

Supplementary Information for

**Visible-light induced photochemical oxygen evolution from water by 3,
4, 9, 10-perylenetetracarboxylic dianhydride nanorod as n-type organic
semiconductor**

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1. Experimental section

1.1 Chemicals

3, 4, 9, 10-perylenetetracarboxylic dianhydride (PTCDA), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{OH})_2$, CoO , Co_3O_4 , AgNO_3 and La_2O_3 were purchased from Alfa Aesar. $\text{Co}(\text{dmgH})_2\text{pyCl}$ (dmgH = dimethylglyoximate, py = pyridine) was purchased from Sigma-Aldrich. All chemicals are of analytical grade without further purification unless otherwise noted. The ultrapure water with 18.2 M Ω cm (Mettler Toledo, FE20, China) was used thorough the experiment.

1.2 Deposition of CoO_x

Typically, 0.5 g PTCDA powder was impregnated into 20 mL water containing a calculated amount of cobalt nitrate and the resulting solution was kept in ultrasonic bath for 5 minutes. After removing water, the as-impregnated powder was calcined in air at 573 K for 1 h. The cobalt oxide cocatalyst was denoted as CoO_x .

1.3 Characterizations

UV/Vis diffuse reflectance spectra were recorded with a Cary 5000 UV-visible-NIR spectrophotometer employed with a lab-sphere diffuse reflectance accessory in the range 200-900 nm. Emissions spectra and time-resolved emission decay were measured by time-correlated-single photon counting (Edinburgh Instruments, FLS-920). In the nanosecond transient absorption spectroscopy experiments, excitation was provided by using an OPO laser at 410 nm. The prober was a xenon lamp on the Edinburgh LP-920 apparatus from analytical instruments. All optical measurements were performed at room temperature under ambient conditions. HRTEM was performed by JEM 2100F (operated at an accelerating voltage of 200 kV). The XPS measurements were performed on an ESCALAB 250 spectrophotometer with Al-K α radiation. The binding energy scale was calibrated using the C 1s peak at 284.6 eV. Gas chromatography (GC) was performed with TIAN MEI 7890 II gas chromatograph using a 5 Å molecular sieve column and a thermal conductivity detector. Electrochemistry measurement was carried out in a three-electrode setup with the working electrode of the sample film electrode, counter electrode of platinum disk, and reference electrode of Ag/AgCl (3.0 M KCl) with electrolyte (0.1 M Na_2SO_4 , pH = 6.8). A Zennium electrochemical workstation (Germany, Zahner Company) was used. The oxygen evolution was analyzed by a Clark-type oxygen electrode (Hansatech Instruments, DW1/AD unit with an S1 electrode). For AQE measurement, a 450 nm blue fiber

coupled semiconductor laser (Changchun New Industries Optoelectronics Technology Co., Ltd., CNI model with PSU-H-LED) and LED light sources with 410 nm, 450 nm, 532 nm and 630 nm were used. The power of laser and LED light sources were measured using a power meter. X-Ray absorption spectroscopic (XAS) data were collected at Beam line 1W1B of the Beijing Synchrotron Radiation Facility (BSRF). The storage ring of BSRF was operated at 2.5 GeV under top-up mode with a constant beam current of 250 mA. pH value was measured with a Model pH-3C meter (Mettler Toledo FE20).

1.4 Photocatalytic reactions for water oxidation

The oxygen evolution was analyzed by a Clark-type oxygen electrode. A 410 nm LED was used as the illumination light source. The reaction vessel was cooled with flowing water adjusted to room temperature. The signal was calibrated using air saturated aqueous solutions ($[O_2] = 276.3 \mu\text{M}$) and fresh prepared $\text{Na}_2\text{S}_2\text{O}_4$ solution ($[O_2] \approx 0$). A 2 mL aqueous solution containing 0.1 mg photocatalyst was adopted, and 3.5 mg AgNO_3 was used as the sacrificial reagent for photocatalytic water oxidation. 4 mg La_2O_3 was added to maintain the pH value of the reaction solution. Before each measurement, the mixture was also purged with Ar gas to provide an oxygen-free solution. In order to confirm the oxygen generation coming from light driven water oxidation, the illumination starts after 2 minutes of flat zero $[O_2]$ signal in dark.

For GC measurement, a 50 mL aqueous solution containing 5 mg photocatalyst, 85 mg AgNO_3 , and 100 mg La_2O_3 . Prior to irradiation, the mixture was evacuated to ensure air completely removed, and then irradiated from the top side with a 300 W xenon lamp using an optical filter ($\lambda \geq 400 \text{ nm}$) to cut off the light in the ultraviolet region. The evolved gases were analyzed by GC.

1.5 The apparent quantum efficiency (AQE) measurement

The oxygen evolution was analyzed by a Clark-type oxygen electrode. A 450 nm blue fiber coupled semiconductor laser was used with illuminance area 1 cm^2 . The maximum reaction rate was determined at the steepest slope of the oxygen evolution curve. And the AQE was calculated using the following equation:

$$AQE = \frac{4 \times \text{the number of evolved } O_2 \text{ molecules}}{\text{the number of incident photons}} \times 100\%$$

1.6 Calculation of average edge energy of Co XANES spectra

We define the average edge energy of Co XANES spectra by an integral method proposed

earlier¹⁻³ according to the following equation:

$$E^{edge} = \frac{1}{\mu_2 - \mu_1} \int_{\mu_1}^{\mu_2} E(\mu) d\mu$$

with μ being the X-ray absorption coefficient and E^{edge} being the average edge energy of reference samples and PTCD/CoO_x composite. Numerical values for an edge-position energy were obtained by calculation of the integral of the edge region calculated between $\mu = 0.03$ and 0.9. For the conversion of the edge position to the average oxidation state of cobalt, Co^{II}O, Co^{II}(OH)₂, Co^{II,III}₃O₄ and Co^{III}(dmgH)₂pyCl with known oxidation states were used to obtain the linear relationship between the average position of cobalt K-edge energy and oxidation states.

The relative populations of Co^{II} and Co^{III} were calculated using:

$$\begin{cases} [Co^{II}] + [Co^{III}] = 1 \\ 2[Co^{II}] + 3[Co^{III}] = z \end{cases}$$

where z is the average oxidation state from XAS analysis.

2. Results of characterizations

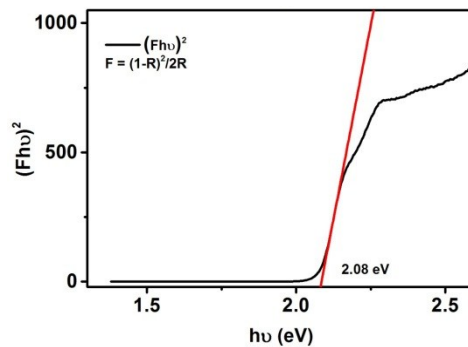


Fig. S1 Kubelka-Munk plot of PTCD used to estimate the band gap.

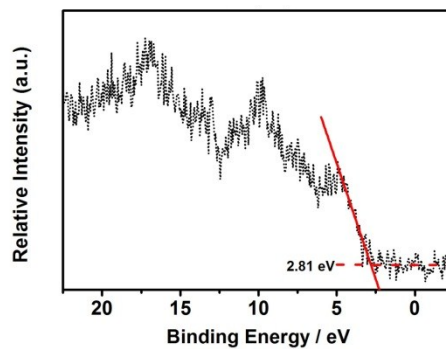


Fig. S2 VB XPS spectra of PTCD.

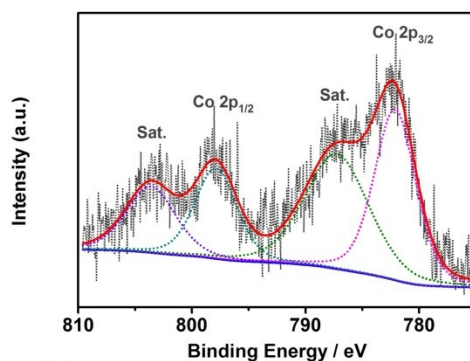


Fig. S3 XPS characterization of PTCDA-CoO_x demonstrated in the energy regions of Co 2p. The binding energy was corrected by C 1s peak (284.6 eV).

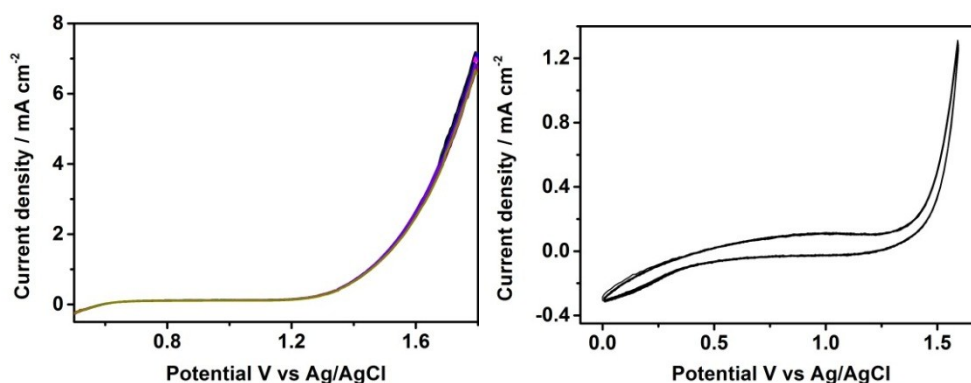


Fig. S4 Polarization (left, 10 circles) and cyclic voltammetry (right, 20 circles) curves for OER on modified FTO electrodes comprising PTCDA-CoO_x composite, using Pt disk counter electrode, Ag/AgCl reference, 50 mV/s scan rate.

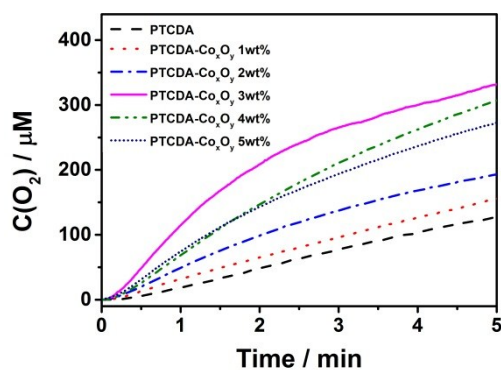


Fig. S5 Kinetics of photochemical oxygen evolution measured by Clark electrode, PTCDA-CoO_x 0.1 mg, La₂O₃ 4 mg, AgNO₃ 3.5 mg, DI H₂O 2 mL, illumination with 410 nm LED.

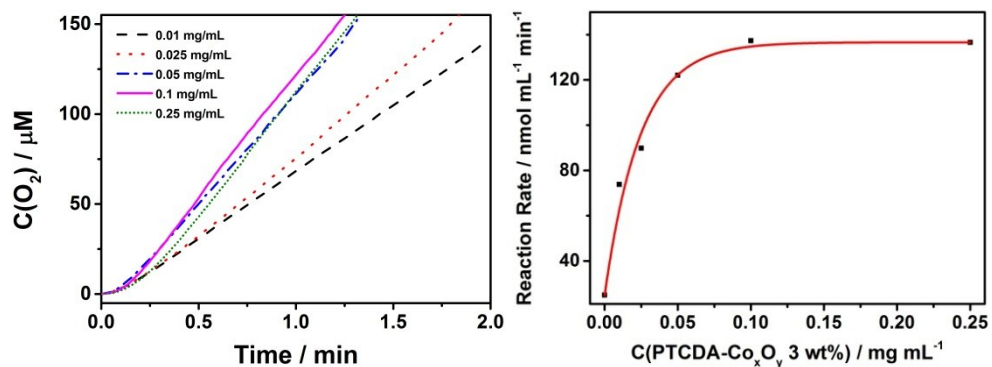


Fig. S6 (a) Kinetics of photochemical oxygen evolution measured by clark electrode, La_2O_3 4 mg, $AgNO_3$ 3.5 mg, DI H_2O 2 mL, illumination with 410 nm LED. (b) Rate of oxygen evolution with different contents of the PTCDA- CoO_x 3 wt%.

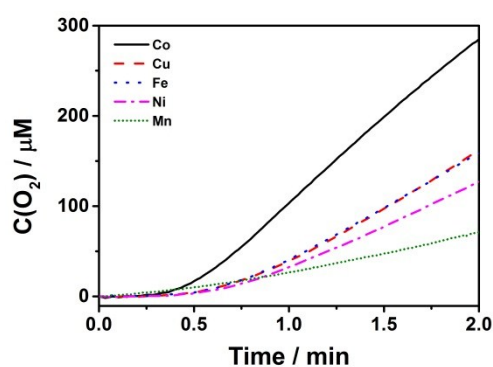


Fig. S7 Kinetics of photochemical oxygen evolution measured by clark electrode, PTCDA- MO_x 0.1 mg, La_2O_3 4 mg, $AgNO_3$ 3.5 mg, DI H_2O 2 mL, illumination with 410 nm LED.

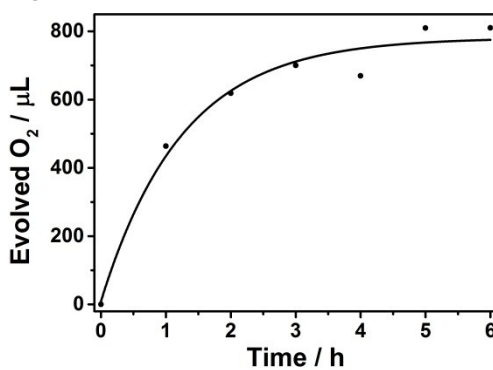


Fig. S8 Kinetics of photochemical oxygen evolution measured by GC, PTCDA- CoO_x 3 wt% 5 mg, La_2O_3 100 mg, $AgNO_3$ 85 mg, DI H_2O 50 mL, illumination with Xe lamp.

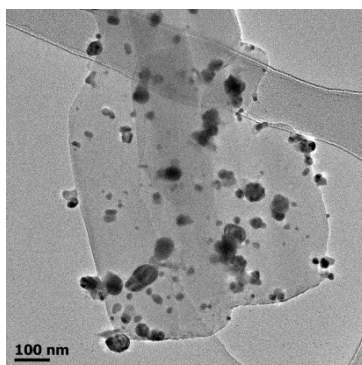


Fig. S9 TEM images of PTCDA-CoO_x 3 wt% after photoillumination.

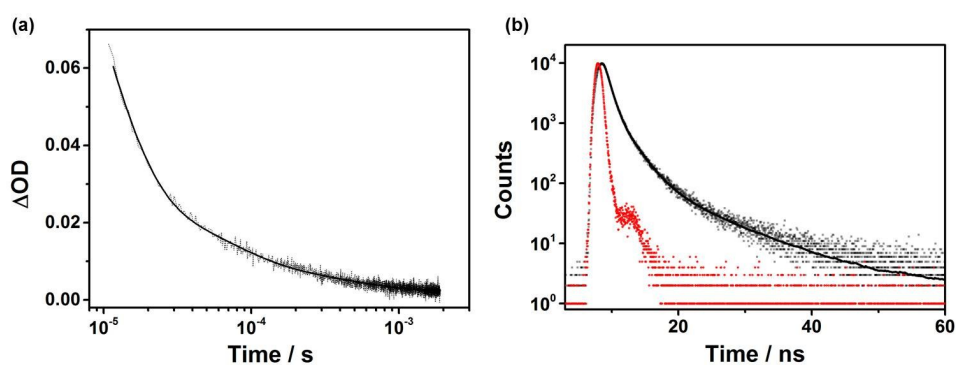


Fig. S10 (a) Transient absorption decay signal for PTCDA powder upon 410 nm excitation probed at 610 nm. (b) Time-resolved emission decay of PTCDA powder at 678 nm. Excitation wavelength: 485 nm.

Reference:

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2. M. Risch, F. Ringleb, M. Kohlhoff, P. Bogdanoff, P. Chernev, I. Zaharieva and H. Dau, *Energy Environ. Sci.*, 2015, **8**, 661-674.
3. J. Huang, J. Chen, T. Yao, J. He, S. Jiang, Z. Sun, Q. Liu, W. Cheng, F. Hu, Y. Jiang, Z. Pan and S. Wei, *Angew. Chem. Int. Ed.*, 2015, **54**, 8722-8727.