq 90\%$ over 6% MX/CN. In addition, the MX/CN also shows high activity for selective oxidation of other non-aromatic and aromatic alcohols. Moreover, the reaction conditions are surveyed and the mechanism has been studied. This study provides a way for HMF conversion under mild conditions.

#### 1. Introduction

The selective oxidation of 5-hydroxyfurfural (HMF) into 2, 5-diformylfuran (DFF) is one of the key reactions in the production of chemical products [1–7]. However, its industrial synthesis requires toxic chemical oxidants, expensive precious metals and high temperatures [1–3]. Therefore, it is important to develop the mild reaction to synthesize DFF.

Recently, visible-light-driven photocatalytic selective oxidation of alcohols into corresponding aldehydes has attracted great attention due to its mild reaction conditions, high selectivity and merit to be driven by solar energy [3-9]. For example, Krivtsov et al. found that metal-free g-C<sub>3</sub>N<sub>4</sub> can selective oxidize HMF into DFF under visible light irradiation [7]. However, the DFF selectivity is low (50%). Later, our group reported that HMF can be transformed into DFF over the relative p-n junction CdS/g-C<sub>3</sub>N<sub>4</sub> under visible light irradiation [5], and photocatalytic selective oxidation of HMF to simultaneously produce DFF and H<sub>2</sub> using 2D/2D-3D NiS/Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> hierarchical structure under visible light irradiation [6]. Compared with traditional synthesis process, photocatalytic method exhibits promising future with features of sustainability and green. It has been demonstrated that 2D nanomaterials or structures are the best for photocatalysts [5-7]. More recently, MXene, a new class of 2D material, has received extensive attention for photocatalysis such as nitrogen fixation, hydrogen evolution and CO<sub>2</sub> conversion [10-16]. Its wonderful geometry and the extraordinary electronic structure as well as the controllable surface chemistry indicate that it is a promising and versatile cocatalyst for preparing composite photocatalysts [10-21].

Herein, we report a noble-metal-free photocatalyst MXene/g-C<sub>3</sub>N<sub>4</sub> (MX/CN) for selective conversion of HMF into DFF at mild reaction conditions for the first time, in which 2D MXene (MX) as a cocatalyst is supported on 2D g-C<sub>3</sub>N<sub>4</sub> (CN). The visible-light-driven CN possesses suitable energy band structure, which can provide feasible redox potential for selective conversion HMF into DFF. The MX can significantly improve the separation and transfer efficiencies of the photogenerated charge carriers of the CN. Thus, the MX/CN exhibits high photocatalytic performance for selective conversion of HMF into DFF under visible light irradiation.

#### 2. Experimental section

All the chemicals used in the experiment were commercially and without further purification. Firstly, the MXene ( $Ti_3C_2$ , MX) was obtained by etching  $Ti_3AlC_2$  (Fig. 1). Then, the dispersed MX nanosheets were prepared via ultrasound treatment of MX suspension, and the g- $C_3N_4$  nanosheets were synthesized by the previous report [22]. The MX/CN composites with different amount of MX were fabricated by a self-assembly method. The synthesis procedure, characterization of photocatalysts and photocatalytic activity tests are shown in the supporting information.

#### 3. Results and discussion

XRD patterns of the samples are presented in Fig. S1. After HF

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Fig. 1. Pictorial representation of the procedure for preparing MX/CN.

etching Ti<sub>3</sub>AlC<sub>2</sub> to remove the Al, the XRD diffraction peak of Ti<sub>3</sub>AlC<sub>2</sub> at  $2\theta = 39^{\circ}$  is disappeared, indicating that Ti<sub>3</sub>AlC<sub>2</sub> has been successfully converted into Ti<sub>3</sub>C<sub>2</sub> (MXene, MX). The as-prepared CN shows two characteristic diffraction peaks (27.5° and 13.1°) of the standard g-C<sub>3</sub>N<sub>4</sub>, it is consistent with the literature [22]. For the MX/CN composites, the characteristic diffraction peaks of MX and CN can be clear observed. It is demonstrated that MX and CN keep pure phases in the MX/CN composites. The result can be further confirmed by the FT-IR spectra (Fig. S2). The XPS analysis was used to detect the chemical composition of MX, CN and MX/CN (Fig. S3). The XPS patterns of MX and CN. It can be clear observed that the MX/CN composite is mainly composed of Ti, C, N, O and F. The O and F elements are derived from the surface group of the MX. This is a comment phenomenon for MX prepared by HF etching method [23].

As shown in Fig. S4, The MX after HF etching exhibits 2D stack shape like a book, which is made up of 2D nanosheets and spacings between 2D nanosheets (Fig. S4a and c). However, after 10 h of sonication, the 2D nanosheets-stack structure is broken and 2D dispersed nanosheets are obtained (Fig. S4b and d). The dispersed 2D MX nanosheets would benefit the deposition of 2D CN nanosheets (Fig. S4e). Additionally, the crystal lattice distortion between MX and CN is about 3%, indicating that CN flat can be well combined with 2D MX (Scheme S1). It can be seen that 2D MX is contacted well with 2D CN (Fig. S4f). The further HRTEM image analysis confirms it. Two different types of areas can be observed in Fig. 2. Specifically, one is the crystalline regions with distinctive lattice fringes; the other is amorphous areas with no lattice fringes. Based on the previous studies [10,17,19,20], the lattice spacing of 0.265 nm is contributed to the MX, while the area with no crystal lattice can be assigned to the CN. Moreover, the EDXmapping images further confirm the composed elements of the MX/CN composite (Fig. S5), which is in line with XPS result. In addition, the distribution of these elements (C, N, Ti, O and F) is consistent with the shape of the MX/CN composite.

The photocatalytic activities of these catalysts were evaluated by selective oxidation of HMF into DFF under visible light irradiation. As shown in Fig. 3a, the yields of DFF over CN and MX are 8.8% and



Fig. 2. HRTEM image of 6% MX/CN.



**Fig. 3.** (a) Photocatalytic selective oxidation HMF to DFF with MX, CN and MX/ CN under visible light irradiation for 2 h. (b) Cyclic photocatalytic oxidation of HMF into DFF over the 6% MX/CN composite under visible light irradiation (reaction time 6 h per circle).

11.8%, respectively. However, the MX/CN composites show higher activities than CN and MX. Among the MX/CN composites, the 6% MX/CN shows the highest activity. The DFF yield is about 32.6%, which are 3.7 times that of CN and 2.8 times that of MX. Importantly, the DFF yield of the 6% MX/CN can be improved by increasing reaction time (Fig. S6a). The yield of DFF can reach up to 90% with high selectivity of 97% under visible light irradiation for 10 h. Interestingly, there is still about half of the yield when the reaction system was performed under nitrogen conditions (Fig. S6b). It may be caused by the fact that the surface of MX is rich in free radicals, which would in favor of HMF conversion. Moreover, the yield and selectivity obtained under pure

oxygen conditions are basically the same with that under air atmosphere (Fig. S6b). It indicates that this reaction can be happened under air atmosphere. The stability of the catalyst is an important property for its application. In order to test the reusability of the MX/CN photocatalyst, all reaction conditions are the same as before. Specifically, after each reaction, the catalyst is separated by centrifugation, washed to remove the residual original reaction solution and finally dried at 60 °C. It can be seen from Fig. 3b that the catalytic activity of the MX/CN decreases slightly with recycling runs, which may due to the fact that a small amount of catalyst loss per use.

To investigate the effect of solvents, acetonitrile (CAN), dimethylsulfoxide (DMSO), ethyl alcohol (ETOH), trifluorotoluene (BTF), and isopropanol were used as solvents (Table S1). It can be seen that BTF is the best solvent to convert HMF into DFF. In addition, the different reactants were used as the substrate (Table S2). It can be found that the MX/CN not only has good activity for non-aromatic alcohols, but also has good reactivity for aromatic alcohols. For example, 84% of p-methoxybenzyl alcohol can be selective oxidized into p-methoxybenzaldehyde with the selectivity of 96%.

The promising activities of MX/CN were then investigated by a series of control experiments. It is known that the photocatalytic performance is mainly influenced by three crucial factors: light absorption, surface area or reactive site, and photogenerated charge separation and transportation [6]. Notably, the last one is demonstrated to be the most crucial factor [6]. As shown in Fig. S7, the light absorption of MX/CN is similar to that of CN. Specifically, the band gaps of CN and the 6% MX/ CN are approximately equal to 2.75 and 2.70 eV, respectively. Moreover, the calculated conduction band (CB) and valence band (VB) of CN are -0.94 and 1.81 V, respectively. After MX loaded on the CN, the CB (0.88 V) and VB (1.82 V) of CN are not changed obviously. Compared to the redox potentials of HMF/DFF (1.61 V) and DFF/oxidized DFF (2.03 V), the CN can provide powder and suitable oxidizing ability for selective oxidation of HMF into DFF. Fig. S8 shows the nitrogen adsorption-desorption isotherms and the corresponding pore-size distribution curves of MX, CN and 6% MX/CN. The surface areas of MX, CN and 6% MX/CN are 23.9, 7.2 and 19.9  $m^2 \ g^{-1},$  respectively. The pore volumes of MX, CN and 6% MX/CN are 0.139, 0.060 and  $0.132\ \text{cm}^3\ \text{g}^{-1},$  respectively. Clearly, the increased surface area and pore volume can promote mass transfer. Fig. S9a shows that the 6% MX/CN catalyst exhibits the highest photocurrent value than other samples, which means that the 6% MX/CN has high electron-hole separation efficiency. In addition, the electrochemical impedance spectra indicate that the transfer efficiency of the photogenerated carriers over the 6% MX/CN is higher than that over MX and CN (Fig. S9b). The recombination of the photogenerated electrons and holes is further analyzed by PL. Among the MX/CN composites, the 6%MX/CN with the best activity has the lowest emission peak, indicating that the photogenerated carrier recombination rate of the 6%MX/CN composite is the lowest. This indicates that the addition of MX in the MX/CN can effectively suppress the recombination of photogenerated electron-hole pairs under visible light irradiation, thereby greatly improving the photocatalytic efficiency. This conclusion is consistent with the photocatalytic activity and the results of photocurrent and impedance.

In order to study the reactive species during photocatalytic oxidation of HMF, different scavengers were added into the reaction system to eliminate the corresponding reactive species, and the effect of the reactive species can be judged by the activity change of the reaction. As shown in Fig. S11, when the introduction of p-benzoquinone (BQ) or triethanolamine (TEOA) into the reaction system, the conversion of HMF and the yield of DFF are significantly decreased. However, the activity of MX/CN is not reduced as isopropanol (IPA) or carbon tetrachloride (CCl<sub>4</sub>) was added into the reaction system. These evidence that  $\cdot O_2^-$  and h<sup>+</sup> are active species for photocatalytic selective oxidation of HMF. Moreover, the  $\cdot$ OH and  $\cdot O_2^-$  were measured by ESR technique. As shown in Fig. S12, the MX/CN and CN show strong DMPO- $\cdot O_2^-$  signals under light irradiation. Importantly, with the



**Fig. 4.** The illustration of the mechanism for selective oxidation of HMF into DFF over the MX/CN under visible light irradiation.

extension of the reaction time, the intensity of the DMPO- $\cdot O_2^-$  signal over MX/CN is increasing. It is in line with the above results that the  $\cdot O_2^-$  is the main active species. However, the ESR signals of DMPO- $\cdot OH$  cannot be observed over both CN and MX/CN (Fig. S13), implying that  $\cdot OH$  cannot be created. It is reasonable to get this result, because the valence band potential of CN is lower than the redox potential of  $\cdot OH$  production [24].

Based on the above experimental data and analysis, we propose a possible photocatalytic mechanism (Fig. 4). First, the main photocatalyst CN provide photogenerated electrons and holes with suitable redox potentials (that is applicable CB and VB positions). The electrons photoexcited on the CB transfer to the cocatalyst MX and are captured by  $O_2$  to form  $\cdot O_2^-$  on the surface. The holes photogenerated on the VB meet the selective oxidation of HMF to DFF, and DFF cannot be converted into the corresponding acid. Therefore, under visible light irradiation, HMF can be oxidized into DFF over MX/CN composite photocatalyst with high selectivity and conversion.

#### 4. Conclusion

The MX/CN composite with applicable CB and VB positions has been successful fabricated. The 6% MX/CN composite exhibits the highest efficiency of separation and transfer of the photogenerated electron-hole pairs under visible light irradiation. Under visible light irradiation for 10 h, the yield and selectivity of DFF can reach up to 90% and 97%, respectively. Besides HMF, aromatic alcohols and other non-aromatic alcohols can also be effectively converted into the corresponding aldehydes over the MX/CN composite under visible light irradiation. This study demonstrates that the MXene is an efficient cocatalyst to improve the reactivity of  $g-C_3N_4$  for selective oxidation of alcohols into fine chemicals under mild reaction conditions.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2020.106152.

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