

SUPPORTING INFORMATION

Article

Porous Hybrid Materials Based on Mesotetrakis(Hydroxyphenyl) Porphyrins and TiO₂ for Efficient Visible-Light-Driven Hydrogen Production

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Experimental section

Materials

Solvents were purified using an MBRAUN MB SPS-800 system. Anhydrous solvents used in the Suzuki coupling reaction were degassed by bubbling with N₂ for 20 min. All other chemicals and reagents were used as received from commercial sources without further purification. Specifically, butyl titanate (Ti(OBu)₄) 99.0%, tetrahydrofuran (THF) 99.0%, acetic acid 99.5%, propionic acid 99.5%, nitrobenzene 99.5%, ethanol 99.5%, methanol 99.5%, TEOA 98.0%, and H₂PtCl₆•6H₂O 99.95% were used.

Characterizations

The ¹H and ¹³C NMR spectra were tested on a Bruker 400 MHz spectrometer. Mass spectra data were obtained on an ultrafleXtreme MALDI-TOF/TOF mass spectrometer (Bruker Daltonics). The absorption spectra were observed with a Shimadzu UV-3600 spectrometer and fluorescence spectra were measured with an Edinburgh Instruments Ltd FLS980 spectrometer. Powder X-ray diffraction (PXRD) was recorded on a Rigaku Smart Lab diffractometer (Bragg-Brentano geometry, Cu-K_{α1} radiation, λ = 1.54056 Å). Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) micrographs, selected area electron diffraction (SAED), and elemental mapping were obtained by a JEM-2100F transmission electron microscope at 300 kV. Scanning electron microscopy (SEM) micrographs were recorded on Hitachi Ultra-high Resolution FE-SEM SU8010 microscope. Gas adsorption measurements were performed using ultra-high purity N₂ and CO₂ gas on Quantachrome Auto-sorb-iQ2-MP analyzer. The Mott-Schottky curves were measured using a CHI760E electro-chemical analyzer (China) in a three-electrode cell. Pt plate was used as counter electrode and Ag/AgCl electrode (3 M KCl) was used as reference electrode. The electrolyte was a 0.5 M Na₂SO₄ aqueous solution. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass by dispersing materials (2 mg) in ethanol (1 mL) with Nafion (10 μL), and the exposed area of the electrode was 1 cm². The photocatalytic hydrogen production system was Perfect Light Lab Solar-IIIAG and H₂ measurement was performed on Agilent 7820A gas chromatography with a thermal conductivity detector (TCD). The amounts of Pt NPs loaded on samples were detected by ICP-AES (spectra range: 120-800 nm, holographic grating, 2924 line/mm,

SPECTRO CIROS VISION). Cyclic voltammograms (CVs) were recorded using a CHI760E electrochemical analyzer with platinum plate as working electrode, Ag/AgCl (3 M KCl) as reference electrode, Pt wire as counter electrode, and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte in THF with a scan rate of 40 mV s⁻¹.

Synthesis

The porphyrin compounds **THPP**, **THPP-Pd** and **THPP-Zn** were synthesized according to the reported literature [1].

Synthesis of 5,10,15,20-tetrakis(4-hydroxyphenyl)-porphyrin, THPP

4 ml nitrobenzene and 8 ml propionic acid are added into a 50 ml three-necked flask and refluxed for 30 min. 5 ml 4-hydroxybenzaldehyde propionic acid solution (1.6 mmol/ml) and 5 ml pyrrole nitrobenzene solution (1.6 mmol/ml) are dropped in the reactionary mixture slowly. The mixture is refluxed for 1.5 h, cooled, blew through by air within 30 min, 10 ml of petroleum ether is flowed, then left in refrigerator overnight. The final product is dark blue solid with a yield of 67% (0.446 g). ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.96 (s, 2H), 9.94 (s, 4H), 8.86 (s, 8H), 7.99 (d, *J* = 8.2 Hz, 8H), 7.20 (d, *J* = 8.3 Hz, 8H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 175.55, 157.77, 135.88, 132.30, 120.37, 114.30, 27.27, 9.47. MALDI-TOF: *m/z* 679.256 ([M+H]⁺), calculated: *m/z* 679.234 ([M+H]⁺).

Synthesis of metalloporphyrin THPP-Pd

A mixture of THPP (0.1 g, 0.15 mmol) and palladium acetate (0.1 g, 0.45 mmol) in 10 mL of DMF was boiled for 1 h. Then the mixture was poured into water. The precipitate was filtered and washed with water and dried at 70 °C. The resulting product was dissolved in ethyl acetate and chromatographed on a column of silica gel using ethyl acetate as eluent. The eluate was evaporated and the complex was precipitate by petroleum ether. The resulting complex was washed and dried in the air at room temperature. Yield: 94%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.93 (s, 4H), 8.83 (s, 8H), 7.94 (d, *J* = 8.4 Hz, 8H), 7.18 (d, *J* = 8.4 Hz, 8H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 157.87, 141.64, 135.51, 131.87, 131.53, 122.21, 114.39. MALDI-TOF: *m/z* 783.143 ([M+H]⁺), calculated: *m/z* 783.123 ([M+H]⁺).

Synthesis of metalloporphyrin THPP-Zn

A mixture of THPP (0.1 g, 0.15 mmol) and zinc acetate (0.1 g, 0.46 mmol) in 10 mL of DMF was boiled for 1 h. Then the mixture was poured into water. The precipitate was filtered and washed with water and dried at 70 °C. The resulting product was dissolved in ethyl acetate and chromatographed on a column of silica gel using ethyl acetate as eluent. The eluate was evaporated and the complex was precipitate by petroleum ether. The resulting complex was washed and dried in the air at room temperature. Yield: 95%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.81 (s, 4H), 8.79 (s, 8H), 7.94 (d, *J* = 8.1 Hz, 8H), 7.16 (d, *J* = 8.1 Hz, 8H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 157.87, 141.64, 135.51, 131.87, 131.53, 122.21, 114.39. MALDI-TOF: *m/z* 741.157 ([M+H]⁺), calculated: *m/z* 741.148 ([M+H]⁺).

Preparation of THPP-TiO₂, THPP-Pd-TiO₂, THPP-Zn-TiO₂ and Gel-TiO₂

Tetrabutyl titanate (1 mL), acetic acid (168 μL), deionized water (106 μL) and THF (1 mL) were added into 20 mL glass bottle and the mixture was stirred at room temperature, and then 12.5 mg of porphyrin (**THPP**, **THPP-Pd** or **THPP-Zn**) dissolved in THF (1 mL) was dropwise added. The transparent gelatum was formed in several minutes and was soxhleted with deionized water for 72 h and then evaporated to dryness. Similarly, Gel-TiO₂ material was prepared though the same procedure but without porphyrin doping.

Preparation of Pt/THPP-TiO₂, Pt/THPP-Pd-TiO₂ and Pt/THPP-Zn-TiO₂ photocatalysts

Hybrid material (100 mg), distilled water (80 mL), methanol (10 mL) and 10 mM H₂PtCl₆ aqueous solution (334 μL) were added into a quartz reactor. The mixture was degassed by vacuuming and irradiating with 300 W xeon lamp (without filter) for 30 min, and then the Pt

nanoparticles were loaded. Pt loading amount (0.5 wt%) was testified by the inductively coupled plasma atomic emission spectrometry (ICP-AES).

Preparation of sensitized Pt/Gel-TiO₂/THPP-Pd photocatalyst

Pt nanoparticles were loaded onto Gel-TiO₂ by the photo deposition method mentioned above. The as-prepared Pt/Gel-TiO₂ powder (100 mg) was dispersed in 0.3 mM THF solution of **THPP-Pd** (10 mL) and stirred at room temperature for 12 h in the dark, and then centrifuged and washed with THF until the eluent was colorless. The solid was dried in vacuum at room temperature for overnight.

Photocatalytic H₂ production

The photocatalytic H₂ production experiments were performed in a glass reactor with quartz cover connected to a closed gas circulation, in which the reaction mixture can be degassed by vacuuming. Specifically, 50 mg photocatalyst was dispersed in 100 mL of 10 vol% TEOA aqueous solution (pH \approx 12). Then the suspension was stirred continuously and irradiated by a 300 W Xe lamp with or without a cut-off filter ($\lambda > 420$ nm). The amount of produced H₂ was determined at an interval of 1 h with online gas chromatography.

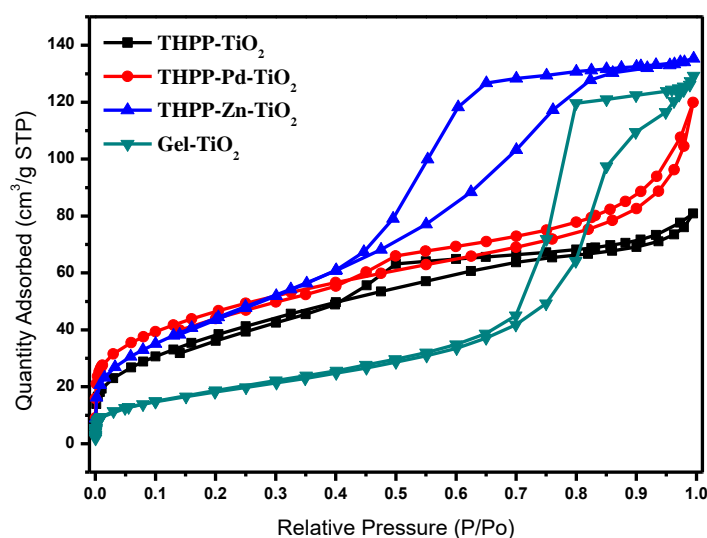


Figure S1. N₂ adsorption-desorption isotherms of Gel-TiO₂, THPP-TiO₂, THPP-Pd-TiO₂ and THPP-Zn-TiO₂ at 77 K.

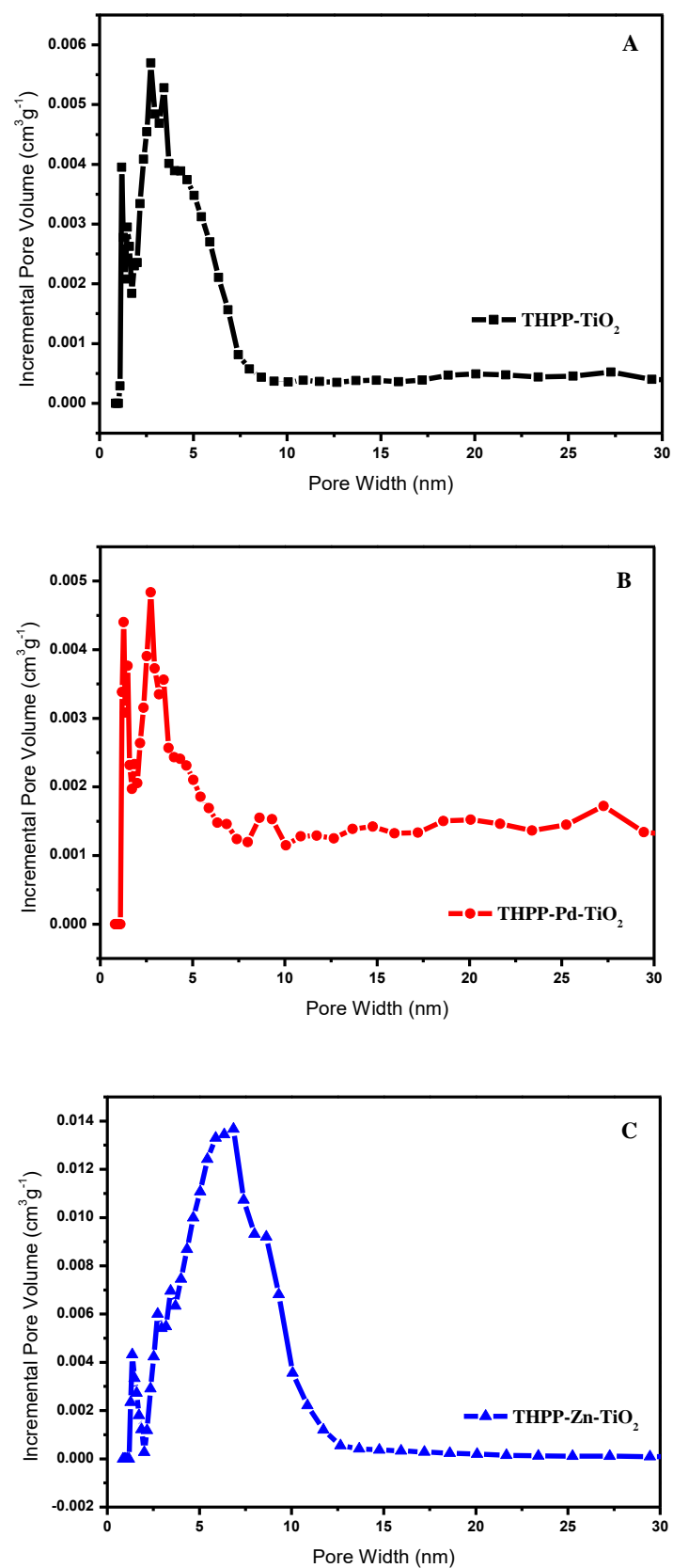


Figure S2. The pore size distributions of A) THPP-TiO₂, B) THPP-Pd-TiO₂ and C) THPP-Zn-TiO₂.

Table S1. BET surface areas, pore volumes and pore widths of Gel-TiO₂, THPP-TiO₂, THPP-Pd-TiO₂ and THPP-Zn-TiO₂ derived from 77 K N₂ sorption isotherms.

	THPP-TiO ₂	THPP-Zn-TiO ₂	THPP-Pd-TiO ₂	Gel-TiO ₂	P25-TiO ₂
	2	TiO ₂	TiO ₂		
Surface Area (m ² /g)	143.4	166.1	168.3	162.9	55.4
Pore Volume (ml/g)	0.125	0.209	0.185	0.233	0.162
Pore width (nm)	1.18/3.49	1.38/5.96	1.26/2.83	1.36/4.41	29.40

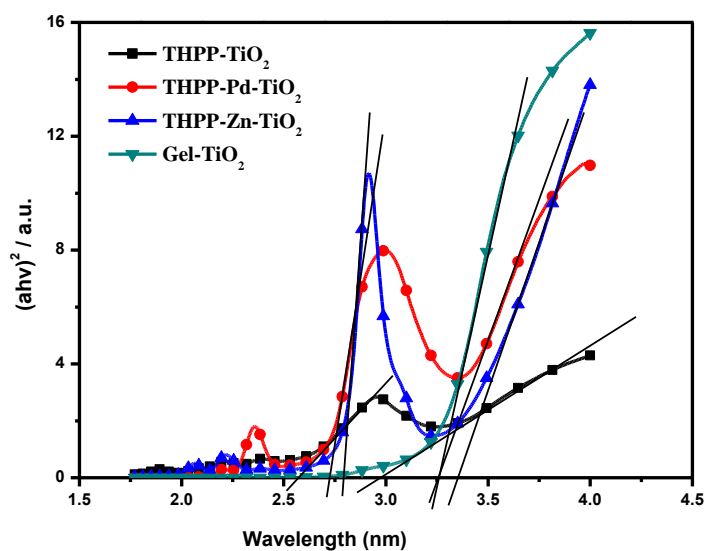


Figure S3. Tauc plots of THPP-TiO₂, THPP-Pd-TiO₂, THPP-Zn-TiO₂ and Gel-TiO₂.

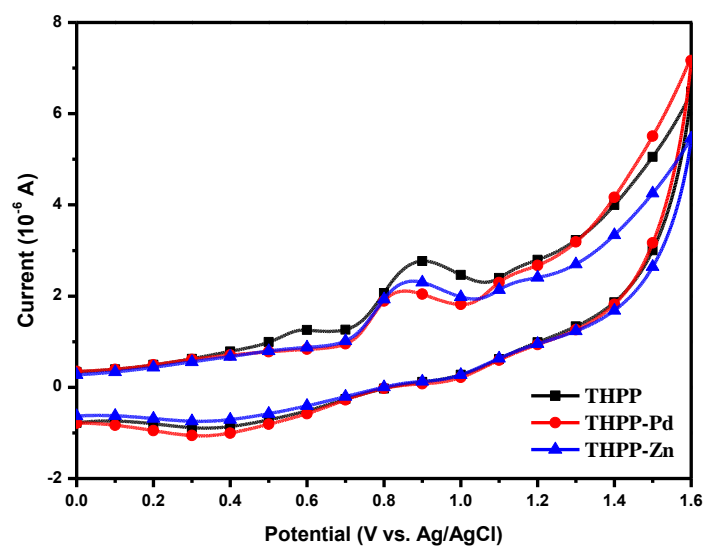
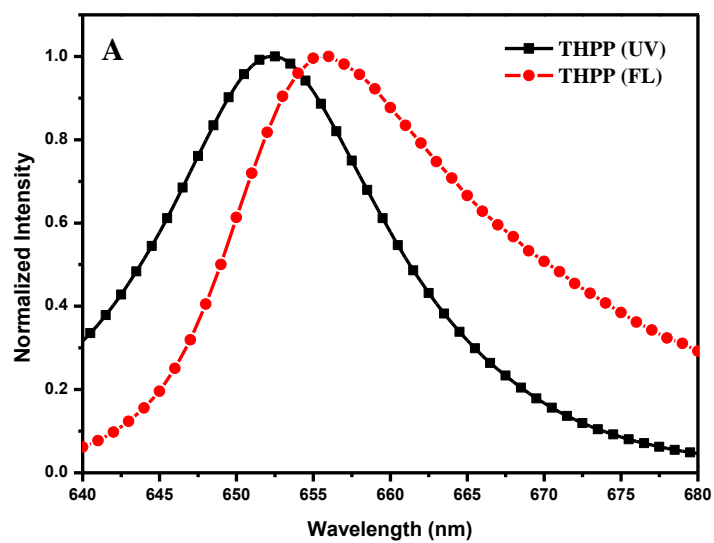


Figure S4. Cyclic voltammogram of THPP, THPP-Pd and THPP-Zn in 0.1 M TBAPF₆ THF solution with a scan rate of 40 mV s⁻¹.



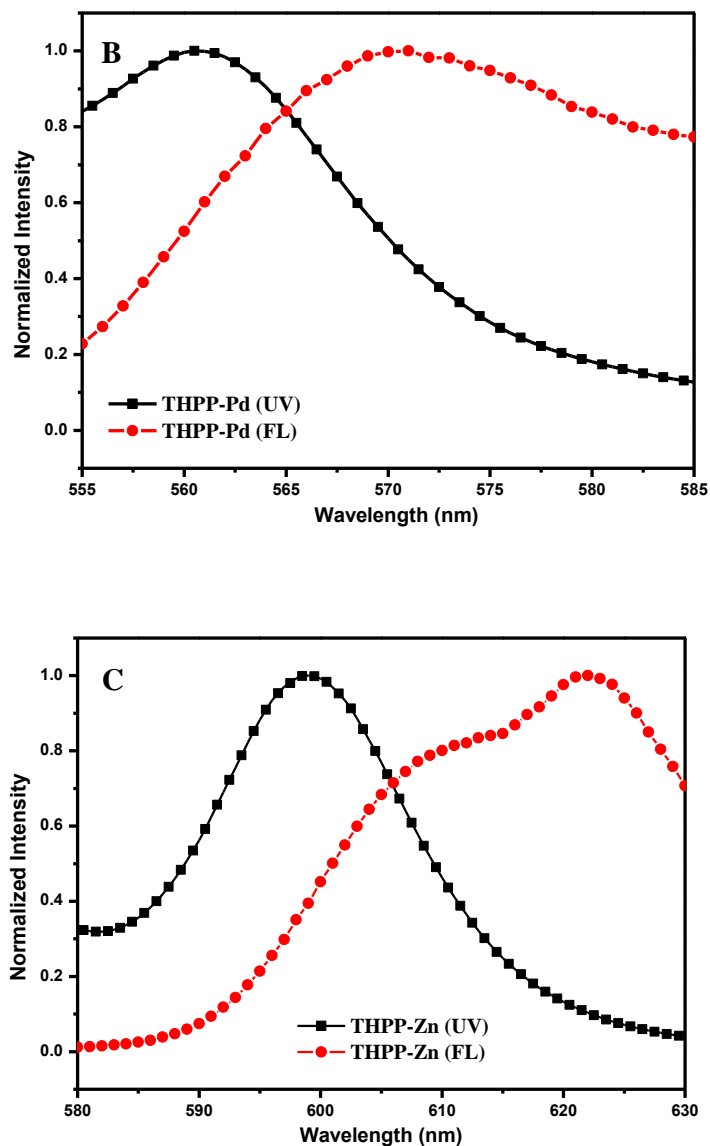


Figure S5. Absorption and emission spectra of A) THPP, B) THPP-Pd, and C) THPP-Zn measured in THF solution.

Table S2. The energy levels and electrochemical data of THPP, THPP-Pd and THPP-Zn.

	E_{ox}/V (vs NHE.)	E_{0-0}/eV (Intersection/nm)	E_{exc}/V (vs NHE.)	E_{HOMO}^a/eV (vs vac.)	E_{LUMO}^a/eV (vs vac.)
THPP	1.12	1.90 (654)	-0.78	-5.62	-3.72
THPP-Pd	1.08	2.19 (565)	-1.11	-5.58	-3.39
THPP-Zn	1.10	2.05 (606)	-0.95	-5.60	-3.55

^aCalculated by the scale: -4.5 eV for 0.0 V versus NHE. from ref. [2].

Table S3. H₂ production data and calculated TON values of hybrid catalysts of THPP, THPP-Pd and THPP-Zn with or without Pt NPs under visible light in 5 h.

Dye	Dye-TiO ₂				Pt/Dye-TiO ₂			
	H ₂ yield ^a /μmol g ⁻¹	H ₂ yield ^b /μmol m ⁻²	TON ^c _{Dye}	TON ^d _{Pt}	H ₂ yield ^a /μmol g ⁻¹	H ₂ yield ^b /μmol m ⁻²	TON ^c _{Dye}	TON ^d _{Pt}
THPP	0	0	0	0	2,884.1	20.1	39	113
THPP-Pd	1,150.6	6.84	18	45	10,126.9	60.2	158	395
THPP-Zn	15.4	0.09	0.2	0.6	6,198.8	37.3	92	242

[a] = the number of moles of H₂ in 5 h / mass of catalyst.

[b] = the number of moles of H₂ in 5 h / surface area of catalyst.

[c] = the number of moles of H₂ in 5 h / the number of moles of doping dye.

[d] = the number of moles of H₂ in 5 h / the number of moles of loading Pt.

Table S4. AQY results for H₂ production of Pt/THPP-TiO₂, Pt/THPP-Pd-TiO₂ and Pt/THPP-Zn-TiO₂ catalysts (6 mg for each sample) after 0.5 h irradiation under 425 nm LED light source.

photocatalyst	n(H ₂) /μmol	AQY/%
Pt/THPP-TiO ₂	0.39	0.153
Pt/THPP-Pd-TiO ₂	1.17	0.456
Pt/THPP-Zn-TiO ₂	0.64	0.249

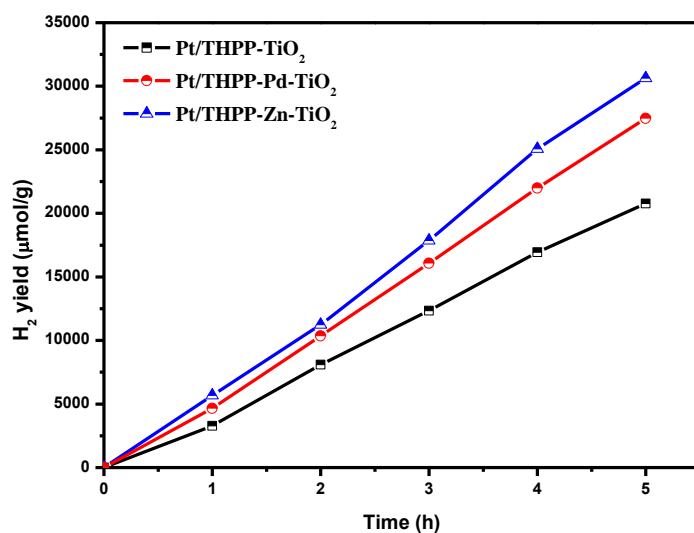


Figure S6. H₂ production curves of Pt/THPP-TiO₂, Pt/THPP-Pd-TiO₂, and Pt/THPP-Zn-TiO₂ in an aqueous solution of 10% TEOA under complete UV-vis irradiation.

Table S5. H₂ production data and calculated TON values of Pt/THPP-Pd-TiO₂ and Pt/THPP-Pd/TiO₂ in cyclic photocatalytic experiment.

Round No.	Pt/THPP-Pd-TiO ₂			Pt/THPP-Pd/TiO ₂		
	H ₂ yield ^a / μmol g ⁻¹	H ₂ yield ^b / μmol m ⁻²	TON ^c _{Pt}	H ₂ yield ^a / μmol g ⁻¹	H ₂ yield ^b / μmol m ⁻²	TON ^c _{Pt}
1	10,127	60.2	395	10,022	61.5	391
2	14,274	84.8	557	6,625	40.7	258
3	17,493	103.9	682	5,552	34.1	217
4	14,191	84.3	554			
5	13,512	80.3	527			
6	13,365	79.4	521			
7	9,114	54.1	356			
8	11,196	66.5	437			
9	13,969	83.0	545			
10	13,780	81.9	538			
Total	131,020	778.5	5111			

[a] = the number of moles of H₂ in 5 h / mass of catalyst.

[b] = the number of moles of H₂ in 5 h / surface area of catalyst.

[c] = the number of moles of H₂ in 5 h / the number of moles of loading Pt.

References

- [1] a) J. Cabrera-Gonzalez, E. Xochitiotzi-Flores, C. Vinas, F. Teixidor, H. García-Ortega, N. Farfan, R. Santillan, T. Parella, R. Nunez, *Inorg. Chem.*, 2015, 54, 5021-5031; b) M. V. Tesakova, A. S. Semeikin, V. I. Parfenyuk, J. Porphyrins Phthalocyanines, 2015, 19, 1032-1038.
- [2] a) A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 2001; b) M. Grätzel, *Nature*, 2001, 414, 338-344.