

Electronic Supporting Information

[Ru(N[□]N[□]N)₂-Ce]-based Framework for Photocatalytic Sulfides

Oxidation and Hydrogen Production

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Experimental

Materials and methods

4'-(4-Methoxycarbonylphenyl)-2,2':6',2''-terpyridine was synthesized according to a published procedure¹. The [(4'-(4-carboxylphenyl)tpy)₂Ru](OTf)₂ (Ru(cptpy)₂) was synthesized according to previous report with slight modifications², and all other chemicals and solvents employed in this work were used without any further purification. Single-crystal X-ray diffraction (SCXRD) data were collected using the Bruker ApexII Duo. IR spectra (KBr pellets) were recorded on Thermo Fisher Scientific FT-IR spectrometer (Thermo IS5). TGA was performed on a Mettler Toledo TGA/DSC 1000 analyzer under N₂ atmosphere at a heating rate of 10°C min⁻¹. Powder X-ray diffraction (PXRD) spectra were measured by Bruker D8 Advance XRD diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). Solid UV-Vis absorption spectra were recorded on a UV-2600 220V CH spectrometer (Shimadzu, Japan). NMR spectra were acquired on a Bruker Avance IIIHD spectrometer (¹H at 400 MHz, ¹³C at 700 MHz). X-ray photoelectron spectroscopy (XPS) was taken on 5000 Versaprobe III. Photocurrent measurements and electrochemical impedance spectroscopy (EIS) were measured on a CHI 760E electrochemical work station. The reactions of photocatalytic sulfides oxidation were carried out on a multi-channel photochemical reaction system featuring 10 W 450 nm LED lamps and monitored by gas chromatograph (GC-2014C Shimadzu). The reactions of photocatalytic hydrogen production were achieved in a top-irradiation reactor attached to a gas-closed glass system equipped with a 300 W Xenon arc lamp (CEL-HXF300, Au-Light, China). The generated H₂ was monitored by gas chromatograph (GC-2014C Shimadzu).

Synthesis of [(4'-(4-carboxylphenyl)tpy)₂Ru](OTf)₂ (Ru(cptpy)₂)

A mixture of RuCl₃·3H₂O (130 mg, 0.5 mmol), 4'-(4-Methoxycarbonylphenyl)-2,2':6',2''-terpyridine (367 mg, 1 mmol), AgOTf (385 mg, 1.5 mmol) and DMA were added to a round-bottomed flask. The solution was refluxed for 24 hours under nitrogen atmosphere. After cooling at room temperature, AgCl was removed by filtration. Then the solvents were evaporated. The product was washed with ethyl acetate and dried to gain the dark red solid [(4'-(4-Methylcarboxylphenyl)tpy)₂Ru](OTf)₂. Finally, [(4'-(4-Methylcarboxylphenyl)tpy)₂Ru](OTf)₂ was dissolved in aqueous solution of LiOH (4 M). After stirring for 12 h at 80 °C, the solution is made acidic with HNO₃ to give a heavy precipitate. The solid is filtered and washed with water, then dried in vacuo, yield 80%.

Synthesis of Ce-1 (Ce[Ru(cptpy)₂](NO₃)₄)

Ce(NO₃)₃·6H₂O (0.045 g, 0.1 mmol), Ru(cptpy)₂ (0.017 g, 0.015 mmol), 2-fluorobenzoic acid (0.112 g, 0.8 mmol) and HNO₃ (3.5 M, 1.3 mL) were added to a 20 mL Pyrex vial with a mixed solvents of DMF (10 mL) and H₂O (0.5 mL), and it was ultrasonized for 10 minutes at room temperature. Then the mixture was placed in a preheated oven at 100 °C for 48 h. Dark red crystals of suitable size for single X-ray analysis were obtained (yield 93% based on (Ru(cptpy)₂). The crystals were washed with DMF and EtOH, and air-dried at room temperature.

Synthesis of Ce-2 (Ce[Ru(cptpy)₂](OH)(NO₃)₃)

Ce(NH₄)₂(NO₃)₆ (0.055 g, 0.1 mmol), Ru(cptpy)₂ (0.017 g, 0.015 mmol), 2-fluorobenzoic acid

(0.112 g, 0.8 mmol) and HNO₃ (3.5 M, 1.3 mL) were added to a 20 mL Pyrex vial with a mixed solvents of DMF (10 mL) and H₂O (0.5 mL), and it was ultrasonized for 10 minutes at room temperature. Then the mixture was placed in a preheated oven at 100 °C for 48 h. Dark red crystals of suitable size for single X-ray analysis were obtained (yield 91% based on (Ru(cptpy)₂). The crystals were washed with DMF and EtOH, and air-dried at room temperature.

Synthesis of Ce/Zr-3 and Zr-3

Ce(NH₄)₂(NO₃)₆ (0.002 g, 0.004 mmol), ZrOCl₂ (0.005 g, 0.016 mmol), Ru(cptpy)₂ (0.034 g, 0.03 mmol), HCOOH (3.25 mL) were added to a 20 mL Pyrex vial with a mixed solvents of DMF (8 mL) and H₂O (4 mL), and it was ultrasonized for 10 minutes at room temperature. Then the mixture was placed in a preheated oven at 120 °C for 48 h. Dark red crystals were obtained. The crystals were washed with DMF and EtOH, and air-dried at room temperature. The **Zr-3** was synthesized according to previous reports.

Single X-ray Analysis

The X-ray diffraction data were collected on a Bruker SMART APEX2-CCD diffractometer with graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) at 296 K. The program SADABS was used for the absorption correction. The structures were solved by the direct method and refined on F² by the full-matrix least squares methods using the SHELX-2014/2018 program package. Crystallographic data collection and refinement results are summarized in Table S1 and Table S2.

Photoelectrochemical measurements

Photocurrent tests of **Ce-1** and **Ce-2** were performed in a standard three-electrode system with the ITO as the working electrode, Pt plate as the counter electrode, and an Ag/AgCl as a reference electrode. The 0.1 M Na₂SO₄ solution was used as electrolyte. 5 mg **Ce-1** or **Ce-2** was dispersed into a mixed solution with 1 mL ethanol and 40 μ L 5 wt% Nafion. Then 80 μ L suspension was dropped onto the surface of the ITO glass with an area of 1 cm² and dried in air. The photo-responsive signals of **Ce-1** or **Ce-2** were recorded under irradiation of a 300 W Xe lamp.

EIS of **Ce-1** and **Ce-2** were performed in a standard three-electrode system with the glassy carbon as the working electrode, Pt plate as counter electrode, and an Ag/AgCl as a reference electrode. The 0.1 M Na₂SO₄ aqueous solution was used as the electrolyte. 5 mg **Ce-1** or **Ce-2** was dispersed into 1 mL ethanol. Then 5 μ L suspension was dropped onto the surface of the glassy carbon and dried in air. The EIS plots of **Ce-1** or **Ce-2** were recorded.

Procedures of Ce-1, Ce-2 and Ce/Zr-3 photocatalyzed sulfide oxidation

0.1 mmol Sulfide, 5 mg **Ce-1**, **Ce-2** or **Ce/Zr-3** and 5 mL CH₃OH were added to a 10 mL quartz bottle pumped with O₂. Subsequently, the sample was irradiated with a 10 W LED light ($\lambda = 450 \text{ nm}$) and stirred at room temperature. After reaction, the products were detected by GC.

Procedures of Ce-1 or Ce-2 photocatalyzed hydrogen production

Photocatalytic hydrogen production experiments were performed in a top-irradiation reactor attached to a gas-closed glass system. 10 mg **Ce-1/Ce-2** was dispersed in a mixed solution of 50 mL water containing 0.01 M TEOA and H₂PtCl₆ aqueous solution (Pt content: 3 wt %). Then the reaction system was degassed under vacuum to remove air. Subsequently, the sample was irradiated

with a 300 W Xenon lamp and stirred at 6 °C. After the reaction, the generated H₂ was analyzed by using a gas chromatograph with high-purity argon carrier gas.

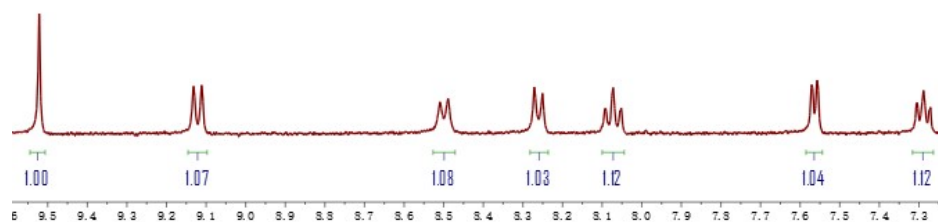


Figure S1. (a) ¹H NMR of Ru(cptpy)₂ in d₆-dmsd at 400 MHz. ¹H NMR (400 MHz, DMSO-d₆, ppm): δ = 9.52 (s, 1H), 9.12 (d, *J* = 8.1 Hz, 1H), 8.50 (d, *J* = 8.1 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.11 – 8.03 (m, 1H), 7.56 (d, *J* = 5.5 Hz, 1H), 7.29 (t, *J* = 6.4 Hz, 1H).

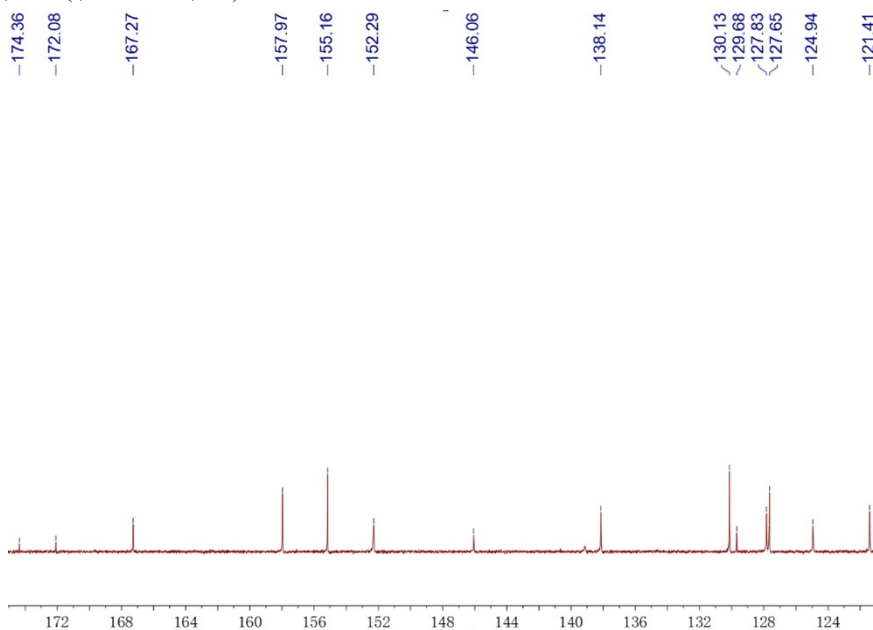


Figure S1. (b) ¹³C NMR of Ru(cptpy)₂ in d₆-dmsd at 700 MHz. ¹³C NMR (700 MHz, DMSO-d₆, ppm): δ = 174.36, 172.08, 167.27, 157.97, 155.16, 152.29, 146.06, 138.14, 130.13, 129.68, 127.83, 127.65, 124.94, 121.41.

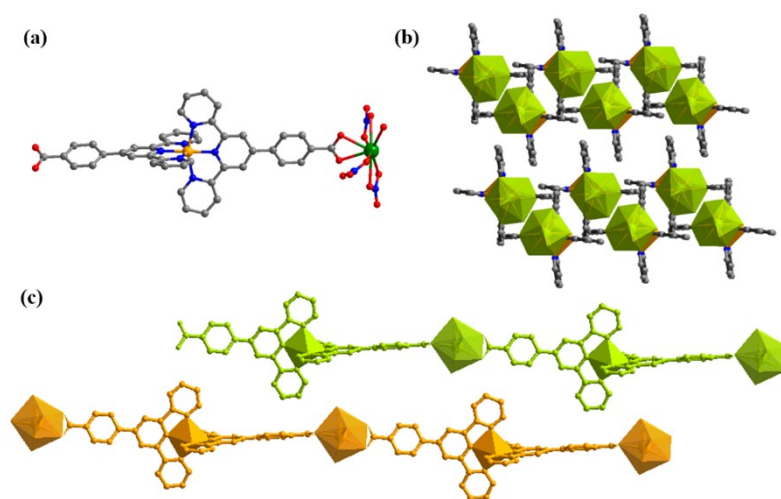


Figure S2. (a) The coordination environments of Ce-2 (color code: Ru, light orange; Ce, lime; C, gray; O, red; N, blue) (b) and (c) View of the 1D chain and 3D network of Ce-2.

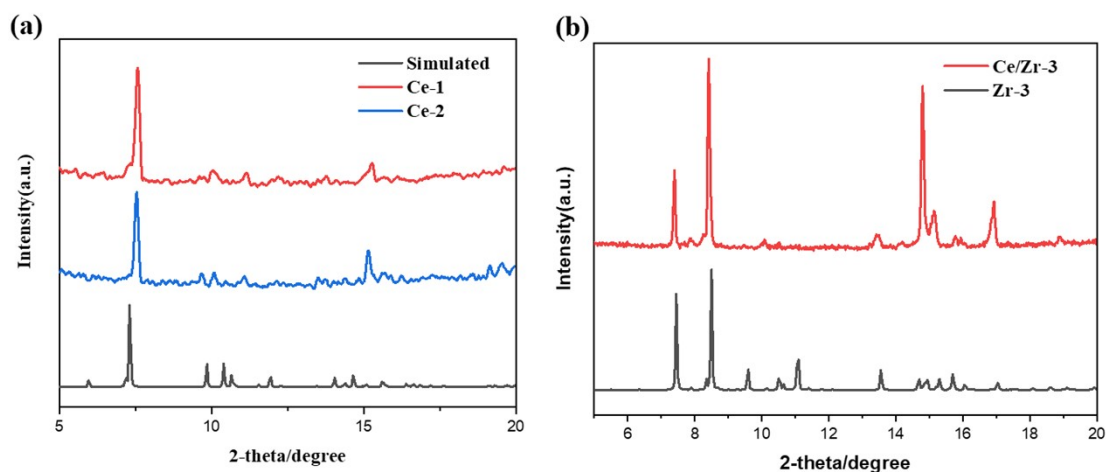


Figure S3. PXRD patterns for as-synthesized samples (a) Ce-1, Ce-2 and (b) Ce/Zr-3.

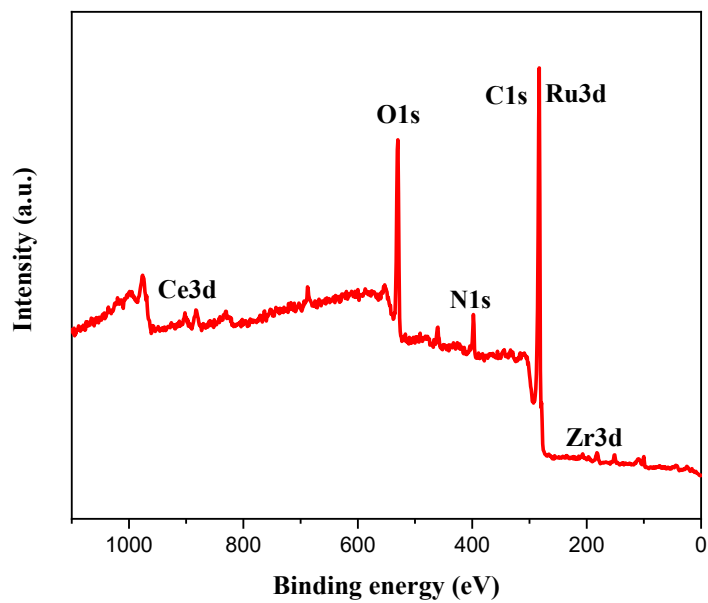


Figure S4. XPS spectrum of Ce/Zr-3.

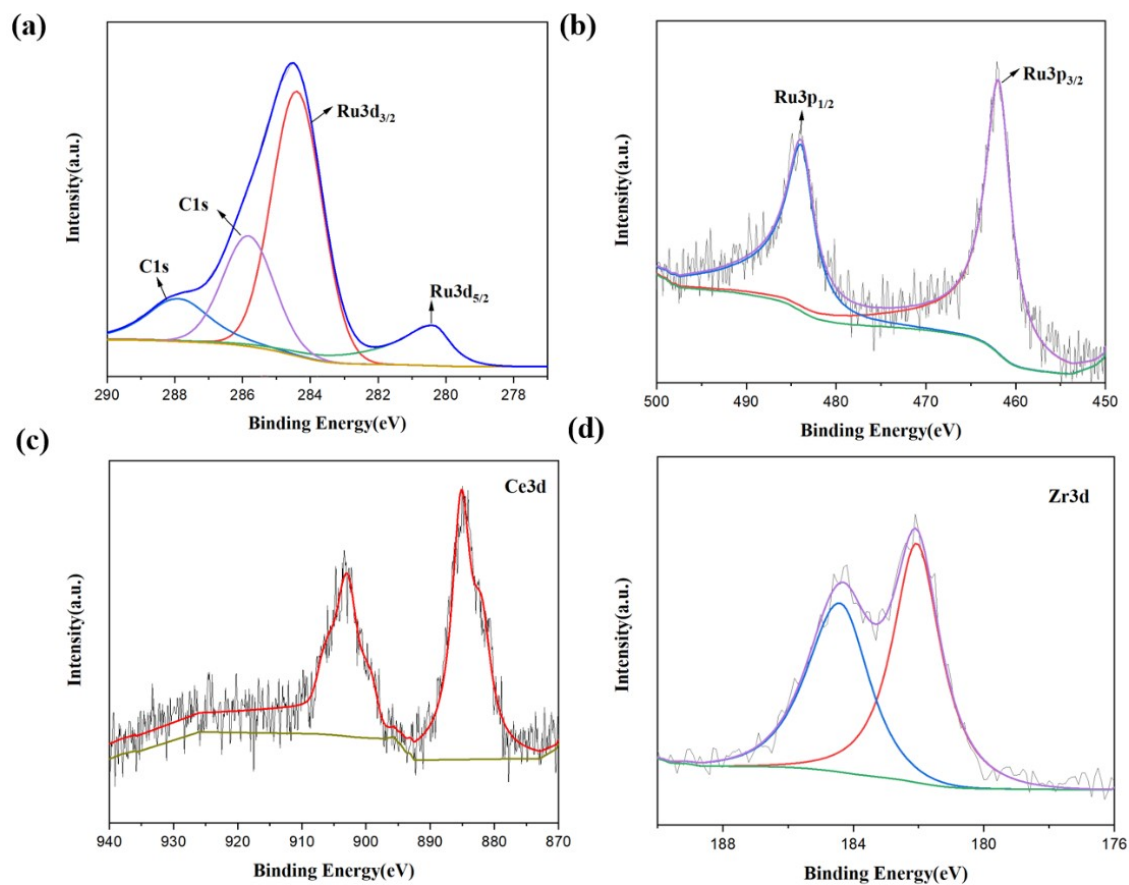


Figure S5. XPS spectrum of complex Ce/Zr-3. (a) Ru 3d, (b) Ru 3p, (c) Ce 3d, (d) Zr 3d.

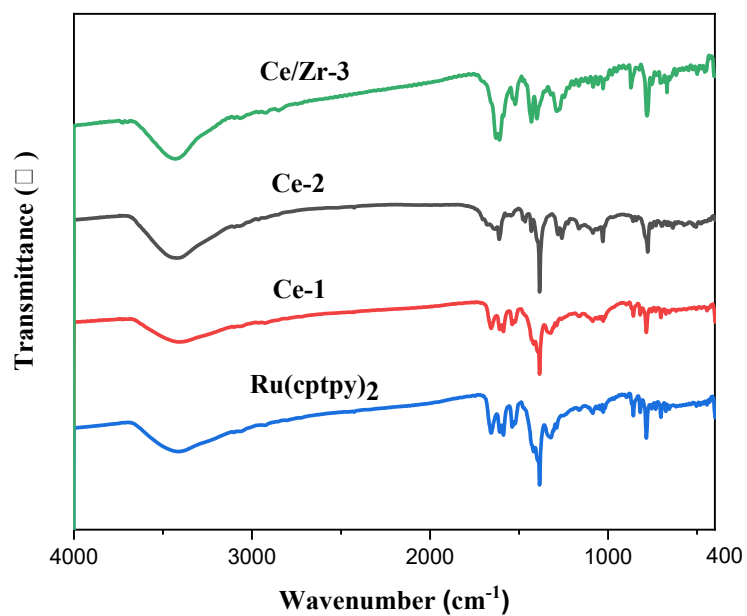


Figure S6. IR spectra of Ru(cptpy)₂, Ce-1, Ce-2 and Ce/Zr-3.

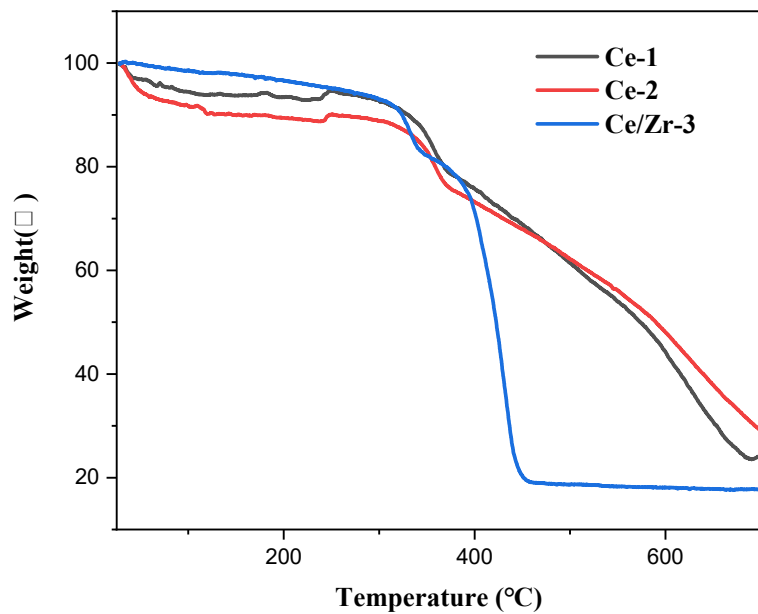


Figure S7. TGA analysis of Ce-1, Ce-2 and Ce/Zr-3.

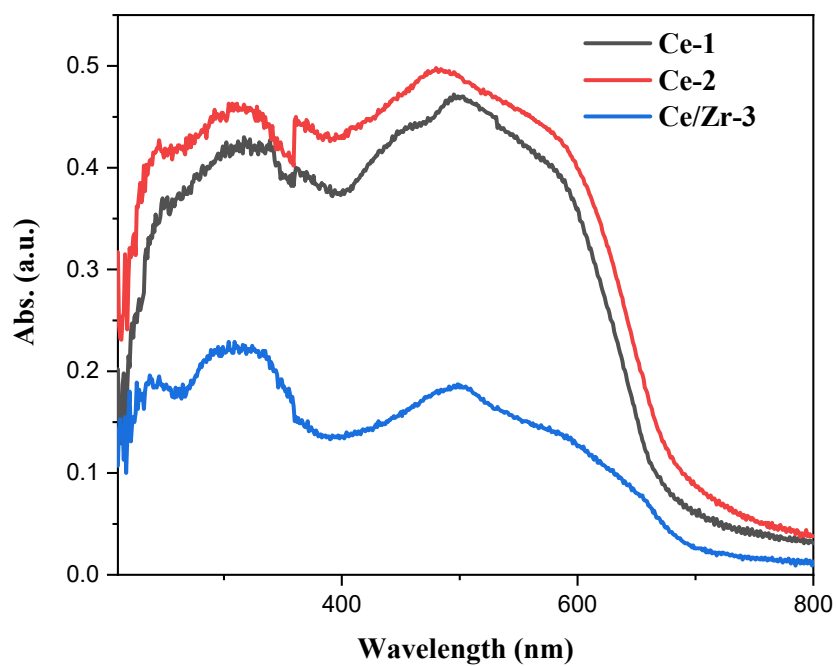


Figure S8. UV-vis absorption spectra of Ce-1, Ce-2 and Ce/Zr-3.

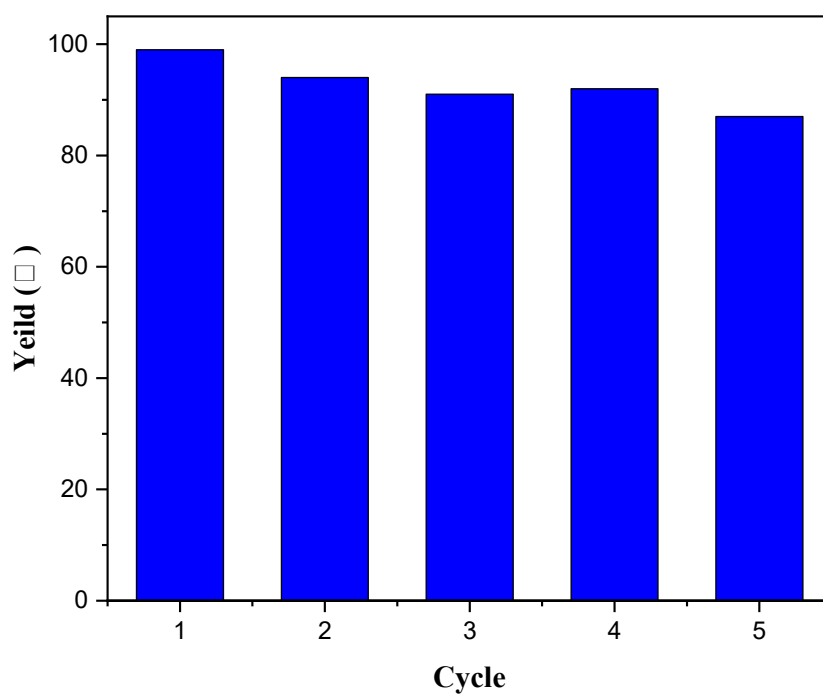


Figure S9. Photocatalytic activity of Ce/Zr-3 on oxidation of methylphenyl sulfide over five cycles.

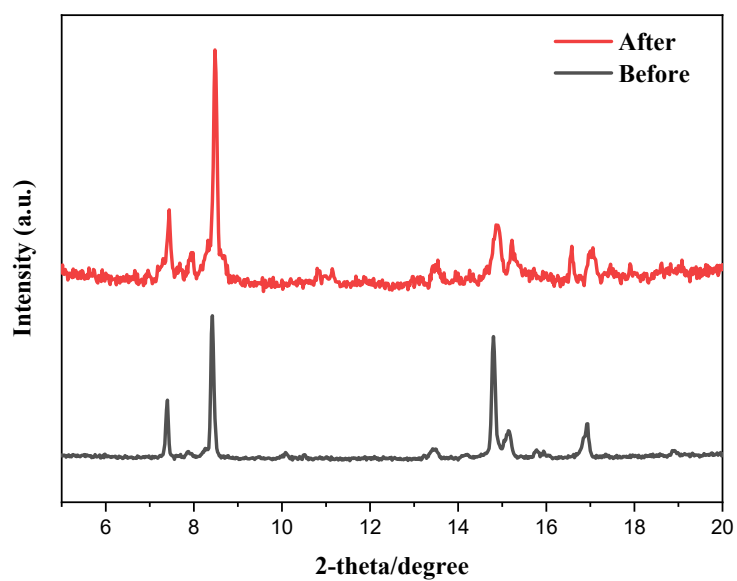


Figure S10. PXRD patterns of as-synthesized Ce/Zr-3 and after recycled reactions.

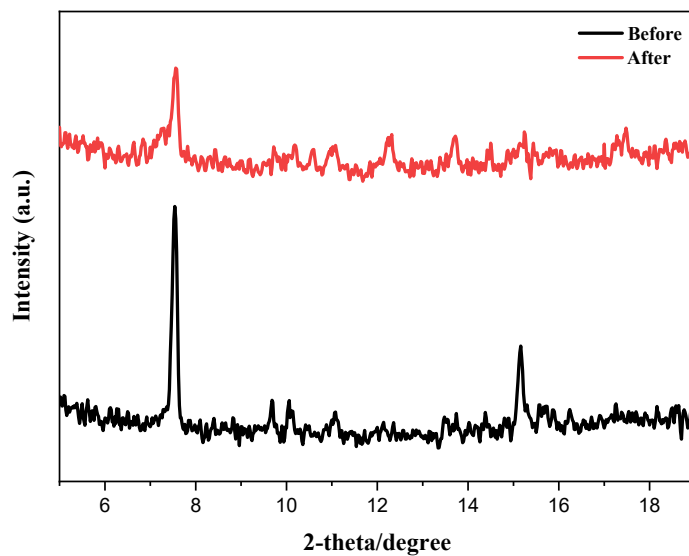


Figure S11. PXRD patterns of as-synthesized Ce-2 and after recycled reactions.

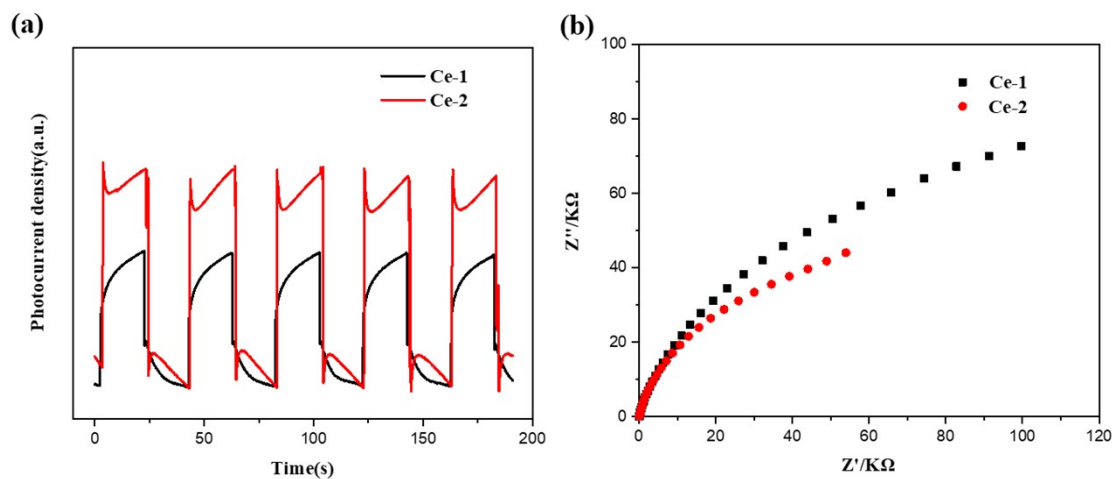
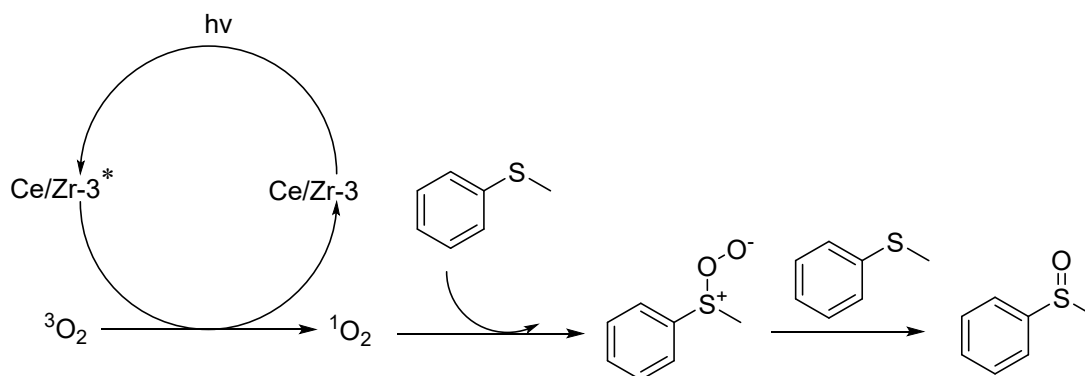
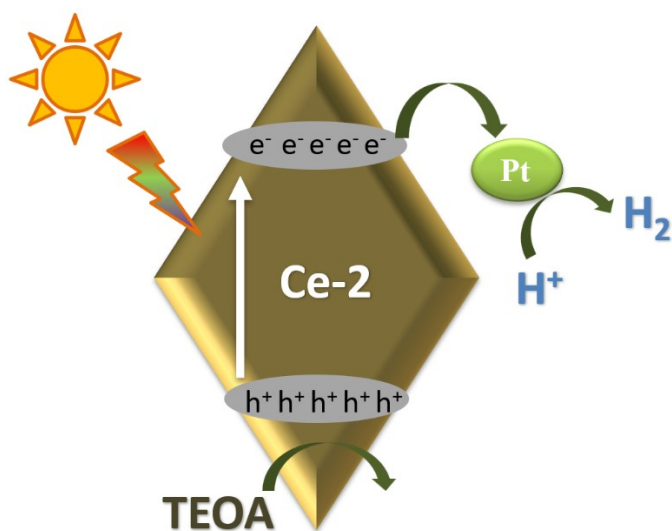


Figure S12. (a) Photocurrent tests and (b) EIS plots of Ce-1 and Ce-2.



Scheme S1. Proposed reaction mechanism for photocatalytic sulfide oxidation.



Scheme S2. Proposed reaction mechanism for photocatalytic hydrogen production with Pt as cocatalyst.

Table S1 Crystal data and structure refinement for **Ce-1**

Empirical formula	C ₄₄ H ₂₈ CeN ₁₀ O ₁₆ Ru
Formula weight	1193.95
Temperature/K	296(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.978(2)
b/Å	14.050(3)
c/Å	16.307(3)
α /°	107.623(6)
β /°	105.164(6)
γ /°	95.164(6)
Volume/Å ³	2688.6(8)
Z	2
ρ_{calc} g/cm ³	1.475
μ /mm ⁻¹	1.189
F(000)	1184.0
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	3.602 to 60.314
Index ranges	-18 \leq h \leq 18, -19 \leq k \leq 19, -22 \leq l \leq 22
Reflections collected	36544
Independent reflections	15335 [R_{int} = 0.0629, R_{sigma} = 0.1021]

Data/restraints/parameters	15335/38/637
Goodness-of-fit on F ²	1.068
Final R indexes [I>=2σ (I)]	R ₁ = 0.0712, wR ₂ = 0.2057
Final R indexes [all data]	R ₁ = 0.1117, wR ₂ = 0.2311
Largest diff. peak/hole / e Å ⁻³	4.57/-4.21
$^aR_1 = \sum F_o - F_c /\sum F_o $; w R ₂ = { $\sum[w (F_o^2-F_c^2)^2]/\sum[w (F_o^2)^2]$ } ^{1/2}	

Table S2 Crystal data and structure refinement for Ce-2

Empirical formula	C ₄₄ H ₂₈ CeN ₉ O ₁₄ Ru
Formula weight	1147.94
Temperature/K	296(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.966(3)
b/Å	14.216(3)
c/Å	16.083(3)
α/°	106.92(3)
β/°	105.88(2)
γ/°	94.314(19)
Volume/Å ³	2688.9(10)
Z	2
ρ _{calc} g/cm ³	1.418
μ/mm ⁻¹	1.182
F(000)	1138.0
Radiation	Mo Kα (λ = 0.71073)
2θrange for data collection/°	2.784 to 50.052
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19
Reflections collected	25432
Independent reflections	9485 [R _{int} = 0.1723, R _{sigma} = 0.1511]
Data/restraints/parameters	9485/42/616
Goodness-of-fit on F ²	1.024
Final R indexes [I>=2σ (I)]	R ₁ = 0.0738, wR ₂ = 0.1691
Final R indexes [all data]	R ₁ = 0.1179, wR ₂ = 0.1890
Largest diff. peak/hole / e Å ⁻³	3.13/-2.00
$^aR_1 = \sum F_o - F_c /\sum F_o $; w R ₂ = { $\sum[w (F_o^2-F_c^2)^2]/\sum[w (F_o^2)^2]$ } ^{1/2}	

Table S3 Control reactions of the photocatalytic H₂ production reaction for the reaction time of 6 h.

Entry	Catalyst	Cocatalyst	Sacrificial reagent	Light	H ₂ production rate
1	Ce-1	Yes	TEOA	Xe lamp	2.6 $\mu\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$
2	Ce-2	Yes	TEOA	Xe lamp	108.5 $\mu\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$
3	Ce-2	Yes	None	Xe lamp	n.d.
4	Ce-2	Yes	TEOA	None	n.d.
5	Ru(cptpy)₂	Yes	TEOA	Xe lamp	n.d.

Supporting References

1. E. C. Constable, E. L. Dunphy, C. E. Housecroft, M. Neuburger, S. Schaffner, F. Schapera and S. R. Batten, *Dalton trans.*, 2007, 38,4323–32.
2. M. Elcheikh Mahmoud, H. Audi, A. Assoud, T. H. Ghaddar and M. Hmadeh, *J. Am. Chem. Soc.*, 2019, **141**, 7115-7121.