

Supporting Information

Improving crystallinity of imine-linked covalent organic frameworks by acetal for enhanced photocatalytic H₂O₂ evolution

Xinyu Li, Qing Yang, Fangli Yi, Yiqi yuan, Hongmei Cao, Kewei Liu, Hongjian Yan*

College of Chemistry
Sichuan University
Chengdu, Sichuan, 610064
P. R. China

*Corresponding Author

E-mail: hjyan@scu.edu.cn

Experimental section

1.1 Materials

Tetrahydrofuran, 2,2',2''-nitrilotris(ethan-1-ol) (TEOA), 1,4-dioxane, mesitylene, acetonitrile, methanol, ethanol, 1-propanol, 1-butanol, ethane-1,2-diol, propane-1,2,3-triol, 2-propanol and 2-methyl-2-propanol were obtained from Chengdu Kelong Chemical Reagent Factory. 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (TaPt), 2,3,5,6-tetrafluoroterephthalaldehyde (TFA) and 3-pentanol were purchased from Zhengzhou Alpha Chemical Co., Ltd. 1-pentanol, pentane-1,2,3,4,5-pentaol and 2,2,2-trifluoroethanol were bought from Adamas-beta. Butane-1,2,3,4-butaol was gained from Aladdin.

1.2 Characterization

Matrix-Assisted Laser Ionization Time of Flight Mass Spectrometry (MALDI-TOF, Shimadzu Biotech Axima Performance), ^{13}C liquid-state nuclear magnetic resonance (^{13}C liquid-state NMR, AVANCE III HD) and Fourier-transformed infrared (FT-IR, Perkin-Elmer spectrometer) were used to characterize the structure of the acetal. FT-IR was also used to characterize the structure of COFs as well as ^{13}C solid-state nuclear magnetic resonance (^{13}C solid-state NMR, AVANCE III). X-ray diffraction (XRD, DX2700) was used to characterize the crystalline structure of COFs. UV-vis (UV3600 · Shimadzu) was applied to detect the absorption of the light. Photoluminescence (PL, Hitachi F-7000) was applied to detect the separation of the excitons. Scanning electron microscope (SEM, JSM-5900LV) and transmission electron microscope (TEM, Tecnai G₂ F20 S-TWIN) were used to capture the images of morphology. Electrochemical impedance spectroscopy (EIS) and photocurrent density (CHI660E) was performed to show the transference of the excitons. N₂ adsorption-desorption measurements were performed to show the pore structure and surface area. Electron paramagnetic resonance (EPR, EMXPlus) was used to capture the signals of radicals (DMPO as the radical-trapping reagent, ·O₂⁻ tested in methanol solution, ·OH tested in water solution).

1.3 Synthesis

Synthesis of 1,4-bis(diethoxymethyl)-2,3,5,6-tetrafluorobenzene.

TFA (18.5 mg, 0.0898 mmol) and ethanol (600 μL , 10.295 mmol) were added into a sample bottle. Kept at room temperature overnight, the bottle was transferred to a desiccator containing silica gel. After drying for 24 hours, the white product was collected.

Synthesis of TFA-TaPt-COFs.

TFA (18.5 mg, 0.0898 mmol) and TaPt (22.9 mg, 0.0647 mmol) were added in mixed solvent of 1,4-

dioxane/mesitylene (1:1 in volume, 2mL) and 600 mL ethanol in a glass pressure tube. After kept at 120 °C for 12 hours, orange sediment was collected by filtering and washed twice with THF. Then the solid was dried at 55 °C for 24 hours.

1.4 Photocatalytic test

Photocatalytic H₂O₂ evolution test.

The photocatalytic H₂O₂ evolution test was conducted in an open glass system. TFA-TaPt-COF (5 mg) was dispersed in mixed solvent of alcohol (5-10 mL) and water (90 mL). 300W xenon lamp equipped with 400 nm filter was used as light source. The temperature was controlled as 10 °C by a cooling system. The mixed solution containing the product (filtered, 4 mL) and the chromogenic liquid (10 mL) were put into a volumetric flask and then added H₂O to 25 mL. After reacting for 1 h, the absorption of the solution was tested by UV-vis absorption spectrophotometer (UV-1800BPC, Mapada).

Photocatalytic H₂ evolution test.

The photocatalytic H₂ evolution test was conducted in a closed glass system. TFA-TaPt-COF (10 mg) was dispersed in mixed solvent of acetonitrile (20 mL) and water (80 mL) containing 10% (in vol.) TEOA as sacrificial reagent. 300W xenon lamp equipped with 400 nm filter was used as light source. The temperature was controlled as 10 °C by a cooling system. The gaseous product was detected by gas chromatograph equipped with TCD detector (GC 112A, molecular 5A, Ar carrier).

Cyclic photocatalytic H₂O₂ evolution test.

The photocatalytic H₂O₂ evolution test was conducted in an open glass system. TFA-TaPt-COF (5 mg) was dispersed in mixed solvent of alcohol (5-10 mL) and water (90 mL). 300W xenon lamp equipped with 400 nm filter was used as light source. The temperature was controlled as 10 °C by a cooling system. The mixed solution containing the product (filtered, 4 mL) and the chromogenic liquid (10 mL) were put into a volumetric flask and then added H₂O to 25 mL. After reacting for 4 h, the absorption of the solution was tested by UV-vis absorption spectrophotometer (UV-1800BPC, Mapada).

Cyclic photocatalytic H₂ evolution test.

The photocatalytic H₂ evolution test was conducted in a closed glass system. TFA-TaPt-COF (10 mg) was dispersed in mixed solvent of acetonitrile (20 mL) and water (80 mL) containing 10% (in vol.) TEOA as sacrificial reagent. 300W xenon lamp equipped with 400 nm filter was used as light source. The temperature was controlled as 10 °C by a cooling system. After reacting for 4h, the gaseous product was detected by gas chromatograph equipped with TCD detector (GC 112A, molecular 5A, Ar carrier).

Figures

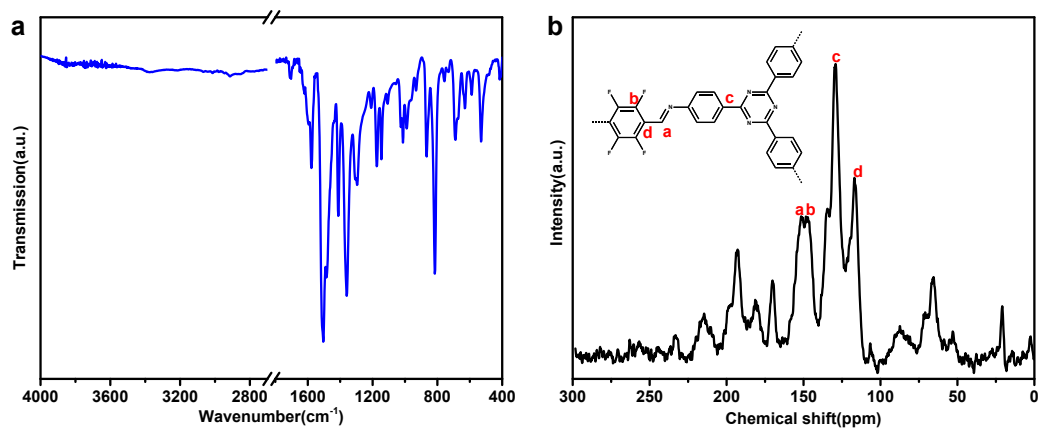


Fig.

S1 The spectrum of (a) FT-IR and (b) Solid-¹³C-NMR of TFA-TaPt-COF

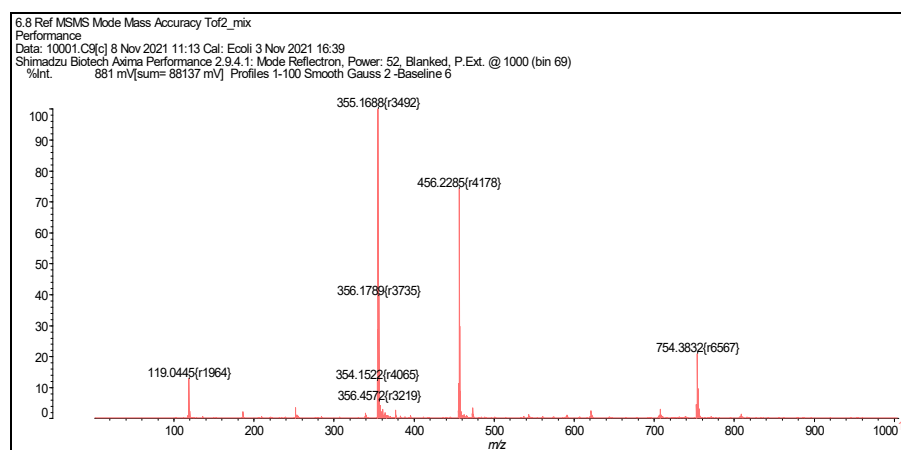


Fig. S2 The MALDI-TOF of 1,4-bis(diethoxymethyl)-2,3,5,6-tetrafluorobenzene

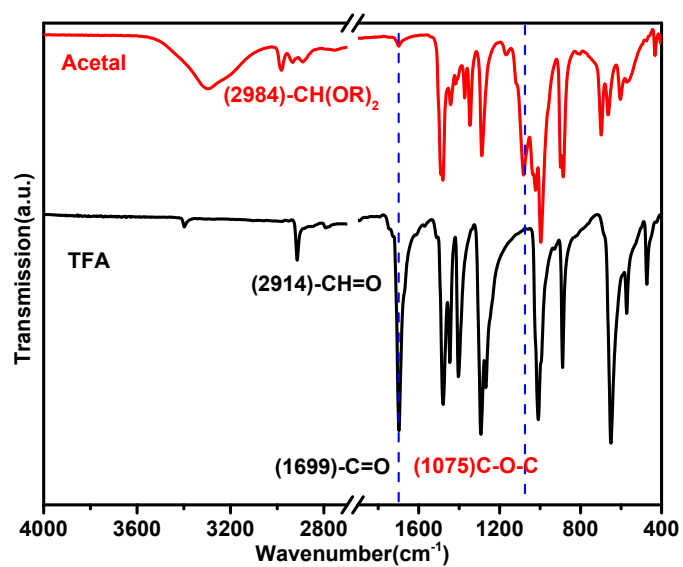


Fig. S3 The FT-IR spectra of the acetal and TFA

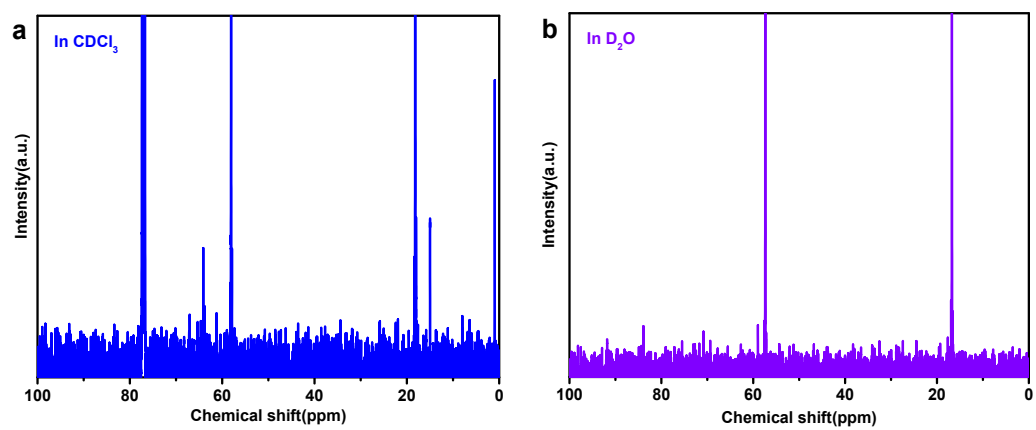


Fig. S4 The liquid ^{13}C -NMR of the acetal (a) in CDCl_3 , (b) in D_2O

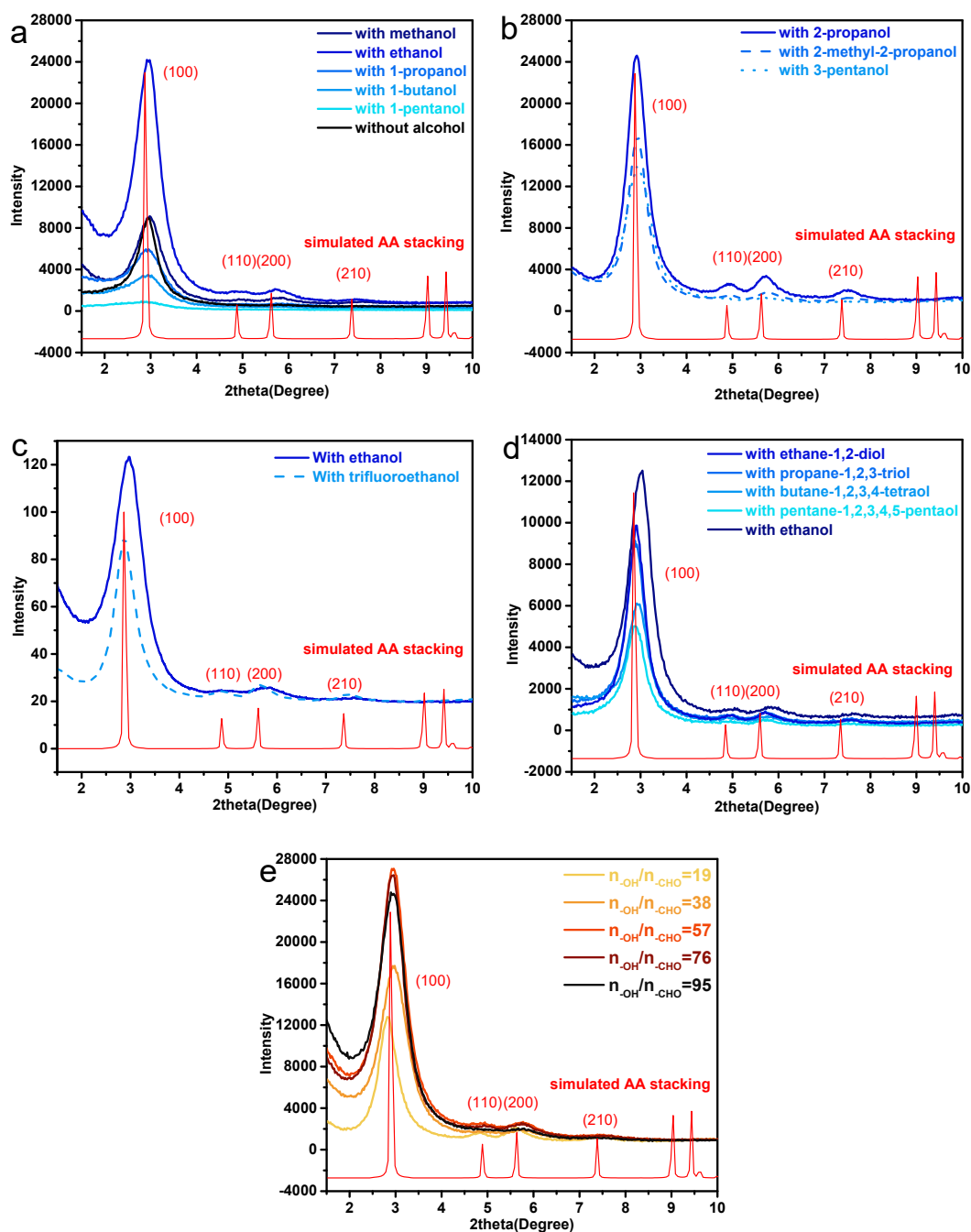


Fig. S5 (a) The XRD patterns of TFA-TaPt-COF synthesized in the presence of primary alcohols. (b) The XRD patterns of TFA-TaPt-COF synthesized in the presence of monohydric alcohols with different alkyl groups. (c) The XRD patterns of TFA-TaPt-COF synthesized in the presence of 2,2,2-trifluoroethanol. (d) The XRD patterns of TFA-TaPt-COF synthesized in the presence of polyhydric alcohols. (e) The XRD patterns of TFA-TaPt-COF synthesized in the presence of ethanol with different amount.

Fig. S5e presented the optimum hydroxyl to aldehyde ratio was about 57. The growing tendency with the $n_{\text{OH}}/n_{\text{CHO}}$ ratio is most likely related to lowering concentration of TFA. In contrast, when the ratio is above 57, excessive ethanol dominates and acts as reactant with imine groups, leading the destruction of COF and lower crystallinity.

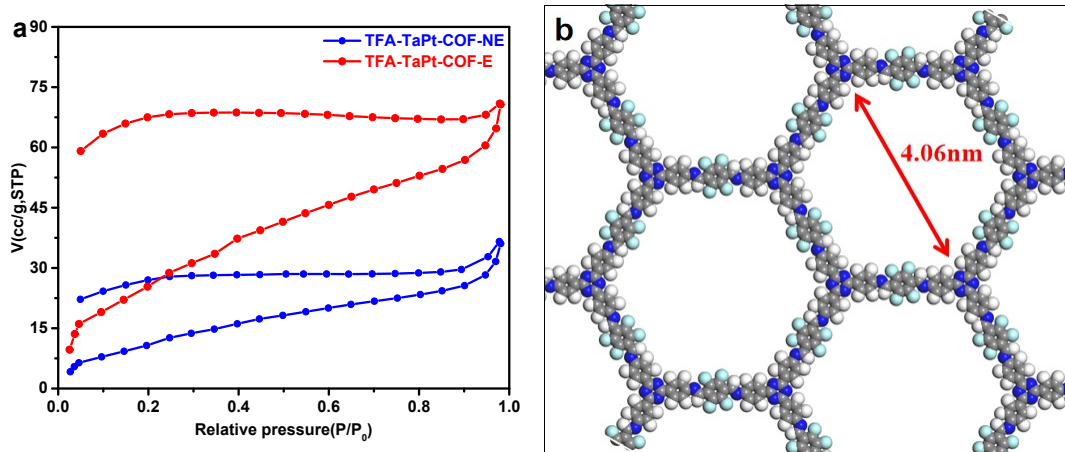


Fig. S6 The N_2 (a) adsorption-desorption isotherms; (b) The theoretical pore size of TFA-TaPt-COF.

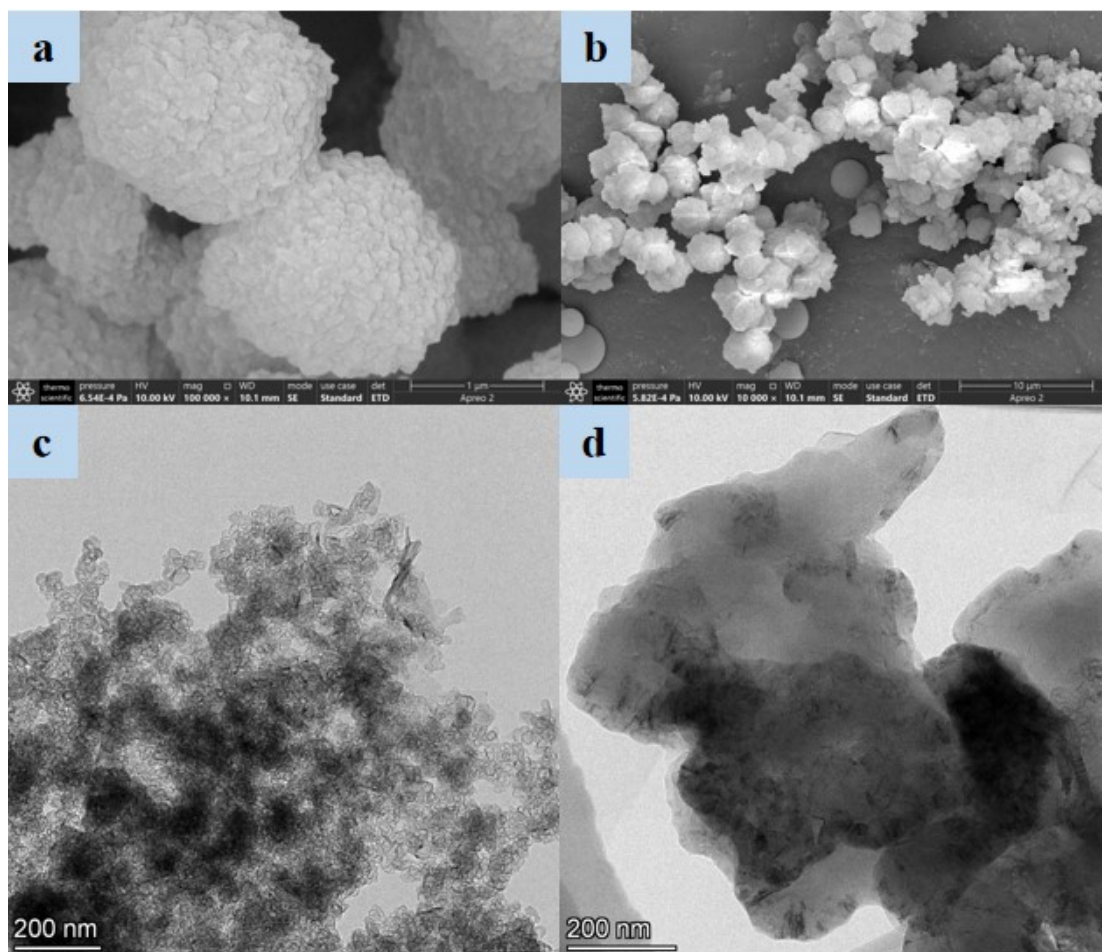


Fig. S7 The SEM images of TFA-TaPt-COFs in the absence (a) and presence (b) of ethanol; The TEM images of TFA-TaPt-COFs in absence (c) and presence (d) of ethanol.

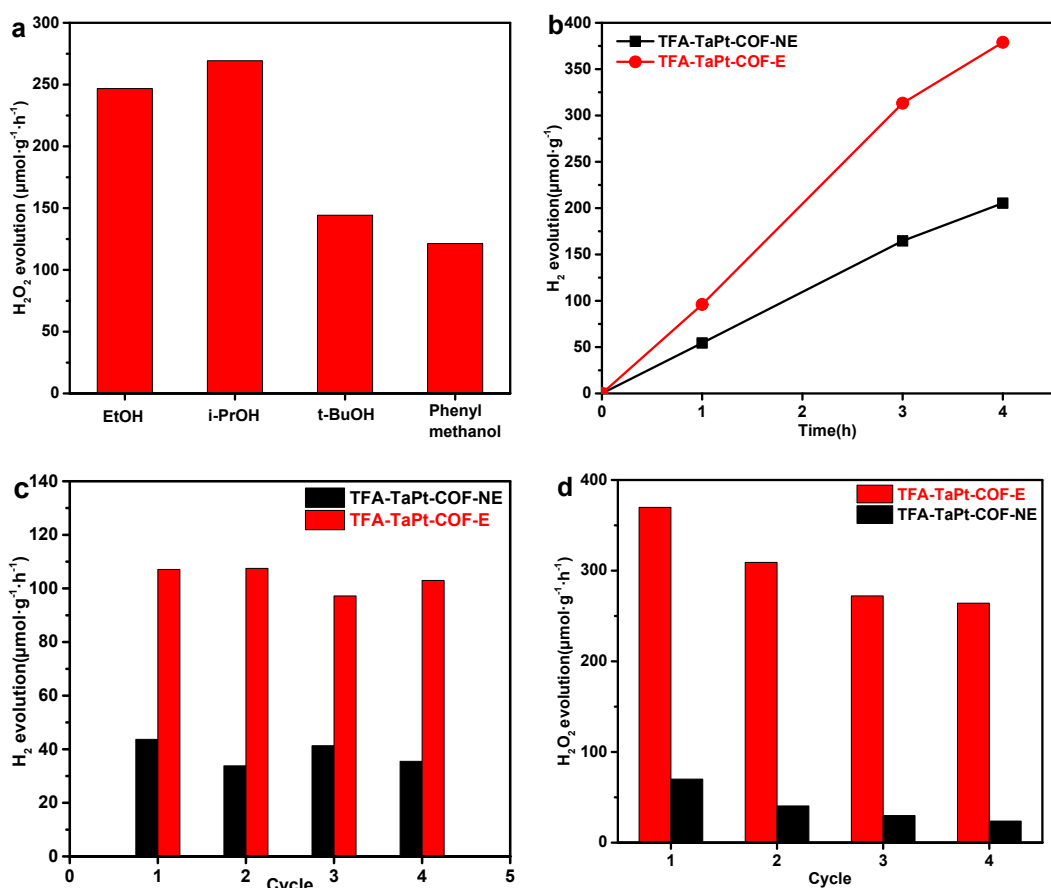


Fig. S8 (a) The photocatalytic H₂O₂ evolution of TFA-TaPt-COF in different sacrificial reagents; (b) The photocatalytic H₂ evolution of TFA-TaPt-COF-E and TFA-TaPt-COF-NE; (c) The cyclic test of photocatalytic H₂ evolution of TFA-TaPt-COF. (d) The cyclic test of photocatalytic H₂O₂ evolution of TFA-TaPt-COF.

The decrease in photocatalytic activity might be ascribed to the loss of catalysts. For every test, the highly dispersed catalysts could not avoid being extracted along with the solution. Thus, the photocatalytic activity decreased. However, the cyclic test of photocatalytic H₂ evolution could prove the stability of TFA-TaPt-COF-E. The calculation formular of apparent quantum yield (AQY) is:

$$\eta = [(2 \times \text{moles of H}_2\text{O}_2 \text{ evolved}) / (\text{moles of the incident photons})] \times 100\%$$

AQY was tested at 425 nm and the results showed 0.13% and 0.03% for TFA-TaPt-COF-E and TFA-TaPt-COF-NE, respectively.

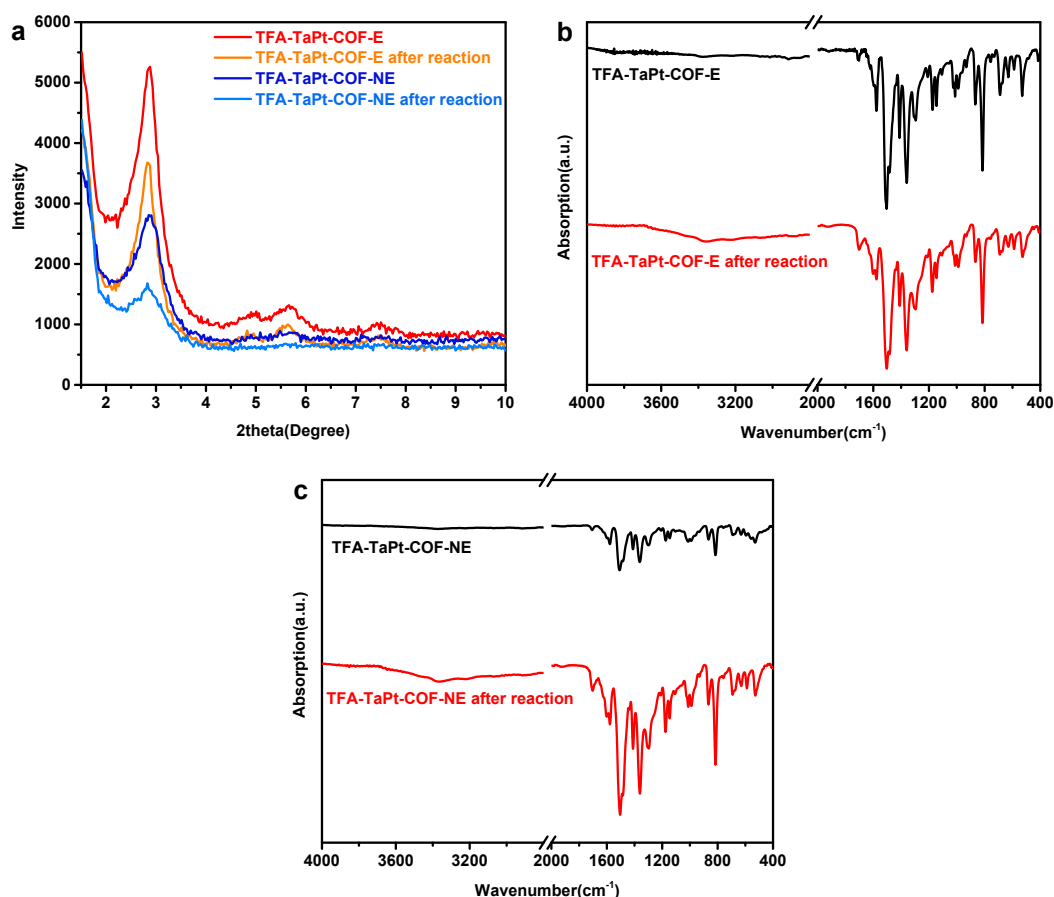


Figure S9 The comparison of XRD patterns of TFA-TaPt-COF (a); The comparison of FT-IR of TFA-TaPt-COF (b and c).

After photocatalytic reaction, the crystallinity of TFA-TaPt-COF-E and TFA-TaPt-COF-NE decreased (Fig S9a), which was attributed to ultrasonic treatment and the deconstruction by H₂O₂. The ultrasonic treatment could crush and strip the COFs in order to disperse them. Whereas the structures were broken as well. Besides, H₂O₂ is oxidative, whose oxidation ability increases along with increasing concentration. During photocatalysis, H₂O₂ could also oxidize part of COFs, causing decreasing in crystallinity. However, the crystallinity of TFA-TaPt-COF-E was still higher than that of TFA-TaPt-COF-NE, indicating TFA-TaPt-COF-E had relatively higher stability. FT-IR results also indicated the deconstruction of COFs (Fig S9b and S9c). The slight increase at about 3000 cm⁻¹ indicated the existence of -CHO, which derived from the broken of imine bonds.

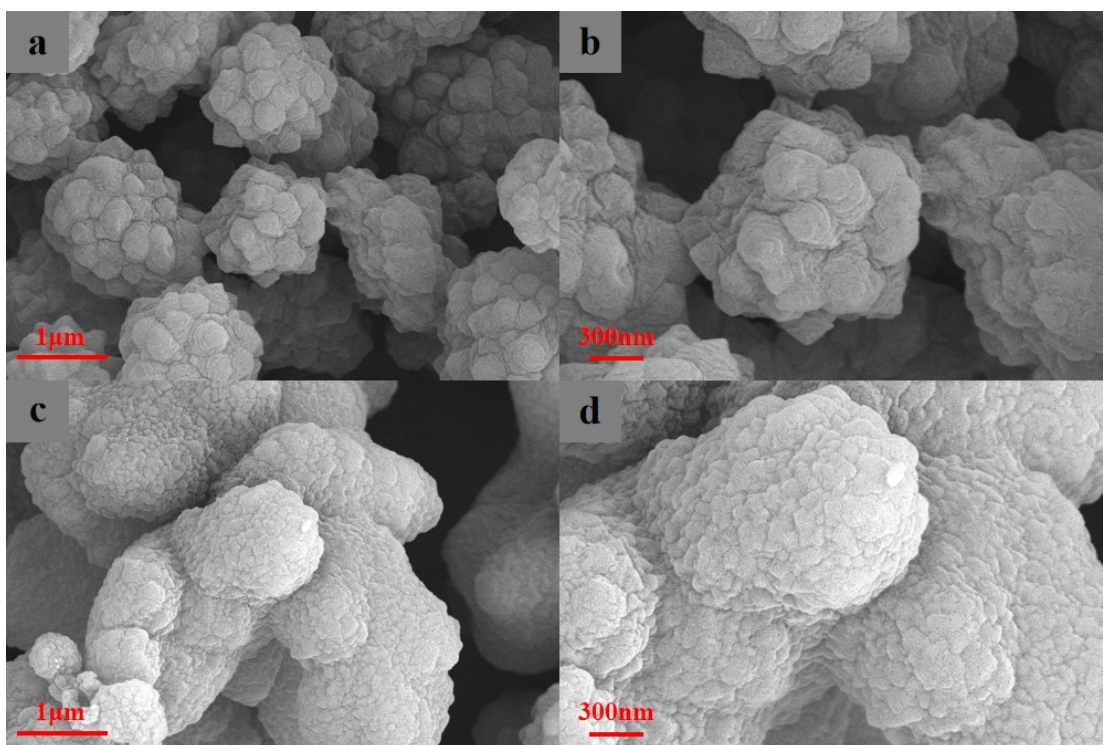


Figure S10 The SEM images of TFA-TaPt-COF-NE (a and b) and TFA-TaPt-COF-E (c and d) after photocatalytic H_2O_2 evolution for 16h.

The SEM images showed the structures of two COFs after reaction. Both of the two COFs showed irregular and some collapsed to sheet-like particles. However, compared with TFA-TaPt-COF-NE (Fig S10a and S10b), TFA-TaPt-COF-E had relatively large particles stacked together (Fig S10c and S10d), which corresponded to morphological images before reaction.