

## Electronic Supplementary Information

### Two-dimensional Metal-Organic Framework Accelerating Visible-Light-driven Hydrogen Production

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## I. Experimental Section

### 1.1 Materials synthetic procedures

All chemicals were purchased from Sigma-Aldrich without further purification.

**Preparation of Co-MOF:** Co-MOF was prepared according to the reported method.<sup>1</sup> Briefly,  $\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.119 g, 0.5 mmol), 1,10-phenanthroline (0.091 g, 0.5 mmol), 4,4'-oxybis(benzoic acid) (0.129 g, 0.5 mmol) and triethylamine (0.101 g, 1 mmol), were added into 10 mL  $\text{H}_2\text{O}$ . The suspension was then transferred into a Teflon-lined autoclave and heated to 160 °C and kept for 6 days and then cooled to room temperature at a rate of 5 K h<sup>-1</sup>. Red crystals were obtained after being washed with water and dried in air.

**Preparation of ultrathin Co-MOF layer (CML):** 100 mg of the as-prepared Co-MOF was added into 100 mL ethanol and the suspension was then probe-ultrasonicated for 10 hours followed by high-speed centrifugation. Then the as-exfoliated 2D CML in the supernatant was preserved for further use.

**Preparation of  $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{S}$  (ZCS):** ZCS was prepared by a precipitation-hydrothermal approach. Briefly, 7.15 g  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and 2.14 g  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 217 mL deionized water and stirred at room temperature for 30 min. After that, 50 mL 0.9 M  $\text{Na}_2\text{S}$  aqueous solution was added dropwise into the above solution followed by stirring for about 2 hours at room temperature. Then the mixture was transferred into a 500 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 12 h. The final products were washed with deionized water and ethanol, respectively, for two times to remove any residuals and then dried at 60 °C under vacuum.

**Preparation of ZCS/CML hybrids:** The ZCS/CML hybrids were fabricated by a self-assembly method using the as-synthesized ZCS and 2D CML ethanol solution. In a typical procedure, 50 mg ZCS nanoparticles were mixed with 2.5, 10.0, 15.0 and 25.0 mL of 2D CML ethanol solution, respectively. Then the suspension was mechanically ground for 5 min. After the ethanol naturally evaporated, the solid left was again ground into powders as the final products. The resulting samples were labelled as ZCS/CML2.5, ZCS/CML10, ZCS/CML15 and ZCS/CML25, respectively.

### 1.2 Physicochemical characterizations

PXRD was performed on Rigaku MiniFlex 600 X-Ray Diffractometer with  $\text{Cu K}\alpha$  to characterize the crystal structure. The morphologies and structures of as-prepared samples were observed by TEM (JEOL ARM-200CF with double Cs correctors, 200 kV). UV-Vis diffuse reflectance spectra were collected for the dry-pressed disk samples with an UV-Vis spectrophotometer (UV2600, Shimadzu, Japan) using  $\text{BaSO}_4$  as the reflectance standard. The PL spectra were recorded on a RF-5301PC

spectrofluorophotometer (Shimadzu, Japan) at room temperature. Time-resolved PL decay curves were obtained on a FLS1000 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK). XPS measurement was conducted on a VG ESCALAB 210 XPS spectrometer with Mg K $\alpha$  source. All the binding energies were referenced to the C 1s peak at 284.8 eV. XANES spectra of the samples were collected at the soft X-ray absorption beamline of the Australian Synchrotron (AS). Elemental contents were determined by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer) on Prodigy 7. The steady-state SPV spectra were acquired on a home-built apparatus.

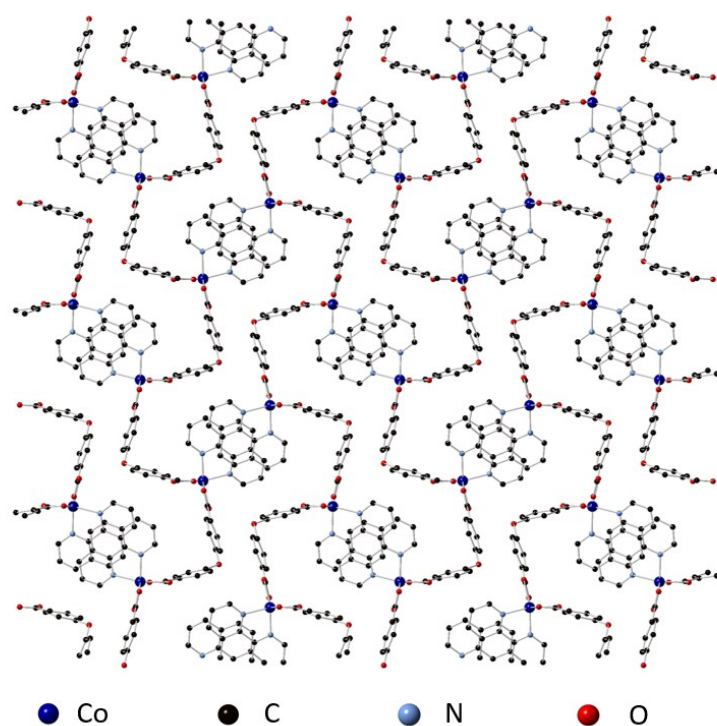
### **1.3 Photocatalytic H<sub>2</sub> production measurement**

The experimental measurements of photocatalytic H<sub>2</sub> production were carried out in a 100 ml Pyrex flask at room temperature and atmospheric pressure. A 300 W Xenon arc lamp with a UV-cutoff filter ( $\lambda > 420$  nm) was utilized as a visible-light source to trigger the photocatalytic reaction. Briefly, 20 mg of the as-prepared photocatalyst was added into 80 ml of lactic acid (88 vol%) solution. Before irradiation, the suspension was purged with Argon for 0.5 h to remove any dissolved air and keep the reaction system under anaerobic conditions. Next, 0.2 ml gas was intermittently sampled through the septum, and H<sub>2</sub> content was analyzed by Gas chromatography (Clarus 480, PerkinElmer, USA, TCD, Ar as a carrier gas and 5 Å molecular sieve column). Before the experiment, all glassware was rinsed carefully with de-ionized water.

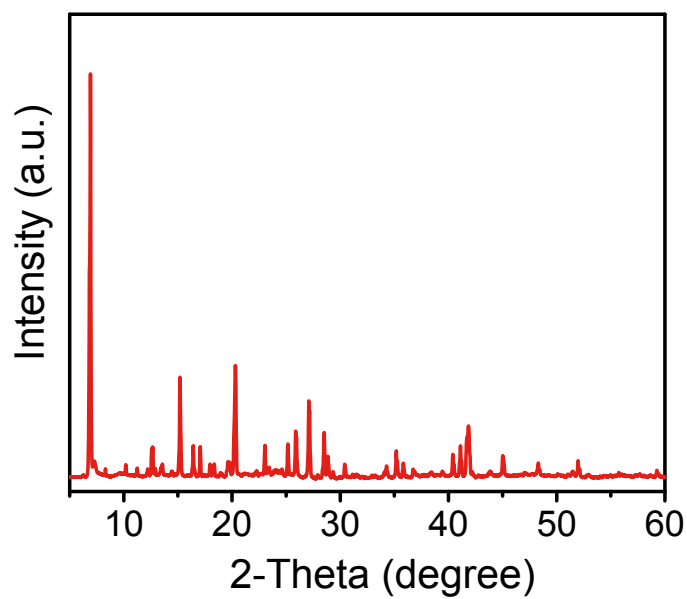
### **1.4 Electrochemical and photoelectrochemical measurements**

EIS measurements were performed on an electrochemical analyzer (CHI650D instruments) in a standard three-electrode system utilizing the synthesized samples as the working electrodes, Ag/AgCl (saturated KCl) as a reference electrode, and Pt wire as the counter electrode. The EIS were recorded over a range from 1 to  $2 \times 10^5$  Hz with an AC amplitude of 0.02 V. 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was utilized as the electrolyte. Transient photocurrent was measured in the same three-electrode system. A 300 W Xenon light with a UV-cutoff filter ( $\lambda > 420$  nm) was applied as the light source. 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. The working electrodes were synthesized as follows: 0.01 g sample and 0.03 g polyethylene glycol (PEG; molecular weight: 20,000) were ground with 2.0 ml of ethanol to make a slurry. Then the slurry was coated onto a 1.2 cm \* 0.8 cm FTO glass electrode by the doctor blade approach. The obtained electrode was dried in an oven and heated at 623 K for 0.5 h under flowing N<sub>2</sub>.

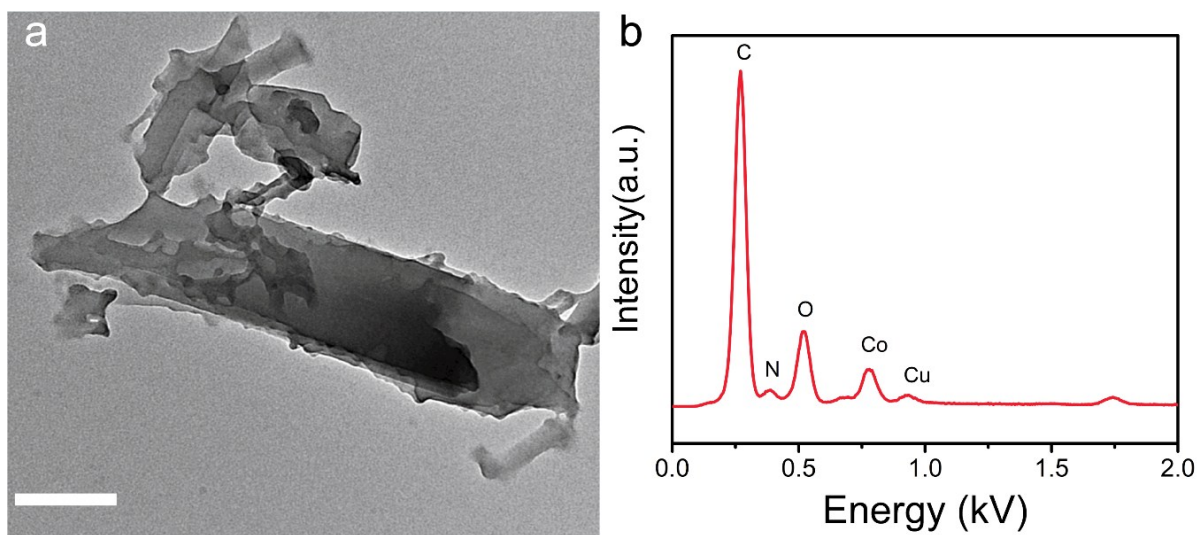
## II. Supplementary Figures



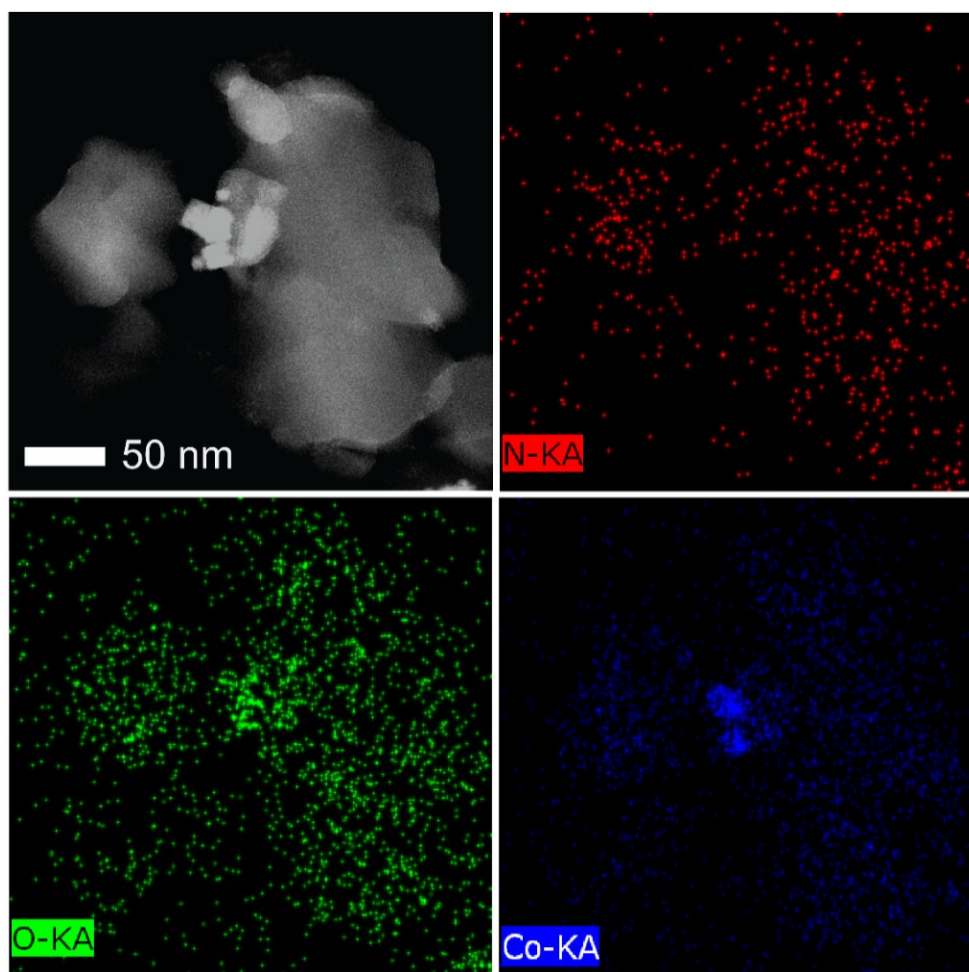
**Figure S1.** Crystal Structure of Co-MOF. (Note: Hydrogen atoms bonded to C, N and O are not shown.)



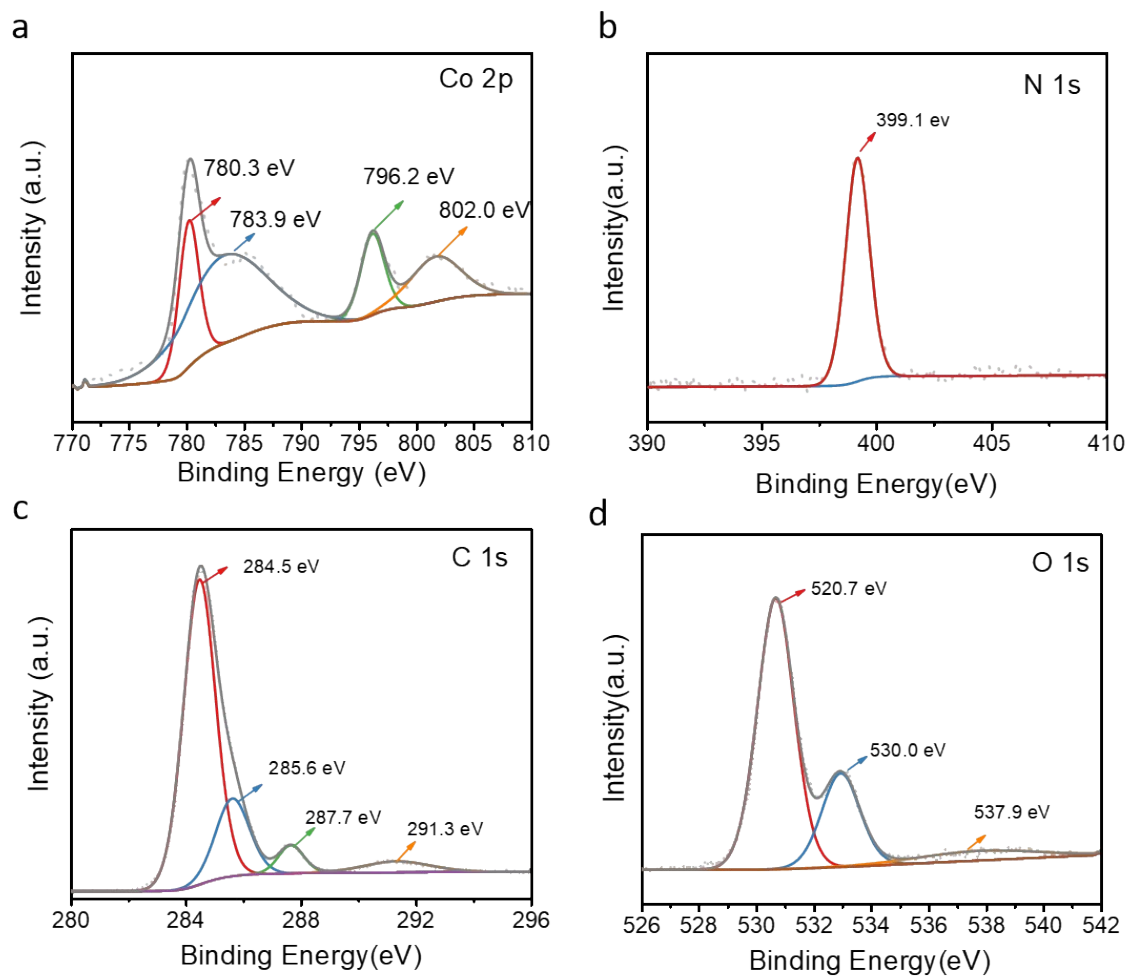
**Figure S2.** PXRD pattern of Co-MOF.



**Figure S3.** (a) TEM image and (b) EDS spectrum of 2D CML (scale bar in a: 200 nm).



**Figure S4.** HAADF-STEM and the corresponding element mapping images of CML.



**Figure S5.** High-resolution XPS spectra of (a) Co 2p, (b) N 1s, (c) C 1s and (d) O 1s in CML.

### III. Supplementary Tables

**Table S1.** A comparison of the photocatalytic H<sub>2</sub>-production activities of the representative noble-metal-free Zn<sub>x</sub>Cd<sub>1-x</sub>S or CdS based systems

<i>Photocatalyst</i>	<i>Co-catalyst</i>	<i>Enhancement factor</i>	<i>H<sub>2</sub> production rate (μmol h<sup>-1</sup> g<sup>-1</sup>)</i>	<i>Light/dose</i>	<i>Ref.</i>
Zn <sub>0.8</sub> Cd <sub>0.2</sub> S/CML15	CML	4.92	18100	λ > 420 nm/ 20 mg	This work
Zn <sub>1-x</sub> Cd <sub>x</sub> S/10 wt.% α-Fe <sub>2</sub> O <sub>3</sub>	α-Fe <sub>2</sub> O <sub>3</sub>	24	540	λ > 420 nm/ 100 mg	[2]
P-ZnCdS/CdS-VS <sub>2</sub>	VS <sub>2</sub>	7.6	192	λ > 400 nm/ 5 mg	[3]
0.5 wt% Fe <sub>0.3</sub> Pt <sub>0.7</sub> -ZnCdS	Fe <sub>0.3</sub> Pt <sub>0.7</sub>	3.06	2230	λ > 400 nm/ 100 mg	[4]
0.5 wt% Pt-ZnCdS	Pt	2.20	1630	λ > 420 nm/ 100 mg	[4]
CdS/CNT	CNT	2.23	1770	λ > 420 nm/ 20 mg	[5]
CdS/Graphene	Graphene	4.87	56000	λ > 420 nm/ 20 mg	[6]
CdS/N-Graphene	N-Graphene	5.25	1050	λ > 420 nm/ 200 mg	[7]
CdS/DWNT/s-MoS <sub>2</sub>	DWNT/s-MoS <sub>2</sub>	N/A	5730	λ > 420 nm/ 20 mg	[8]

**Table S2.** Fitted results of resistance obtained from electrochemical impedance spectra

<i>Resistance</i>	<i>ZCS</i>	<i>ZCS/CML15</i>
R <sub>s</sub> (ohm)	47.15	43.10
R <sub>t</sub> (ohm)	3818	3186

## IV. Supplementary references

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