Supporting information

Constructing biomimetic $TiOF_2$@PCN-222-Fe Z-Scheme heterojunction through self-assembled *L*-cysteine for CO_2 visible light photoreduction

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Supporting information

Experimental Section

Materials.

Glacial acetic acid (99.5%), tetrabutyl titanate (AR), and L-cysteine (99%) from Macklin Reagent Company. $ZrOCl_2 \cdot 8H_2O$ from Heowns. Meso-Tetra(4-carboxyphenyl) porphine, 5,10,15,20-Tetrakis-(4-carboxyphenyl)-porphine-Co, and 5,10,15,20-Tetrakis-(4-carboxyphenyl)-porphyrin-Fe-(III) Chloride from Shanghai Tengqian Biotechnology Co., Ltd, DMF from Fuchen (Tianjin) Chemical Reagent Co., Ltd, trifluoroacetic acid from Energy Chemical. Titanium(Ⅳ) oxide, rutile (99.8%) from Shanghai D&B Biological Science and Technology Co. Ltd. Zirconium dioxide (99%) from Tianjin Guangfu Fine Chemical Research Institute. Potassium bromide (99.5%) from Shanghai Aladdin Biochemical Technology Co., Ltd. Cystine (98.0%) from Shanghai Anpu Experimental Technology Co., Ltd.

The synthesis of $TiOF_2$ powder.

First, 10 mL of glacial acetic acid, 2 mL of 40 wt% hydrofluoric acid and 5mL of tetrabutyl titanate solution were mixed in a polytetrafluoroethylene lining, stirred at room temperature for 15 min, then transferred to a high-temperature oven. The solvent thermal reaction was carried out at 200 °C for 12 h. After the reaction kettle is reduced to room temperature, the production was washed three times with alcohol and then dried. $TiOF_2$ powder can be obtained.

The synthesis of PCN-222 series catalysts.

Taking PCN-222 as an example, 325.8 mg $ZrOCl_2 \cdot 8H_2O$, 93 mg TCPP ligand, 30 mL of DMF solution and 1.35 mL trifluoroacetic acid were successively mixed in a PTFE liner for hydrothermal reaction at 120 °C for 18 h, until it was reduced to room temperature, centrifuged, and washed with ethanol, and dried in a 60 °C oven for 10 h to obtain PCN-222 powder. Similarly, change TCPP to Co-TCPP or Fe-TCPP-Cl. PCN-222-Co or PCN-222-Fe can be obtained.

The synthesis of composite catalysts

Taking $TiOF_2$@PCN-222-Fe as an example, firstly, 80 mg PCN-222-Fe, 20 mg $TiOF_2$ and 100 mg cysteine were dissolved in 100 mL ethanol in a beaker, stirred for 30 min, ultrasonic for 30 min, then the beaker was put on a stirrer, and the powder was obtained by stirring at 80 °C for 4 h until the solvent is all evaporated. $TiOF_2$@PCN-222-Fe was obtained by transferring the powder into a crucible, moving it to a tube furnace, heating it at a heating rate of 10 °C/min for 2 h at 200 °C in nitrogen atmosphere. When it reduced to room temperature, $TiOF_2$@PCN-222-Fe was obtained.

The preparation method of other composite catalysts is similar.

Characterization

The crystal structure and phase composition of the sample were determined by an X-ray powder diffractmeter (Rigaku MiniFlex 600) at 298 K in the range of 3-50° using CuKα radiation (λ=0.154178 nm). $^1H/^{13}C$ solid-state nuclear magnetic resonance (Bruker, Avance III WB 400) verified the structural characteristics of the catalyst. The potentiometric acid-base titration curve was obtained by ZDJ-4B automatic potentiometric titrator. The morphology of the samples was observed by scanning electron microscope (SEM, JSM-7800 F) and transmission electron microscope (TEM, JEM-2800). Infrared spectra were measured by an FT-IR spectrometer (Bruker TENSOR-37). X-ray photoelectron spectroscopy (XPS) results were performed on Kalpha from Thermo Scientific. The thermogravimetric curve in this paper was measured using the Thermo plus EVO2 synchronous thermal analyzer, the test atmosphere was argon, the test temperature range was 25-800 °C, and the heating rate was 10 °C per minute. The UV-vis diffuse spectroscopy results in this article were tested using the Thermo Fisher Evolution 220 instrument. Test results were obtained using dry barium sulfate as a blank background sample, using a dry and homogeneous sample. For ease of analysis, the test results are normalized. The paramagnetic signal was detected at room temperature using an electron paramagnetic resonance (EPR) spectrometer (EMX plus-6/1). Fluorescence spectroscopy (Hitachi, F-4600) and room-temperature transient fluorescence spectroscopy (EDINBURGH, FS5) were used to analyze the recombination and lifetime of photogenerated electrons and holes. Specific surface area, pore volume, and pore size at 77 K were measured using ASAP 2460 micromertics based on the BET model. Inductively coupled plasma atomic emission spectroscopy (ICP-OES, Agilent 5110) was used to analyze the elemental content. Ultraviolet photoelectron spectroscopy (UPS) was operated on a Thermo Scientific ESCALAB 250Xi with a monochromatic Al Kα source (150 W, 1486.6 eV, the C 1s 284.8 eV was chosen as the internal standard for the calibration of binding energies) was employed to study the valence state and valence band of the catalysts and He I (hν=21.22 eV) as the exciting source for UPS. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive spectroscopy (EDS) images were recorded using FEI Titan cubic Themis G2 300 at 300 kV and a spherical aberration corrector.

Electrochemical measurements

The electrochemical performance test was carried out in a three-electrode system using an electrochemical workstation (IVIUM). Add 1 mg of catalyst to 1 mL of ethanol and 80 μL of Nafion. After sonication, evenly coat 1.5×1 cm^2 ITO glass and dry overnight. The 0.5×0.5 cm^2 platinum sheet electrode, the saturated Ag/AgCl electrode, and the catalyst-coated ITO glass were used as the counter electrode, reference electrode, and working electrode, respectively. The Mott-Schottky (MS) curve measures at a frequency of 1000 Hz and voltages from -1.0 V (vs. Ag/AgCl) to 1.0 V (vs. Ag/AgCl). Under the irradiation of a 300 W Xenon lamp, the change in photocurrent is recorded. Mott-Schottky, and photocurrent measurements were all performed in 0.5 M Na_2SO_4 solution. 211.95 mg potassium ferrocyanide (II) (K_4FeCN_6), 1.65 mg potassium ferrocyanide (K_3FeCN_6), and 745.5 mg potassium chloride (KCl) were dissolved in 100 mL of water as cyclic voltammetry (CV) electrolytes. The CV test was performed at voltages between -1.0 V (vs. Ag/AgCl) and 1.0 V (vs. Ag/AgCl).

For electrochemical impedance (EIS) testing, the solution containing a catalyst is dropwise applied to 1 cm^2 of carbon paper as a working electrode. The Hg/HgO (1 M KOH) was used as the reference electrode. A Pt plate with an area of 1 cm^2 was used as the counter electrode. And electrochemical impedance (EIS) testing was performed in the frequency range of 10,000 Hz. Electrochemical impedance was performed in 0.5 M Na_2SO_4 solution.

X-ray Absorption Spectroscopy (XAS)

Fe K-edge analysis was performed with Si(111) crystal monochromators at the BL11B beamlines at the Shanghai Synchrotron Radiation Facility (SSRF) (Shanghai, China). Before the analysis at the beamline, samples were pressed into thin sheets with 1 cm in diameter and sealed using Kapton tape film. The XAFS spectra were recorded at room temperature using a 4-channel Silicon Drift Detector (SDD) Bruker 5040. Fe K-edge extended X-ray absorption fine structure (EXAFS) spectra were recorded in transmission mode. Negligible changes in the line-shape and peak position of Fe K-edge XANES spectra were observed between two scans taken for a specific sample. The titanium element test is the same as that of iron. The XAFS spectra of these standard samples (Fe foil, Ti foil, Fe_2O_3 and TiO_2) were recorded in transmission mode. The spectra were processed and analyzed by the software codes Athena and Artemis. The Demeter software package was used to process and analyze XAS data. A linear function is subtracted from the pre-edge region and normalized using Athena software.[1] The 3-10 $Å^{-1}$ window function ($\Delta k = 1.0$ $Å^{-1}$) was used to perform a Fourier transform on k^2-weighted $\chi(k)$ data. Artemis software was used to fit the EXAFS equation nonlinearly into the Fourier transform data of r space, and the structural parameters were obtained by least squares optimization.

Photocatalytic activity measurements

In a typical photocatalytic test, 50 mg of catalyst is weighed and uniformly dispersed on a quartz boat inside a 141 mL volume quartz reactor. A 300 W Xenon lamp (CEL-HXF300) with a 420 nm filter was used as the visible light source and placed vertically about 15 cm above the quartz boat. First, ultra-high purity CO_2 (99.999%) is introduced into the reactor for about 40 min to ensure that the reactor is completely filled with CO_2 gas. Then, 2 mL of deionized water was injected into the reactor, a process that avoids contact with the catalyst with water. The temperature of the quartz reactor is maintained at around 25±2°C by a condensation circulation device outside the reactor. During the reaction, the entire reactor and light source should be placed in a dark box. Turn on the xenon lamp, let the reaction proceed for 4 h, draw the gas (0.4 mL) from the quartz reactor, and analyze the concentration of the reduced product using a gas chromatography (GC- 2030N, SHIMADZU). At least two stitches were drawn from each sample and averaged.

OER performance test

Electrochemical measurements were carried out by an electrochemical workstation (Ivium V53517, Netherlands) using a standard three-electrode system in 1 M KOH. A solution containing a catalyst is dropwise applied to 1 cm^2 of carbon paper as a working electrode. The Hg/HgO (1 M KOH) was used as the reference electrode. A Pt plate with an area of 1 cm^2 was used as the counter electrode in OER. Between 1.014 and 1.514 V versus RHE for OER with a scan rate of 100 mV s^{-1}, and the corresponding LSV curves were recorded. All the electrochemical measurements were corrected using 90% iR compensation and calibrated to the reversible hydrogen electrode (RHE) using the Nernst equation: $E_{RHE} = E_{Hg/HgO} + 0.098\ V + 0.059 \times PH$, where the pH values of 1 M KOH electrolytes were measured to be 13.81.

We have also performed the photocatalytic activity for OER of H_2O using $TiOF_2$@PCN-222-Fe. The test conditions are as follows: Typically, 0.1 g of $TiOF_2$@PCN-222-Fe was added to 100 mL of aqueous solution containing $AgNO_3$ (10 mM) as a hole sacrificial reagent and 0.1 g of La_2O_3 (99.9%, Aladdin Chemical Reagent) was added to the solution to adjust the pH value to be about 8.5. The reactor was thoroughly evacuated by connecting to the system and was maintained at about 283 K. The photocatalytic reaction was conducted under a 300W xenon lamp with a cut-off filter, and the produced O_2 gas was analyzed by an online gas chromatography.

Zeta potential test

Zeta potential test was performed on ZetaSizer Nano ZS90, which was preheated for 30 min. The teat temperature was set to 25 °C. The sample was dissolved in ethanol, and after 5 minutes of sonication, the mixed solution was added to the DTS1070 potential cell, before being inserted into the device for potential testing.

DFT calculations

First-principles calculations based on density functional theory (DFT) were performed using the Vienna Ab initio Simulation Package (VASP) [2,3] within the projector augmented-wave formalism. Generalized gradient approximation (GGA) [4,5] in the parameterization of Perdew, Burke, and Ernzerhof (PBE) [6] pseudopotential was used to describe the exchange–correlation electric field potential. All atomic structures were fully relaxed geometry optimization with a converging tolerance of 0.02 eV/Å for residual force and 10^{-6} eV for energy. The plane-wave cutoff was set to 520 eV. The Brillouin Zone was sampled with the Gamma centered mesh with a 4 × 3 × 1 k-point grid for geometry relaxation. A vacuum space in the z-direction was set to 15 Å to prevent the interaction between periodic images. The van der Waals interactions were described by the Grimme's semi-empirical DFT-D3 method [7]. The Gibbs free energy changes ΔG was defined as $\Delta G = \Delta E + \Delta ZPE -$

T*ΔS, where ΔE denotes the calculated DFT energy, ΔZPE means the zero-point energy difference, and ΔS represents the entropy change during the reaction [8,9].

References

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Results

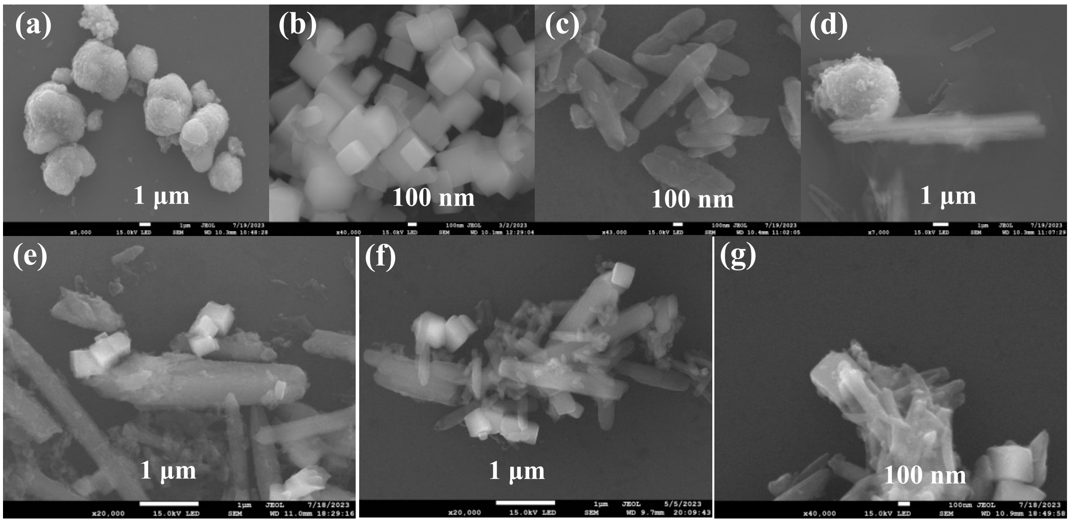


Figure S1. SEM images of (a)TiO_2, (b)$TiOF_2$, (c)PCN-222-Fe, (d)TiO_2@PCN-222, (e)$TiOF_2$@PCN-222, (f)$TiOF_2$@PCN-222-Co and (g)$TiOF_2$@PCN-222-Fe.

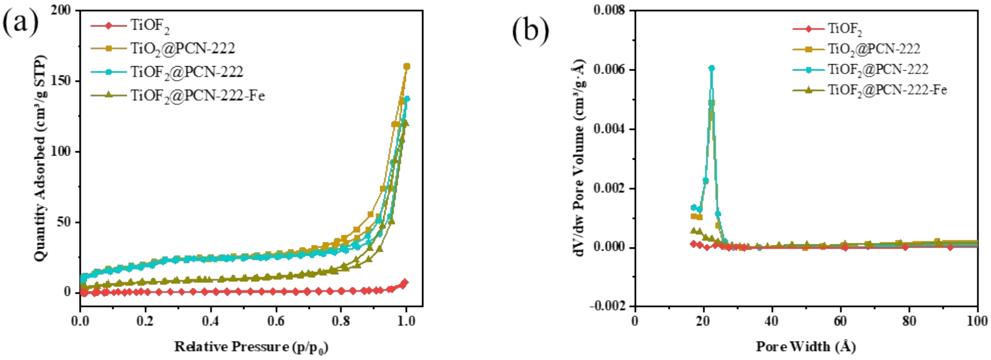


Figure S2. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution curves of $TiOF_2$, TiO_2@PCN-222, $TiOF_2$@PCN-222, and $TiOF_2$@PCN-222-Fe.

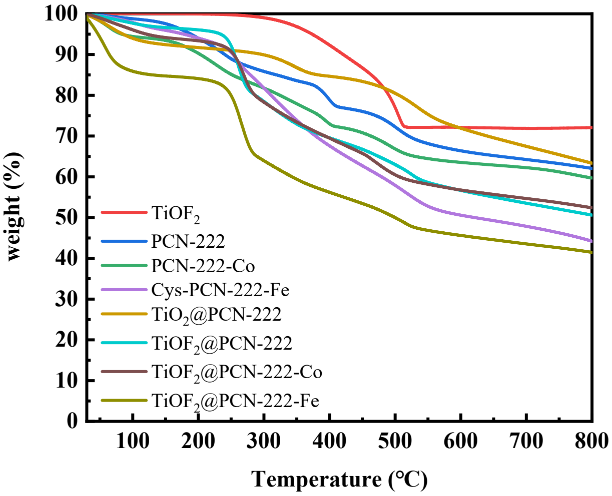


Figure S3. TGA curves of $TiOF_2$, PCN-222/-Co, Cys-PCN-222-Fe and complexes.

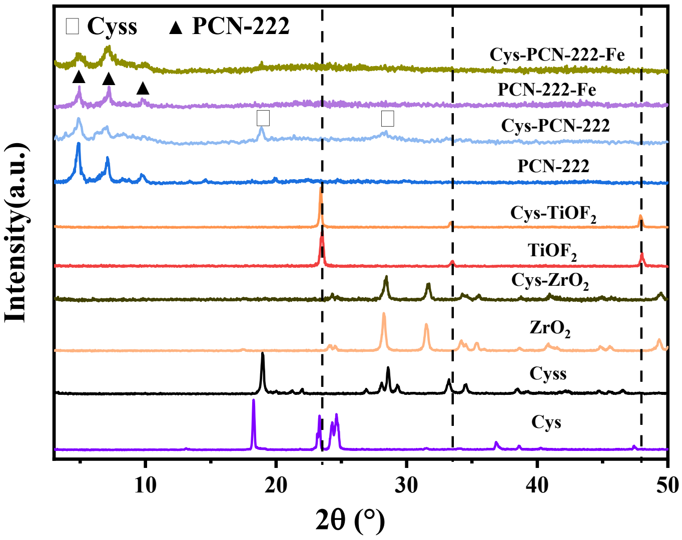


Figure S4. The PXRD patterns of Cys, Cyss, ZrO_2, $TiOF_2$, PCN-222, PCN-222-Fe and cysteine-treated samples.

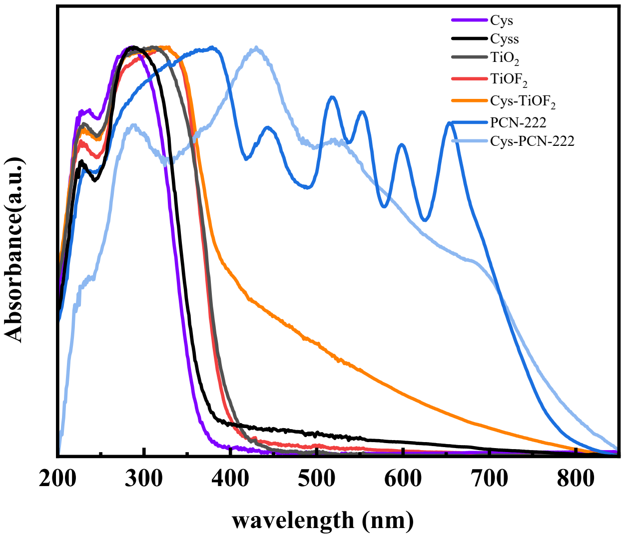


Figure S5. UV-vis plot of cysteine, cystine, TiO_2, $TiOF_2$, PCN-222 and cysteine compounds.

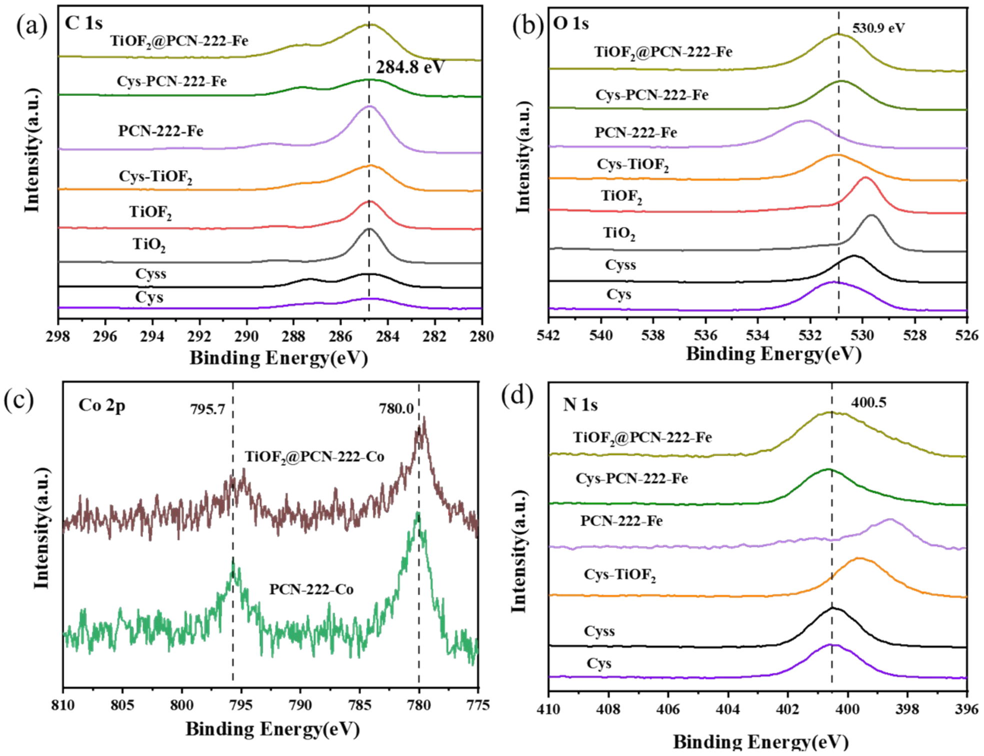


Figure S6. XPS results. (a) C 1s and (b) O 1s of Cys, Cyss, TiO$_2$, TiOF$_2$, Cys-TiOF$_2$, PCN-222-Fe, Cys-PCN-222-Fe and TiOF$_2$@PCN-222-Fe, (c) Co 2p of PCN-222-Co and TiOF$_2$@PCN-222-Co and (d) N 1s of Cys, Cyss, Cys-TiOF$_2$, PCN-222-Fe, Cys-PCN-222-Fe and TiOF$_2$@PCN-222-Fe.

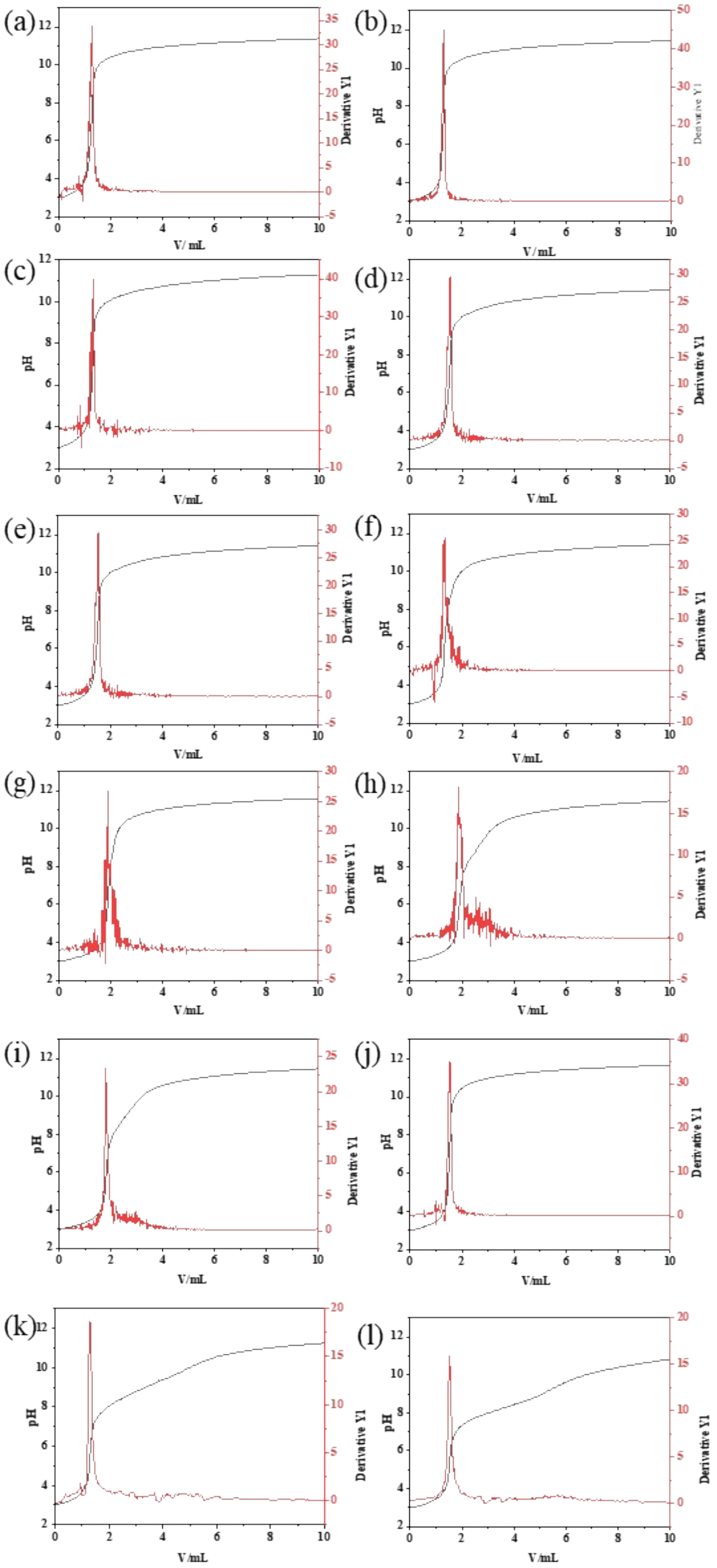


Figure S7. Acid−base titration curve and first derivative curve for (a) TiO_2, (b) $TiOF_2$, (c) PCN-222, (d) PCN-222-Co, (e) PCN-222-Fe, (f) TiO_2@PCN-222, (g) $TiOF_2$@PCN-222, (h) $TiOF_2$@PCN-222-Co, (i) $TiOF_2$@PCN-222-Fe, (j) ZrO_2, (k) Cys, (l) Cyss.

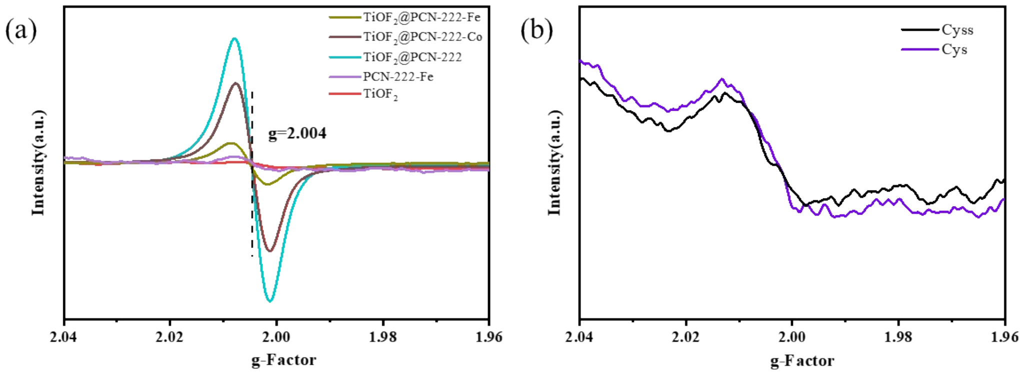


Figure S8. g-factor of (a) $TiOF_2$ and PCN-222-Fe and composites, (b) Cys and Cyss.

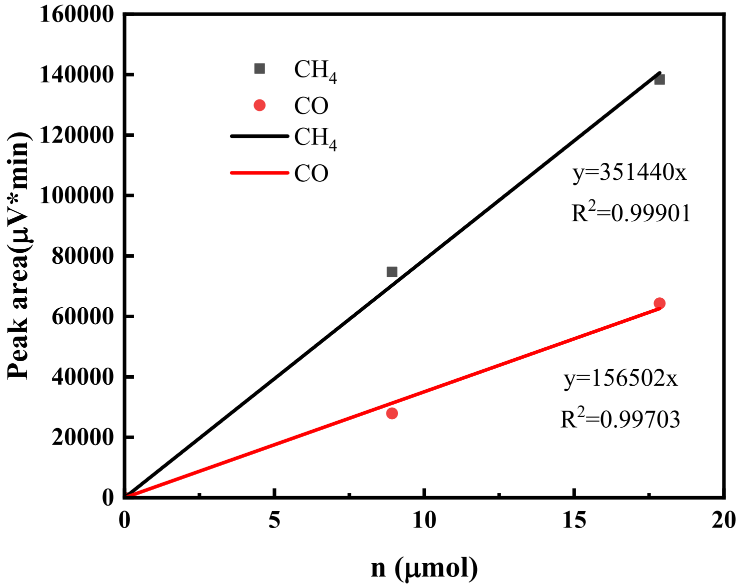


Figure S9. Gas chromatograph standard curve of CO and CH_4.

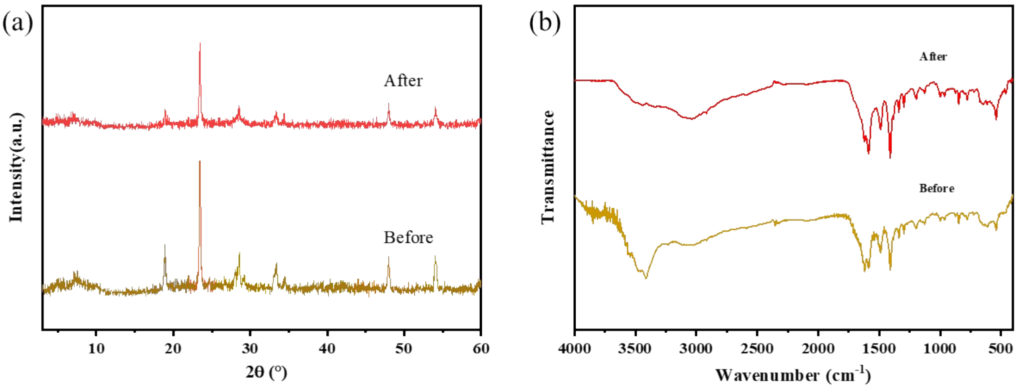


Figure S10. (a)The PXRD patterns and (b) FT-IR of $TiOF_2$@PCN-222- Fe before and after the reaction.

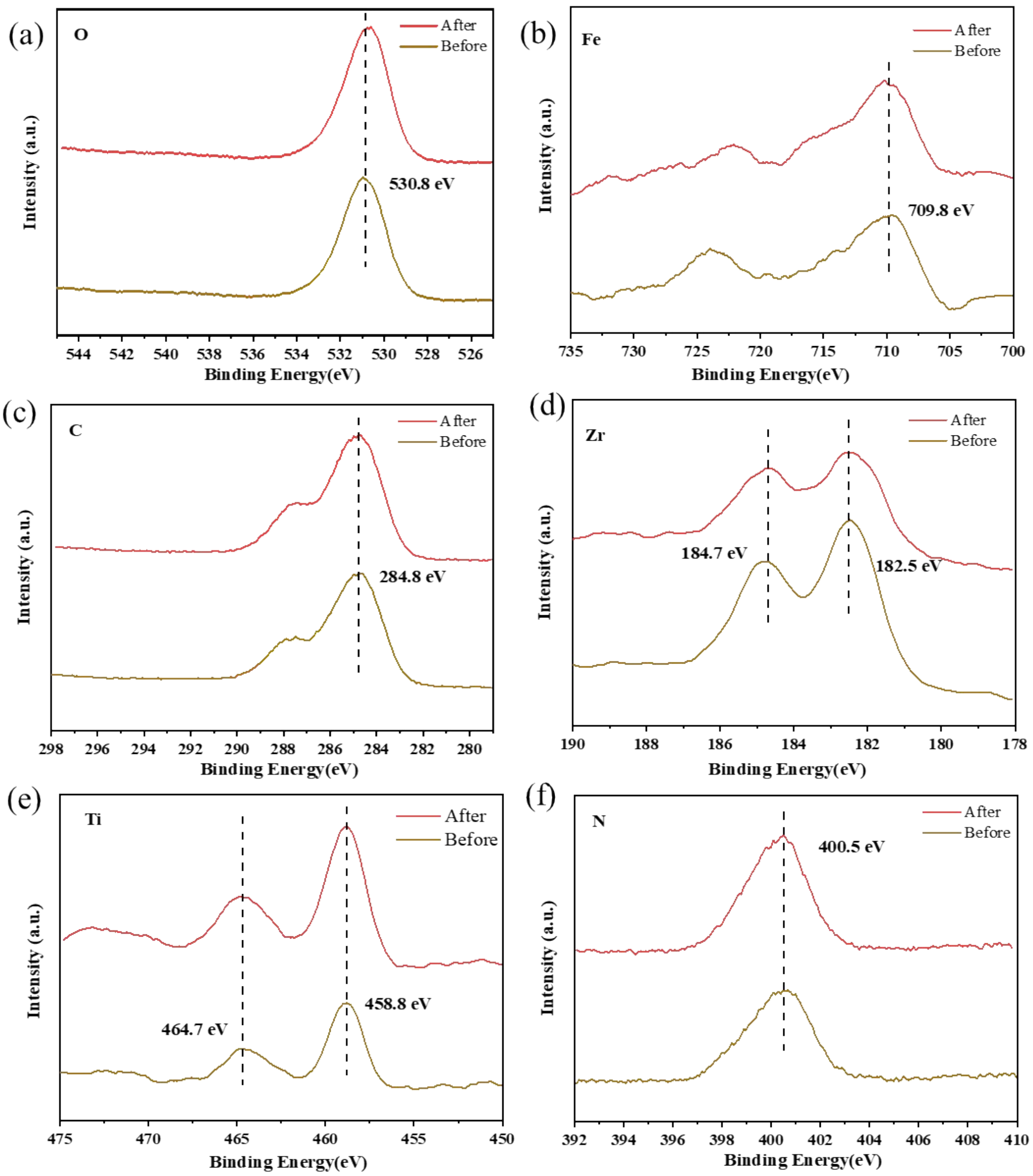


Figure S11. XPS of $TiOF_2$@PCN-222-Fe before and after the reaction.

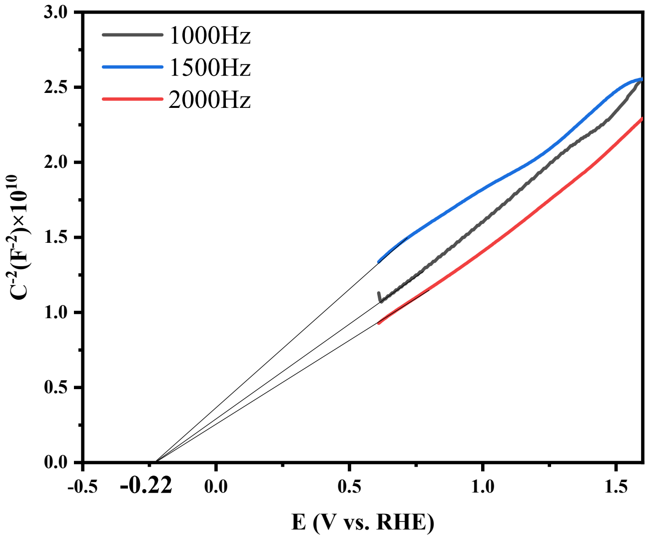
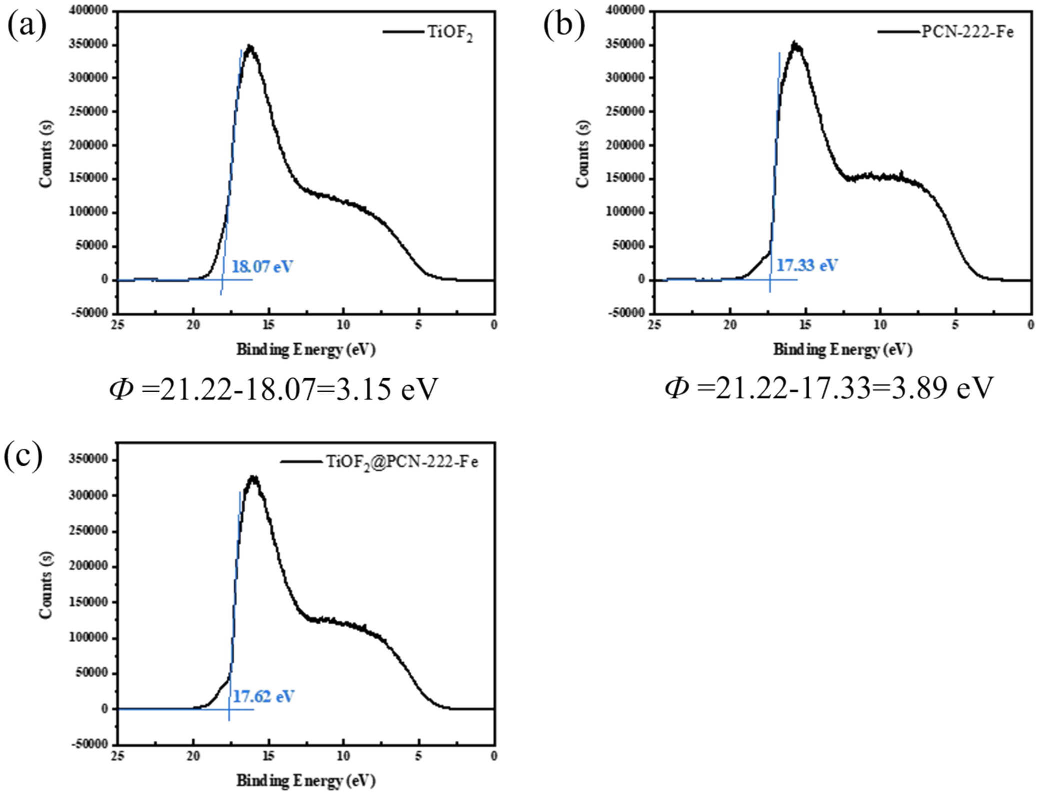


Figure S12. Mott−Schottky plots of $TiOF_2$@PCN-222-Fe in different frequency.



Φ =21.22-18.07=3.15 eV

Φ =21.22-17.33=3.89 eV

Φ =21.22-17.62=3.60 eV

Figure S13. The work functions calculated from the UPS plots of the samples with 5V bias voltage, (a) TiO_2, (b) $TiOF_2$, and (c) $TiOF_2$@PCN-222-Fe.

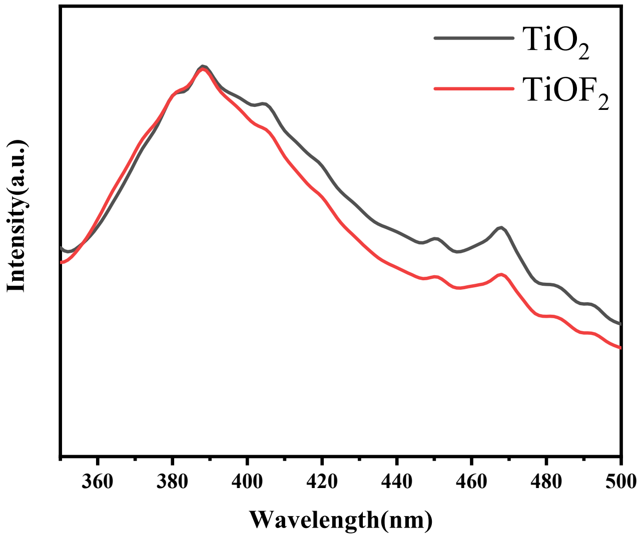


Figure S14. Photoluminescence spectra of samples.

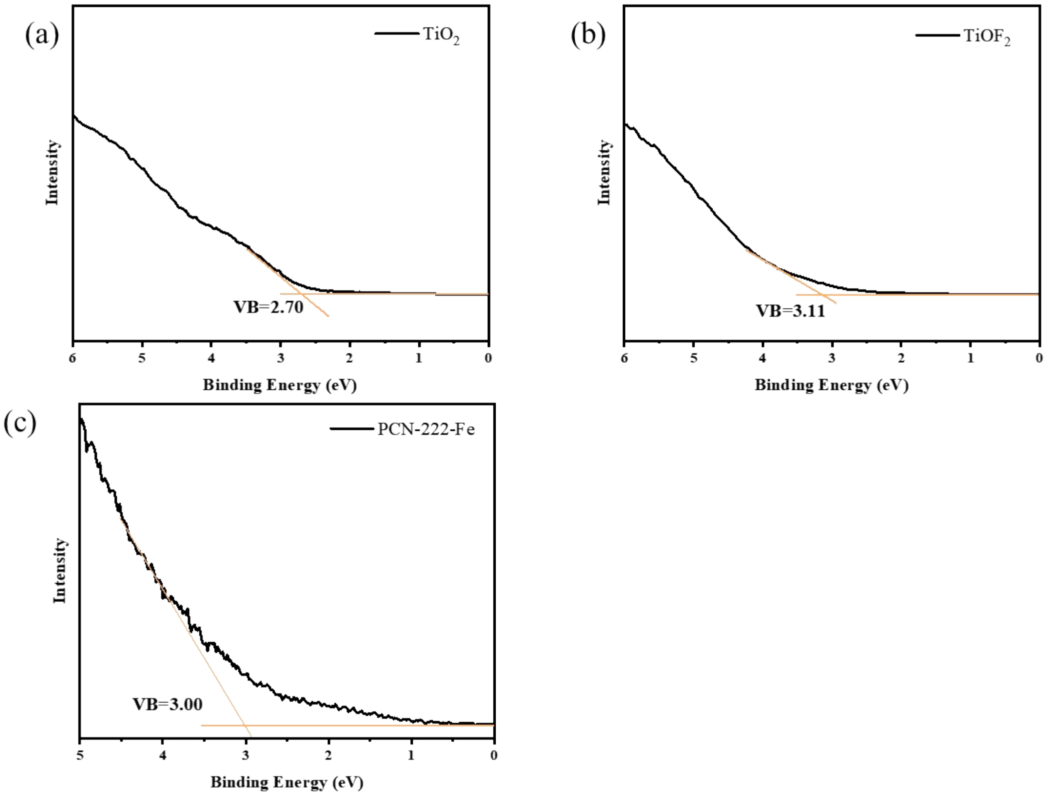


Figure S15. The valence bands calculated from the UPS plots of the samples. (a) TiO_2, (b) $TiOF_2$, and (c) PCN-222-Fe.

Table S1. Surface area and pore volume of the catalysts.

	BET Surface (m^2/g)	**Pore Volume (cm^3/g)**
$TiOF_2$	2.8	0.004
TiO_2@PCN-222	70.7	0.106
$TiOF_2$@PCN-222	75.8	0.085
$TiOF_2$@PCN-222-Fe	26.2	0.070

Table S2. ICP-OES results of the samples.

Sample	Co (wt%)	Fe (wt%)	Ti (wt%)	F (wt%)
PCN-222-Co	1.35			
PCN-222-Fe		1.96		
$TiOF_2$@PCN-222-Co	1.43		7.17	3.59
$TiOF_2$@PCN-222-Fe		1.35	7.97	3.38

Table S3. Acid−base titration results of the samples.

sample	V_{NaOH}/mL	pK_a	$n_{NaOH}/10^{-5}$mol
TiO_2	1.28	3.30	6.00
$TiOF_2$	1.32	3.32	6.18
PCN-222	1.34	3.38	6.22
PCN-222-Co	1.54	3.33	7.20
PCN-222-Fe	1.42	3.30	6.60
TiO_2@PCN-222	1.34	3.31	6.28
$TiOF_2$@PCN-222	1.88	3.31	8.80
$TiOF_2$@PCN-222-Co	1.88	3.30	8.76
$TiOF_2$@PCN-222-Fe	1.80	3.30	8.38
ZrO_2	1.52	3.30	7.12
Cyss	1.28	3.30	6.14
Cys	1.50	3.28	7.20

Table S4. Transient fluorescence of samples.

Sample	τ_1	Rel %	τ_2	Rel %	τ_{avg}
TiO_2	0.1891	55.20	2.0200	44.80	1.83
$TiOF_2$	0.1982	58.98	2.3567	41.02	2.12
PCN-222-Fe	0.1975	48.99	1.9269	51.01	1.77
$TiOF_2$@PCN-222-Fe	0.1900	46.40	2.1750	53.60	2.04