# Electronic Supporting Information (ESI)

**for**

## Co-MOF Derived $Co_9S_8$@NS-C Electrocatalyst for Efficient Hydrogen Evolution Reaction

Yun-Wu Li,* Qian Wu, Rui-Cong Ma, Xiao-Qi Sun, Dan-Dan Li, Hong-Mei Du, Hui-Yan Ma,* Da-Cheng Li, Su-Na Wang* and Jian-Min Dou

[a] *Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, and School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252000, P. R. China.*

*Corresponding authors.

E-mails: liyunwu@lcu.edu.cn; mahuiyanyan@163.com (H. Y. Ma); wangsuna@lcu.edu.cn (S.-N. Wang)

## S1 Additional Experimental Section

### S1.1. Syntheses of $\{[H_2N(CH_3)_2]_2[Co(BPTC)]\cdot 4DMAC\cdot 5H_2O\}_n$ (LCU-105).

A mixture of $Co(NO_3)_3\cdot 6H_2O$ (87.31 mg, 0.3 mmol) and $H_4BPTC$ (99 mg, 0.3 mmol) in DMAC (6 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), which was heated at 120 °C for 4 days and then cooled to room temperature at a rate of 10 °C·h$^{-1}$. Block-like purple crystals of **LCU-105** were collected. Yield: 30 % based on Co. Elemental analysis (%) for activated sample **LCU-105a**, $C_{20}H_{22}O_8N_2Co$ (M = 477.33): *Calcd.*: C, 50.32; H, 4.65; N, 5.87; *Found*: C, 50.41; H, 4.56*;* N, 5.81;. IR (KBr disk, cm$^{-1}$) see **Fig. S3** in **SI**.

**S1.2. Crystal data for Co-MOF (LCU-105).**

**Table S1. Crystal Data and Structure Refinement Parameters for LCU-105.**

| **Co-MOF** | | **LCU-105** | |
|---|---|---|---|
| Formula | $C_{36}H_{68}O_{17}N_6Co$ | Crystal system | Monoclinic |
| $F_w$ | 915.89 | Space group | $P2/c$ |
| $\lambda$/Å | 0.71073 | $Z$ | 4 |
| $T$/K | 100(2) | $D_c$/Mg·m$^{-3}$ | 1.113 |
| $a$ [Å] | 19.601(4) | $F$(000) | 1144 |
| $b$ [Å] | 9.3797(19) | Reflections collected/unique | 26897/5995 |
| $c$ [Å] | 18.630(4) | $R_{int}$ | 0.2573 |
| $\alpha$[°] | 90 | Data/Restraints/Parameters | 5995/116/352 |
| $\beta$ [°] | 95.69(3) | $R_1/wR_2$ [$I>2\sigma(I)$] [a] | 0.0.1492/0.3669 |
| $\gamma$[°] | 90 | $R_1/wR_2$ [(all data)] [a] | 0.2352/0.4167 |
| $V$ ( Å $^3$) | 3408.3(12) | GOF on $F^2$ | 1.130 |

[a] $R_1 = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$ $wR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2/(\Sigma w|F_0|^2)^2]^{1/2}$.

## S2. Figures in Supporting Information

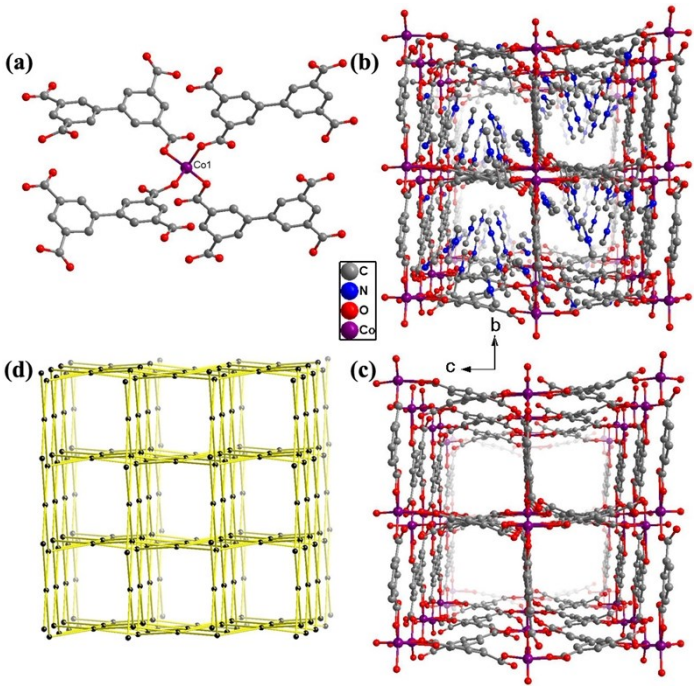


**Fig. S1.** (a) The ball and stick mode of coordination environment around $Co^{2+}$ in **LCU-105**; (b) the 3D structure including $[NH_2(CH_3)_2]^+$ cations and DMAC solvents of **LCU-105** along *a* axis; (c) the 3D microporous framework without $[NH_2(CH_3)_2]^+$ cations and DMAC solvents of **LCU-105a** along *a* axis; (c) the simplified **pts** topology of **LCU-105**. Color codes: blue, N; gray, C; red, O; violet, Co. (The hydrogen atoms are omitted for clarity)

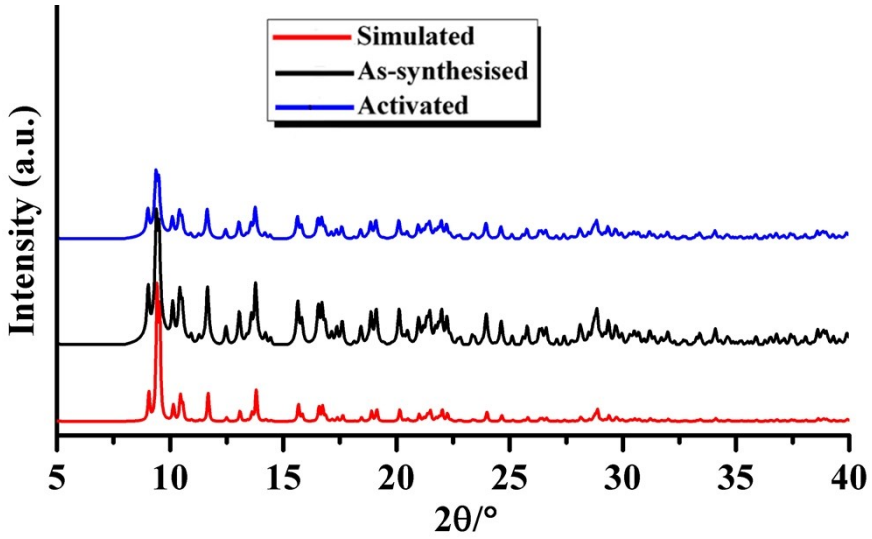


**Fig. S2.** PXRD patterns of **LCU-105** and **LCU-105a**.

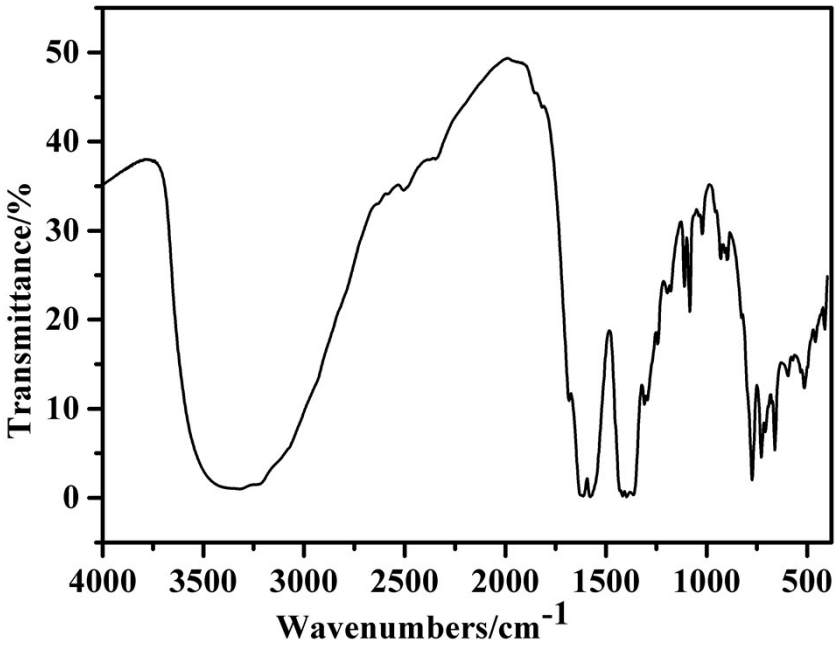


**Fig. S3.** IR spectra of compound **LCU-105**.

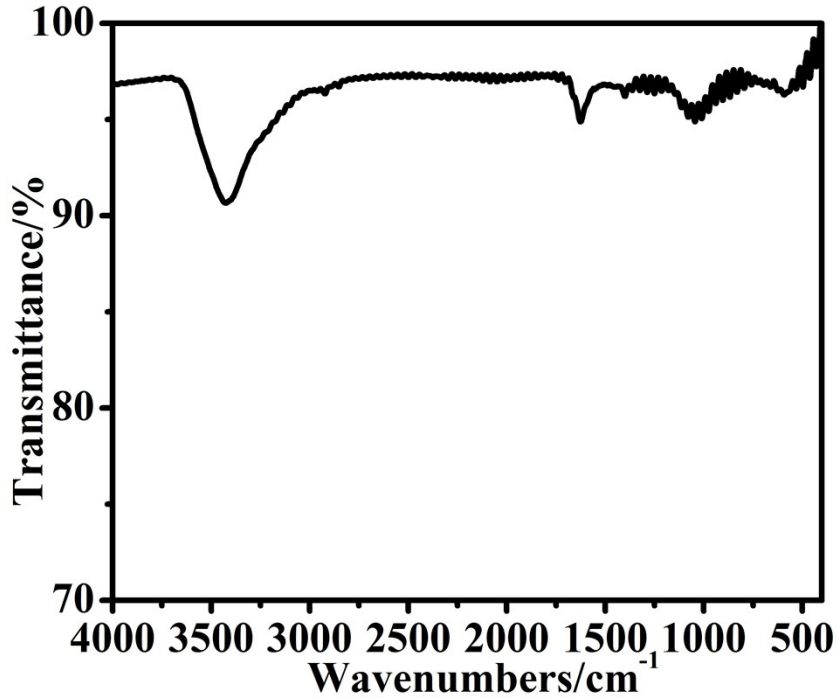


**Fig. S4.** IR spectra of $Co_9S_8$@NS-C-900 composite.

**Table S2.** Comparison of HER performances of $Co_9S_8$@NS-C-900 with recently reported cobalt based catalysts in KOH.

| Catalysts | $\eta$ (mV) at $J$ = 10 mA cm$^{-2}$ | Tafel slope (mV dec$^{-1}$) | References |
|---|---|---|---|
| **$Co_9S_8$@NS-C-900** | **86.4** | **81.1** | **This work** |
| $Co_9S_8$@$MoS_2$/CNFs | 190 | 110 | *Adv. Mater.*, 2015, **27**, 4752−4759. |
| $Co_9S_8$/CNFs | 304 | 140 | *Adv. Mater.*, 2018, **30**, 1707301. |
| $Co_9S_8$/1L $MoS_2$ | 95 | 71 | |
| $Co_9S_8$/2L $MoS_2$ | 124 | 92 | |
| $Co_9S_8$/3L $MoS_2$ | 175 | 101 | |
| $Co_9S_8$/4L $MoS_2$ | 181 | 108 | |
| $Co_9S_8$/5L $MoS_2$ | 208 | 145 | |
| $Co_9S_8$/NSG-220 | 147 | 97 | *ACS Sustainable Chem. Eng.*, 2019, **7**, 19442−19452. |
| $Co_9S_8$/N,S-rGO | 266 | 75.5 | *Sci. Rep.*, 2019, *9*, 1951. |
| $Co_9S_8$@N-S-HPC | 173 | 78 | *App. Catal. B: Environ.*, 2019, **254**, 186−193. |
| $Co_9S_8$/$MoS_2$@NSOC | 194 | 118 | *J. Energy Chem.*, 2020, **44**, 90−96. |
| $Co_9S_8$ Nanotubes | 320 ($J_{20}$) | -- | *Am. J. Anal. Chem.,* 2016*,* **7***,* 210−218. |
| $CoS_2$ pyramids | 244 | 133 | *Electrochimica Acta*, 2014, **148**, 170−174. |
| $CoS_2$/rGO/CNTs | 143 | 51 | *Angew. Chem. Int. Ed.*, 2014, **53**, 12594−12599. |
| $CoS_2$ | 327 | 148 | |
| $CoS_2$/rGO | 278 | 82 | |
| Co@N-Doped Carbon | 200 ($J_{13.6}$) | 79.3 | *Chem. Mater.*, 2015, *27*, 2026−2032. |
| $CoS_2$ nanowires | 145 | 51.6 | *J. Am. Chem. Soc.*,2014, **136**, 10053−10061. |
| Co NPs@NC | 210 | 108 | *J. Mater. Chem. A*, 2014, **2**, 20067−20074. |
| $CoN_x$/C | 170 | 75 | *Nat. Commun.*, 2015, **6**, 7992. |
| Co-N-doped Graphene | 187 | 82 | *Nat. Commun.*, 2015, **6**, 8668. |
| Co@N-CNTs@rGO | 108 | 55 | *Adv. Mater.*, 2018, **30**, 1802011. |
| Co-NC/CNT | 201 | 121 | *J. Mater. Chem. A*, 2016, **4**, 16057−16063. |
| Co-NRCNTs | 370 | -- | *Angew. Chem. Int. Ed.*, |

| | | | |
|---|---|---|---|
| | | | 2014, **53**, 4372−4376. |
| Co-P@$Co_3O_4$/CC | 73 | 85 | *Chem. Commun.*, 2018, **54**, 2150−2153. |
| Co-NC/CF | 157 | 109 | *Energy Environ. Sci.*, 2020, **13,** 545−553. |
| Co@NG/NRGO | 70 | 64 | *Chem. Commun.*, 2020, **56**, 567−570. |
| CoO@MOFC | 190 | 98 | *Chem*, 2017, **2**, 791−802. |
| Carbon paper/carbon tubes/cobalt-sulfide | 190 | 138 | *ACS Nano*, 2016, **10**, 2342−2348. |