

## Supporting Information

### Controllable synthesis of hollow COFs for boosting Photocatalytic Hydrogen Generation

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## 1. Experimental details

### Materials

1,3,5-triformylbenzene (TFB, purchased from Energy Chemical). Pentyl alcohol and glycerol (purchased from Meryer). All reagents and solvents were obtained from Aladdin and used without further purification, including sodium chloride and 1,4-phenylenediamine (PA), et al.

### 2. Sample preparation

**Synthesis of sodium chloride template.** The fabrication of cubic NaCl was prepared through an anti-solvent method according to the previous work. Typically, 5.6 g of sodium chloride was dissolved into 60 mL of glycerol at 140 °C under stirring for 0.5 h. Then, 400  $\mu$ L of NaCl solution was dropwise added into 20 mL of pentyl alcohol at 0 °C (ice water bath) under vigorously stirring for 1 min. The precipitate was collected after centrifugation and drying at 80 °C for 12 hours, thus resulting in cubic NaCl template.

**Synthesis of hollow COF.** TFB (48.6 mg, 0.3 mmol), Pa (48 mg, 0.45 mmol), a certain amount of sodium chloride template, and the solution of 1:1 mesitylene/dioxane (3 mL) were added into a 50 mL Pyrex tube and ultrasonicated for 15 min to get a homogeneous mixture. After stirring 4 h, 0.25 mL of 6 M acetic acid was added, then stirring 0.5 h and the tube was degassed by three freeze-pump-thaw cycles and heated at 120 °C for 72 h. The resultant yellow precipitate was filtrated and washed with N, N-dimethylformamide (DMF) and acetone, respectively. After a solvent exchange process by using anhydrous acetone and NaCl removal procedure by using water, the hollow COF samples were obtained after drying at 80 °C under vacuum for 12 h. The usage of cubic NaCl was varied from 400 to 800 mg, and the corresponding samples were denoted as COF-LZU1-400, COF-LZU1-600, and COF-LZU1-800, respectively. For comparison, COF-LZU1 was also fabricated via a similar procedure with COF-LZU1-X except for the using of NaCl template.

### 3. Characterization

The morphology of prepared samples was investigated by using field emission scanning

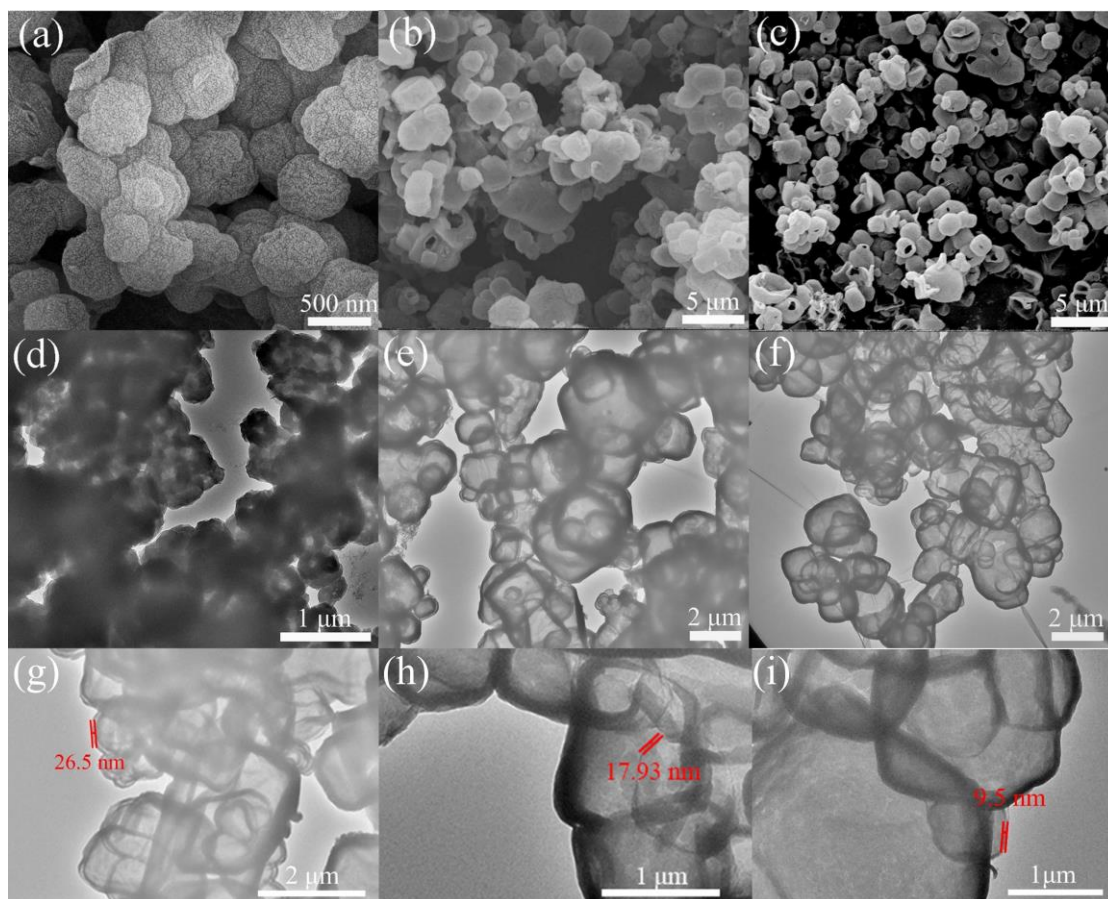
electron microscopy (FE-SEM, Nova Nano-SEM 200, USA) and transmission electron microscopy (TEM, JEM-2100F, Japan). The crystal phases of samples were examined by X-ray diffraction (XRD, D8 Advance, Germany). Fourier transform infrared spectroscopy (FT-IR) was conducted on a Nicolet 50 spectrometer (Thermo Scientific, USA). The UV–visible diffuse reflectance spectroscopy (UV–vis DRS, Shimadzu 2450, Japan) were obtained by using BaSO<sub>4</sub> as a standard. X-ray photoelectron spectroscopy (XPS) was measured by using Al K $\alpha$  radiation as an excitation. (XPS, ESCALAB 250Xi, Thermo Scientific). N<sub>2</sub> adsorption-desorption isothermals were recorded on a Micromeritics ASAP2020 HD88 instrument. Photo-luminescence (PL) spectra were obtained on a Hitachi F-7000 instrument with an excitation wavelength of 365 nm. Time-resolved PL (TR-PL) characterization was recorded on an Edinburgh FLS 1000 instrument with excitation wavelength of 380 nm and the obtained curves were fitted by a single exponential. Contact angle was conducted on a KRUSS K100 instrument. Thermogravimetric analysis (TGA) was recorded on a Diamond TG/DTA analyzer (Perk in Elmer) under N<sub>2</sub> atmosphere.

#### **4. Photoelectrochemical measurements**

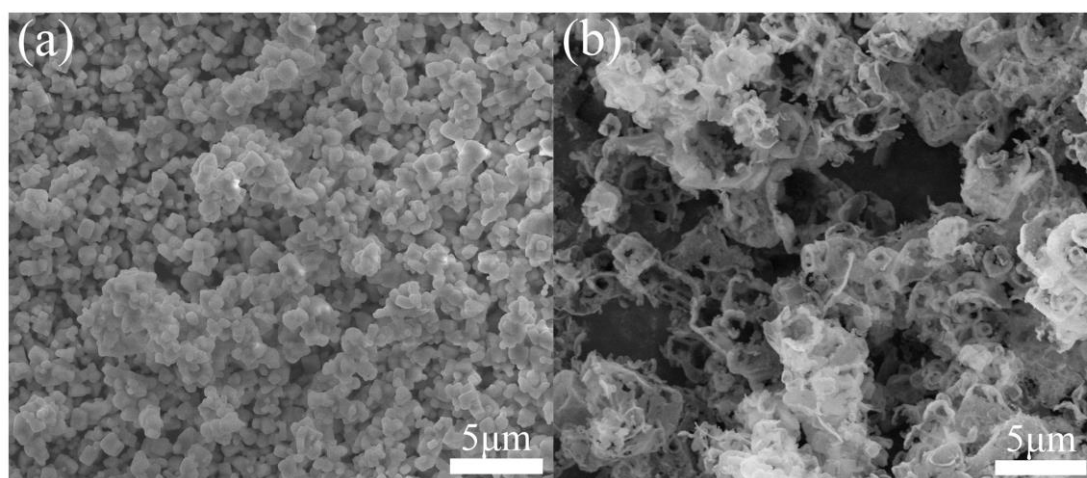
The photoelectrochemical properties were measured by using a three-electrode system. 0.5 M Na<sub>2</sub>SO<sub>4</sub> (pH = 7) was used as the electrolyte. The Ag/AgCl and Pt plate were the reference electrode and counter electrode, respectively. For preparing work electrode, 5 mg of samples was well dispersed into 5 wt% Nafion (40  $\mu$ L) and 1:1 ethanol/glycol (0.5 mL). Then, 80  $\mu$ L of the above mixture was dropwise coated on FTO glass surface, after drying at 60 °C for 12 h, the work electrode was obtained. Electrochemical impedance spectroscopy (EIS) was measured at frequency ranging from 1 to 100 kHz. The photocurrent-time (i-t) curve was performed under chopped light irradiation. Mott-Schottky plots were tested at the alternating current (AC) frequency of 1, 3 and 5 kHz. According to the Nernst equation, the potential with Ag/AgCl ( $V_{Ag/AgCl}$ ) was converted to the potential with the ordinary hydrogen electrode (NHE, pH = 0).  $V = V_{Ag/AgCl} + 0.059 \times pH + 0.197$

#### **5. Photocatalytic test**

The hydrogen production performance of the as-synthesized samples was measured by using an online system (Labsolar-6A, Beijing Perfectlight), and gas chromatography (GC, Agilent 7890A) equipped with thermal conductivity detector (TCD) was used to record the H<sub>2</sub> yield. A 300 W xenon lamp was used as light source with a 420 nm cutoff filter. 10 mg of photocatalysts was dispersed into 100 mL of distilled water containing 0.95 g of ascorbic acid (AA), and 3 wt% Pt was photo-deposited on photocatalyst surface serving as H<sub>2</sub> evolution cocatalyst. The reaction temperature was kept at 6 °C. Before illumination, the system was degassed with a vacuum pump. During the photocatalytic process, the reaction system is kept under vigorous stirring to ensure the homogenous dispersion of photocatalyst. Cyclic measurements were conducted to investigate the stability of the prepared samples. Specifically, after 4 h reaction, the light was turned off, and the system was evacuated. Then, another reaction cycle was conducted.



**Fig. S1** (a–c) SEM images of COF-LZU1, COF-LZU1-400 and COF-LZU1-800; (d–f) TEM images of COF-LZU1, COF-LZU1-400 and COF-LZU1-800, (g–i) TEM images of COF-LZU1-400, COF-LZU1-600 and COF-LZU1-800.



**Fig. S2** SEM images of KCl (a) and COF-LZU1-KCl (b).

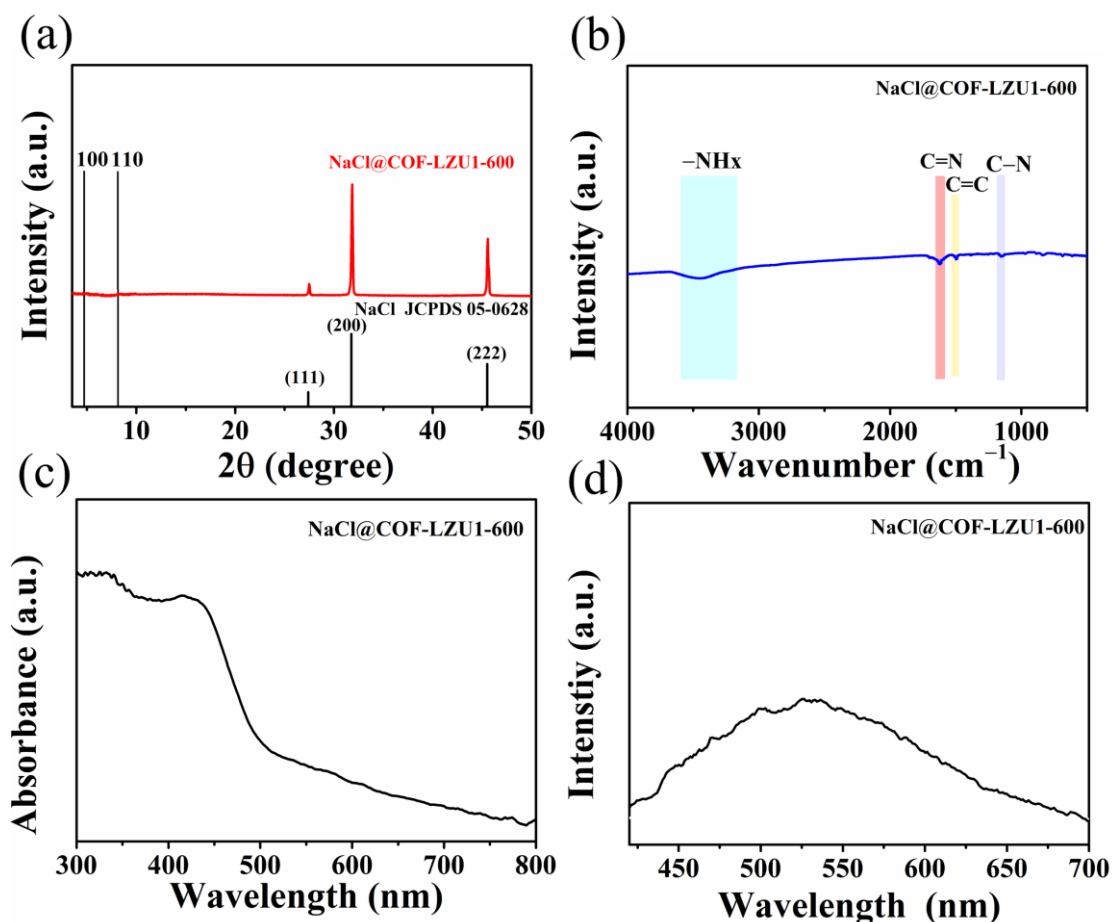


Fig. S3 (a) XRD pattern, (b) FT-IR spectrum, (c) UV-vis DRS and (d) PL of NaCl@COF-LZU1-600.

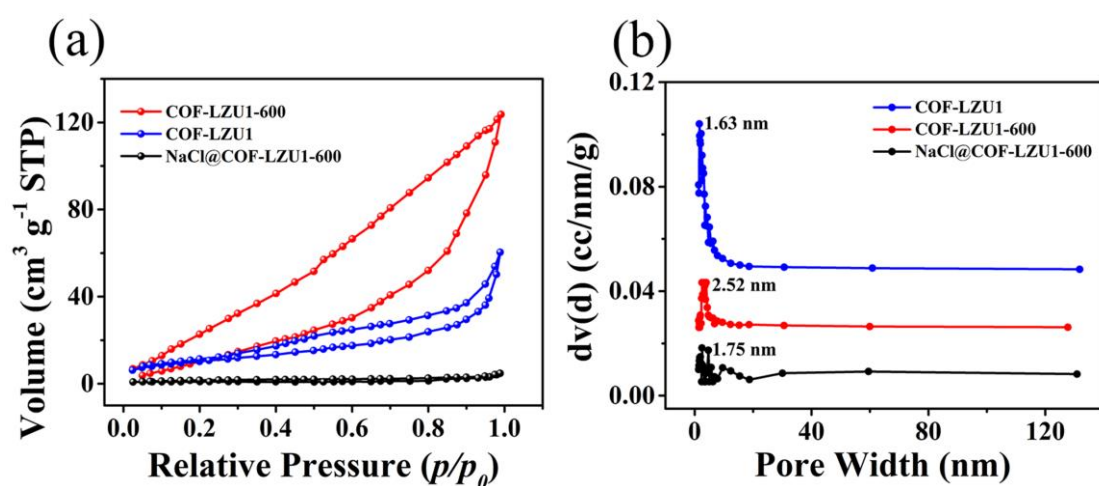
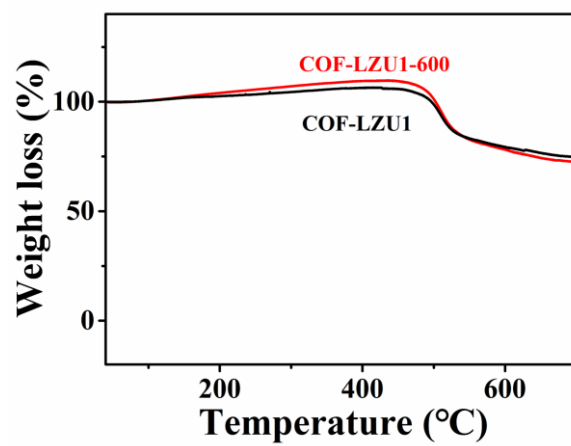
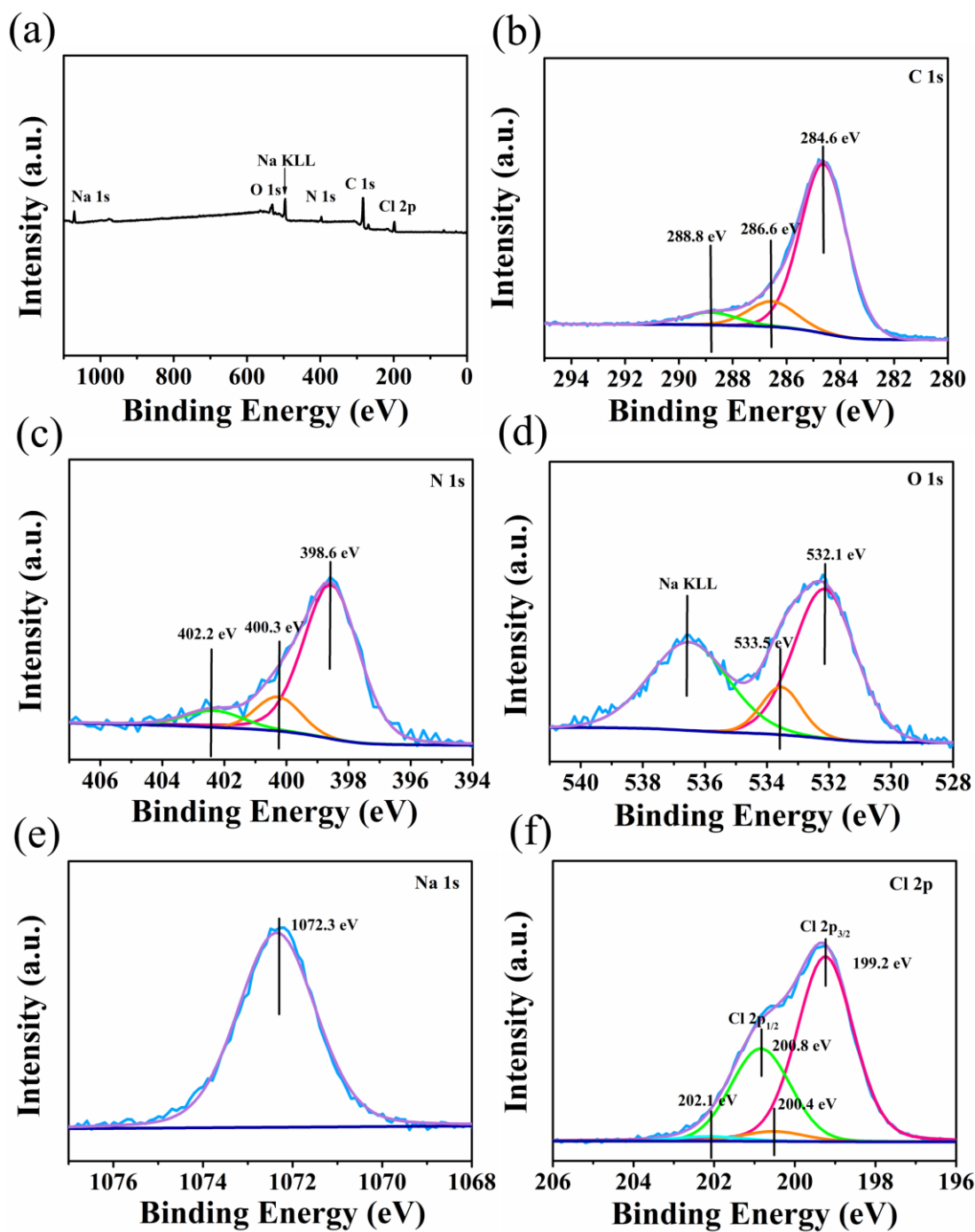


Fig. S4 (a) N<sub>2</sub> adsorption and desorption isotherms and (b) the corresponding pore size distribution for samples.



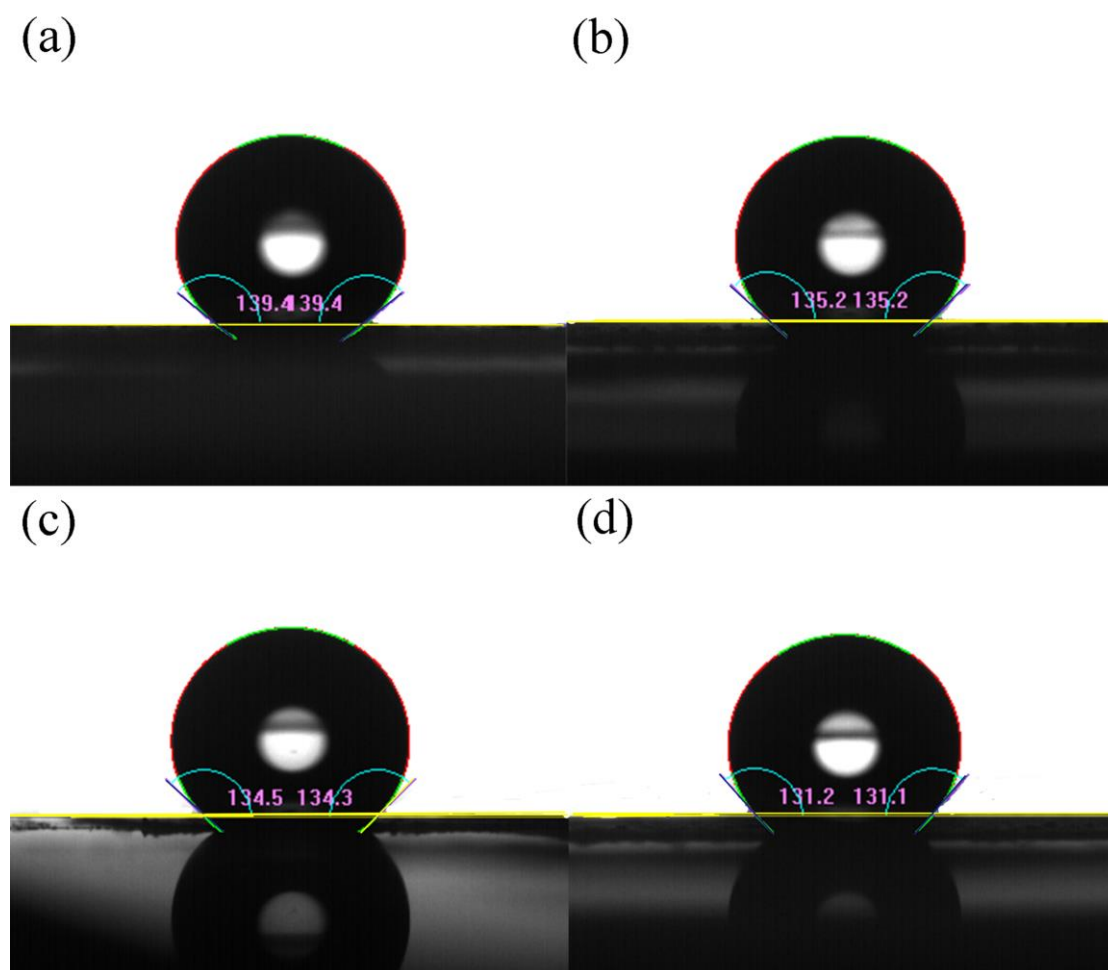
**Fig. S5** TGA thermograms of COF-LZU1 and COF-LZU1-600.



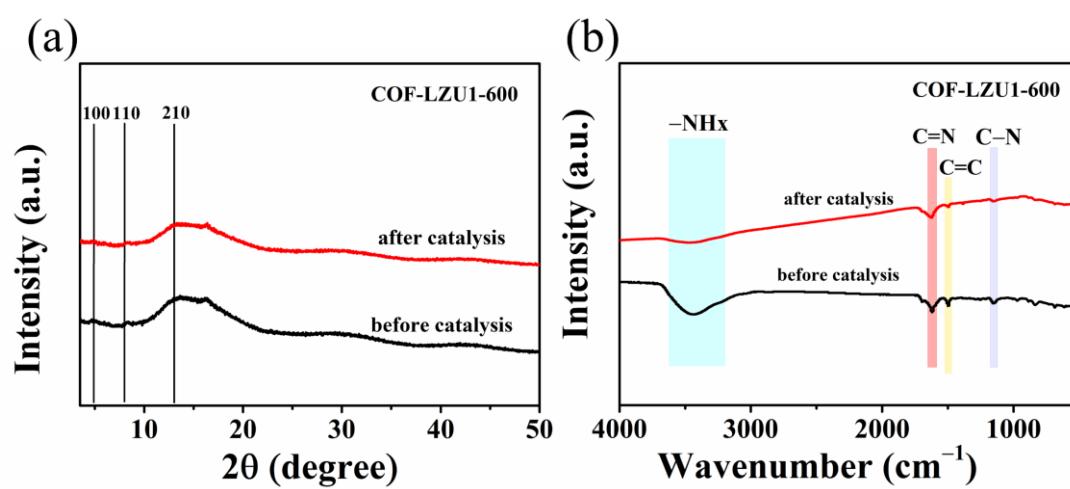
**Fig. S6** (a) The survey spectrum, (b) High-resolution spectra of C 1s, (c) N 1s and (d)

O 1s, (e) Na 1s and (f) Cl 2p of NaCl@COF-LZU1-600.





**Fig. S7** (a–d) Contact angle of COF-LZU1, COF-LZU1-400, COF-LZU1-600 and COF-LZU1-800.



**Fig. S8** (a) XRD patterns and (b) FT-IR spectra of COF-LZU1-600 before and after photocatalytic reaction.

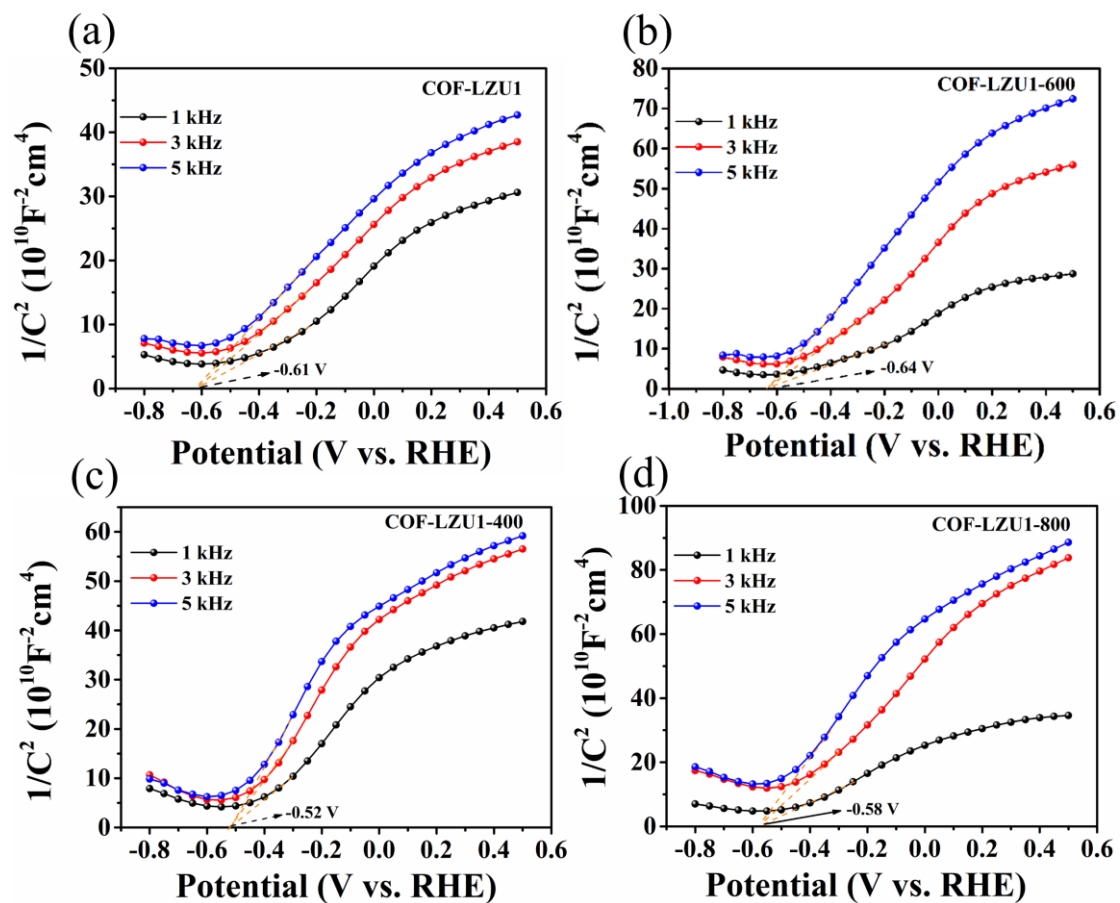


Fig. S9 Mott-Schottky plots of prepared samples.

Table S1 The corresponding structural parameters of different materials.

Samples	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Average pore size (nm)	Pore volume ( $\text{cm}^3/\text{g}$ )
COF-LZU1	220.8	1.63	0.23
COF-LZU1-600	54.9	2.52	0.22
NaCl@COF-LZU1-600	6.9	1.75	0.008

**Table S2** The element contents obtained by XPS analysis.

Samples	Atomic concentration of elements (%)				
	C	N	O	Na	Cl
COF-LZU1	71.65	17.31	11.05	-	-
COF-LZU1-600	60.03	29.33	10.64	-	-
NaCl@COF-LZU1-600	71.72	7.08	11.85	4.41	4.93

**Table S3** Comparison of photocatalytic H<sub>2</sub> reduction efficiency of COF-LZU1 with other COF-based materials.

Photocatalyst	Cocatalyst	Sacrifice reagent	Light source	HER rate $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	Ref.
COF-LZU1-600	3 wt% Pt	AA	> 420 nm	651	This work
COF-LZU1	3 wt% Pt	AA	> 420 nm	28	1
COF-LZU1	4.92 wt% Pd	TEOA	> 420 nm	0	2
LZU1/CdS	No	Na <sub>2</sub> SO <sub>3</sub> /Na <sub>2</sub> S	> 420 nm	8670	3
TFPT-COF	2.2 wt% Pt	Sodium ascorbate	> 420 nm	230	4
COF-LZU1@BiFeO <sub>3</sub>	No	Only water	≥ 420 nm	202.6	5

## References

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