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# Covalent organic framework with sulfonic acid functional groups for visible light-driven CO<sub>2</sub> reduction†

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In this study, a covalent organic framework (TpPa-SO<sub>3</sub>H) photocatalyst with sulfonic acid function groups was synthesized using a solvothermal method. The morphologies and structural properties of the as-prepared composites were characterized by X-ray diffraction, infrared spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy, N<sub>2</sub> adsorption-desorption measurements, and field emission scanning electron microscopy. An electrochemical workstation was used to test the photoelectric performance of the materials. The results show that TpPa-SO<sub>3</sub>H has -SO<sub>3</sub>H functional groups and high photocatalytic performance for CO<sub>2</sub> reduction. After 4 h of visible-light irradiation, the amount of CO produced is 416.61 μmol g<sup>-1</sup>. In addition, the TpPa-SO<sub>3</sub>H photocatalyst exhibited chemical stability and reusability. After two testing cycles under visible light irradiation, the amount of CO produced decreased slightly to 415.23 and 409.15 μmol g<sup>-1</sup>. The XRD spectra of TpPa-SO<sub>3</sub>H were consistent before and after the cycles. Therefore, TpPa-SO<sub>3</sub>H exhibited good photocatalytic activity. This is because the introduction of -SO<sub>3</sub>H narrows the bandgap of TpPa-SO<sub>3</sub>H, which enhances the visible light response range and greatly promotes the separation of photogenerated electrons.

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## Introduction

Rapid industrial development is associated with the combustion of fossil fuels. However, fossil fuels are a limited resource, and dependence on them will result in an energy crisis. Moreover, burning fossil fuels increases the concentration of CO<sub>2</sub> in the atmosphere. CO<sub>2</sub> is one of the main greenhouse gases responsible for global warming, which could affect the development and survival of human beings.<sup>1,2</sup> As environmental issues attract increasing attention worldwide, the utilization of resources and the reduction of CO<sub>2</sub> emissions have become important considerations. Therefore, it is imperative to develop clean and green CO<sub>2</sub> conversion technology.<sup>3,4</sup>

Semiconductor photocatalysis technology can transform solar energy into chemical energy without pollution, and they are considered to be the most effective means of alleviating the energy crisis and environmental pollution.<sup>5,6</sup> As early as 1979, Fujishima used photocatalytic technology to reduce CO<sub>2</sub>,<sup>7</sup> and there have since been many reports on photocatalysts. Common CO<sub>2</sub> reduction photocatalysts include inorganic

semiconductors,<sup>8-10</sup> metal-organic frameworks (MOFs),<sup>11</sup> and covalent organic frameworks (COFs).<sup>12</sup> In particular, TiO<sub>2</sub> is widely used for photocatalytic CO<sub>2</sub> reduction because of its low cost, high stability, and low toxicity.<sup>13</sup> However, it has a wide band gap (3.2 eV) so efficient photocatalytic performance cannot be achieved with visible light. Therefore, it is necessary to use physical or chemical methods to modify TiO<sub>2</sub> and improve its photocatalytic efficiency.<sup>14</sup> In contrast, g-C<sub>3</sub>N<sub>4</sub> has a narrow band gap (2.7 eV), which results in high photocatalytic activity and an excellent visible light response.<sup>15</sup> However, owing to the short recombination lifetime of fast charge carriers, the charge separation of g-C<sub>3</sub>N<sub>4</sub> is insufficient. Moreover, it has low crystallinity and a small specific surface area, so it cannot make full use of light, and its photocatalytic performance is limited.<sup>16</sup> MOFs can effectively capture light, shorten the carrier transmission distance, and enhance the separation of electrons and holes, so they can be used as new functional materials for photocatalysts.<sup>17,18</sup> However, MOFs are not functionalized or synthesized with heterojunction materials, and they do not have high photocatalytic activity and stability. Therefore, it is often necessary to modify MOFs to improve their photocatalytic performance.<sup>19</sup> Conjugated microporous polymers (CMPs) can capture light and have an effective charge separation capability, so they have been extensively studied in the field of photocatalysis.<sup>20-22</sup> However, the formation of CMPs is controlled by kinetics, and they are linked by irreversible

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Fig. 1 Schematic diagram of synthesis of the TpPa-SO<sub>3</sub>H and TpPa photocatalysts.

organic covalent bonds. Therefore, the structure is amorphous and forms a disordered microporous polymer.<sup>23</sup>

COFs are new two- or three-dimensional organic crystalline polymer materials composed of light elements (*e.g.*, C, N, O, and B), which have adjustable pore diameters, low density, and strong stability.<sup>18,24</sup> Moreover, they have excellent semiconductor characteristics for photocatalysis, such as good absorption of visible light, a suitable band gap, and fast charge carrier mobility.<sup>25,26</sup> COFs have  $\pi$ - $\pi$  conjugated units, which can maintain good chemical stability under acidic and alkaline conditions and in different organic solvents.<sup>27,28</sup> Furthermore, COFs have a large specific surface area, which exposes more photocatalytic sites, thereby increasing the light absorption capacity. Owing to their excellent characteristics, COFs are widely used as efficient photocatalytic catalysts for CO<sub>2</sub> reduction,<sup>29</sup> degradation of organic pollutants,<sup>30</sup> Cr(VI) reduction,<sup>31</sup> water decomposition,<sup>32</sup> hydrogen evolution,<sup>33,34</sup> *etc.*

Herein, we report the covalent organic framework TpPa-SO<sub>3</sub>H with a sulfonic acid function groups for the photocatalytic reduction of CO<sub>2</sub> (Fig. 1). Compared to TpPa, TpPa-SO<sub>3</sub>H is expected to exhibit excellent light absorption ability and abundant photocatalytic activity sites under visible-light illumination. The introduction of -SO<sub>3</sub>H group can reduce the band gap, it will effectively promote the transfer and separation of interface charges, accelerate the migration of carriers, and inhibit the recombination of electrons and holes. Thus, TpPa-SO<sub>3</sub>H will have great potential in visible light-driven reduction of CO<sub>2</sub> emissions.

## Experimental

### Synthesis and characterization

The TpPa-SO<sub>3</sub>H and TpPa were synthesized according to a solvothermal procedure. We synthesized two kinds of imine-linked COFs through the reaction of 2,4,6-trihydroxy-1,3,5-benzenetricarbaldehyde (Tp) with two different monomers 2,5-diaminobenzenesulfonic acid (Pa-SO<sub>3</sub>H) and *p*-phenylenediamine (Pa) (Fig. S1 and S2†). Thermogravimetric analysis (TGA) showed that TpPa-SO<sub>3</sub>H and TpPa had similar thermogravimetric curves. Compared to TpPa-SO<sub>3</sub>H, TpPa showed higher thermal stability, but both materials exhibited good thermal stability at room temperature ( $\sim 25$  °C) and pressure (Fig. S3†). X-ray diffraction (XRD) was used to determine the crystal structural of TpPa-SO<sub>3</sub>H and TpPa (Fig. 2a and b). The XRD pattern of TpPa-SO<sub>3</sub>H showed two main characteristic

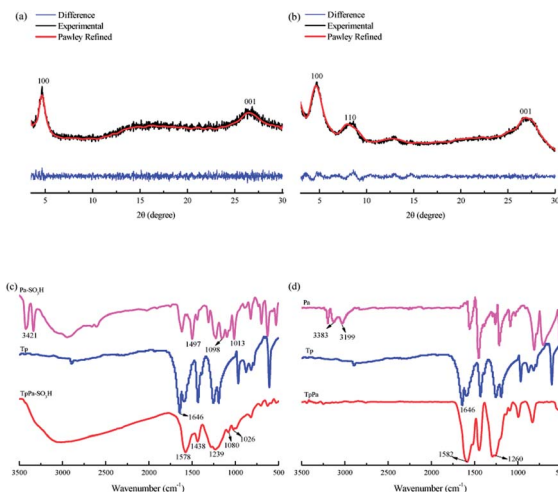


Fig. 2 XRD patterns of (a) TpPa-SO<sub>3</sub>H and (b) TpPa. FT-IR spectra of (c) TpPa-SO<sub>3</sub>H and (d) TpPa.

peaks at  $2\theta = 4.67^\circ$  and  $26.62^\circ$ , which correspond to the 100 and 001 planes, respectively. TpPa showed a main diffraction peak at  $4.79^\circ$ , which corresponds to the 100 plane. There was a slightly wider diffraction peak at  $8.54^\circ$ , which can be attributed to the 110 plane. Finally, the diffraction peak at  $27.04^\circ$  is assigned to the 001 plane. The peak positions of the synthesized COFs were consistent with the simulated positions, indicating that TpPa-SO<sub>3</sub>H and TpPa were successfully synthesized. The structures of TpPa-SO<sub>3</sub>H and TpPa were investigated using FT-IR (Fig. 2c and d). Fig. 2c shows that Tp had a stretching vibration absorption peak associated with C=O at  $1646\text{ cm}^{-1}$ , and Pa-SO<sub>3</sub>H had a telescopic vibration associated with -NH<sub>2</sub> at  $3421\text{ cm}^{-1}$ . There were also symmetric and asymmetric stretching bands associated with O=S=O at 1013, 1098, and  $1497\text{ cm}^{-1}$ , indicating the presence of sulfonic acid groups. The stretching bands at  $1646\text{ cm}^{-1}$  for C=O and  $3421\text{ cm}^{-1}$  for -NH<sub>2</sub> disappeared in the synthesized products. Symmetric and asymmetric stretching bands were observed at  $1578\text{ cm}^{-1}$  for C=C and  $1239\text{ cm}^{-1}$  for C-N, and 1026, 1080, and  $1438\text{ cm}^{-1}$  for O=S=O. This indicates that TpPa-SO<sub>3</sub>H was synthesized successfully. The Fourier transform infrared spectrum of TpPa showed that the C=O stretching band of Tp at  $1643\text{ cm}^{-1}$  and the stretching vibration bands of the NH<sub>2</sub> group of Pa at 3383 and  $3199\text{ cm}^{-1}$  disappeared, indicating that the monomers were completely consumed. Moreover, new C=C and C-N stretching vibration bands appeared at 1582 and  $1260\text{ cm}^{-1}$ , respectively. Thus, TpPa was synthesized successfully. Full-spectrum and energy dispersive X-ray (EDX) elemental mapping showed that TpPa-SO<sub>3</sub>H is composed of four elements: C, N, O, and S (Fig. S4 and S6a†). The C 1s spectrum was convolved into three peaks with binding energies of 284.8, 286.16, and 289.64 eV, corresponding to C-C, C=N or C-O, and C=O bonds, respectively. The high-resolution XPS spectrum of O 1s deconvolved into two peaks with binding energies of 531.5 and 532.85 eV corresponding to C-O and C=O bonds, respectively. The high-resolution X-ray photoelectron spectroscopy (XPS) spectrum of S 2p. One binding energy is attributed to S



2p<sub>3/2</sub> at 168.1 eV, and the other to S 2p<sub>1/2</sub> at 169.3 eV. This confirms that the TpPa-SO<sub>3</sub>H structure was formed (Fig. S4†). Similarly, TpPa is composed of C, N, and O elements (Fig. S5 and S6†). C 1s was convolved into three peaks with binding energies of 284.8, 285.93, and 289.25 eV, corresponding to C-C, C=N or C-O, and C=O bonds, respectively. The high-resolution XPS spectrum of O 1s deconvolved into two peaks with binding energies 530.98 and 532.76 eV corresponding to C-O and C=O bonds, respectively (Fig. S5†). Within the relative pressure range  $P/P_0 < 0.1$ , the proportion of TpPa-SO<sub>3</sub>H and TpPa increased sharply. This may be due to some structural condensation in the synthesis process. According to the IUPAC classification, under relative pressure, both materials have an H3 hysteresis loop, and the isotherms are similar to type IV isotherms. Therefore, owing to the existence of mesopores. The Brunauer-Emmett-Teller (BET) specific surface areas of TpPa-SO<sub>3</sub>H and TpPa were 63.61 and 779.62 m<sup>2</sup> g<sup>-1</sup>, respectively. The BET specific surface area of TpPa was higher than that of TpPa-SO<sub>3</sub>H, possibly owing to the introduction of the -SO<sub>3</sub>H group to the benzene ring. The pore size of TpPa-SO<sub>3</sub>H is smaller than that of TpPa owing to the introduction of the -SO<sub>3</sub>H group. The pore sizes of TpPa-SO<sub>3</sub>H and TpPa are 3.68 and 4.28 nm, respectively, and the pore volumes are 1.22 and 0.52 cm<sup>3</sup> g<sup>-1</sup>, respectively (Fig. 3). The maximum CO<sub>2</sub> adsorption capacities of TpPa-SO<sub>3</sub>H and TpPa were 34.28 and 57.47 cm<sup>3</sup> g<sup>-1</sup> (Fig. S7†), respectively. The adsorption enthalpy  $\Delta H$  is the isosteric heat of adsorption  $Q$  produced during the adsorption process. This is calculated using the Clausius-Clapeyron equation,  $\ln P = -\Delta H/RT + C$ . Therefore, the CO<sub>2</sub> isosteric heat of adsorptions  $Q$  of TpPa-SO<sub>3</sub>H and TpPa are -34.08 and -33.61 kJ mol<sup>-1</sup>, respectively. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the TpPa-SO<sub>3</sub>H and TpPa show that the surface of TpPa is smooth and flat with a clustered structure, and the introduction of -SO<sub>3</sub>H makes the surface rough, with an obvious fibrous structure. Ordered structures can provide efficient transport paths for reactants, and more active sites for the photocatalytic reactions (Fig. S8†). UV-vis diffuse reflectance spectroscopy (DRS) was used to study the light absorption and photochemical properties of the two materials. The semiconductor bandgap energy  $E_g$  was calculated using the Tauc plot method. The bandgap energy  $E_g$  of a semiconductor can be calculated using the equation  $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$ , where  $\alpha$  is the optical absorption coefficient,  $h$  is the photon energy,  $\nu$  is the frequency,  $E_g$  is the forbidden

bandwidth of the material,  $A$  is a proportional constant, and the  $n$  indicates the type of optical transition of the semiconductor. Here, the value of  $n$  is 2, therefore, both materials are indirect bandgap semiconductors. The light absorption range of TpPa-SO<sub>3</sub>H is greater than that of TpPa. Thus, according to the Tauc mapping method, the electron energies of TpPa-SO<sub>3</sub>H and TpPa are 1.61 and 1.97 eV, respectively. The bandgap of TpPa-SO<sub>3</sub>H was narrower than that of TpPa. Therefore, TpPa-SO<sub>3</sub>H has stronger visible-light absorption capability (Fig. 4a and b). The photoelectric properties of TpPa-SO<sub>3</sub>H and TpPa were tested using a CHI660e three-stage electrochemical workstation, and the carrier separation efficiency was investigated further. Mott-Schottky (MS) curves with frequencies of 500,

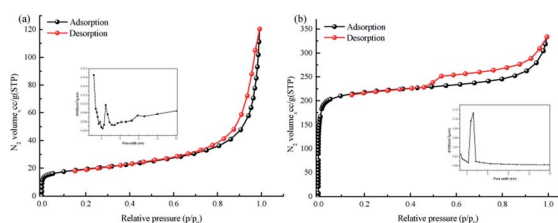


Fig. 3 N<sub>2</sub> adsorption-desorption isotherms of (a) TpPa-SO<sub>3</sub>H and (b) TpPa.

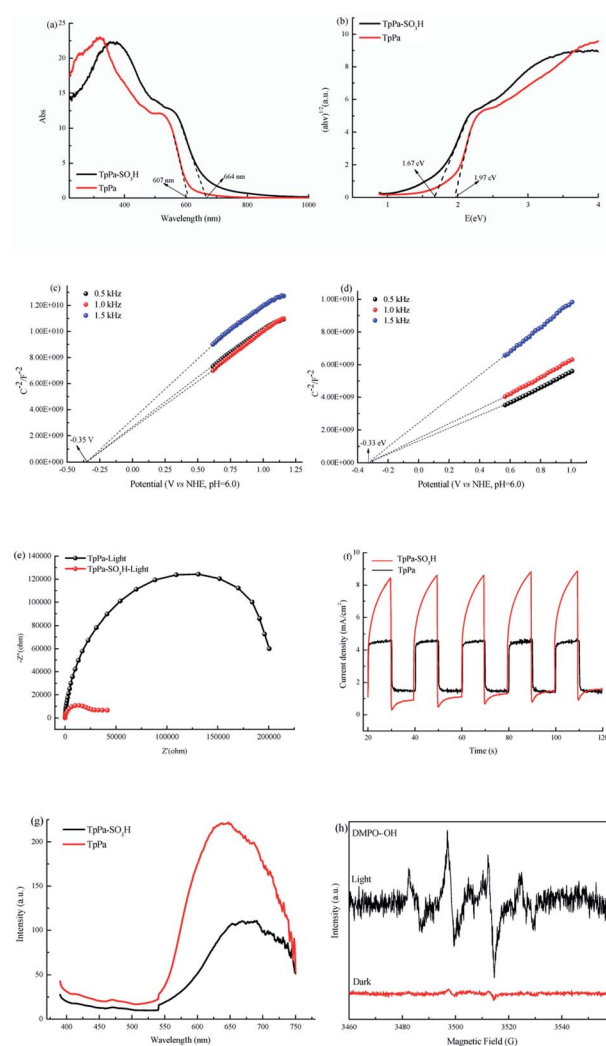


Fig. 4 UV-vis DRS images of (a) TpPa-SO<sub>3</sub>H and TpPa. (b) Plots of  $(\alpha h\nu)^{1/2}$  as a function of energy ( $h\nu$ ) for bandgap energies of TpPa-SO<sub>3</sub>H and TpPa. Mott-Schottky (MS) plots of (c) TpPa-SO<sub>3</sub>H and (d) TpPa. (e) Nyquist plot of electrochemical impedance spectra (EIS) of TpPa-SO<sub>3</sub>H and TpPa. (f) Transient photocurrent response of TpPa-SO<sub>3</sub>H and TpPa. (g) Photoluminescence (PL) emission spectra of TpPa-SO<sub>3</sub>H and TpPa. (h) Electron spin resonance (ESR) spectra of DMPO-•OH under visible light irradiation.



1000, and 1500 Hz were used under dark conditions (Fig. 4c and d). The MS method was used to analyze the conduction bands of TpPa-SO<sub>3</sub>H and TpPa. That is, a straight line was drawn from the MS curve to the *x*-axis to obtain the conduction band potentials, which were -0.35 and -0.33 V for TpPa-SO<sub>3</sub>H and TpPa, respectively. Fig. 4c and d shows that the slopes of the MS curves for TpPa-SO<sub>3</sub>H and TpPa were positive, which confirms that both materials are n-type semiconductors. Electrochemical impedance spectroscopy (EIS) and transient photocurrent (PC) response measurements were used to further study the carrier separation efficiency. Under illumination, Nyquist semicircle radius of TpPa-SO<sub>3</sub>H was much smaller than that of TpPa (Fig. 4e). This shows that the introduction of -SO<sub>3</sub>H can improve the charge-transfer ability of the material. To evaluate the charge separation abilities of TpPa-SO<sub>3</sub>H and TpPa, the switching period photocurrent responses of the two materials under light irradiation were measured (Fig. 4f). The photocurrent distribution is shown in Fig. 4f, TpPa-SO<sub>3</sub>H produced a stronger photocurrent than TpPa. This shows that the introduction of the -SO<sub>3</sub>H group can effectively promote charge separation and accelerate the separation of charge carriers. Compared to TpPa, TpPa-SO<sub>3</sub>H showed a lower PL intensity (Fig. 4g). The PL decay profiles, fitting parameters and average lifetimes (Fig. S9 and Table S1†) reveal that the PL lifetime ( $\tau$ ) of TpPa-SO<sub>3</sub>H (0.5 ns) is shorter than those of TpPa (0.7 ns), the results show that the recombination rate of  $e^-h^+$  in TpPa was very high, and the introduction of the SO<sub>3</sub>H group provided more effective  $e^-h^+$  separation.

### Photocatalytic reduction of CO<sub>2</sub>

The photocatalytic activities of TpPa-SO<sub>3</sub>H and TpPa were evaluated based on the photocatalytic reduction of CO<sub>2</sub> under simulated visible light (Fig. 5a and b). In the absence of CO<sub>2</sub>, the other conditions remained unchanged. COFs do not produce

CO when they decompose, so this can be excluded from consideration. Fig. 5a and b show that without the photocatalysts, the photocatalytic activity of CO<sub>2</sub> was very low, and after 4 h of visible light irradiation only 2.61  $\mu\text{mol g}^{-1}$  of CO was produced. The addition of a photocatalyst was the main factor affecting the reduction of CO<sub>2</sub>. After 4 h of simulated sunlight irradiation, the CO yields with TpPa-SO<sub>3</sub>H and TpPa were 416.61 and 380.68  $\mu\text{mol g}^{-1}$ , respectively. After 2 h of illumination, there are almost no increase of CO amount over TpPa-SO<sub>3</sub>H, the reason may be that the amount of photocatalyst is low and the active sites are insufficient. This shows that the photoreduction ability of CO<sub>2</sub> can be improved by adding -SO<sub>3</sub>H substituents to the monomers of synthetic materials. To demonstrate the high selectivity and stability of the photocatalyst materials under visible light, the materials were recovered and subjected to cyclic testing (Fig. 5c and d). The photodegradation efficiency of TpPa-SO<sub>3</sub>H did not change significantly. After two reaction cycles, an excellent constant CO yield was obtained. This indicates that TpPa-SO<sub>3</sub>H has good photocatalytic stability. To further prove the stability of the TpPa-SO<sub>3</sub>H photocatalytic material, XRD was used to determine whether the crystallinity had changed (Fig. S10†). There were no obvious differences in the XRD patterns before and after the reaction, indicating that the material had good structural stability. Next, the energy-band structure of the material was calculated (Fig. 6). Under visible-light illumination, the CB potentials of TpPa-SO<sub>3</sub>H and TpPa had larger negative values than those of the CO<sub>2</sub>/CO redox potential. Thus, the photocatalytic activity for CO<sub>2</sub> conversion was higher, and the thermodynamic requirements for CO<sub>2</sub>/CO conversion were satisfied. Electron spin resonance (ESR) analysis was conducted to identify free radicals. After testing, no  $\cdot\text{O}_2^-$  signals were observed, but the  $\cdot\text{OH}$  signal was observed (Fig. 4h). Therefore, we propose a possible mechanism for this process. TpPa-SO<sub>3</sub>H is photoexcited to the conduction band by electrons ( $e^-$ ) in the valence band, which generates holes ( $h^+$ ) in the valence band. Then,  $e^-$  and  $h^+$  can be transferred to the surface of the catalyst, where  $h^+$  oxidizes H<sub>2</sub>O into  $\cdot\text{OH}$  and H ions ( $\text{H}^+$ ). Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was introduced as a photosensitizer to capture light and improve the efficiency of the photocatalytic reduction of CO<sub>2</sub>. [Ru(bpy)<sub>3</sub>]<sup>2+</sup> can effectively receive photogenerated  $e^-$  and  $\text{H}^+$  reduces CO<sub>2</sub> to CO. Meanwhile, TEOA was introduced as

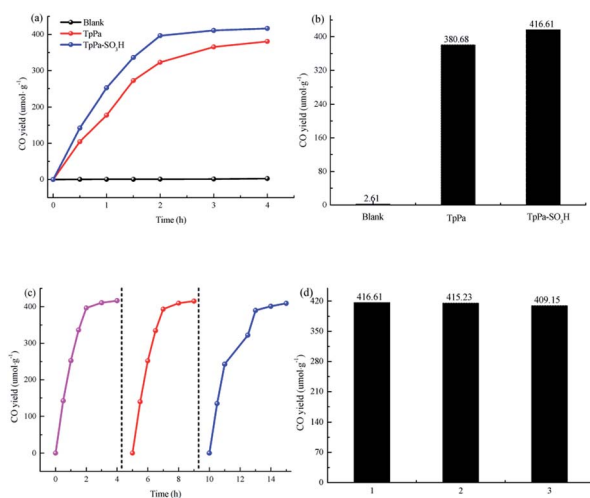


Fig. 5 (a and b) Photocatalytic activity of the samples. (c and d) Repetitive testing of the CO<sub>2</sub> photoreduction process with TpPa-SO<sub>3</sub>H under simulated solar light irradiation.

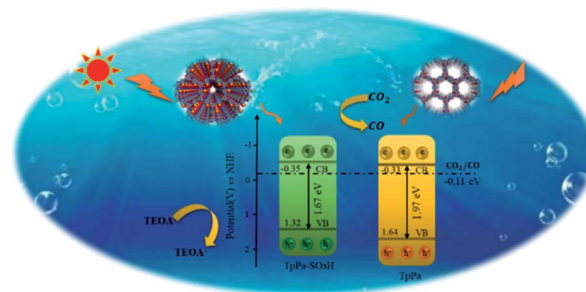
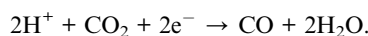
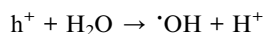
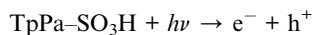


Fig. 6 Schematic illustration of the photocatalysis process of TpPa-SO<sub>3</sub>H and TpPa.





a sacrificial agent to prevent the recombination of photo-generated  $e^-$  and  $h^+$ . The  $h^+$  in the valence band easily accepts the  $e^-$  from TEOA, which is then oxidized to  $TEOA^+$ . This can be summarized by the equations:



The photocatalytic reduction efficiencies of TpPa- $SO_3H$  and TpPa under visible-light irradiation were compared with various other photocatalysts (Table S2†). Compared to most photocatalytic materials, TpPa- $SO_3H$  has greater photocatalytic activity, and a higher photocatalytic CO production rate. The results show that the COFs synthesized by introducing  $-SO_3H$  group into the monomer had a positive effect on the photocatalytic activity for  $CO_2$  reduction.

## Conclusions

In summary, 2D covalent organic framework TpPa- $SO_3H$  and TpPa photocatalysts, were synthesized and applied to visible light-driven  $CO_2$  reduction. The results show that the introduction of sulfonic acid function groups gives TpPa- $SO_3H$  high photocatalytic activity for  $CO_2$  reduction. TpPa- $SO_3H$  showed excellent light absorption ability and abundant photocatalytic activity under visible light. Moreover, it exhibited a higher yield and greater stability than TpPa. After 4 h of visible light irradiation, TEOA was introduced as a sacrificial agent, and  $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$  was used as photosensitizer, the photocatalytic reduction of  $CO_2$  by TpPa- $SO_3H$  produced CO with a yield of  $416.61 \mu mol g^{-1}$ . The  $-SO_3H$  group can affect the catalytic activity, it can promote  $H_2O$  to produce more  $H^+$ . Under light irradiation, synergistic effect of  $H^+$  and  $e^-$  promoted the reduction of  $CO_2$  to CO. This study provides a method for the design of COFs photocatalysts. In addition, it can be used to effectively reduce environmental pollution and alleviate the energy crisis.

## Conflicts of interest

There are no conflicts to declare.

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