

Supporting Information

A sulfur-containing two-dimensional covalent organic framework with electrocatalytic hydrogen evolution in alkaline medium

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Section S1. Materials and characterization

S1.1 Materials and instruments

All starting materials and solvents, unless otherwise noted, were obtained from J&K scientific LTD. Fourier transform infrared (FT-IR) spectra were acquired on a Thermoscientific Nicolet 4700 Fourier Transform Infrared Spectrometer with KBr pellet. Thermogravimetric analysis (TGA) was recorded on a STA 449 F3 *Jupiter* thermal analyzer with N₂ flow rate of 20 mL min⁻¹ at a heating rate of 5 °C min⁻¹ to 800 °C. PXRD data were collected on a PANalytical B.V. Empyrean powder diffractometer using a Cu K α source ($\lambda = 1.5418 \text{ \AA}$) over the range of $2\theta = 2.0\text{--}40.0^\circ$ with a step size of 0.02° and 2 s per step. The sorption isotherm for N₂ was measured by Micromeritics ASAP 2460 analyzer with ultra-high-purity gas (99.99% purity). To estimate the pore size distributions, nonlocal density functional theory (NLDFT) was applied to analyze the N₂ isotherm on the basis of the model of N₂@77K on carbon with slit pores and the method of non-negative regularization. The SEM images were obtained on JEOL 8100 scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was obtained by Escalab 250XI X-ray electron spectrometer (VG Scientific, America).

S1.2 Electrochemical measurements

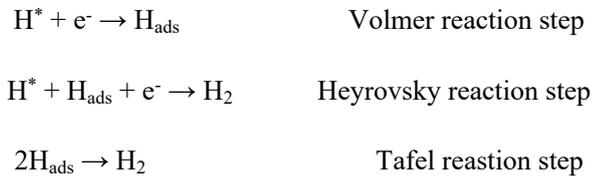
The electrocatalytic properties of the catalysts for hydrogen evolution reaction were evaluated with a three-electrode configuration on a CHI 760E electrochemical workstation (CHI Instruments, Shanghai, China). To prepare the working electrode, 2 mg of the electrocatalyst combined with 300 μL of ethanol and 4 μL of Nafion was treated by ultrasonication for 20 min. Then, the as-prepared suspension (12 μL , corresponding to a mass loading of 1.14 mg cm^{-2}) was slowly deposited on glassy carbon (GC, 3 mm diameter) electrode. After continuous purging with N₂ to remove dissolved gases, 1.0 M KOH solutions was used as alkaline electrolytes. The as-prepared sample was directly used as the working electrode. Hg/HgO and graphite rods were used as reference and counter electrodes in 1.0 M KOH solutions. Potential measurements were all converted to potential values relative to the reversible hydrogen electrode (RHE) based on $E_{(\text{vs. RHE})} = E_{(\text{vs. Hg/HgO})} + 0.0591 \cdot \text{pH} + 0.098$. LSV curves were obtained in a nitrogen-saturated

electrolyte at a sweep rate of 10 mV/s. The ohmic potential drop (iR) losses that arise from the solution resistance were all corrected. The EIS was tested in the constant potential mode in the frequency range 1 Hz to 100 kHz. Cyclic voltammetry (CV) curves of the samples in different electrolytes were tested at different scan rates (20, 40, 60, 80 and 100 mV/s) and further calculated to obtain the bilayer capacitance value C_{dl} .

S1.3 The HER reaction process

In alkaline medium, the HER reaction process is assigned to the Volmer-Heyrovsky pathway^[1,2].

Electrochemical reaction step:



Where H^* represents the catalytic site with an adsorbed H-species.

S1.4 The Tafel equation is presented as:

$$\eta = a + b \log(i/i_0)$$

η is the overpotential, i is current density, i_0 is the exchange current density, b is the Tafel slope and a is the constant term.

S1.5 Double layer capacitance (C_{dl}) calculation:

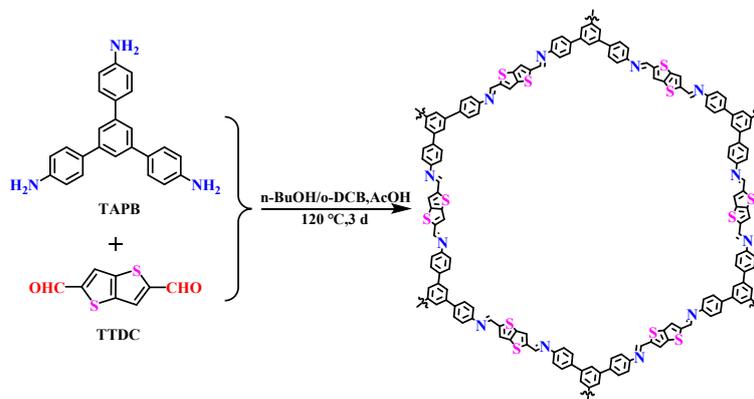
The double layer capacitance (C_{dl}) was evaluated according to the following equation: $C_{dl} = \Delta j/v$, which Δj is the current density difference between anode and cathode at the potential corresponding to 0.25 V and v is the scan rate. The slope of the line plots corresponds to the double of C_{dl} .

S1.6 Faraday efficiency calculation:

$$\text{The Faraday efficiency calculation: } \text{FE}\% = \frac{(\text{Amount of H}_2 \text{ generated experimentally})}{(\text{Amount of H}_2 \text{ generated theoretically})} = \frac{nNF}{Q} \times 100\%$$

Where n equals to 2, N is the number of Hydrogen produced during the experiment (mol) and Q is the total charge passed through the reaction.

S1.7 Synthesis of JLNU-300



1,3,5-Tris(4-aminophenyl) benzene (TAPB) (0.04 mmol, 14.06 mg) and Thieno[3,2-b]thiophene-2,5-dicarboxaldehyde (TTDC) (0.06 mmol, 11.78 mg) were weighted into a Pyrex tube (volume: *ca* 20 ml with both length of 10 cm, neck length of 9 cm) Butanol (0.75 ml), 1,2-dichlorobenzene (0.25 ml) and 0.1 ml of aqueous acetic acid (6.0 mol/L) was added to the mixture. The tube was flash frozen at 77 K (LN₂ bath), evacuated to an internal pressure of 0.15 mmHg and flame sealed. Upon sealing the length of the tube was reduced to *ca.* 13 cm. The reaction mixture was heated at 120 °C for 72 h to afford a orange precipitate which was isolated by filtration over a medium glass frit and washed with anhydrous acetone (3 × 20 ml). The yield is about 71.0% (18.3 mg). The solvent was removed under vacuum at 80 °C to afford the corresponding products as orange powder of JLNU-300. Anal. Calcd for C₇₂H₄₂N₆S₆: C: 73.10; H: 3.55; N:7.11; S: 16.24. Found: C:72.98; H: 3.54; N: 7.09; S: 16.39. Solid-state ¹³C NMR (500MHz): 103.107, 116.58, 122.64, 126.77, 141.82, 148.00 ppm. FT-IR (KBr): 3316, 3223, 1660, 1578, 1480, 1408, 1220, 1146, 870, 832 cm⁻¹.

Section S2: Gas adsorption isotherms

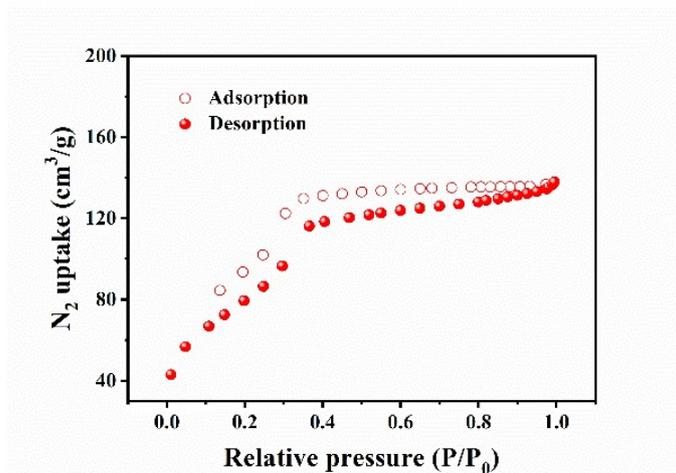


Figure S1. N_2 adsorption-desorption isotherms of JLNU-300.

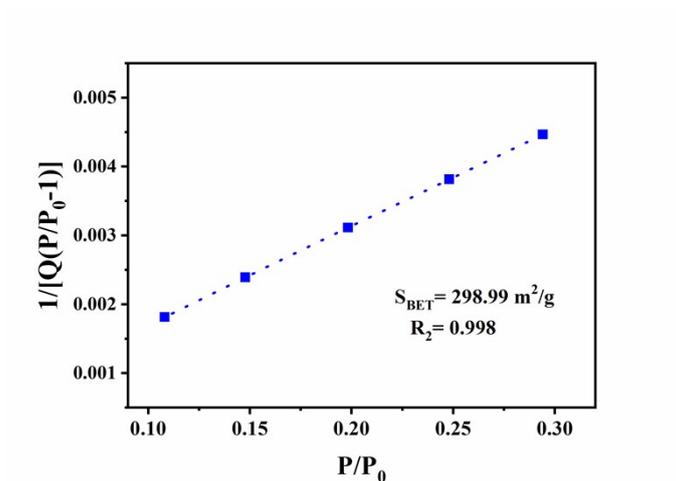


Figure S2. BET pore of JLNU-300 calculated from N_2 adsorption isotherm at 77 K.

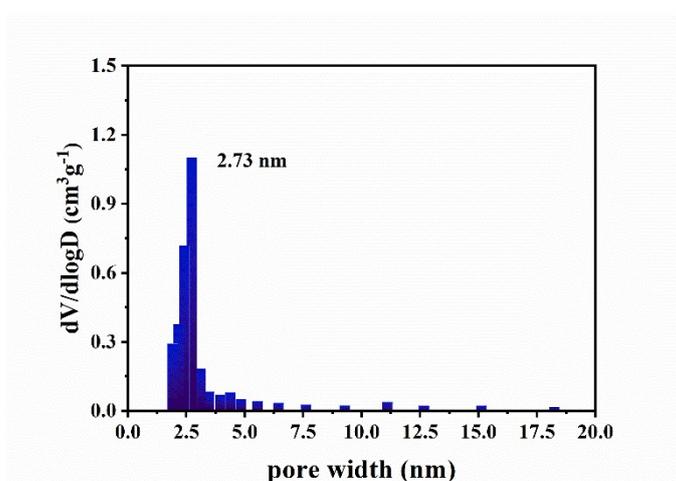


Figure S3. The pore size distribution curve of JLNU-300.

Section S3: TGA

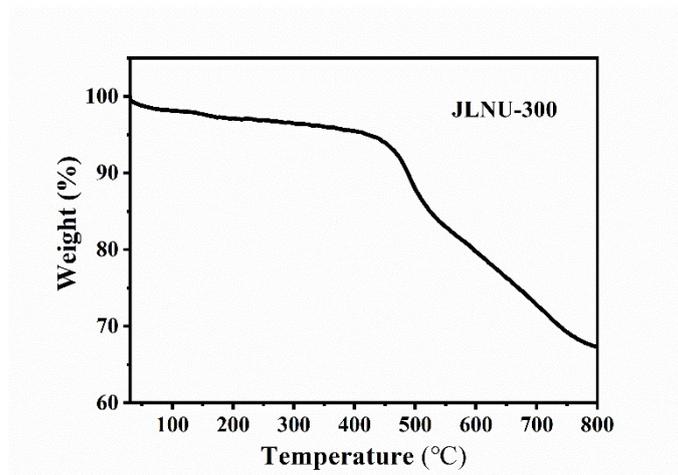


Figure S4. Thermogravimetric curves of JLNU-300 in N₂ atmosphere.

Section S4: Stability test

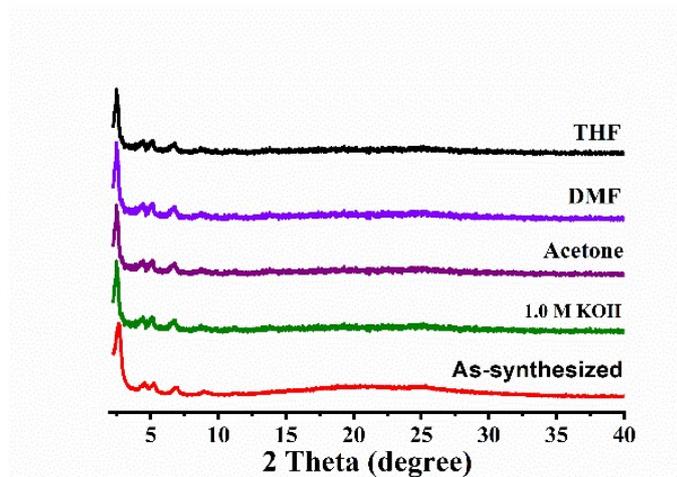


Figure S5. PXRD patterns of JLNU-300 after 3 d treatment in different organic solvents and 1.0 M KOH solutions.

Section S5: Unit cell parameters and fractional atomic coordinates

Table S1. Unit cell parameters and fractional atomic coordinates for JLNU-300 were calculated on the basis of staggered **hcb** net.

Space group		<i>P6</i> (No. 168)	
Calculated unit cell		a = b = 39.9266 Å, c = 3.5538 Å, $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	
Measured unit cell		a = b = 38.7246 Å, c = 3.2531 Å, $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	
Pawley refinement		$R_{\omega p} = 4.98\%$ and $R_p = 3.87\%$	
Atom	x	y	z
C1	0.31524	0.62643	0.000
C2	0.35573	0.64836	0.000
C3	0.37926	0.62913	0.000
C4	0.41981	0.65109	0.000
C5	0.44203	0.63298	0.000
C6	0.42413	0.59266	0.000
C7	0.38359	0.5705	0.000
C8	0.3614	0.58863	0.000
N9	0.44772	0.57499	0.000
C10	0.43357	0.53787	0.000
C11	0.45882	0.52107	0.000
C12	0.49902	0.5433	0.000
C13	0.48642	0.48122	0.000
S14	0.43995	0.47161	0.000
H15	0.30014	0.5935	0.000
H16	0.43459	0.68401	0.000
H17	0.47494	0.65111	0.000
H18	0.36866	0.53758	0.000
H19	0.32848	0.57051	0.000
H20	0.4009	0.51766	0.000
H21	0.51373	0.57621	0.000

Section S6. References

- [1] E. Skúlason, V. Tripkovic, M. E. Björketun, S. Gudmundsdóttir, G. Karlberg, J. Rossmeisl, T. Bligaard, H. Jónsson and J. K. Nørskov, *J. Phys. Chem. C*, **2010**, 114, 18182-18197.
- [2] M. Chhetri, S. Maitra, H. Chakraborty, U. V. Waghmare, C. N. R. Rao, *Energy Environ. Sci.* **2016**, 9, 95-101.