Modified crystal structure and improved photocatalytic activity of

MIL-53 via inorganic acid modulator

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1 Abstract

Metal-organic frameworks (MOFs) as photocatalysts have attracted considerable 2 3 attention due to their potential for environment remediation, of which MIL-53 is a representative member of MOFs. However, the photocatalytic performance was 4 affected by the recombination of photo-generated electron-hole pairs. On the one hand, 5 6 acid-modulated MOFs have received much attention, however, more attention have been paid to the adsorption capacity and there is still a big gap in the application of 7 8 photocatalysis. This work focused on the effect of HCl modulator on crystal structure 9 and photocatalytic activity. In the morphology aspect, the presence of smaller crystals and layer structure and mesoporous distribution was due to t 10 Regulatory effect of HCl, and it had a double function: slowing down the hydroxsis of 11 eCl3 6H2O as well as conteracting the deprotonation of the dissovled carboxylic acids. Notablely, 12 confirmed by XRD, the change of crystal form from MIL-53 to MIL-88 was 13 attributed to the presence of 40 μ L. Increased s ecific surface area could provide 14 more active sites, including adsorption and cat stic ones. Compared with the MIL-53, 15 the photocatalytic activity of acid regulard MIL-53 increased by 1.5 times. 16 in Jetween the photocatalytic activity and the Meanwhile, the quantitative relation 17 $\mathbf{1}_{\mathbf{V}} \cdot \mathbf{O}_2$ and $\mathbf{\bullet} \mathbf{OH}$ as the main active free radicals in content of HCl was revealed 18 Fin s were confirmed from the EPR analysis. This work photocatalytic degradat 19 эп рі pplication of modulated MOFs by acid modulator in provides a basis 20 photocatalysis. 21

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23 Keywords: MOFs, acid modulator, crystal structure, photocatalytic activity, band gap

24 1.Introduction

Metal-organic frameworks (MOFs) as a class of porous crystalline materials, based on the coordination bonds between metal clusters have attracted considerable attention over the past few decades [1-3]. The abundant pore size and adjustable structure make the MOFs widely used in many fields [4-7], including gas storage and separation, catalysis, drug transport, proton conductors, *etc.* In particular, some MOFs with semiconductor properties can be used for the photocatalytic degradation of organic pollutants [8-11].

Defects, refer to irregular arrangement of crystal atoms, and they are widely exist 32 in MOFs, which aroused great interest among the researchers. 33 **R** ctural disorder and heterogeneity within MOFs breaks the periodic arrangement of atoms and greatly 34 influences the pore/aperture sizes as well as the surface properties of the resulting 35 materials, which subsequently modifies their performance [12-14]. The targeted 36 incorporation of defects into MOFs, *i.e.*, the synthetic control of the concentration and 37 til today [15]. The methods of chemical nature of defect, remains challengh 38 39 prepared defects reported divided into two wegories, (i) the "de novo" synthesis, ker approach, fast crystal growth. (ii) the including modulation approach, 40 sch ding mechanical treatment, acid/base treatment, post synthetic treating synth 41 лз, • To date, the modulator strategy, as the most common harsh activation procedure 42 of large amounts modulator in addition to the linker one, refers to the ddi 43 molecules into the precursor solution during the MOF synthesis. It is generally 44 accepted that small amounts of modulator slow down the speed of crystallization by 45 impacting the equilibrium reaction and in turn the formation of defects. It is worth 46 47 noting that the existing modulator are applied to MOFs with carboxylic acid as linker, typically UiO-66 was the mode system for many works [17-19]. 48

In recent years, the study on the effect of crystal morphology and properties by the modulators has been updated gradually. Compare to UiO-66, the TFA (Trifluoroacetic acid)-modulated UiO-66 sample was found to be significantly more active. Modulator-dependent defect engineering can also be used as a tool for pore design in order to facilitate diffusion and to incorporate different catalytically active

species. The particle size of the $Cu_3(BTC)_2$ (HKUST-1) could be tuned from 300 nm 54 to 2.4 µm by varying the amount of CA added [20]. The intrinsic microporous 55 56 structure of HKUST-1 is maintained while the larger pores' size distributed in the range of 30 to 100 nm. After encapsulation, a superior catalytic activity with a high 57 conversion rate is achieved. TMA (Trimesic acid) as a modulator, could optimize the 58 59 HKUST-1 with nano-size and the modulated one exhibited the increased adsorption for CO₂ with the adsorption capacity of 2.5 mmol /g [21]. In the work of Bagherzadeh, 60 61 et al., acetic acid and formic acid were chosen as monoligand modulated agents for MIL-88 A. At low modulator content, the primary diamondlike characteristic 62 morphology of the particles was preserved. While acetic arcmildly altered the 63 morphology of the MOF and narrowed its particle-size distribution, on the other hand, 64 formic acid is more potent than acetic acid, which drastically changed the morphology 65 of the MOF particles to those resembling dendrites 2]. Atzori *et al.* recently reported 66 on the specific influence of benzoic acid modulator toward the formation of missing 67 cluster defects. Specially, the quantitative relationship between defects and modulator 68 was confirmed from the combination of PND, dissolution/¹H NMR spectroscopy 69 C and Jiang reported on the hierarchical and N₂ sorption measurements 70 using acetic/octanic/dodecanic acid as modulators UiO-66 containing mesopo 71 лs [24]. The pore diameter chained defective UiO-66 systems was systematically 72 n th turned via altering the le and concentration of the modulator, resulting in smaller 73 or bigger mesopores within the microporous UiO-66. The defect-induced formation of 74 mesopores allows for the incorporation of larger catalytically active species like 75 polyxometallates, which then can be used in the catalytic methanolysis of styrene 76 77 oxide. Except the novo synthesis, generally, defects can be formed by post-synthetic 78 treatment (such as acid/based treatment and solvent exchange).

However, the current studies focused on the adsorption and catalytic properties of modulated MOFs by acid modulator, and there is still a gap in the effect of modulator on the photocatalytic properties. In this work, Fe(III)-based MOFs with photocatalytic activity, as a member of the MIL family, were selected as the research object for the photocatalytic degradation of tetracycline with persistance and potential

harm to the environment. MIL-53, as a typical porous Fe-MOF, possesses a strong 84 Fe-O clusters as light absorbing component responsible for photocatalytic activity; 85 however, the photocatalytic performance of which was affected by the recombination 86 of photo-generated electron-hole pairs. There was much space retained to improve the 87 photocatalytic activity, mainly, additional electron acceptors and heterojunction 88 89 structures, and both are conductive to charge and holes separation. The hydrogen peroxide (H₂O₂), persulfate (PS) and peroxymonosulfate (PMS) as electron acceptors 90 91 accelerated the photocatalytic process by promoting the separation of photogenerated 92 electrons and holes [21-25]. In addition, the heterojunction based on MIL-53, including the MIL-53/AgI [26-28], MIL-53/Ag₃PO₄ [28, 29], **NL**-53/SnS [30] and 93 MIL-53/g-C₃N₄ [31-33] are effective in photocatalytic vegradation of organic 94 pollutants. However, the increased photocatalytic activity of shale crystal MIL-53 by 95 acid modulator has not been reported until now. This work focused on the effect of 96 acid modulator on the crystal morphology, size and photoelectric properties, the 97 emphasis on the photocatalytic activity. In part ala, the quantitative relation between 98 99 the content of HCl modulator and the photocallytic activity has been revealed. This work provides a basis for the ap of modulated MOFs by acid modulator in 100 On photocatalysis. 101

102 **2. Materials and methods**

103 **2.1 Materials**

104 1,4-Benzenedicurboxylic acid (H₂BDC, 99%), N,N-dimethyformadie (DMF, 105 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 106 Iron (III) chloride hexahydrate (FeCl₃•6H₂O, 99%) and hydrochloric acid (HCl) were 107 supported by Macklin chemical Reagent Co., Ltd (Shanghai, China). All the reagents 108 were obtained from commercial channels and were of analytic grade without further 109 purification.

110 2.2 Synthesis of single crystal MIL-53

MIL-53 (Fe) was prepared by a facile solvothermal method [34]. A mixture of FeCl₃•6H₂O, H₂BDC and DMF with a molar ratio of 1: 1: 280 was stirred until the formation of bright yellow clear liquid. Then, the reaction mixture was heated at 170 °C for 24 h in a Teflon-lined stainless steel autoclave. The sample was vacuum filtered
and cleaned by DMF and methanol three times. The obtained orange-yellow
precipitate was dried under vacuum at 70 °C.

117 **2.3 Synthesis of defective MIL-53**

Defective MIL-53 (Fe) was prepared by the acid modulation method on the basis of as-obtained MIL-53. Different amounts of HCl (10 μ L-40 μ L) (1 M/L) was added into the mixture of FeCl₃•6H₂O, H₂BDC and DMF until a nice mixture. Then, the reaction mixture was heated at 170 °C for 24 h in a Teflon-lined stainless steel autoclave. The filtration, cleaning and drying processes are similar to MIL-53. 10 μ L, 20 μ L, 30 μ L, 40 μ L, 50 μ L, 100 μ L HCl modulated camples were denoted as D-1, D-2, D-3 and D-4, D-5 and D-10.

125 **2.4 Characterization**

The crystals structures of the samples were determined by X-ray diffaction 126 (XRD, XRD-6100, Shimadzu) with Cu Ka radiation, operating at 2 θ range from 127 to 80° . Fourier transformation infrared (FDR) spectra on KBr pellets of the 10° 128 samples were analyzed on a Nicolet FTIR 57 spectrometer at a resolution of 4 cm⁻¹. 129 The specific surface areas and pore size distribution The Brunauer-Emmett-Teller (BF 130 rea analyzer (Belsorp-miniII, BEL) by nitrogen were measured on a surface 131 Franchotoelectron spectroscopy (XPS) was analyzed on a adsorption-desorption. 132 , Thermo) using an Al Ka X-ray source (1486.6 eV). The spectrometer (Escarb 2 133 ultraviolet visible diffused reflectance spectra (UV - vis DRS) were collected on an 134 UV - vis spectrophotometer (Cary 300, Varian) in the wavelength range from 300 nm 135 to 800 nm with BaSO₄ as the reference. The optical band gap of MIL-53(Fe) could be 136 calculated according to the energy dependence relation of $ahv=A(hv-E_g)^{n/2}$, where 137 a,h,Eg, and A are absorption coefficient, Plant constant, light frequency, optical band 138 gap and a constant, respectively and n is determined by the type of optical transition 139 in the semiconductor (n=1 for a direct transition). The photoluminescence (PL) 140 spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer at an 141 excitation wavelength of 340 nm. The photocurrent, impedance and Mott-Schottky 142 measurements were conducted with a CHI760E electrochemical workstation. For the 143

preparation of photoelectrodes, the photocatalysts were dispersed in polyvinyl alcohol 144 solution to form a 2 mg/L solution and ultrasonicated for 60 min. Then, indium doped 145 tin oxide (ITO) conductive glass was covered with 100 μ L colloidal solution and dry 146 at 60 °C. The measurements were performed in a standard three-electrode system, 147 including working electrode (ITO), the counter electrode (Pt), and the reference 148 electrode (saturated calomel electrode) and 0.5 M Na₂SO₄ aqueous solution as the 149 electrolyte. The electron spin response (ESR) signals of free radical were examined on 150 151 a spectrometer (JES-FA200, JEOL) under visible light irradiation ($\lambda > 420$ nm) using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as spintrapped reagent 152

2.5 Photocatalytic activity tests

The photocatalytic activities of MIL-53 and defective M e evaluated by 154 we the targeted tetracycline TC under visible light irradiation. Visible illumination was 155 obtained by a 300 W Xe lamp (CEL-HXF300, Cealight) equipped with a 420 nm 156 cutoff filter. Typically, 50 mg of the sample was depended into a 100 mL of 20 mg/L 157 TC aqueous solution. Prior to irradiation the spensions were fiercely magnetically 158 159 stirred for 60 min in the dark to reach the aborption-desorption equilibrium. Then, TC solution can be treated under sor ditions. Every 30 min, 4 mL of the reaction 160 Itered out the photocatalyst power, and the suspensions were taken of 161 ai priored by an UV-vis spectrophotometer (UV-2700, concentration of TC 162 citation wavelength. The removal efficiency (DE, %) was Shimadzu) under 55 163 calculated by the following equation: 164

165 $DE(\%) = (C_0 - C_t)/C_0 \times 100\%$

166 Where C_0 is the initial concentration of TC, and C_t is the TC concentration at time t.

- 167 **3. Result and discussion**
- 168 **3.1 Characterization of materials**

Fig. 1a shows the XRD patterns of MIL-53, D-1, D-2, D-3 and D-4. In the XRD patterns of MIL-53, the diffraction peaks located at 9.238° (110), 9.785° (200), 16.630° (112), 18.551° (220) respectively, which were in good agreement with the simulated patterns [35, 36]. Meanwhile, the crystalline nature of the products was confirmed by the sharp diffraction peak and high diffraction peak intensity [37]. In the

XRD, with the increased dosage of HCl (10, 20 to 30 μ L), the peak intensities of 174 XRD was obviously reduced, interestingly, when the dosage of HCl increased to 40 175 µL, the new diffraction peak corresponding to MIL-88(Fe) appeared. The results 176 showed that HCl plays an important role in the transformation between different 177 crystals forms of Fe-based MOFs. Sanil [38] reported the effect of dodecanoic acid on 178 the crytallinity and morphology of MOF of copper 1,3,5-benzenetricarboxylate 179 (Cu-BTC). The modulated samples show wellresoved prominent diffraction peaks 180 181 characteristic of CuBTC crystals. A line-broadening and lower of main peak in the XRD patterns. In the study of Zhao [39], acetic acid was used as an effective 182 coordination modulator to modulate the size, morphology 183 and crystal form of MIL-101 (Fe). A good yield and product quality could be reached compared to 184 experiments without addition of acetic acid. With increased addition of acetic acid 185 (5,10,15,20,25,30mL), the XRD peak intensity decreased. Notably, while the patterns 186 of A-35(mL) and A-40(mL) possessed a stronger reflection at 2 θ =10.92°, which 187 pointed to the rod-like by-product (MIL-33). ers benzoic acid played an important 188 role in the conversion between MIL-22 and VIL-101(Cr) [40] . HBC-0, HBC-1 and 189 HBC-3 samples, when using 0,1 nivelents of the benzoic acid additive, exhibit 190 ology, characteristic of MIL-101(Cr). Interestingly, particles with an octahedral 191 ъrр. id concentration to nearly double or more, which the increase of benze 192 5, 8 or 10 equivalents, caused the formation of lesser corresponds to the 193 amounts or no MIL 101(Cr). Indeed, for HBC-8, the content of nano-MIL-101(Cr) 194 decreases further and the rod-like MIL-88B (Cr) became dominant, while for HBC-10 195 196 only the micrometer-sized rod-like crystals of MIL-88B (Cr) were observed. Thereby 197 an interesting effect of a relatively sharp change of crystallization outcome depending on the concentration of the benzoic acid was observed, with a higher concentration 198 favoring the MIL-88(Cr) form. During the crystal formation, HCl had a double 199 function: it slowed down the hydrolysis of FeCl₃ 6H₂O and counteracted the 200 201 deprotonation of the dissolved carboxylic acids. The proper acid-base environment of the reaction system governed deprotonation of the organic linker and the crystal 202 203 nucleation process [41]. The other is that the HCl as a capping agent inhibited



Fig. 1. (a) XRD patterns of MIL-53 , D-1, D-2, D-3 and D-4; (b) FTIR spectra of MIL-53, D-1, D-4 ; (c) N_2 absorption-desorption isotherms of MIL-53, D-1 D-2, D-3 and D-4; (d) Pore size distribution of MIL-53, D-1,D-2, D-3 and D-4; (e) Quantitative relationship between amount of HCl and BET surface area.

210 The effect of HCl modulator on the functional group of MIL-53 was reflected in the infrared spectrum (FTIR). Since defects in the MOF lattice may play a major role 211 in the electronic and optical properties of the material [42], the defects and their 212 densities were investigated by FTIR spectroscopy. Typical IR vibration spectra of the 213 samples prepared with different HCl dosages are shown in Fig. 1b. In addition to the 214 215 characteristic adsorption band, the IR spectra characteristic vibrations of defects, which are correlated with the uncoordinated carboxylic group. In detail, the vibration 216 217 band at 1700 cm-1 corresponds to the C-O vibration of coordinated carboxylic groups and the vibration bands at 1547 cm-1 are representative of the asymmetric and 218 symmetric vibrations of free carboxylic group [43], meanwhilg ne peak at 747 cm-1 219 was identified as the formation of Fe-O bond [44]. Control groups with acid 220 coordinators added, the results shown that the IR spectrosci blue shift of C-O 221 vibration of coordinated carboxyl groups with the seaken peak intensity, indicating 222 that C-O-Fe bond changed with the HCl moculator. On the other hand, the 223 visualization of free carboxyl group indicated that the presence of more uncoordinated 224 ligands due to the absence of the metal cluster dissolved in HCl. 225

This speculation has been of ent with the weakening of the iron oxide peak 226 ree-acid synthesis, the IR band intensity of located at 747 nm. Com 227 are is roughly 1/2 and 1/4 for the modified MOFs with defect-related band at 228 0010 μ L HCl and Φ in the synthesis solutions. The similarly decreased peak I. 229 intensity in equal proportion was reflected in the defect -related Fe-O bands, and it is 230 reasonable to infer that the absence of metal clusters dissolved in HCl modulator is 231 232 the main cause of the defects.

Nitrogen sorption isotherms of HCl-modulated MIL-53 are shown in **Fig.1c**, which are typical I(b) isotherms are reported in the literature for MIL-53. The porosity results are shown in **Fig.1d** and the quantitative relationship between the Brunauer-Emmett-Teller (BET) surface area and the dosage can be seen in **Fig.1e**. The BET surface area and porosity results and the degree of roughness were shown in S Table 1. In the pore size distribution, the appearance of mesoporous structure is the most remarkable feature, in the presence of 10-30 μ L, which may be related to the

increased photocatalytic activity. Notablely, the disappearance of mesoporous 240 structure may contribute to the poor photocatalytic activity of D-4. Similarly, in the 241 facile synthesis of nano-sized MIL-101(Cr) with the addition of acetic acid, under too 242 high acetic acid concentration, there is no positive effect for MIL-101(Cr) synthesis, 243 and the by-product MIL-53 showed much lower porosity. In terms of specific surface 244 area, 10 µ L HCl played an important role in the increasing the specific surface area. 245 The increase in the specific surface area is noticeable in the presence of 10-30 μ L, 246 247 which may provide more active sites including adsorptive and catalytic ones for photocatalysis. The results were consistent with the study of Shearer[44], the BET 248 surface areas of UiO-66 vary significantly, ranging from 1175r 249 (no modulator) to 1777 m²/g (36Trif), which is one of the highest BET surface areas e 250 er reported for UiO-66 (the current record is $1890 \text{ m}^2/\text{g}$). 251

SEM is the most direct and effective means to characterize materials, as can be seen 252 the in Fig.2, under the action of acid regulation, crys al change from columnar to 253 double spindle is a remarkable feature A the remarkable feature is that the 254 255 appearance of smaller crystals, which were consisted with the XRD diffraction peaks that become wider and shorter. It tudy of Huang *et al.*, the irregular morphology 256 medulated by three alkaline nitrogen heterocycles existed in the modulated U 257 -6 miss [45]. In addition, tran n electron microscopy is an important technique to 258 acture. Because MOFs are generally quite sensitive to the characterization the 259 electron beam, it is lifficult to obtain highquality images, which was consistent with 260 the study of Zhou etal [46]. The mesoporous structures are clearly identified form D-1 261 and D-4. 262

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Fig. 3 TEM images of MIL-53(a,b); D-1 (c,d); D-2 (e,f)

The surface chemical compositions and states of surface element for MIL-53, D-1 and D-4 were characterized by XPS. The XPS survey spectrum verified that MIL-53 consisted of C, O and Fe. The high resolution XPS C1s spectrum in **Fig. 4a** was fitted into two peaks with the binding energies at 284.4 eV and 288.7 eV, corresponding to the C=C, C-H of the H₂BDC linkers and Fe–COOH functional groups [47]. The acreage ratio of Fe-COOH to C=C and C-H is 0.205 in MIL-53, while in D-1 it decreased to 0.189, then in D-4 it further decreased to 0.174, indicating that the breakage of Fe-O bond was resulted from the absence of the metal clusters. Compared to MIL-53, the red shift occurred when the binding energy of the two main peaks moved to the higher direction [48].

In the high resolution XPS O 1s spectrum (Fig. 4b), which comprise of two main 285 peaks located in 531.1 eV and 531.9 eV, derived from the oxygen atoms in the 286 carboxylic groups of the H₂BDC linker and the Fe-O bonds of the MIL-53, 287 288 respectively [49]. Compared to MIL-53, the red shift also occurred when the binding energy of the two main peaks moved to the higher direction. Meanwhile, the acreage 289 ratio of Fe-O to COOH is 0.849 in MIL-53, while in D-1 it decreased to 0.797, then in 290 D-4 it further decreased to 0.754, indicating that the share is shrinki 291 g attributed to the defect of metal clusters. XPS is helpful in analyzing the visital defects. XPS peak 292 position and strength contributed to the analysis on the coordination environment of 293 metal clusters and ligands. In the study of Xuan 1501, the defect sites of Trifluroacetic 294 acid (TFA) modulated UiO-66 was studied by PS The high resolution Zr 3d spectra 295 of UiO-66-X are studied. The spectra 296 Zr Meould be deconvoluted into two peaks. ed to Zr 3d_{5/2} of the zirconium atoms in Zr6 The peak at ~ 182.8 eV can be 297 Let n be ascribed to Zr $3d_{3/2}$ of the zirconium atoms clusters, and the peak at ~ 1 298 $-OH_2$ and Zr–OH). It can be seen that the increased in missing-linker defec 299 amount of TFA dic e proportion of Zr $3d_{5/2}$ and increase the proportion of Zr eas 300 3d_{3/2} due to the increased missing-linker defects in UiO-66-X. Besides, compare to 301 UiO-66-O, both the binding energy of Zr3d 5/2 and Zr 3d 3/2 for UiO-66-X synthesized 302 303 with TFA modulation shift to lower value. In our work, the XPS peak position and peak strength of the Fe 2p were slightly affected by the trace acid (Fig. 4c), the 304 significant effect was exhibited by 40 μ L HCl may be due to the changed coordination 305 environment of Fe from MIL-53 to MIL-88. Meanwhile, for binding energy, the red 306 307 shift indicates that the coordination bond of Fe-O changes. The FTIR combine with 308 the XPS analysis confirmed that the defect was caused by the sacrifice of the metal clusters. 309

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Therefore, acid regulation strategy has a great influence on the structure and

morphology of MIL-53. Structurally, the crystal growth was inhibited by 10 μ L HCl treatment and then smaller crystals were obtained; however, layer crystal structure regulated by 40 μ L HCl exhibited. Due to the contribution of HCl regulator, the increased specific structure and the pore structure transformed from microporous to mesoporous structure. It is essential to confirm the defect of the metal clusters from the FTIR and XPS analyses. These changes in structural may have an effect on their properties, such as the photoelectric properties, and they got further exploration.







Fig. 4 XPS Spectra of the MIL-53, D-1 and D-4 (a) C 1s of MIL-53, D-1 and D-4; (b)

327 **3.2 Photocatalytic activity of MIL-53 and D-MIL-53 (Fe)**

328 **3.2.1 Different photocatalytic activity**

Due to the widespread existence and perniciousness of organic pollution, antibiotic 329 wastewater by virtue of degradation-resistant was selected as the study object to 330 evaluate the photocatalytic activity of different materials [51-53]. Depicted in Fig. 5a 331 shows the comparison of TC removal efficiency on photocatalysts MIL-53 and 332 D-MIL-53 (D-1 - D-10). Obviously, all the samples could adsorb TC to some degree 333 334 in the darkness, which was due to the good adsorption ability of MOFs with mesoporous structure [54]. As a typical porous material, adsorption property of MOFs 335 could not be ignored. Both the adsorption and the photocr 336 anytic capacity were improved of D-1, D-2 and D-3. The increased adsorption wacity was due to the 337 contribution of increased specific surface area and pore volume which was consistent 338 with the previous BET characterization. The photoc talytic degradation efficiency of 339 MIL-53 was 60.1%, however, small amount of HCL (10 µL, 20 µL and 30 µL) could 340 dramatically improve the photocatalytic etivit (99.1%, 79.2% and 69.2%). Notably, 341 the photocatalytic activity of D-1 was 15 time enhanced compared to that of MIL-53. 342 degradation efficiency was reduced to 52%, On the other hand, the photoca 343 41 µL, 50 µL, 100 µL HCl into precursor solution. 42% and 37% when further, 344 HCl over 40 µL exh negative impact on the photocatalytic performance, 345 леа indicating that the of acid modulator affected the photocatalytic activity of 346 mò materials. In addition, the quantitative relationship between the photocatalytic 347 activities the photocatalyst and the modulators are as shown in **Fig. 5b**. Furthermore, 348 regular linear results exhibited by the plots of $-\ln(C_t/C_0)$ versus irradiation time (t) 349 350 indicated that photocatalytic process followed the first order kinetic equation [55]. The photocatalytic activities of different materials were analyzed and the reaction 351 kinetic constants of different photocatalysts were calculated. The datas in Fig.5 were 352 fitted, the calculated first-order reaction kinetic constants were 0.01042, 0.00701, 353 0.00556, 0.004 and 0.00338, and the corresponding correlation coefficients (R^2) were 354 0.96232, 0.97312, 0.96866, 0.93659, 0.95528. Compared with MIL-53, the reaction 355 rates of D-1, D-2, D-3 and D-4 were increased by 2.6, 1.8, 1.4 and 0.85 times. The 356

results showed that the acid is sensitive in enhanced photocatalytic reactivity.

358 3.2.2 The effect of initial TC concentrations

Actually, the concentration of TC varies largely in the natural environment, and 359 high concentration of wastewater may have passivation effect on photocatalysts. Thus, 360 it is essential to discuss the effect of initial TC concentration on the photocatalytic 361 362 performance of the photocatalyst. Based on the above results, the D-1 by virtue of its excellent photocatalytic activity was selected as the research object and the response 363 of different concentration antibiotic wastewater was studied. Fig. 5c displayed the 364 effect of different initial TC concentration on the degradation efficiency of D-1. 365 Obviously, it can be seen that the degradation rate is af **Exted** by the initial 366 concentration to some extent. D-1 has the best removal result for the degradation of 367 10 mg/L TC wastewater and almost complete degradation was where (96.9%). The 368 removal efficiencies of TC declined to 79.1% when the initial TC concentration 369 increased to 40 mg/L. It may be that dense to cacyoline molecules restric light 370 transmition. The adsorption sites are competed to prent molecules and intermediates, 371 which leads to low photocatalytic efficiency 372 5.571.

373 **3.2.3** The removal efficiency of total product carbon (TOC)

ni carbon (TOC) was used to measure the degree The variation of the tot 374 I OI shall be degradation pollutants. As shown in Fig. S1, the of mineralization of ph лоса 375 or the D-4, MIL-53 and D-1 were 12.3 %, 18.7 % and TOC removal efficience 376 21.9 % under 30 mm light exposure, when the light increased to 150 mins, the TOC 377 removal efficiencis increased to 39.8%, 50.5% and 61.3%. The results demonstrate 378 379 that the defective MIL-53, based on he mineralization ability, has good photocatalytic 380 activity. The identification of intermediates and inference of photocatalytic degradation pathway based on mineralization process was aided by LC-MS/MS and 381 3D EEMs. 382

383 **3.2.4 Possible photocatalytic degradation pathway of TC**

The pathway of photocatalyic degradation was clarified in the process of photocatalytic degradation. The degradation intermediates of TC in the presence of D-1 were identified by LC-MS/MS, as shown in **Fig. S2**. Based on the detected

intermediates, the photocatalytic degradation pathway was speculated as shown in Fig. 387 **S3.** The generated intermediate TC 1 was attributed to the reaction of TC deamidation, 388 while the transformation from TC 1 to TC 2 was based on the loss of dimethylamino 389 group. Then the TC 2 was fragmented into TC 3 through a series of transformations, 390 including dehydroxylation, opening rings of benzene, deethylation and additional 391 392 reaction. In the end, the deacetylation and oxidation reaction was responsible for the change from TC 3 to TC 4. The presumed photocatalytic degradation pathway was 393 394 consistent with that of Yang et al. by Ag@AgI/V_I-BOI photocatalyst [58].

Additional, 3D EEMs can also explain the TC degradation pathway to a certain 395 extent. As revealed in Fig. S4 (a) and (b), there was no sig Recant difference the 396 original solution and the solution obtained after 60 min dam adsorption, suggesting 397 that in the dark reaction stage, adsorption played a hadag role. Conversion 398 conditions to provide a visible light source, the flucture peak located at $\lambda ex/\lambda em$ 399 $= (340-350 \text{ nm})/(500-510 \text{ nm}) \text{ and } \lambda \text{ex}/\lambda \text{em} = (33)$ 34 nm)/(495–505 nm) appeared 400 Fig. S4 (c), suggesting the structure of intermed tate products are similar to the fulvic 401 402 acid and humic acid [59,60]. With the passage of time to 150 min Fig. S4 (d), the offimed in depth by the deepen intensity of the photocatalytic degradation has be 403 re consistent with the inferred photocatalytic fluorescence peak, and the 404 St degradation pathway. A intermediates may evolve further into CO₂ and H₂O. 405 a th

406 3.2.5 Reusability and subjects

The reusability and stability of materials are important for practical application. As 407 shown in **Fig. S5**, compared to 90.1% degradation efficiency of D1 under the 20 mg/L, 408 it reduced to 74.3% after four times recycle, suggesting that the modulated MOFs was 409 410 stable and reusable. Good stability and reusability are important guarantees for practical application. Interestingly, as can be seen in **Fig.S6** the diffraction of XRD 411 changed obviously after photocatalytic reaction, the diffraction of which was 412 413 consistent with MIL-88 [61], indicating that irradiation is the driving force of crystal transformation. In the study of Nguyen etal [62], the photocatalytic activities of 414 MIL-88 and that of MIL-53 were compared, it of MIL-88 was slightly lower than that 415 of MIL-53. This also explains why MIL-53 photocatalytic activity decreases after 416

417 several cycles, and the key to the problem lies in the crystal transformation. In the study of Zhou, in the preparation of CTAB/CA (CTAB, cetyltrimethylammonium 418 bromide; CA, citric acid) modulated Cu₂(BTC)₃, for the samples synthesized with 419 high CTAB/CA ratios, their X-ray diffraction patterns are in good agreement with that 420 reported for Cu₂(BTC)₃. Nonetheless, an excess amount of CA favors the generation 421 of a new crystalline phase with a typical diffraction line at $2\theta = 10.1^{\circ}$. The 422 incorporation of excessive CA into frameworks should be responsible for the new 423 424 phase. However, the formation of composite photocatalyst can increase the stability of MIL-53, such as Ag₃PO₄/MIL-53 [63], SnS/MIL-53 [64], the stability of 425 photocatalyst was confirmed by the diffraction peaks that remained consistent before 426 and after the reflection. In addition, we provided the SEM mages after degradation, 427 which was important to analyze the mechanism and subject of photocatalytic 428 degradation. As can be seen in Fig. S7, after the reaction, the most remarkable feature 429 is the appearance of many regular hexahedral exystals, which represented the typical 430 XFD characterization. structure of MIL-88 and were consisted with th 431

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Fig.5 (a) The different photocatalytic activity of MiL-53, D-1, D-2, D-3, D-4, D-5 and
D-10; (b) (inner) Kinetic curves of a C legradation by MIL-53, D-1, D-2, D-3 and
D-4; (b) The qualitative relation in oet seen different of HCl content and the removal
efficiency; (c) The impact of initial TC concentration on D-1.

450 **3.3 Mechanism of different photocatalytic activity**

The optication perties play important roles in assessing the photocatalytic 451 abilities for photocatalysts. The light-absorption property of MIL-53, D-1 and D-4 452 453 were tested through the UV-vis DRS measurements. As shown in Fig. 6a, MIL-53, including the perfect and modulated types, displayed a strong absorption within the 454 visible light range, signifying their potential capacity for visible-light harvesting 455 [65]. In the UV-vis DRS spectrum of MIL-53, the absorption peak at 445 nm, it of 456 D-1 and D-4 are similar with that of MIL-53, which was attributed to the 457 spin-allowed d-d transition ($[^{6}A_{1g} \rightarrow 4A_{1g} + {}^{4}Eg(G)]$) of Fe³⁺ in MOFs [67]. Similar 458 band gap of MIL-53, D-1 and D-4 located at 2.70 eV, 2.70 eV, 2.60 eV (Fig. 6b), 459 based on the relation of Eg=1240/ λ , which were similar to the existing findings. In 460

461 the study of Du *et al.* [35], it can be observed that the absorption edge of the as-prepared MIL-53(M) photocatalysts is gradually shifted to longer wavelength by 462 altering metal ions from Al to Cr and to Fe. The onset of the main absorption edge 463 of MIL-53 (Al), MIL-53 (Cr) and MIL-53 (Fe) was 320 nm, 395nm and 455 nm, 464 which corresponds to the band gaps (Eg) of 3.87, 3.20 and 2.72 eV 465 (Eg=1240/wavelength). In the study of Nguyen et al. [66], the MIL-53(Fe) samples 466 show the strong absorption bands in the range of 200-450 nm, which can be 467 468 assigned to absorption induced by ligand-to-metal charge transfer (LMCT) of O (II) \rightarrow Fe(III). A band gap of MIL-53(Fe) was estimated to be 2.72 eV. In addition, in 469 the study of Liang et al. [67], the main optical absorption e of MIL-53-0.5% 470 1240/2 RGO is estimated to be 455 nm. Based on the relation Exthe calculated 471 optical band gap of which is 2.72 eV. Other similar work has been reported in the 472 study of Bai et al. [37], Lin et al. [68], and et al. [69]. Considering the 473 photoactivity, the band gap may not be the or affecting the photocatalytic 474 na 475



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Fig.6 (a) UV-visible light spectra of MIL-53, D-1 and D-4; (b) Band-gap of MIL-53,
D-1 and D-4.





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488 Fig.7 The photoelectric characterization (a) Photoluminestence spectra for MIL-53,
489 D-1 and D-4; (b) Transient photocurrent responses of MIL-53, D-1 and D-4; (c) EIS
490 Nyquist plots of MIL-53, D-1 and D-4;(d) Transient flurrescence lifetime of MIL-53,
491 D-1 and L-4

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th photocatalytic activity was analyzed from The separation of photocarriers related w 492 three aspects:(1) Photoluminesc emission was considered as a reference for 493 n¢, the separation system of photogenic carriers [70]. Generally, a lower PL intensity 494 corresponding to a high photocatalytic activity was due to the enhanced photo-excited 495 electron-hole pairs eration efficiency [71]. Fig. 7a revealed the differences on the 496 PL spectra of MIL-5, D-1 and D-4 under an excitation wavelength of 340 nm. Upon 497 photoexcitation at 340 nm, the MIL-53 photocatalyst exhibited a broad band at 498 400-500 nm with peaks at 425 nm, 465 nm and 490 nm, respectively. The reduced PL 499 intensity of D-1, compared to the MIL-53, indicated the delayed combination of 500 photo-induced electron-hole pairs due to the HCl modualtor. At the same time, there 501 was a significant red shift. Meanwhile, the deformation of photoluminescence 502 spectrum may be related to the structural change of D-4. (2) Photocurrent (PC) 503 represents the migration of photogenic carriers. As shown in Fig. 7b, the photocurrent 504 of the D-1 is the most prominent, indicating that the fast separation rate of 505

photo-excited charges was controlled by defect. This may be the defect sites as a traps 506 to capture the generated electrons and holes, resulting in the prolonged the charge 507 carriers lifetime [72]. Besides, Fig. 7c showed the EIS analysis. it is obvious that the 508 relative size of art is in the order of D-4 > MIL-53 > D-1, suggesting that defective 509 MIL exhibited a more efficient charge separation and electron transfer ability. In 510 addition, simulated equivalent circuit of impedance analysis was shown in Fig. S8, 511 and the fitting degree values of D-1, MIL-53 and D-4 are 2.32E⁻³, 2.17E⁻³, 3.49E⁻³, 512 respectively. Combining all the optical representations, the defect strategy by acid 513 modulator can regulate the optical properties. To illustrate the separation and 514 recombination of photogenic carriers, we further tested the fl Descence lifetime of 515 the materials including D-1, D-4 and MIL-53, as shown in Fig. 7d. Refer to 516 multi-exponential fitting, the fluorescence lifetimes of MA-3 D-1 and D-4 were 517 0.80 ns, 0.85ns, 0.77 ns, and the results showed that acid regulation prolongs the life 518 of the photogenic carriers. The reduced fluorescence life of D-4 was attributed to the 519 changed crystal form from MIL-53 to MIL-88 (h) increase of fluorescence lifetime 520 521 makes photogenic carriers more likely to participate in photocatalytic reaction before recombination. 522

It is necessary to determine the VBM of the samples by UPS, and accurate 523 information was provided to determine the energy level structure of the material. The 524 bandgap energy (E) of MIL-53, D-1 and D-4 were determined to be 2.70 eV, 2.70 eV 525 and 2.60 eV, respectively. Next, ultraviolet photoelectron spectroscopy (UPS) 526 provides a basis for determining the energy level structure. As shown in **Fig.8**, the 527 valence band energy (ECB) were 6.20 eV, 5.82 eV, 5.90 eV for MIL-53, D-1 and D-4. 528 Moreover, the cutoff energy (Ecutoff) of MIL-53, D-1 and D-4 are 18.34 eV,18.30 eV 529 530 and 18.52 eV on the basis of fermi level (E_f) are 0 eV. According to the following equation, $e\Phi = hv - |E_{cutoff} - E_f|$, their work function (e Φ) were equal to 2.86 eV, 2.90 531 eV and 2.68 eV, as shown in **Fig.9**. The transport of photogenic carriers is driven by 532 larger work function, thus, the high photocatalytic activity may be related to the large 533 work function. In addition, the VB can be determined by virtue of XPS, as shown in 534

Fig.S9. The VB of MIL-53, D-1 and D-4 are 1.60 eV,1.60 eV and 1.50 eV, the results showed that the two technologies including UPS and XPS-VB used different light sources and the values are highly similar.



Fig.9 The energy level structure of MIL-53, D-1 and D-4.

Free radicals provide the power for photocatalytic reactions and some 547 oxygen-containing such as O_2^- (superoxide radicals) and OH (hydroxyl radicals) 548 have been confirmed in free radicals capture experiments. For D-1 with the highest 549 photocatalytic activity, there was no signal under dark conditions, instead, the signal 550 peak with equal spacing of 1: 1: 1: 1 appeared at 5 min and was considered to be O_2^{-} , 551 as shown in Fig. 10a. Attributed to the more negative reduction potential of O_2/O_2^{-1} 552 (-0.33 eV vs NHE), it makes it impossible for O₂ to react with the electrons on the CB 553 of D-1 to the generation of O_2^{-} . The signal peak was strengthened, when increasing 554 time to 10 mins, indicating that more active O_2^- were generated. The change trend 555 of O_2^- was consisted with that of the TC degradation, indicating that they were the 556 driving force of photocatalytic degradation. The similar trend 557 was bserved in the MIL-53 (Fig. S10a) and D-4(Fig. S10c). 558

On the other hand, the signal peak with equal spacing of 1:2:2:1 was deemed as the 559 signal peak of OH. As show in Fig. 10b, the characteristic signals of OH could be 560 ignored in dark while it appeared at 5 and 1 mil. The generation of OH mainly 561 comes from two aspects: (1) The reduction O^{2-} via the routes of $O^{2-} \rightarrow H_2O_2$ 562 NHE) of D-1 was less then the oxidation \rightarrow OH, as the VB potential (2) 563 NLE), which failed to oxidize the H₂O surface or potential of OH^{-/} OH (2.40, 564 errated from the electrons reaction with dissolved O₂ OH^{-} to form OH; (2) 565 $_2\mathcal{O}_2$ and H⁺, then which soul further transformed to generate OH as reaction: e_{CB} + 566 $H_2O_2 \rightarrow OH + OH [73]$, indicating that OH as another important driver propel the 567 photocatalytic reactions. The similar trend was observed in the MIL-53 (Fig. S10b) 568 and D-4 (Fig. S10d). Thus, O²⁻ and OH are provided by modulated MOFs as driving 569 570 forces to demineralize the organic pollutants.



Fig. 10 The active drivers associated with the photocatalytic process in D-1 (a) O_2^- ; (b) OH.

578 4. Conclusions

It is interesting and meaningful to application of HCl-modulated MIL-53 for the 579 580 photocatalytic degradation of organic pollutants, providing another possibility for the removal of organic pollutants. The effect of acid modulator on structure and the 581 photocatalytic activity were emphasically investigated. Structurally, the increased 582 583 specific surface and new mecroporous structures caused by acid modulator may be related with the defects due to the absence of metal clusters. The differences in 584 585 properties, in particular, the photocatalytic properties affected by the differences in structure. Compare with MIL-53, the photocatalytic activity of acid-regulated MIL-53 586 increased by 1.5 times due to the easier separation of photomerated carriers, in 587 addition, the quantitative relationship between the content of modulator and the 588 photocatalytic activity was revealed. Good recycling unth the fourth cycles is an 589 important guarantee for reuse. In addition, form the ERP analysis, O2 and OH are 590 provided by modulated MOFs as driving forces to a mireralize the organic pollutants. 591

592 Acknowledgements

he Program for the National Natural 593 This study was financially supported by N1 / Science Foundation of China (51 1579098, 51779090, 51709101, 51521006, 594 51,08177), the National Program for Support of 51809090, 51278176, 5137 595 as of China (2014), the Program for Changjiang Top - Notch Young P 596 лes Scholars and Info Besearch Team in University (IRT-13R17), and Hunan 597 otiv Provincial Science and Technology Plan Project (2018SK20410, 2017SK2243, 598 2016RS3026), and the Fundamental Research Funds for the Central Universities 599 (531109200027, 531107051080, 531107050978). 600

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