Ti₃C₂ Mxene/porous g-C₃N₄ interfacial Schottky junction for boosting spatial charge

2

separation in photocatalytic H₂O₂ production

- 3 Yang Yang ^{a, 1}, Zhuotong Zeng ^{b,1}, Guangming Zeng ^{a, *}, Danlian Huang ^{a, *}, Rong Xiao ^{b, *}, Chen
- 4 Zhang^a, Chengyun Zhou^a, Weiping Xiong^a, Wenjun Wang^a, Min Cheng^a, Wenjing Xue^a, Hai Guo^a,
- 5 Xiang Tang^a, Donghui He^a
- ⁶ ^a College of Environmental Science and Engineering, Hunan University and Key Laboratory of
- 7 Environmental Biology and Pollution Control, Ministry of Education (Hunan University), Changsha

×'

- 8 410082, P.R. China
- 9 ^b Department of Dermatology, Second Xiangya Hospital, Central Scott University, Changsha

- 10 410011, P.R. China
- 11
- 12
- 13

^{*} Corresponding authors at: College of Environmental Science and Engineering, Hunan University, Changsha, 410082, PR China. *E-mail addresses*: zgming@hnu.edu.cn (G. Zeng), huangdanlian@hnu.edu.cn (D. Huang) and xiaorong65@csu.edu.cn (R. Xiao). ¹These authors contribute equally to this article.

14 Abstract

The development of efficient photocatalysts for the production of hydrogen peroxide (H_2O_2) is a 15 promising strategy to realize solar-to-chemical energy conversion. Graphitic carbon nitride $(g-C_3N_4)$ 16 presents giant potential for photocatalytic H₂O₂ production, but the sluggish charge separation 17 depresses its photocatalytic performance. Herein, an interfacial Schottky junction composed of Ti₃C₂ 18 nanosheets and porous $g-C_3N_4$ nanosheets (TC/pCN) is constructed by a facile electrostatic self-19 assembly route to significantly boost the spatial charge separation to promote the activation of 20 molecular oxygen for H_2O_2 production. As the optimal sample, TC/pCN-2 sesses the highest H₂O₂ 21 production rate (2.20 µmol L⁻¹ min⁻¹) under visible light irradiation 22 $2\overline{0}$ nm), which is about 2.1 times than that of the porous $g-C_3N_4$. The results of supervise radical detection and rotating disk 23 electrode measurement suggest that the two-step size electron reduction of oxygen is the 24 predominant reaction step during this photocata tic H₂O₂ production process. The enhanced 25 hation of Schottky junction and subsequent built-in photocatalytic performance is ascribed 26 electric field at their interface, which accelerate the spatial charge separation and restrain the charge 27 ides an in-depth understanding of the mechanism of photocatalytic recombination. This work 28 pro H_2O_2 production, and gives ideas for the design of highly active materials for photocatalytic H_2O_2 29 production. 30

Keywords: Photocatalytic H₂O₂ production; Ti₃C₂ Mxene; Porous g-C₃N₄; Schottky junction; Spatial
 charge separation

34 1. Introduction

Hydrogen peroxide (H₂O₂) is a clean and multifunctional oxidant whose byproduct is only water 35 [1, 2]. It has been widely used in the field of chemical industry and environmental management, such 36 as pulp bleaching, organic synthesis, disinfection, and water remediation [3-7]. Recently, H_2O_2 has 37 also attracted tremendous interest as an ideal fuel cell energy carrier that can replace H₂ [8-10]. On the 38 one hand, H_2O_2 can be stored and transported more conveniently and safely than that of H_2 due to its 39 water solubility [11-13]. On the other, compared to two-compartment H₂ based fuel cell, the structure 40 and scale of single-compartment direct peroxide-peroxide fuel cell (DIPEC are more advanced [14, 41 15]. However, the anthraquinone method as the most used method 42 \mathbf{p}_2 production is limited by its complicated routes, high costs, and toxic by-products [16] Moreover, the synthesis of H₂O₂ in the 43 presence of H_2 and O_2 though noble metal catalysts has the problem of potentially explosive nature, 44 and the method of obtaining H₂O₂ via electrocate vic oxygen reduction reaction (ORR) is also 45 restricted by its high energy consumpting . Therefore, the safe and efficient, environmental-46 friendly and low cost technology for H_2 production is urgently desired [19-21]. 47

ng riethods for H_2O_2 production, semiconductor photocatalysis owns 48 As one of the most omis the advantages of safety, pollution-free, and energy conservation [22-25]. In this process, 49 photogenerated electrons on the conduction band originated from semiconductor materials can reduce 50 O_2 to produce H_2O_2 . Among the various semiconductor materials, graphitic carbon nitride (g- C_3N_4) 51 has drawn much attentions owing to its efficient visible light absorption, proper conduction band edges, 52 high chemical stability, and excellent environmental benignity [26-28]. Since Shiraishi et al. [29] 53 firstly reported that g-C₃N₄ could highly selective produce H₂O₂ in an alcohol/water mixture with O₂ 54 under visible light irradiation ($\lambda > 420$ nm) due to the efficient formation of 1,4-endoperoxide species, 55

many investigations have been made in this field [30, 31]. Nevertheless, the bulk $g-C_3N_4$ usually presents poor photocatalytic activity because of the low separation and transfer efficiency of photogenerated charge carriers. Therefore, various strategies have been developed for $g-C_3N_4$, such as defects engineering [32-34], heteroelements incorporating [35], and other species introducing [36, 37], aiming at boosting the spatial charge separation, and thus improving the yield of H₂O₂ production.

Mxenes, a novel family of two-dimensional (2D) materials obtained by selectively etching the A 61 layers from the MAX phases (M represents early transition metal, A represents A-group element, and 62 X represents C and/or N element), have stimulated growing concerns ricer [38, 39]. Among them, 63 Ti_3C_2 as a typical Mxene has been widely investigated since it w oxted in 2011 because of its 64 unique features, such as superior electrical conductivity, goo structural stability, and excellent visible 65 light harvesting ability [40]. Moreover, Ti₃C₂ could be combined with semiconductor photocatalysts 66 to form Schottky junctions, which greatly promote the separation of photogenerated charge carriers. 67 Thus, in addition to the bright future in of Li-ion batteries and supercapacitors, Ti₃C₂ also 68 presents great potentials in photoc talys [41, 42]. For example, Ran et al. [43] demonstrated that 69 Ti₃C₂ could remarkably memory the photocatalytic H₂ production performance of CdS under visible 70 light irradiation ($\lambda \ge 420$ nm). The H₂ production activity and the apparent quantum efficiency (AQE) 71 of CdS/Ti₃C₂ hybrid photocatalyst could reach to 14342 μ mol h⁻¹ g⁻¹ and 40.1%, respectively, which 72 could be ascribed to the excellent electrical conductivity, desirable Fermi level position and the 73 formation of Schottky junction. Besides, Cao et al. [44] also found that the 2D/2D Ti₃C₂/Bi₂WO₆ 74 heterostructure exhibited significantly enhanced activity toward photocatalytic CO₂ reduction. 75 Benefiting from the improved charge transfer ability, the total yield of CH₄ and CH₃OH on 76 Ti₃C₂/Bi₂WO₆ was 4.6 times than pristine Bi₂WO₆. These reports demonstrated that Ti₃C₂ could 77

greatly promote the separation and transfer of photogenerated charge carriers, and thus improving the photocatalytic performance. Theoretically, when the metal's work function is greater than the n-type semiconductor's work function, a Schottky junction can be established after their intimate contact [45-47]. As the work function of Ti_3C_2 is greater than that of g-C₃N₄, it can be reasonably deduced that the interfacial Schottky junction composed of 2D Ti_3C_2 nanosheets and 2D porous g-C₃N₄ nanosheets might be a superior catalyst for photocatalysis, which may own enhanced visible light absorption, accelerated spatial charge separation, and a desirable yield of H₂O₂ [40, 48].

In this study, a novel Ti₃C₂ Mxene/porous g-C₃N₄ (TC/pCN) interf al Schottky junction is 85 fabricated via a facile electrostatic self-assembly process. The perf of TC/pCN photocatalyst 86 for H₂O₂ production under visible light irradiation ($\lambda > 420$ m) is investigated. Based on the results 87 of superoxide radical detection, rotating disk electrode medsurement, photoelectrochemical properties 88 and band structure analysis, the possible production mechanism of H₂O₂ over the TC/pCN 89 photocatalyst is proposed. The introduc $_{3}C_{2}$ into g-C₃N₄ not only boosts the spatial charge 90 separation, but also promotes the production of H₂O₂ under visible light. 91

92 2. Experimental section

- 93 2.1. Preparation of samples
- 94 2.1.1. Preparation of the porous $g-C_3N_4$ nanosheets

The porous g-C₃N₄ nanosheets were prepared by a chemical exfoliation method. Bulk g-C₃N₄ was first obtained by the thermal pyrolysis of urea on a semiclosed crucible at 520 °C for 2.5 h with a heating rate of 10 °C min⁻¹. Then 1 g of the bulk g-C₃N₄ was dispersed in 200 mL of 0.5 mol L⁻¹ hydrochloric acid (HCl) solution under ultrasonic treatment. After ultrasonication for 1 h, the mixture was stirred for 4 h, then filtered and washed with deionized water until the pH \geq 6. Finally, the porous 100 g-C₃N₄ nanosheets were obtained by drying the product at 60 $\,^{\circ}$ C for 12 h.

101 2.1.2. Preparation of the Ti_3C_2 nanosheets

102 The Ti_3C_2 nanosheets were prepared according to the previous report [44]. Typically, 1 g of Ti₃AlC₂ was dispersed in 20 mL of hydrofluoric acid (HF) solution (content \geq 40.0%). After stirring 103 for 72 h, the suspension was centrifuged, washed with deionized water until the pH \geq 6, and dried for 104 8 h under vacuum at 60 °C. Then, the precursor was added into 20 mL of dimethyl sulfoxide (DMSO) 105 and kept stirring for 12 h. The mixture was centrifuged, washed with deionized water for several times 106 to remove the remainder DMSO, and dried for 8 h under vacuum at 60° Eubsequently, 0.5 g of the 107 dried sample was dispersed in 50 mL of deionized water and un 108 ind-treated for 1 h under N₂ protection followed by 1 h of centrifugation at 3500 rpm to move the unexfoliated sample. Finally, 109 the supernatant of Ti_3C_2 nanosheets was obtained, and is concentration was measured to be 1 mg mL⁻¹. 110 2.1.3. Preparation of the Ti_3C_2 /porous g-C₃N₄($T\dot{C}/p$ CN) sample 111

The Ti₃C₂/porous g-C₃N₄ (TC/pCI was prepared by a facile electrostatic self-assembly 112 method. Typically, 0.3 g of the porous g-C₃N₄ was dispersed in 50 mL of deionized water and 113 sequently, a certain volume of the Ti_3C_2 solution was added dropwise ultrasound-treated for 0. 114 into the above suspension and ultrasound-treated for another 0.5 h to delaminate and strengthen the 115 interfacial interaction. The mixture was then stirred for 4 h to build the mutual electrostatic attraction 116 117 The mass ratios of Ti₃C₂ to porous g-C₃N₄ were set as 1%, 2%, and 5% by controlling the added 118 volume of Ti_3C_2 solution, and the obtained samples were designated as TC/pCN-X (X = 1, 2, 5). The 119 porous $g-C_3N_4$ with no Ti_3C_2 solution adding was defined as pCN. 120

121 2.2. Characterization

122	Zeta potential was detected by a Zetasizer Nano ZS (Malvern, UK). Transmission electron
123	microscopy (TEM) images were collected on a Tecnai G2 F20 S-TWIN electron microscope (FEI,
124	USA). Atomic force microscopy (AFM) images were acquired on a Dimension Edge (Bruke,
125	Germany). Energy-dispersive X-ray spectroscopy (EDS) mapping images were obtained on a Quanta
126	250 field emission scanning electron microscopy (FESEM, FEI, USA). Brunauer-Emmett-Teller (BET)
127	specific surface areas were measured by N_2 adsorption-desorption method using an ASAP 2020 HD88
128	instrument (Micromeritics, USA). X-ray diffraction (XRD) patterns were tested on a D8 Advance X-
129	ray diffractometer (Bruke, Germany) with Cu Ka radiation. Fourier transform infrared (FTIR) spectra
130	were monitored using a KBr pellet on a TENSOR 27 spectrometer (Brake, Germany). Ultraviolet
131	visible diffuse reflectance spectra (UV-vis DRS) were measured on a Cary 300 spectrophotometer
132	(Varian, USA). X-ray photoelectron spectroscopy (X/S) was performed on a Escalab 250Xi
133	spectrometer (Thermo, USA) with Al Ka radiation. Photoluminescence (PL) spectra were conducted
134	on a F-7000 fluorescence spectrophotomete (Fitachi, Japan) under 320 nm excitation. Time-resolved
135	photoluminescence (TRPL) spectrowere recorded on a FLS 980 fluorescence spectrophotometer
136	(Edinburgh Instruments, UK). Ultraviolet photoemission spectroscopy (UPS) was carried out on a
137	Escalab 250Xi spectrometer Thermo, USA) using He I resonance lines (21.2 eV).

138 2.3. Photocatalytic H₂O₂ production

The photocatalytic H_2O_2 production experiments were carried out as follows. First, 50 mg of catalyst powder was uniformly dispersed into 50 mL of aqueous solution containing 10 vol% isopropanol (IPA) with ultrasonication for 10 min. Then O_2 was continually bubbled through the suspension and stirred in the dark for 1 h to achieve the adsorption-desorption equilibrium before irradiation. Finally, the suspension was irradiated with a 300 W xenon lamp (PLS-SXE300/300UV, Perfect Light, China) equipped with a 420 nm cutoff filter under stirring. At certain time intervals, 3 mL of the suspension was collected. After removing the catalyst powder by centrifugation and filtration with a millipore filter (0.45 μ m), the H₂O₂ concentration was measured by iodometry [30]. The H₂O₂ decomposition behavior of the photocatalysts was studied by dispersing 50 mg of sample in 50 mL of 1 mmol L⁻¹ H₂O₂ solution and irradiating for 1 h visible light under continuous stirring. To evaluate the stability and recyclability of the photocatalysts, after reaction, the samples were collected by centrifugation and washed with deionized water and ethanol respectively, and dried for the cycle

151 experiments.

152 2.4. Superoxide radical detection



The electron spin response (ESR) signal of $\cdot O_2^$ obtained from a JEOL JES-FA200 153 where 5,5-dimethyl-1-pyrroline N-oxide spectrometer under visible light irradiation ($\lambda > 420$ np. 154 (DMPO) was used as spin-trapped reagent. The concentration of $\bullet O_2^-$ was evaluated by nitroblue 155 tetrazolium (NBT) transformation test, 0 mg of the sample was dispersed in 50 mL of 0.01 156 mmol L⁻¹ NBT aqueous solution NBT concentration was measured by a Shimadzu UV-2700 157 ristic absorbance peak (260 nm). spectrophotometer at its 158 arac

159 2.5. Electrochemical and phytoelectrochemical measurement

Rotating disk electrode (RDE) measurement was conducted on a Chenhua CHI 760E electrochemical workstation with a three-electrode cell. The Ag/AgCl electrode and Pt wire electrode were used as the reference electrode and counter electrode, respectively. The working electrode was prepared as follows: 5 mg of the sample was added into 0.5 mL of 10 vol% Nafion solution (diluted with ethanol). Then 5 μ L of the suspension was uniformly dropped on a glassy carbon electrode (diameter of 5 mm) and the electrode was dried at room temperature. The linear sweep voltammetry 166 (LSV) curves were collected in an O₂-saturated 0.1 mmol L^{-1} phosphate buffer solution (pH 7) with a 167 scan rate of 10 mV s⁻¹.

168 The transient photocurrent response curves, electrochemical impedance spectroscopy (EIS) and Mott-Schottky plots were obtained on a Chenhua CHI 760E electrochemical workstation with a three-169 electrode cell. The Ag/AgCl electrode and Pt wire electrode were used as the reference electrode and 170 counter electrode, respectively. The working electrode was prepared as follows: 5 mg of the sample 171 was added into 1 mL of 0.5% nafion solution under ultrasonication for 1 h. The suspension was then 172 dropped on a fluorine-doped tinoxide (FTO) glass $(1 \times 2 \text{ cm}^2)$ which we pre-cleaned by acetone, 173 ethanol and deionized water, respectively. The obtained electrode ried at 80 °C for 4 h and 174 calcined at 120 °C for 1 h. 0.2 mmol L⁻¹ Na₂SO₄ aqueous Lution was used as the electrolyte. The 175 light source was provided by a 300 W xenon lam XE300/300UV, Perfect Light, China) 176 equipped with a 420 nm cutoff filter. The transient shotocurrent response was tested on an applied 177 ectrochemical impedance spectroscopy (EIS) was voltage of 0 V with the light on or o 178 collected on an applied voltage of V with an amplitude of 0.005 V over a frequency between 10^{-2} 179 curves were also collected at the frequency of 1000 Hz. and 10⁵ Hz. Moreover, N 180

- 181 **3. Results and discussion**
- 182 3.1. Synthesis and physicochemical properties

Fig. 1 displays the synthetic process of TC/pCN interfacial Schottky junction. Initially, Ti_3AlC_2 MAX phase was etched into multilayer Ti_3C_2 by HF. The multilayer Ti_3C_2 was subsequently exfoliated into few-layer ultrathin Ti_3C_2 nanosheets under a DMSO assisted ultrasonication. Meanwhile, the porous g-C₃N₄ was obtained from the delamination of bulk g-C₃N₄ by HCl assisted ultrasonication. Zeta potential analysis shows that the potential of Ti_3C_2 (Fig. S1a) and porous g-C₃N₄ (Fig. S1b) surface is negative (-27 mV) and positive (21 mV), respectively. Thus, the spontaneous self-assembly between the positively charged porous $g-C_3N_4$ and the negatively charged Ti_3C_2 was realized by the electrostatic interaction.

The morphology and microstructure of the samples were characterized by TEM. As displayed in 191 Fig. 2a, the Ti₃C₂ nanosheets are almost transparent, indicating the existence of ultrathin nanostructure. 192 The darker color is observed in some place, which can be ascribed to the crumple of highly flexible 193 Ti₃C₂ nanosheets [49]. As for g-C₃N₄ (Fig. 2b), it presents typical sheet-like and porous morphology. 194 Meanwhile, it can be clearly seen from Fig. 2c that the TC/pCN-Lpa esses 2D nanostructure 195 consisted of Ti₃C₂ nanosheets and porous g-C₃N₄ nanosheets. 196 cause of the electrostatic attraction between the two parts, their contact is quite in mate. Moreover, high-resolution TEM 197 (HRTEM) was performed to obtain more information about me two species. From Fig. 2d, no clear 198 fringe can be observed in the part of porous \underline{g} - C_3 N, due to its low crystallinity, whereas an obvious 199 lattice fringe with the measured spacing m can be found in Ti_3C_2 , which is in good agreement 200 [41] Besides, AFM image (Fig. 2e) and the corresponding height with the $(0\overline{1}10)$ crystal plane of T₁₃C 201 at the TC/pCN-2 possesses typical 2D hierarchical nanostructure. distribution profile (Fig. S) sho 202 Additionally, FESEM-EDS lemental mapping was collected to further authenticate the presence of 203 the hybridization. As shown in Fig. 2g, the elements of C, N, Ti, F and O distribute across the TC/pCN-204 2 uniformly, and no other foreign elements can be detected, thereby validating the elemental 205 composition of the sample qualitatively. Therefore, these results demonstrate the successful assembly 206 of Ti₃C₂ nanosheets with porous g-C₃N₄ nanosheets for TC/pCN-2 interfacial Schottky junction. The 207 208 BET specific surface area of the samples were analyzed by N₂ adsorption-desorption isotherms shown in Fig. S2. The BET specific surface area of the pCN, TC/pCN-1, TC/pCN-2, TC/pCN-5 and Ti₃C₂ 209

samples are 52.37, 54.70, 59.34, 56.37 and 8.45 m² g⁻¹, respectively. As the content of Ti_3C_2 increases, the specific surface area of the composite gradually increases and the TC/pCN-2 sample has the largest surface area. With further increasing the Ti_3C_2 content, the specific surface area of the composite decreases because of the relatively small surface area of Ti_3C_2 .

The crystal structure of the samples was analyzed by XRD. The sample with intense peaks in Fig. 214 3a can be assigned to MAX phase Ti₃AlC₂. After HF etching treatment, the diffraction peaks of (002) 215 and (004) shift to lower degrees and the most intense diffraction peak at 39.0 ° disappears, suggesting 216 the removal of Al element in Ti₃AlC₂ and successful transformation $T_{i_3}AlC_2$ to $T_{i_3}C_2$ [41]. 217 Meanwhile, most of the peaks in Ti₃C₂ become weaker and broad empared to Ti₃AlC₂, which is 218 ascribed to the thinner layered structure of Ti₃C₂. Fig. 3 splays the XRD patterns of TC/pCN 219 samples with different Ti₃C₂ contents. All of the sample esent two similar diffraction peaks. The 220 peak (002) at 27.5 ° is indexed to the stacking reflection of conjugated planes, and the other peak (110) 221 s [50]. No distinct diffraction peaks of Ti₃C₂ can be at 13.1 ° represents the repetition of non 222 detected, indicating the well distribution and limited amount of Ti₃C₂ in the TC/pCN samples. Fig. 3c 223 samples. No clear peaks can be observed in the Ti_3C_2 and the framework of shows FTIR spectra of the 224 TC/pCN is similar to that of g-C₃N₄, suggesting that the signals in TC/pCN are from g-C₃N₄. 225 Specifically, the peak around 810 cm⁻¹ is ascribed to the breathing vibration of triazine units, and the 226 peaks between 1200 and 1700 cm⁻¹ are assigned to the skeletal stretching of C-N heterocycles [51, 52]. 227 Additionally, the peaks between 3000 and 3400 cm⁻¹ belong to the -NH and -OH stretching vibrations 228 because of the free amino groups and adsorbed hydroxyl species [53, 54]. The optical absorption 229 properties of the samples were studied by UV-vis DRS. As displayed in Fig. 3d, pristine porous g-230 C₃N₄ exhibits an absorption band around 450 nm. The bare Ti₃C₂ presents a broad and intense 231

absorption from 300 to 800 nm. After hybridizing porous $g-C_3N_4$ with Ti_3C_2 , the visible-light harvesting ability is significantly enhanced. The absorbance in the visible light region of the TC/pCN becomes stronger as the content of Ti_3C_2 increases. These changes are further evidenced by the physical appearance changes. As shown in the insert image of Fig. 3d, the color of the sample change from bright yellow to dark yellow with the increase of Ti_3C_2 content.

The surface chemical composition and states of the samples were investigated by XPS. As 237 displayed in the XPS survey spectra (Fig. 4a), C, N and O elements related to g-C₃N₄ can be seen in 238 TC/pCN-2, while Ti and F elements related to Ti₃C₂ cannot be clearly a reverved due to their weak 239 intensity. The presence of Ti and F elements in TC/pCN-2 are further 240 enfied by the high-resolution spectra, demonstrating that the Ti_3C_2 are successfully incorrected into the g-C₃N₄. Fig. 4b shows the 241 $_{2p}$ spectrum of Ti₃C₂ are deconvoluted high-resolution Ti 2p spectra of Ti₃C₂ and TC/pCN-2 TP 242 into five peaks, in which 455.3 and 461.3 eV can be ssigned to Ti-C, 457.3 and 463.2 eV is related to 243 red to Ti₃C₂, the binding energies of all Ti-related Ti-O, and 459.3 eV belongs to Ti-F [4 244 peaks in TC/pCN-2 exhibit a negative shift. The high-resolution F 1s spectra of Ti₃C₂ and TC/pCN-2 245 b. to peaks at 684.9 and 689.8 eV can be detected, corresponding to are provided in Fig. 4c. 246 F-Ti and F-C, respectively [3]. In comparison with the F 1s spectrum of Ti₃C₂, the binding energies 247 in TC/pCN-2 also show a negative shift. In addition, Fig. 4d displays the high-resolution C 1s spectra 248 of the samples. All the binding energies at 284.8 eV are ascribed to C-C (adventitious carbon) [50]. 249 Ti₃C₂ presents three characteristic peaks at 281.8, 286.3 and 288.9 eV, which are attributed to the C-250 Ti, C-O and C-F, respectively [44]. As for TC/pCN-2, the binding energy of C 1s in 285.8 and 288.4 251 252 are assigned to the C-N and C-N=C [55], which exhibits a positive shift in comparison with that in the g-C₃N₄. No obvious C-Ti can be detected in TC/pCN-2 because of the limited content of Ti₃C₂. Fig. 253

4e demonstrates that the O 1s region of Ti_3C_2 can be divided into three species (O-Ti, OH-Ti and adsorbed H₂O or CO₂) [44], which are located at 529.6, 530.8 and 531.8 eV, respectively. Only peak about adsorbed H₂O or CO₂ can be obviously found in TC/pCN-2. Besides, TC/pCN-2 presents N 1s spectrum similar to pCN, as shown in Fig. 4f, the peaks located at 398.9, 399.9, 401.2 and 404.2 eV are related to C-N=C, N-C₃, C-NH and charging effects in heterocycles, respectively [56]. These changes demonstrate that electrons transfer from g-C₃N₄ to Ti₃C₂ in the TC/pCN-2 sample due to the strong Schottky effect between the g-C₃N₄ and Ti₃C₂, increasing the electron density of Ti₃C₂.

261 *3.2. Spatial charge separation ability*

The spatial charge separation ability of the TC/pCN interfa 262 ottky junction during the photocatalysis was investigated. Fig. 5a displays the transport photocurrent response curves of the 263 samples on typical cycles of visible light irradiation on those which directly interrelates with their 264 spatial charge separation ability [57-59]. With the light on, the current is generated immediately, 265 demonstrating the high photo-sensitiv ficient spatial charge separation of the samples. 266 Compared to pCN, all the TC/pCN X (X = 1, 2, 5) samples show elevated photocurrent response, and 267 p plotocurrent density, indicating that the Ti_3C_2 can greatly accelerate TC/pCN-2 presents the ma 268 vimu the spatial charge separation on the samples. Moreover, the spatial charge separation efficiency of the 269 samples was examined by the PL technique [60, 61]. As shown in Fig. 5b, a broad PL band (425-550 270 nm) with a peak at 465 nm is observed on pCN, which can be ascribed to the radiative recombination 271 272 of electron-hole pairs. The introduction of Ti₃C₂ leads to substantial suppression of radiative electronhole recombination in g-C₃N₄. The TC/pCN-2 presents the weakest PL intensity, implying the fastest 273 274 spatial charge separation [62, 63]. To get more information about spatial charge separation and transfer, TRPL test were conducted. As shown in Fig. 5c, the fluorescence decay curves can be fitted by a 275

276 biexponential model (Eq. (1)):

$$R(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2)$$
(1)

Where B_1 and B_2 are the weight factor, and τ_1 and τ_2 are the short and long fluorescent lifetime, respectively. Clearly, both the short and long lifetimes of TC/pCN-2 ($\tau_1 = 2.75$ ns, 41.09%; $\tau_2 = 10.52$ ns, 58.91%) are prolonged in comparison with those of pCN ($\tau_1 = 2.51$ ns, 37.01%; $\tau_2 = 9.12$ ns, 62.99%). Therefore, the average fluorescent lifetime (Ave. τ) is calculated via the following Eq. (2):

282
$$\tau_{\text{ave}} = \frac{B_1 \tau_1^2 + B_2 \tau_2^2}{B_1 \tau_1 + B_2 \tau_2}$$
(2)

and the average fluorescent lifetime increases from 8.20 ns (pCN) 9.32 ns (TC/pCN-2), 283 demonstrating that the incorporation of Ti₃C₂ on g-C₃N₄ can effic 284 celerate the spatial charge separation and depress the charge recombination, and thus longate the lifetime of photogenerated 285 charge carriers [43, 57]. EIS are employed to reflect the ectronic conductivity and the interfacial 286 charge transfer behavior of the samples [64, 65]. s displayed in Fig. 5d, TC/pCN-2 presents an 287 obvious decrease in the semicircle diam bared with that of pCN, implying that the TC/pCN-288 2 interface has a better electrical conductivity, which is beneficial for achieving efficient spatial charge 289 separation and transfer de otocatalytic process. 290

291 3.3. Photocatalytic H_2O_2 production

The photocatalytic H₂O₂ production ability of the TC/pCN interfacial Schottky junction was evaluated by O₂ reduction from isopropanol solution under visible light irradiation ($\lambda > 420$ nm). As shown in Fig. 6a, the yield of H₂O₂ is distinctly increased by compounding Ti₃C₂ with porous g-C₃N₄. The TC/pCN-2 presents the best photocatalytic performance, the amount of H₂O₂ (131.71 µmol L⁻¹) produced after 60 min of visible light irradiation is about 2.1 times than that of the pCN (61.63 µmol L⁻¹). Fig. S3 displays the UV-vis absorption spectrum changes on TC/pCN-2 among the H₂O₂ production process. It can be clearly observed that the absorbance at 350 nm significantly increases with the prolongation of irradiation time. However, when the mass ratio of Ti_3C_2 to porous g-C₃N₄ is excessive (TC/pCN-5), the yield of H₂O₂ decreases presumably because of the light shielding effect. Meanwhile, control experiments reveal that H₂O₂ can hardly be detected in the absence of photocatalyst or only in the presence of Ti₃C₂, indicating the decisive role of photocatalysis in the H₂O₂ production process.

In the process of photocatalytic H_2O_2 production, the formation and decomposition of H_2O_2 exist simultaneously since H_2O_2 can be decomposed by photogenerated charge conjects. Therefore, the zeroorder kinetic (H_2O_2 formation) and first-order kinetic (H_2O_2 decomposition) are utilized to evaluate the behavior of H_2O_2 production. The kinetic model shown in Eq. (3) provides the H_2O_2 concentration as a function of reaction time [66].

[

309

$$H_2 O_2] = \frac{K_f}{T} (T \exp(-K_d t))$$
 (3)

L⁻¹ min⁻¹) and decomposition rate constant (min⁻¹), $K_{\rm f}$ and $K_{\rm d}$ are the formation rate consta 310 respectively. The values of K_f and K_d are estimated by fitting the data in Fig. 6a into Eq. (3) and the 311 $K_{\rm f}$ the K_f value significantly increases by the introduction of Ti₃C₂, results are displayed in 312 reaching a maximum at TCpCN-2 which is approximately 2.1 times than pCN (from 1.12 to 2.38 313 μ mol L⁻¹ min⁻¹), while the K_d value of TC/pCN-2 (2.38×10⁻³ min⁻¹) is smaller than that of pCN 314 $(2.65 \times 10^{-3} \text{ min}^{-1})$. The positive effect of Ti₃C₂ on the K_f is well matched with the overall H₂O₂ 315 production. These results demonstrate that the combination of porous g-C₃N₄ with Ti₃C₂ can promote 316 the formation of H_2O_2 and depress decomposition of H_2O_2 . 317

To further investigate the decomposition behavior of H_2O_2 in the presence of photocatalysts under visible light irradiation, the H_2O_2 decomposition experiments were performed with an initial H_2O_2 concentration of 1 mmol L⁻¹. As exhibited in Fig. 6c, the H₂O₂ decomposes about 17.5% on TC/pCN-2 after 60 min of visible light irradiation, which is lower than that on pCN (19.0%). In the absence of photocatalysts, the decomposition of H₂O₂ is negligible. The decomposition rate constant (K_d ') are estimated by the following Eq. (4):

324

$$K'_d = \frac{-\ln(C_t/C_0)}{t} \tag{4}$$

Where C_t is the H₂O₂ concentration at time t, C_0 is the initial concentration of H₂O₂ (1 mmol L⁻¹). The results in Fig. S4 illustrate that the K_d ' value of TC/pCN-2 (3.21×10⁻³ min⁻¹) is smaller than that of pCN (3.49×10⁻³ min⁻¹). The results further confirm the inhibition of H₂O decomposition in the TC/pCN-2, which will elevate the yield of H₂O₂ production.

Besides, the recyclability and physicochemical stability of the TC/pCN-2 in the photocatalytic 329 H₂O₂ production were also investigated. The cyclic experiments were conducted and the results are 330 exhibited in Fig. 6d. Obviously, the yield of H₂O can still reach to 123.83 μ mol L⁻¹ after four 331 consecutive cycles. The physicochemi ties of the TC/pCN-2 after photocatalytic H₂O₂ 332 production for four times were further characterized by the XRD (Fig. S5), FTIR (Fig. S6) and XPS 333 viols changes can be seen, demonstrating that the photocatalyst is (Fig. S7) techniques, and 334 no d stable. Moreover, the H₂O₂ production activity of TC/pCN-2 (131.71 μ mol g⁻¹ h⁻¹) is higher than most 335 of other g-C₃N₄-based photocatalysts reported previously (Table 1), suggesting that Ti₃C₂/porous g-336 C_3N_4 photocatalyst is a promising photocatalytic system for H_2O_2 production. 337

339 Table 1

340	Comparison	with other	g-C ₃ N ₄ based	photocataly	vsts for H2O2	production.
J 1 0	Comparison	with other	g-Corve Dascu	photocatar	ysts 101 11202	production.

Photocatalysts	Dosage	Reaction solution	Light source	H ₂ O ₂ production activity	Ref.
	(g L ⁻¹)			(µmol g ⁻¹ h ⁻¹)	
g-C ₃ N ₄ /PDI	1.67	Water (30 mL)	$2 \text{ kW XL} (\lambda > 420 \text{ nm})$	21.08	[36]
g-C ₃ N ₄ /PDI/rGO	1.67	Water (30 mL)	$2 \text{ kW XL} (\lambda > 420 \text{ nm})$	24.17	[37]
3DOM g-C ₃ N ₄ -PW ₁₁	1.00	Water (100 mL)	$300 \text{ W XL} (\lambda > 320 \text{ nm})$	35.00	[14]
Ag@U-g-C3N4-NS	1.00	Water (100 mL)	$300 \text{ W XL} (\lambda > 420 \text{ nm})$	≈ 67.50	[31]
g-C ₃ N ₄ -CoWO	1.00	Water (100 mL)	$300 \text{ W XL} (\lambda \geq 420 \text{ nm})$	97.00	[12]
g-C ₃ N ₄ -CNTs	1.00	10 vol% FA (100 mL)	$300 \text{ W XL} (\lambda \!\geq\! 400 \text{ nm})$	487.00	[9]
g-C ₃ N ₄	4.00	90 vol% EA (5 mL)	$2 \text{ kW XL} (\lambda > 420 \text{ nm})$	125.00	[29]
Mesoporous g-C ₃ N ₄	4.00	90 vol% EA (5 mL)	$2 \text{ kW XL} (\lambda > 420 \text{ nm})$	≈ 183.50	[32]
KPD-CN	0.50	10 vol% EA (40 mL)	$300 \text{ W XL} (\lambda \!\geq\! 420 \text{ nm})$	≈ 485.50	[35]
DCN	0.83	20 vol% IPA (60 mL)	AM1.5 (λ > 420 nm)	96.80	[33]
OCN	1.00	10 vol% IPA (50 mL)	$300 \text{ W XL} (\lambda > 420 \text{ nm})$	200.00	[30]
Ti ₃ C ₂ /porous g-C ₃ N ₄	1.00	10 vol% IPA (50 mL)	$300 \text{ W XL} (\lambda > 420 \text{ nm})$	131.71	This work

341 PDI: pyromellitic diimide; rGO: reduced graphene oxide; 3DOM g-C₃N₄: three dimension ally ordered macroporous graphitic carbon

342

nitride; PW11: polyoxometalate (POMs) cluster of [PW11O39]7-; U-g-C3N4-NS: ultrathin g a nanosheets; CoWO: POMs-derived metal oxides; CNTs: carbon nanotubes; KPD-CN: (K, P, and O)-incorporated pomeric carbon nitride; DCN: defective g-C₃N₄; OCNs: 343

344 oxygen-enriched carbon nitride polymer; FA: formic acid; EA: ethanol; IPA: i oprop ol; XL: Xenon lamp.

To clarify the route of H₂O₂ production in the photo atalytic process, some control experiments 345 were performed. As displayed in Fig. 7a, th H_2 can hardly be examined in the absence of visible 346 ro action is accomplished by photocatalysis. Moreover, no light irradiation, indicating that the 347 detectable amount of H₂O₂ is produced when O₂ is replaced by N₂, and the generation of H₂O₂ is 348 TIPA. These results suggest that the H₂O₂ is mainly produced from the suppressed in the absence 349 electron reduction of O_2 rather than the oxidation of H_2O by the photogenerated holes [8]. Fig. 7b 350 shows the ESR spectra of DMPO- \cdot O₂⁻ adduct for the pCN and TC/pCN-2 samples. It is obvious can 351 be seen that the DMPO-•O₂⁻ adduct signal of TC/pCN-2 is much stronger than that of pCN under 352 visible light irradiation, which is ascribed to the accelerated spatial charge separation and transfer, 353 resulting in the enhanced intensity of DMPO- $\cdot O_2^-$ adduct signal. The amount of $\cdot O_2^-$ formed in the 354 photocatalysis is estimated by the NBT transformation method. As exhibited in Fig. S8, the intensity 355

of characteristic absorption peak of NBT (260 nm) declines after photocatalytic process. According to the reaction relationship between $\cdot O_2^-$ and NBT (4:1 in molar ratio), the average $\cdot O_2^-$ generation rates of pCN and TC/pCN-2 are evaluated to be 3.15 and 5.47 µmol L⁻¹ h⁻¹ (Fig. 7c). This result demonstrates the increased formation of $\cdot O_2^-$, which will further promote the production of H₂O₂.

360 To further investigate the pathway of O₂ reduction, rotating disk electrode (RDE) analysis of oxygen reduction reaction (ORR) were performed [67, 68]. Fig. 7d and e depicts the linear sweep 361 voltammetry (LSV) curves of pCN and TC/pCN-2 measured on a RDE in an O₂-saturated 0.1 mol L⁻¹ 362 phosphate buffer solution (pH 7) at different rotating speeds, respectively. The difference between Fig. 363 7d and e is not significant due to the limited content of Ti_3C_2 , index that the loading of limited 364 content of Ti_3C_2 has no obvious impact on the pathway of kygen reduction reaction for porous g-365 C_3N_4 . The Koutecky-Levich plots of the data at -1. g/AgCl are presented in Fig. 7f. The 366 average number of electrons (n) involved in the overall reduction of O_2 is obtained by the linear 367 regression of the plots using the follow and Eq. (6): 368

369

370

$$j_{k}^{-1} = j_{k}^{-1} + B^{-1}\omega^{-1/2}$$
(5)

$$B = 0.2nFv^{-1/6}CD^{2/3}$$
(6)

Where *j* is the measured current density, j_k is the kinetic current density, ω is the rotating speed (rpm), *F* is the Faraday constant (96485 C mol⁻¹), *v* is the kinetic viscosity of water (0.01 cm² s⁻¹), *C* is the bulk concentration of O₂ in water (1.26×10⁻³ mol cm⁻³), and *D* is the diffusion coefficient of O₂ (2.7×10⁻⁵ cm² s⁻¹), respectively [69]. According to the intercept of the Koutecky-Levich plots, the j_k values of pCN and TC/pCN-2 are estimated to be 10.15 and 12.71 mA cm⁻², respectively, indicating that O₂ is reduced more efficiently on TC/pCN-2 [32]. The n values of pCN and TC/pCN-2 are 1.54 and 1.59, which are determined by the slope of the Koutecky-Levich plots. This result suggests that two-step single-electron O_2 reduction occurs on the pCN and TC/pCN-2, and the loading of Ti_3C_2 on g-C₃N₄ can promote the generation of electrons [11, 34]. Therefore, The H₂O₂ production reaction in this photocatalytic process can be described as follows:

$$e^- + 0_2 \to \cdot 0_2^- \tag{7}$$

$$\cdot 0_2^- + e^- + 2H^+ \to H_2 0_2$$
 (8)

383 *3.4. The mechanism of activity enhancement*

The band gap energy (E_g) of pCN is determined to be 2.63 eV using Kubelka-Munk remission 384 function (Fig. S9). Next, ultraviolet photoelectron spectroscopy (UPS) w employed to investigate 385 the band structure of the samples. As shown in Fig. 8a, the vale d energy $(E_{\rm VB})$ of pCN is 386 determined to be 5.83 eV. And the conduction band energy (CB) is calculated to be 3.2 eV. Because 387 the reference standard for which 0 V vs reversible years en electrode (RHE) equals -4.44 eV vs 388 vacuum level [70], the E_{VB} and E_{CB} of pCN can be estimated to be about 1.39 V and -1.24 V vs RHE, 389 respectively. Moreover, the cutoff energy of Ti₃C₂, pCN and TC/pCN-2 are 17.89, 18.67 and 390 18.46 eV (Fig. 8b and c), while their fermi level (E_f) are all 0 eV. Accordingly, their work functions 391 $(e\Phi)$ can be calculated to 53 and 2.74 eV according to the following equation, $e\Phi = hv - |$ 392 E_{cutoff} - E_{f} [71, 72]. Obviously, the work function of Ti₃C₂ is greater than that of g-C₃N₄, thus a 393 Schottky junction can be established after their contact. Such an upshift (0.21 eV) of the work function 394 between pCN and TC/pCN-2 also verifies the existence of Schottky effect [71]. Besides, the slopes of 395 396 the Mott-Schottky plots (Fig. 8d) demonstrate that porous g-C₃N₄ is n-type semiconductor and TC/pCN-2 presents larger carrier density owing the formation of Schottky junction. 397

398 On the basis of the above results, a possible photocatalytic mechanism over Ti_3C_2 /porous g-C₃N₄ 399 Schottky junction is proposed in Fig. 9. As mentioned above, the work functions of Ti_3C_2 ($e\Phi_{TC}$) and

porous g-C₃N₄ ($e\Phi_{pCN}$) are determined to be 3.31 and 2.53 eV, respectively. When Ti₃C₂ and porous g-400 C₃N₄ are in contact, the visible-light induced electrons on porous g-C₃N₄ will flow to Ti₃C₂ at the lower 401 402 energy level to achieve an equilibrium state between the fermi levels of Ti_3C_2 (E_{fTC}) and porous g- $C_{3}N_{4}$ (E_{fpCN}). A space charge layer thus can be generated on the side of porous g-C₃N₄, making the 403 upward bending of energy band and inducing the formation of Schottky barrier (φ_{SB}). As a result, the 404 electrons trapped by Ti₃C₂ can't flow back to conduction band (CB) of porous g-C₃N₄, which can 405 highly efficient boost the spatial charge separation. Therefore, the Ti₃C₂ nanosheets can create a 406 Schottky junction with the host porous g-C₃N₄ nanosheets to impro tocatalytic activity, and 407 meanwhile, serve as the active sites for the H₂O₂ production. 408

409 **4. Conclusion**

4 was designed and fabricated via the Interfacial Schottky junction of Ti₃C₂ Mxene/portus 410 electrostatic self-assembly method. Benefitting from the Schottky effect and the accompanying built-411 in electric field, the photogenerated porous g-C₃N₄ can be effectively separated and 412 transferred. The TC/pCN-2 has the highest activity with an H_2O_2 production rate up to 2.20 µmol L⁻¹ 413 $\lambda > 420$ nm). The mechanism analysis demonstrate that the twomin⁻¹ under visible light 414 radi step single-electron reduction of oxygen is the predominant reaction step during the photocatalytic 415 H₂O₂ production process. This work promotes understanding of the mechanism of photocatalytic 416 H₂O₂ production and provides a new idea for the design and synthesis of new materials for the 417 production of H₂O₂. 418

419 Acknowledgments

This study was financially supported by the Program for the National Natural Science Foundation
of China (81773333, 51521006, 51879101, 51579098, 51779090, 51709101, 51809090, 51278176,

- 422 51378190), the National Program for Support of Top-Notch Young Professionals of China (2014),
- 423 the Program for Changjiang Scholars and Innovative Research Team in University (IRT-13R17), and
- 424 Hunan Provincial Science and Technology Plan Project (2018SK20410, 2017SK2243, 2016RS3026),
- 425 and the Fundamental Research Funds for the Central Universities (531119200086, 531118010114,
- 426 531107050978).

427 **References**

- 428 [1] Y. Wang, Y. Zhu, Y. Hu, G. Zeng, Y. Zhang, C. Zhang, C. Feng, Small (2018) 1703305.
- 429 [2] H. Yi, D. Huang, G. Zeng, C. Lai, L. Qin, M. Cheng, S. Ye, B. Song, X. Ren, X. Guo, Appl. Catal. B: Environ.
- 430 239 (2018) 408-424.
- [3] J. Gong, B. Wang, G. Zeng, C. Yang, C. Niu, Q. Niu, W. Zhou, Y. Liang, J. Hazaro Mater. 164 (2009) 15171522.
- [4] K. He, G. Chen, G. Zeng, A. Chen, Z. Huang, J. Shi, T. Huang, M. Peng, L. Ju, Appl. Catal. B: Environ. 228
 (2018) 19-28.
- 435 [5] X. Tang, G. Zeng, C. Fan, M. Zhou, L. Tang, J. Zhu, J. Wan, D Huang, M. Chen, P. Xu, Sci. Total Environ. 636
 436 (2018) 1355.
- 437 [6] W. Xue, D. Huang, G. Zeng, J. Wan, C. Zhang, R. Xu, N. Cheng, R. Deng, J. Hazard. Mater. 341 (2018) 381438 389.
- 439 [7] W. Xiong, Z. Zeng, G. Zeng, Z. Yang, R. Xiao, A. Li, J. Cao, C. Zhou, H. Chen, M. Jia, Y. Yang, W. Wang, X.
 440 Tang, Chem. Eng. J. 374 (2019) 91-99.
- 441 [8] Y. Zheng, Z. Yu, H. Ou, A.M. Asiri, Y. Cher, X. Wing, Adv. Funct. Mater. 28 (2018) 1705407.
- 442 [9] S. Zhao, T. Guo, X. Li, T. Xu, B. Yr Ig, X. Sho, Appl. Catal. B: Environ. 224 (2018) 725-732.
- [10] M. Cheng, Y. Liu, D. Huang, C. Lai, G. Zong, J. Huang, Z. Liu, C. Zhang, C. Zhou, L. Qin, W. Xiong, H. Yi, Y.
 Yang, Chem. Eng. J. 362 (2019) 865-876
- 445 [11] S. Zhao, X. Zhao, J. Cat J. 56 (2018) 98-106.
- 446 [12] S. Zhao, X. Zhao, Appl. Ctal. B: Environ. 250 (2019) 408-418.
- [13] W. Xiong, Z. Zeng, X. Li, G. Zeng, R. Xiao, Z. Yang, H. Xu, H. Chen, J. Cao, C. Zhou, L. Qin, Chemosphere
 232 (2019) 186-194.
- [14] S. Zhao, X. Zhao, H. Zhang, J. Li, Y. Zhu, Nano Energy 35 (2017) 405-414.
- [15] L. Zhang, J. Zhang, G. Zeng, H. Dong, Y. Chen, C. Huang, Y. Zhu, R. Xu, Y. Cheng, K. Hou, Bioresour. Technol.
 261 (2018) 10.
- [16] S. Ye, G. Zeng, H. Wu, C. Zhang, J. Dai, J. Liang, J. Yu, X. Ren, H. Yi, M. Cheng, Crit. Rev. Biotechnol. 37
 (2017) 1-15.
- [17] P. Xu, G. Zeng, D. Huang, C. Feng, S. Hu, M. Zhao, C. Lai, Z. Wei, C. Huang, G. Xie, Sci. Total Environ. 424
 (2012) 1-10.
- 456 [18] L. Qin, G. Zeng, C. Lai, D. Huang, C. Zhang, P. Xu, T. Hu, X. Liu, M. Cheng, Y. Liu, L. Hu, Y. Zhou, Sensor.
- 457 Actuat B: Chem. 243 (2017) 946-954.
- 458 [19] C. Zhang, W. Wang, A. Duan, G. Zeng, D. Huang, C. Lai, X. Tan, M. Cheng, R. Wang, C. Zhou, W. Xiong, Y.
- 459 Yang, Chemosphere 222 (2019) 184-194.

- 460 [20] C. Zhang, G. Zeng, D. Huang, C. Lai, M. Chen, M. Cheng, W. Tang, L. Tang, H. Dong, B. Huang, X. Tan, R.
- 461 Wang, Chem. Eng. J. 373 (2019) 902-922.
- 462 [21] L. Li, C. Lai, F. Huang, M. Cheng, G. Zeng, D. Huang, B. Li, S. Liu, M. Zhang, L. Qin, M. Li, J. He, Y. Zhang,
- 463 L. Chen, Water Res. 160 (2019) 238-248.
- [22] Y. Yang, C. Zhang, C. Lai, G. Zeng, D. Huang, M. Cheng, J. Wang, F. Chen, C. Zhou, W. Xiong, Adv. Colloid
 Interface Sci. 254 (2018) 76-93.
- 466 [23] H. Wang, Z. Zeng, P. Xu, L. Li, G. Zeng, R. Xiao, Z. Tang, D. Huang, L. Tang, C. Lai, D. Jiang, Y. Liu, H. Yi,
- 467 L. Qin, S. Ye, X. Ren, W. Tang, Chem. Soc. Rev. 48 (2019) 488-516.
- 468 [24] J. Cao, Z. Yang, W. Xiong, Y. Zhou, Y. Peng, X. Li, C. Zhou, R. Xu, Y. Zhang, Chem. Eng. J. 353 (2018) 126469 137.
- 470 [25] X. Li, P. Xu, M. Chen, G. Zeng, D. Wang, F. Chen, W. Tang, C. Chen, C. Zhang, X. Tan, Chem. Eng. J. 366
 471 (2019) 339-357.
- 472 [26] D. Huang, Z. Li, G. Zeng, C. Zhou, W. Xue, X. Gong, X. Yan, S. Chen, W. Wang, M. Cheng, Appl. Catal. B:
 473 Environ. 240 (2019) 153-173.
- 474 [27] D. Huang, S. Chen, G. Zeng, X. Gong, C. Zhou, M. Cheng, W. Xue, X. Yan, J. Li, Coord. Chem. Rev. 385 (2019)
 475 44-80.
- 476 [28] G. Liao, Y. Gong, L. Zhang, H. Gao, G. Yang, B. Fang, Energy Environ Sci. (2017) 10.1039/c9ee00717b.
- [29] Y. Shiraishi, S. Kanazawa, Y. Sugano, D. Tsukamoto, H. Sakamoto, S. Ichikawa, T. Hirai, ACS Catal. 4 (2014)
 774-780.
- 479 [30] Z. Wei, M. Liu, Z. Zhang, W. Yao, H. Tan, Y. Zhu, Energ. Environ. Sci. 11 (2018) 2581-2589.
- 480 [31] J. Cai, J. Huang, S. Wang, J. Iocozzia, Z. Sun, J. Sun, Y. Yor, XLe, Z. Lin, Adv. Mater. (2019) e1806314.
- 481 [32] Y. Shiraishi, Y. Kofuji, H. Sakamoto, S. Tanaka, S. Ichikawa, T Hirai, ACS Catal. 5 (2015) 3058-3066.
- 482 [33] L. Shi, L. Yang, W. Zhou, Y. Liu, L. Yin, X. Hai, H. Song, J. Ye, Small 14 (2018) 1703142.
- [34] S. Li, G. Dong, R. Hailili, L. Yang, Y. Li, F. Wang, Y. Zong, C. Wang, Appl. Catal. B: Environ. 190 (2016) 2635.
- 485 [35] G.-h. Moon, M. Fujitsuka, S. Kim, T. Mijina, X. Vang, W. Choi, ACS Catal. 7 (2017) 2886-2895.
- [36] Y. Shiraishi, S. Kanazawa, Y. Kofur, H. Salanoto, S. Ichikawa, S. Tanaka, T. Hirai, Angew. Chem. Int. Edit.
 53 (2014) 13454-13459.
- [37] Y. Kofuji, Y. Isobe, Y. Shiraisi, H. Jakamoto, S. Tanaka, S. Ichikawa, T. Hirai, J. Am. Chem. Soc. 138 (2016)
 10019-10025.
- [38] M. Naguib, O. Mashtalir, Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M.W. Barsoum, Acs Nano 6 (2012)
 1322.
- 492 [39] H. Wang, Y. Wu, X. Yuan, G. Zeng, J. Zhou, X. Wang, J.W. Chew, Adv. Mater. 30 (2018) e1704561.
- [40] Y. Xu, S. Wang, J. Yang, B. Han, R. Nie, J. Wang, Y. Dong, X. Yu, J. Wang, H. Jing, J. Mater. Chem. A 6 (2018)
 15213-15220.
- [41] T. Cai, L. Wang, Y. Liu, S. Zhang, W. Dong, H. Chen, X. Yi, J. Yuan, X. Xia, C. Liu, S. Luo, Appl. Catal. B:
 Environ. 239 (2018) 545-554.
- 497 [42] H. Wang, Y. Sun, Y. Wu, W. Tu, S. Wu, X. Yuan, G. Zeng, Z.J. Xu, S. Li, J.W. Chew, Appl. Catal. B: Environ.
 498 245 (2019) 290-301.
- 499 [43] J. Ran, G. Gao, F. Li, T. Ma, A. Du, S. Qiao, Nat. Commun. 8 (2017) 13907.
- 500 [44] S. Cao, B. Shen, T. Tong, J. Fu, J. Yu, Adv. Funct. Mater. 28 (2018) 1800136.
- 501 [45] C. Zhou, S. Wang, Z. Zhao, Z. Shi, S. Yan, Z. Zou, Adv. Funct. Mater. 28 (2018) 1801214.
- 502 [46] H. Zhong, C. Yang, L. Fan, Z. Fu, X. Yang, X. Wang, R. Wang, Energ. Environ. Sci. 12 (2019) 418-426.
- 503 [47] X. She, H. Xu, Y. Yu, L. Li, X. Zhu, Z. Mo, Y. Song, J. Wu, S. Yuan, H. Li, Small 15 (2019) e1804613.

- [48] Y. Sun, D. Jin, Y. Sun, X. Meng, Y. Gao, Y. Dall'Agnese, G. Chen, X. Wang, J. Mater. Chem. A 6 (2018) 9124 9131.
- [49] J. Xuan, Z. Wang, Y. Chen, D. Liang, L. Cheng, X. Yang, Z. Liu, R. Ma, T. Sasaki, F. Geng, Angew. Chem. Int.
 Edit. 128 (2016) 14789-14794.
- 508 [50] C. Zhou, C. Lai, D. Huang, G. Zeng, C. Zhang, M. Cheng, L. Hu, J. Wan, W. Xiong, M. Wen, X. Wen, L. Qin,
- 509 Appl. Catal. B: Environ. 220 (2018) 202-210.
- 510 [51] Y. Yang, C. Zhang, D. Huang, G. Zeng, J. Huang, C. Lai, C. Zhou, W. Wang, H. Guo, W. Xue, R. Deng, M.
- 511 Cheng, W. Xiong, Appl. Catal. B: Environ. 245 (2019) 87-99.
- [52] W. Wang, Z. Zeng, G. Zeng, C. Zhang, R. Xiao, C. Zhou, W. Xiong, Y. Yang, L. Lei, Y. Liu, Chem. Eng. J.
 (2019) 10.1016/j.cej.2019.122132.
- 514 [53] C. Zhou, P. Xu, C. Lai, C. Zhang, G. Zeng, D. Huang, M. Cheng, L. Hu, W. Xiong, X. Wen, L. Qin, J. Yuan, W.
- 515 Wang, Chem. Eng. J. 359 (2019) 186-196.
- 516 [54] W. Wang, P. Xu, M. Chen, G. Zeng, C. Zhang, C. Zhou, Y. Yang, D. Huang, C. Lai, M. Cheng, L. Hu, W. Xiong,
- 517 H. Guo, M. Zhou, ACS Sustain. Chem. Eng. 6 (2018) 15503-15516.
- [55] L. Qin, D. Huang, P. Xu, G. Zeng, C. Lai, Y. Fu, H. Yi, B. Li, C. Zhang, M Cheng, J. Colloid Interf. Sci. 534
 (2019) 357-369.
- 520 [56] C. Zhou, D. Huang, P. Xu, G. Zeng, J. Huang, T. Shi, C. Lai, C. Zhan, M. Shong, Y. Lu, Chem. Eng. J. 370 (2019) 1077-1086.
- [57] H. Guo, C. Niu, D. Huang, N. Tang, C. Liang, L. Zhang, X. Wan, Y. Yang, W. Wang, G. Zeng, Chem. Eng. J.
 360 (2019) 349-363.
- 524 [58] Y. Lin, S. Wu, C. Yang, M. Chen, X. Li, Appl. Catal. B: Environ 246 (2019) 71-86.
- 525 [59] W. Xue, Z. Peng, D. Huang, G. Zeng, X. Wen, R. Deng, Varig, X. Yan, Ceram. Int. 45 (2019) 6340-6349.
- [60] H. Guo, H. Niu, C. Liang, C. Niu, D. Huang, L. Zhang, N. Tang, Y. Yang, C. Feng, G. Zeng, J. Catal. 370 (2019)
 289-303.
- [61] B. Li, C. Lai, G. Zeng, L. Qin, H. Yi, D. Huang, C. Thou, X. Liu, M. Cheng, P. Xu, C. Zhang, F. Huang, S. Liu,
 ACS Appl. Mater. Interface 10 (2018) 18824-18826
- [62] H. Yi, M. Yan, D. Huang, G. Zeng, C. La, M. Li, X. Huo, L. Qin, S. Liu, X. Liu, B. Li, H. Wang, M. Shen, Y.
 Fu, X. Guo, Appl. Catal. B: Environ 250 (2017) 52-62.
- [63] S. Ye, M. Yan, X. Tan, I. Lian, G. Zeng, H. Wu, B. Song, C. Zhou, Y. Yang, H. Wang, Appl. Catal. B: Environ.
 250 (2019) 78-88.
- [64] Y. Lin, S. Wu, X. Li, X. Wu, C. Yang, G. Zeng, Y. Peng, Q. Zhou, L. Lu, Appl. Catal. B: Environ. 227 (2018)
 557-570.
- [65] Y. Yang, Z. Zeng, C. Zhang, D. Huang, G. Zeng, R. Xiao, C. Lai, C. Zhou, H. Guo, W. Xue, M. Cheng, W. Wang,
 J. Wang, Chem. Eng. J. 349 (2018) 808-821.
- 538 [66] H.I. Kim, O.S. Kwon, S. Kim, W. Choi, J.H. Kim, Energ. Environ. Sci. 9 (2016) 1063-1073.
- [67] C. Zhang, C. Lai, G. Zeng, D. Huang, L. Tang, C. Yang, Y. Zhou, L. Qin, M. Cheng, Biosens. Bioelectron. 81
 (2016) 61-67.
- [68] C. Lai, S. Liu, C. Zhang, G. Zeng, D. Huang, L. Qin, X. Liu, H. Yi, R. Wang, F. Huang, ACS sensors 3 (2018)
 2566-2573.
- 543 [69] Y. Liu, H. Liu, C. Wang, S. Hou, N. Yang, Environ. Sci. Technol. 47 (2013) 13889-13895.
- 544 [70] X. She, J. Wu, H. Xu, J. Zhong, Y. Wang, Y. Song, K. Nie, Y. Liu, Y. Yang, M.-T.F. Rodrigues, R. Vajtai, J. Lou,
- 545 D. Du, H. Li, P.M. Ajayan, Adv. Energy Mater. 7 (2017) 1700025.
- 546 [71] Z. Zhuang, Y. Li, Z. Li, F. Lv, Z. Lang, K. Zhao, L. Zhou, L. Moskaleva, S. Guo, L. Mai, Angew. Chem. Int.
- 547 Edit. 57 (2018) 496-500.

[72] Z. Li, Z. Zhuang, F. Lv, H. Zhu, L. Zhou, M. Luo, J. Zhu, Z. Lang, S. Feng, W. Chen, Adv. Mater. 30 (2018)
1803220.

550

Acerted

- 551 **Figure captions**
- **Fig. 1.** Schematic illustration of synthetic process of Ti_3C_2 /porous g-C₃N₄ (TC/pCN) interfacial Schottky junction.
- **Fig. 2.** TEM images of (a) Ti₃C₂, (b) pCN and (c) TC/pCN-2; (d) HRTEM image, (e) AFM image and
- (f) the corresponding height distribution profile, and (g) FESEM-EDS elemental mapping of TC/pCN-
- 556 2.
- 557 **Fig. 3.** (a) XRD patterns of Ti₃AlC₂ and Ti₃C₂; (b) XRD patterns of pCN and TC/pCN samples; (c)
- 558 FTIR spectra of the samples; (d) UV-vis DRS spectra and a photograph (ipper) of the samples.
- **Fig. 4.** XPS spectra of Ti_3C_2 , pCN and TC/pCN-2: (a) total survey, (b) Ti^2 p, (c) F 1 s, (d) C 1 s, (e)
- 560 O 1s and (f) N 1s.
- Fig. 5. (a) Transient photocurrent response curves, b) L spectra, (c) TRPL spectra and (d) EIS
 Nyquist plots of the samples.
- **Fig. 6.** (a) Time-dependent production of H₂O₂ under visible light irradiation; (b) Formation rate constant (K_f) and decomposition are constant (K_d) for H₂O₂ production; (c) The photocatalytic decomposition of H₂O₂ (1 mpol/L⁻¹) under visible light irradiation; (d) Cycling runs for the photocatalytic H₂O₂ production over TC/pCN-2.
- 567 Fig. 7. (a) Comparison of the photocatalytic production of H_2O_2 under different conditions for
- 568 TC/pCN-2; (b) ESR spectra of DMPO-• O_2^- adduct and (c) time-dependent concentration plots of • O_2^-
- 569 for pCN and TC/pCN-2; LSV curves of (d) pCN and (e) TC/pCN-2 measured on a RDE at different
- 570 rotating speeds; (f) Koutecky-Levich plots of the data obtained at the constant electrode potential (-1.0
- 571 V vs. Ag/AgCl).
- 572 **Fig. 8.** UPS spectra of (a) pCN and (b) Ti₃C₂; (c) UPS spectra and (d) Mott-Schottky plots of pCN and

- 573 TC/pCN-2.
- **Fig. 9.** The photocatalytic mechanism of the Ti_3C_2 /porous g-C₃N₄ system.





Fig. 1











Fig. 4













Fig. 9

