Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Nonconjugated AIE Polymer from Enol-Conjugated ACQ Curcumin through Nucleophilic Substitution Polymerization-Induced Emission towards Enhanced Photocatalytic Hydrogen Evolution

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†Electronic supplementary information (ESI) available. See DOI:

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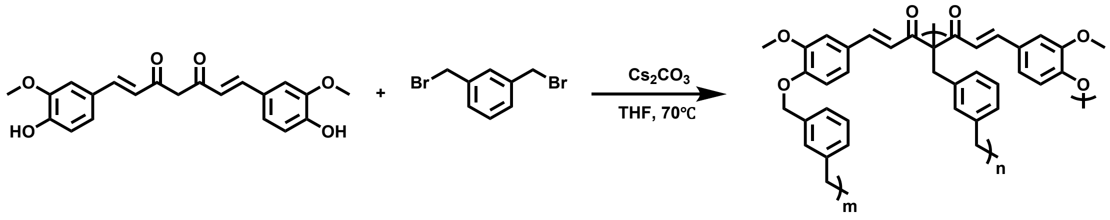
Experimental details

Materials

Curcumin, 1,3-bis(bromomethyl)benzene, benzyl bromide, Cs_2CO_3 were supplied by Energy Chemical (Shanghai, China). Titanium tetraisopropoxide was provided by Sigma-Aldrich (Shanghai, China). Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) was purchased from Aladdin (Shanghai, China). Tetrahydrofuran, petroleum ether, ethyl acetate, sodium hydroxide (NaOH), sodium borohydride ($NaBH_4$, >98.0%), 2,2,6, 6-tetramethylpiperidin-1-oxygen radical (TEMPO), were all analytical grade and supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Sodium fluoride (NaF) was purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). All reagents were used without further purification.

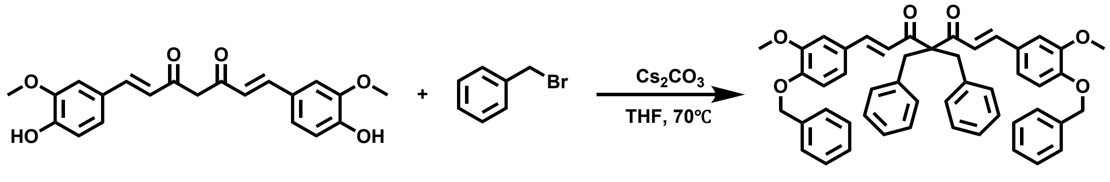
Synthesis of HPCB.



In a Schlenk tube containing Cs_2CO_3 (3.3 mmol, 3 equiv), curcumin (1.1 mmol, 1equiv) and 1,3-bis(bromomethyl)benzene (2.2 mmol, 2equiv) were put into the reaction solution and dissolved in THF (5 mL). The mixed solution was slowly stirred in air at 70°C for 24h. After 24h, the reaction solution was allowed to cool to room temperature. Then the Cs_2CO_3 in the mixture was filtered and the reaction tube was rinsed with THF (3×5 mL) for 3 times, and the mixture was concentrated under reduced pressure to 2 mL. The product was precipitated into an excess of petroleum ether, filtered and vacuum-dried to give HPCB as a yellow solid powder in 86% yield.

^1H NMR (400 MHz, $CDCl_3$): δ: 7.83-6.40 (broad, 16H), δ: 5.26-4.91 (broad, 4H), δ: 3.95-3.65 (broad, 6H), δ: 3.41-3.18 (broad, 2H).

Synthesis of M-HPCB.



In a Schlenk tube containing Cs_2CO_3 (3.3 mmol, 3equiv), curcumin (1.1 mmol, 1 equiv) and benzyl bromide (4.4 mmol, 4 equiv) were put into the reaction solution and dissolved in THF (5 mL). The mixed solution was slowly stirred in air at 70°C for 24h. After 24h, the reaction solution was allowed to cool to room temperature. Then the Cs_2CO_3 in the mixture was filtered and the reaction tube was rinsed with THF (3×5 mL) for 3 times, the solvent was removed by vacuum rotary evaporation, and the residue was subjected to silica gel chromatography (petroleum ether/ethyl acetate=10:1), to obtain M-HPCB in 48% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.72-7.65 (m,2H), δ:7.44 -7.30(m,12H), δ:7.26-7.16(m,7H), δ:7.14-7.08(m,2H), δ:7.04-6.98(m,2H), δ:6.90(s,2H), δ:6.86-6.80(m,2H), δ:5.19(s,4H), δ:3.89(s,6H), δ:3.38 (s,4H).

Synthesis of TiO_2

TiO_2 was prepared via a sol–gel method. Typically, titanium tetraisopropoxide was hydrolyzed under acidic conditions until pH=4 to obtain a TiO_2 sol. Then, a microwave was employed to dehydrate the TiO_2 sol to obtain the TiO_2 gel. After that, the gel was placed in a muffle furnace with an alumina crucible and heated to 300°C for 5h at a rate of 5°C/min.

Synthesis of HPCB-TiO_2 CT complex

Taking HPCB-TiO_2 CT as an example, X (X=1, 5, 10, 20, 30) mg of HPCB was dissolved in 10 mL of DCM, and 100 mg of TiO_2 was then added. The compound was stirred for 1h and washed with DCM five times to remove the unstable HPCB from the surface of TiO_2. Finally, the products were dried at 60°C for 2h and named as 1%HPCB-TiO_2, 5%HPCB-TiO_2, 10%HPCB-TiO_2, 20%HPCB-TiO_2, 30%HPCB-TiO_2, respectively. For 20%curcumin-TiO_2, the process was similar to that of 20%HPCB-TiO_2, except that the HPCB was replaced with curcumin.

Synthesis of Pt-TiO_2 and Pt-HPCB-TiO_2

Pt-HPCB-TiO_2 was synthesized via a photo deposition method. 50 mg of HPCB-TiO_2 was added to a quartz reaction vessel, followed by the addition of 4 ml of deionized water, 4 mL of methanol, and 66.5 µl of a 10 mg/mL chloroplatinic acid solution. Nitrogen gas was bubbled through the reaction vessel for 10 minutes to remove air. The mixture was subsequently irradiated under ultraviolet light for 1 hour. After washing three times with deionized water, the resulting product was dried at 60°C for 12 hours to obtain Pt-HPCB-TiO_2. The synthesis steps are shown in Scheme 1. Pt-TiO_2 was synthesized via the same method, except that HPCB-TiO_2 was replaced by TiO_2.

Synthesis of Pt-HPCB-TiO_2-F

To obtain TiO_2–F, 200 mg TiO_2 was added into 40 mL of a NaF solution with a concentration of 0.5 mol/L. The mixture was stirred continuously at 25°C for 10h, washed with DI water after centrifugation, and dried in an oven at 60°C for 12h. Then, 20 mg of HPCB was dissolved in 10 mL of DCM, and 100 mg of TiO_2-F was then added. HPCB-TiO_2-F was obtained by employing DCM centrifugation and washing. The Pt-HPCB-TiO_2-F sample can be obtained by loading Pt cocatalysts using the chemical reduction method described above.

Characterization methods

Nuclear magnetic resonance (NMR) spectroscopy. The ^{1}H NMR measurements were performed on Bruker-BioSpin AVANCE III HD 400 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard.

Gel permeation chromatography (GPC). Weight-average molecular weight (M_w) and polydispersity index (PDI) of the polymers were estimated on an Agilent 1260 Infinity II equipped with a G7110B isocratic pump and G7162A refractive index detector. Polystyrene standards were utilized, and DMF was used as the eluent at a flow rate of 1.0 mL/min at 50^{o}C.

UV-vis absorption. Sample transmittances at 500 nm were acquired in THF/water mixtures with different water fractions (*fw*, vol%) on a Shimadzu UV-2450 UV-vis spectrophotometer at room temperature.

Luminescence spectroscopy. The spectrum was performed on a Shimadzu RF 5301pc fluorescence spectrophotometer in a quartz cuvette with a path length of 1 cm.

Aggregation-induced emission (AIE) property. The measurements of the polymer in solvent/nonsolvent mixtures were tested. In this study, THF was selected as good solvent for polymers and water as nonsolvent. The luminescent spectra of polymers in THF/H_2O mixtures with different water content were recorded respectively on a Shimadzu RF5301pc fluorescence spectrophotometer.

X-ray powder diffraction was carried out on a Bruker D8 advance instrument operated at 40 kV and 40 mA with Cu Kα radiation in the 2θ range from 5° to 80°.

Fourier transform infrared (FT-IR) spectra were characterized by employing a Nicolet Nexus 670 Fourier transform infrared spectrometer.

Raman spectroscopy was performed on a Thermo Fischer instrument with a 532 nm laser.

N_2 adsorption-desorption measurements were performed using a BELSORP-mini II instrument at −196 °C. Prior to the measurements, the fresh catalyst was degassed under vacuum at 120 °C for 2 h.

X-ray photoelectron spectroscopy (XPS) was characterized by a Thermo Scientific K-Alpha+ (America).

UV–vis-NIR diffuse reflectance spectra (DRS) were measured with a Shimadzu UV-3600i Plus (Kyoto, Japan) by using $BaSO_4$ as a reflectance standard.

Electron paramagnetic resonance (EPR) measurement was analyzed on a Magnettech ESR5000 spectrometer (Bruker).

Photocatalytic measurements

The photocatalytic H_2 evolution was tested in a quartz reactor. Typically, 10 mg of photocatalyst was dispersed in 10 mL of 10 vol% TEOA in a quartz reactor. The mixture was purged with Ar gas for 5 min to remove dissolved oxygen and air. A 300 W Xe lamp (PLS-SXE300/300UV, Perfectlight) equipped with a UV cutoff filter ($\lambda > 420$ nm) was used as the light source. The amount of H_2 generated was analyzed using a gas chromatograph equipped with a thermal conductivity detector (TCD) (GC-9790 Plus, FuLi, China).

Photoelectrochemical measurements

In this work, a standard three-electrode system equipped with a xenon light source ($\lambda > 420$ nm) was used for photoelectrochemical characterization on an electrochemical workstation (CHI 760e, Shanghai). The powder sample was dispersed uniformly on fluorine-doped tin oxide (FTO) glass. A Pt plate and an Ag/AgCl electrode were employed as the counter electrode and the reference electrode, respectively. The electrochemical impedance spectroscopy (EIS) measurement and transient photocurrent were performed using an electrochemical workstation (CHI 760e, Shanghai) with 0.1 M KCl and 0.1 M Na_2SO_4 as the electrolyte.

Table S1. Optimization of S_NP conditions for HPCB

Entry	eq (a: b: Base)	a/g	Solvent	solvent quantity/mL	Base	T/°C	Yield/%
1	1: 1: 3	0.2	THF	3	Cs_2CO_3	70	50.1
2	1: 2: 3	0.2	THF	3	Cs_2CO_3	70	86.6
3	1: 3: 3	0.4	THF	6	Cs_2CO_3	70	84.1
4	1: 4: 3	0.4	THF	6	Cs_2CO_3	70	86.1
5	1: 5: 3	0.4	THF	6	Cs_2CO_3	70	82.5
6	1: 2: 0.5	0.2	THF	3	Cs_2CO_3	70	51.2
7	1: 2: 1	0.2	THF	3	Cs_2CO_3	70	66.6
8	1: 2: 2	0.2	THF	3	Cs_2CO_3	70	68.2
9	1: 2: 4	0.2	THF	3	Cs_2CO_3	70	72.2
10	1: 2: 5	0.2	THF	3	Cs_2CO_3	70	43.6
11	1: 2: 3	0.2	THF	3	Cs_2CO_3	RT	23.3
12	1: 2: 3	0.2	THF	3	Cs_2CO_3	40	39.1
13	1: 2: 3	0.2	THF	3	Cs_2CO_3	60	63.4
15	1: 2: 3	0.2	THF	3	Cs_2CO_3	80	70.1
16	1: 2: 3	0.2	DMF	3	Cs_2CO_3	70	51.2
17	1: 2: 3	0.2	DMSO	3	Cs_2CO_3	70	66.6
18	1: 2: 3	0.2	DCM	3	Cs_2CO_3	RT	23.3
19	1: 2: 3	0.2	THF	3	$Ca(OH)_2$	70	38.9
20	1: 2: 3	0.2	THF	3	KOH	70	47.3
21	1: 2: 3	0.2	THF	3	K_2CO_3	70	35.8
22	1: 2: 3	0.2	THF	3	NaOH	70	-

Table S2. The comparison of photocatalytic H_2 production over different catalysts

Photocatalyst	**Pt(%w/w)**	**Light source**	**Hydrogen evolution ($\mu mol \cdot g^{-1} \cdot h^{-1}$)**	**Ref.**
TiO_2@Carbon layer	0.0	300 W Xe (λ= 360 nm)	416	[1]
Ti^{3+} self-doping black TiO_2/g-C_3N_4	0.0	A 300W Xe arc lamp with 100 mW/cm^{-2}	808.9	[2]
C/Pt/TiO_2	0.5	AM 1.5 G light from 150 W Xe lamp	＞3300	[3]
Pt/TiO_2@Carbon layer	1.0	300 W Xe (λ= 360 nm)	6250	[1]
carbon-coated TiO_2	0.0	A 300 W Xenon lamp with an output light intensity 200 mW cm^{-2} (λ: 350–780 nm)	434.9	[4]
2D/2D COF-TpPa-1/TiO_2	0.0	A xenon lamp (300 W) equipped with a filter (λ＞ 420 nm)	1370	[5]
Pt-choistan-TiO_2	0.5	A xenon lamp (300 W) equipped with a filter (λ＞ 420 nm)	2804	[6]
Pt-20%HPCB-TiO_2	0.5	A xenon lamp (300 W) equipped with a filter (λ＞ 420 nm)	3122.5	This work

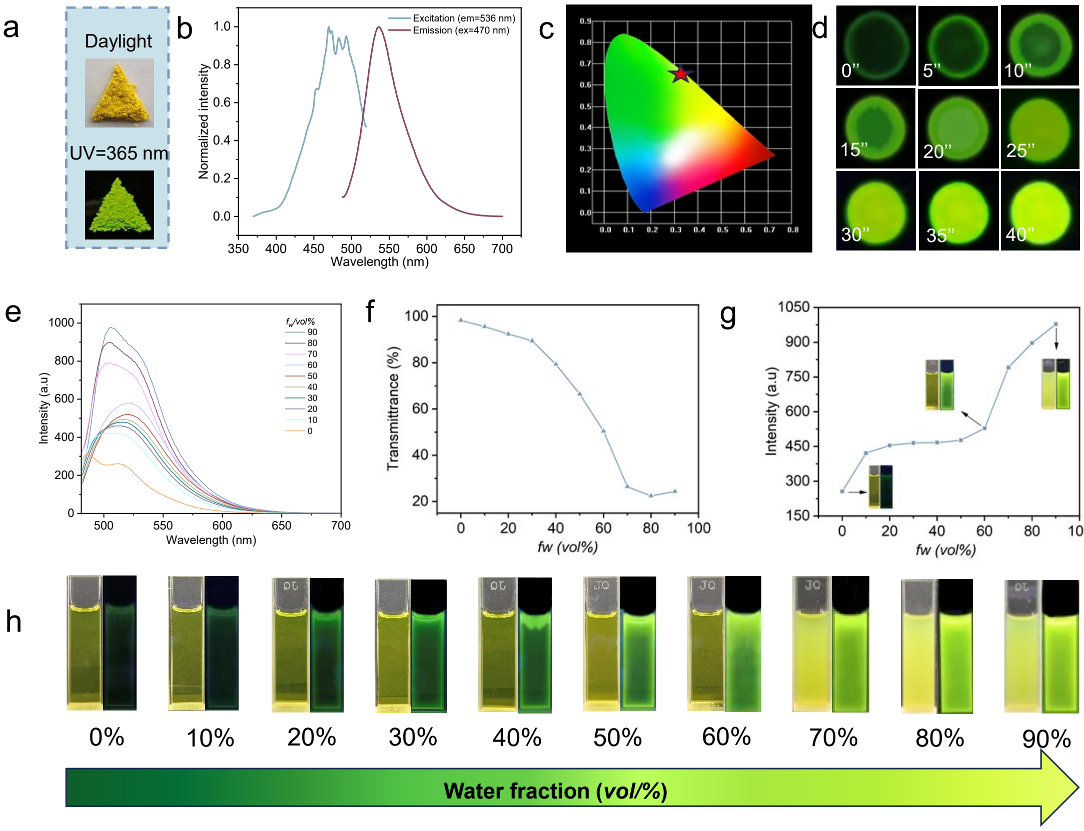


Figure S1. Luminescent properties of M-HPCB. (a) Digital photographs of M-HPCB under daylight and UV lamp at 365 nm. (b) Normalized excitation and emission spectra of M-HPCB at solid state. (c) CIE coordinates of M-HPCB. (d) Digital photos of M-HPCB solution (5 mg/mL of THF solution) on thin-layer chromatography at different time (time unit is second) of evaporation (under UV irradiation at 365 nm). (e) Emission spectra of M-HPCB (0.5 mg/mL) in H_2O/THF mixtures with different water volume fractions (f_w, vol%) (excitation wavelength of 469 nm). (f) The transmission of M-HPCB in H_2O/THF mixtures with different water volume fractions (f_w, vol%) at 500 nm. (g) Emission spectra of M-HPCB in H_2O/THF mixtures with different water volume fractions (f_w, vol %) of M-HPCB (0.5 mg/mL). (h) Digital photos of M-HPCB (0.5 mg/mL) in H_2O/THF mixtures with different water volumetric fractions (f_w, vol%) from 0% to 90% (under UV irradiation at 365 nm).

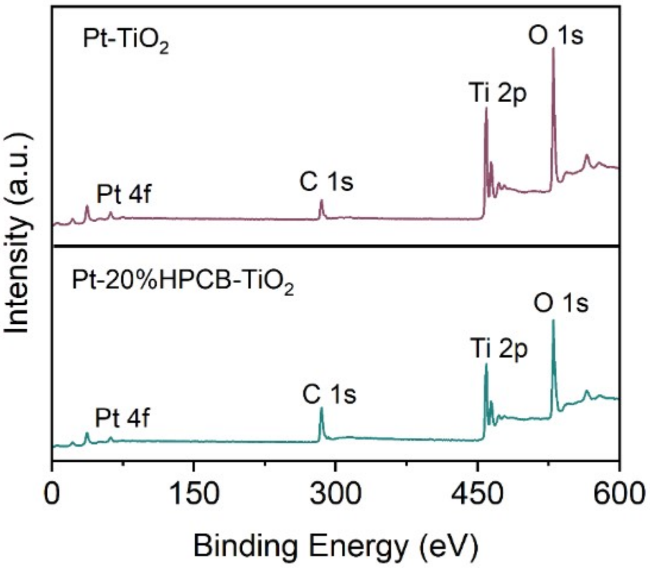


Figure S2. XPS survey spectra of Pt-TiO$_2$ and Pt-20%HPCB-TiO$_2$.

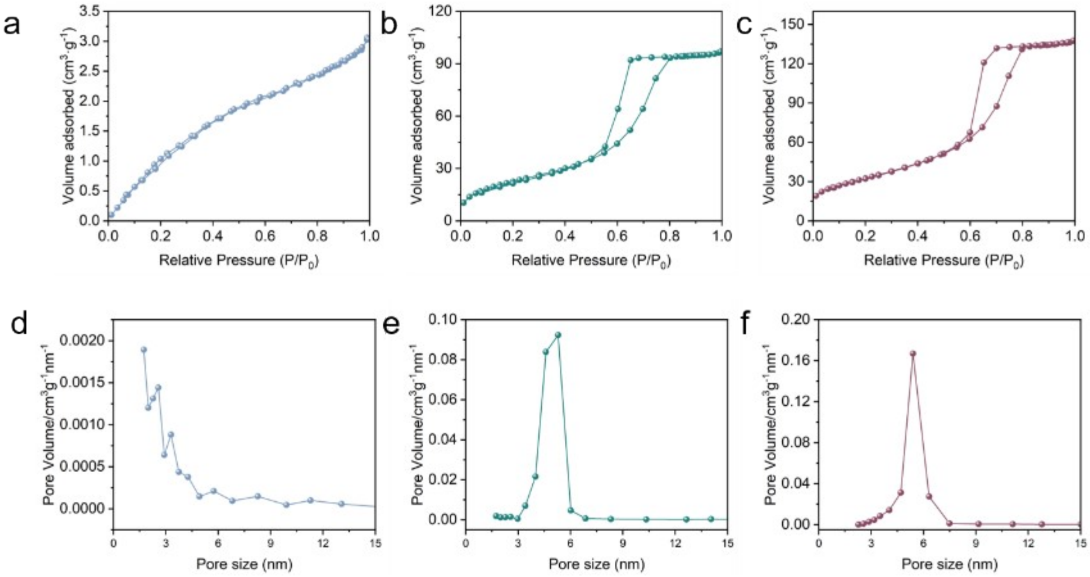


Figure S3. N_2 adsorption–desorption isotherms of (a) HPCB, (b) 20%HPCB-TiO_2, (c) TiO_2, the Barrett-Joyner-Halenda (BJH) of (d) HPCB, (e) 20%HPCB-TiO_2 and (f) TiO_2.

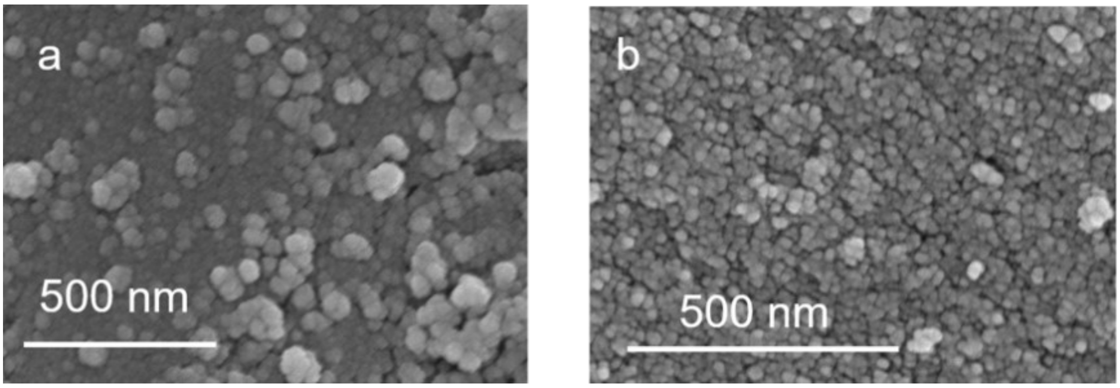


Figure S4. SEM images of (a) Pt-TiO_2 and (b) Pt-20%HPCB-TiO_2.

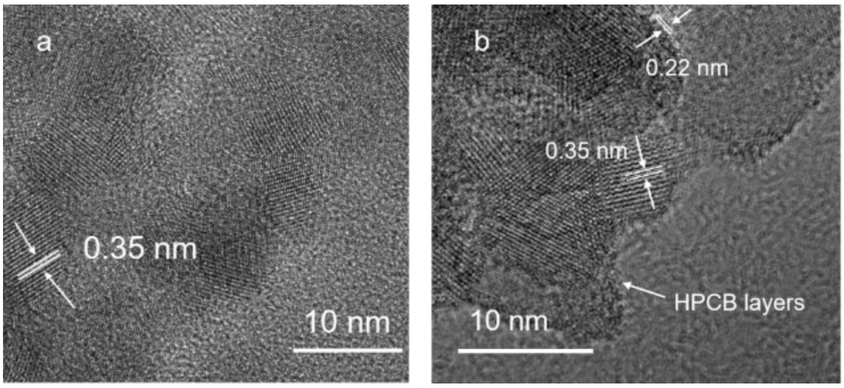


Figure S5. HRTEM image of (a) Pt-TiO_2 and (b) Pt-20%HPCB-TiO_2.

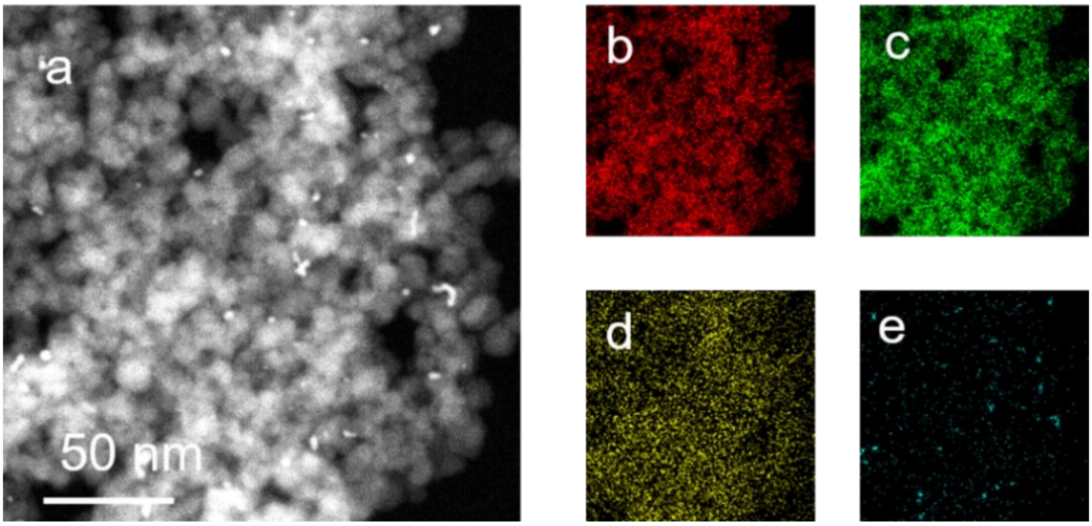


Figure S6. Elemental mapping images of (a) Pt-20%HPCB-TiO_2: (b) Ti, (c) O, (d) C and (e) Pt.

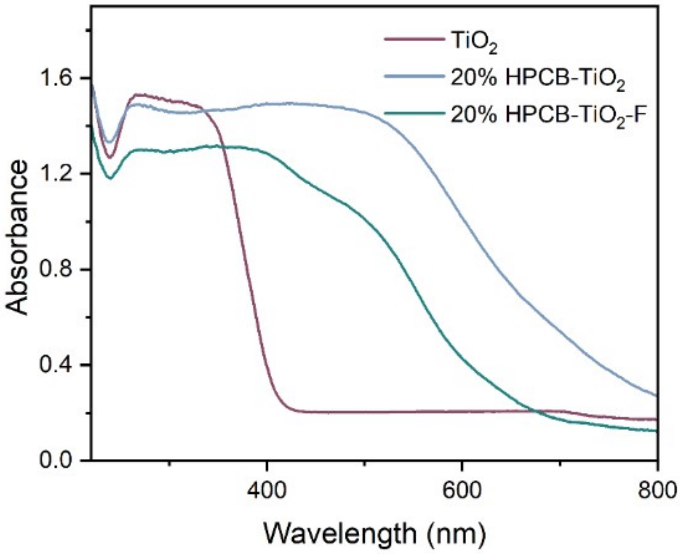


Figure S7. UV–Vis DRS of the as prepared samples.

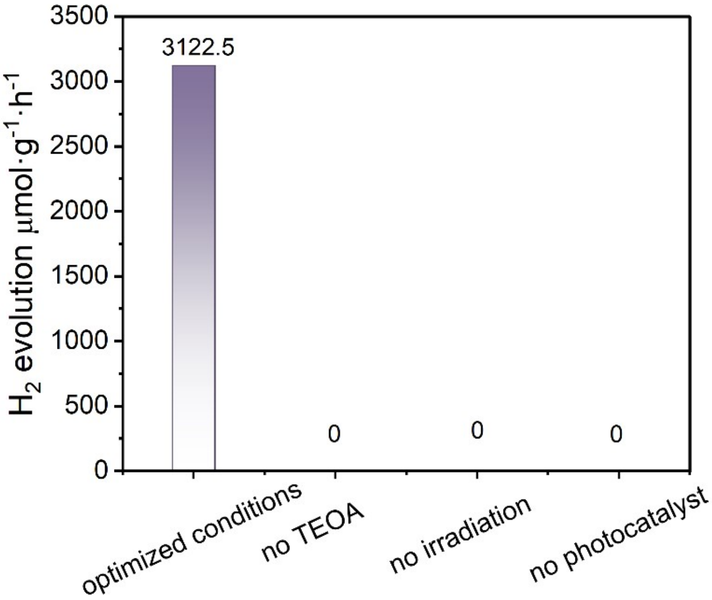


Figure S8. Control experiments for photocatalytic H_2 evolution reaction over Pt-20%HPCB-TiO_2.

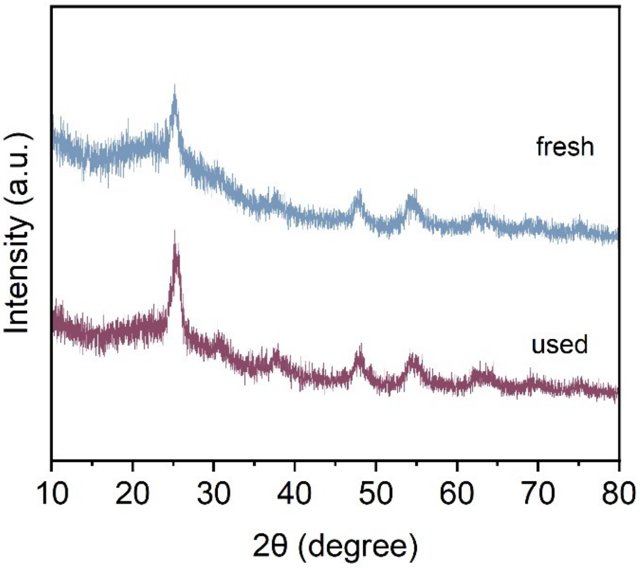


Figure S9. XRD patterns of Pt-20%HPCB-TiO_2 before and after the reaction.

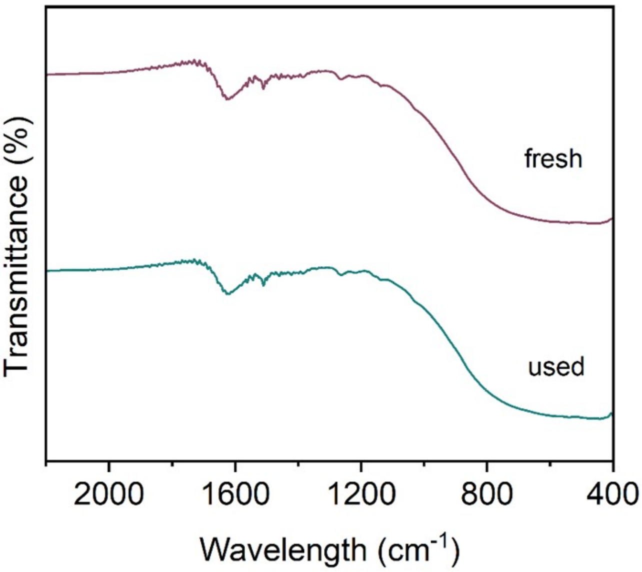


Figure S10. FT-IR spectra of Pt-20%HPCB-TiO_2 before and after the reaction.

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