

## Supporting Information

### A cobalt porphyrin-bridged covalent triazine polymer derived electrode for efficient hydrogen production

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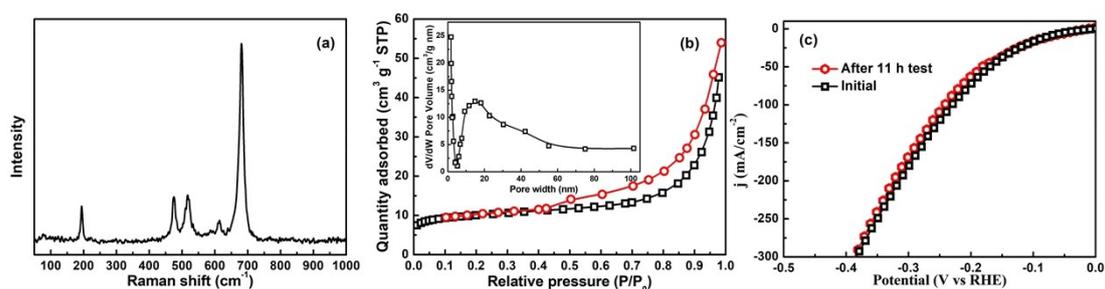


Figure S1. (a) Raman spectrum, (b) N<sub>2</sub> adsorption-desorption isotherm of Co<sub>5.47</sub>N/N,Co-C-800 (Inset is pore size distribution), and (c) LSV curves of Co<sub>5.47</sub>N/N,Co-C-800 before and after stability measurement.

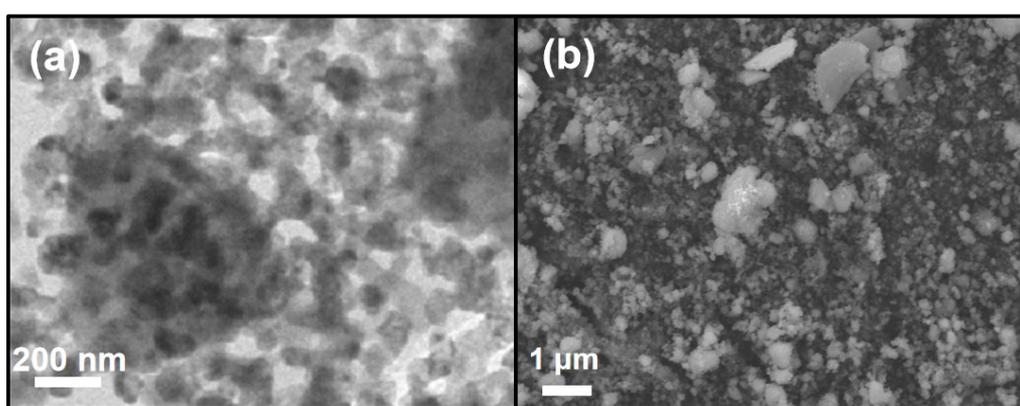


Figure S2. (a) TEM and (b) SEM images of Co<sub>5.47</sub>N/N,Co-C-800 after stability measurement.

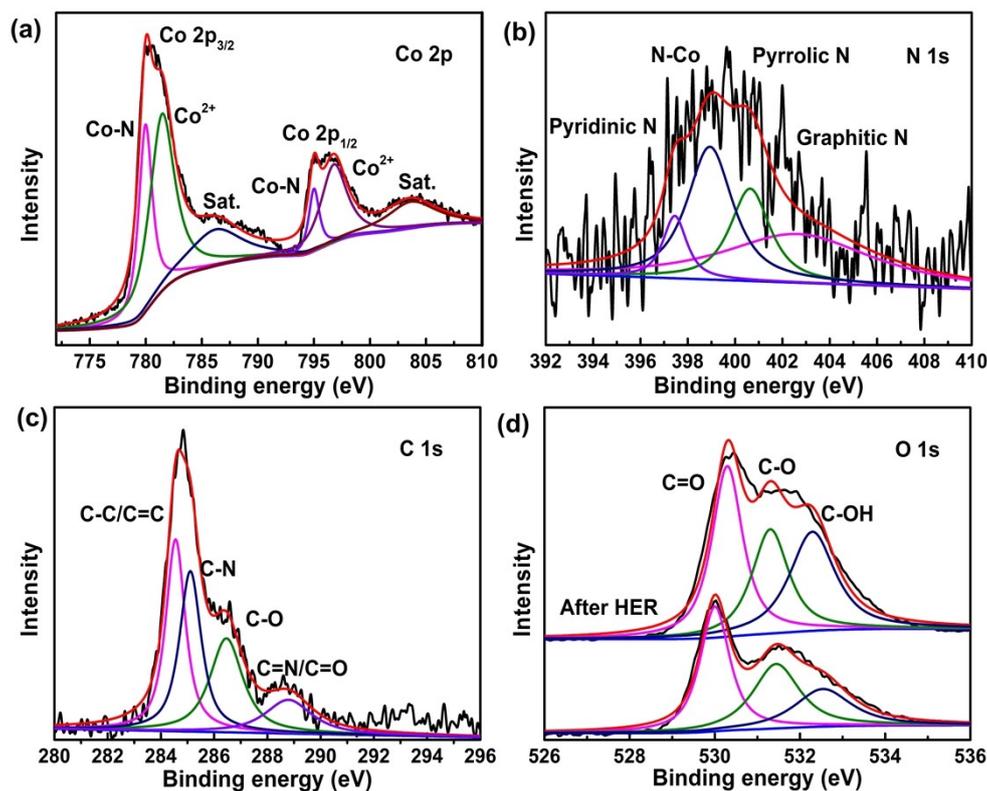


Figure S3. High-resolution XPS spectra of (a) Co 2p, (b) N 1s, and (c) C 1s core levels in  $\text{Co}_{5.47}\text{N}/\text{N},\text{Co-C-800}$  after HER; (d) High-resolution O 1s XPS spectra of  $\text{Co}_{5.47}\text{N}/\text{N},\text{Co-C-800}$  before and after HER.

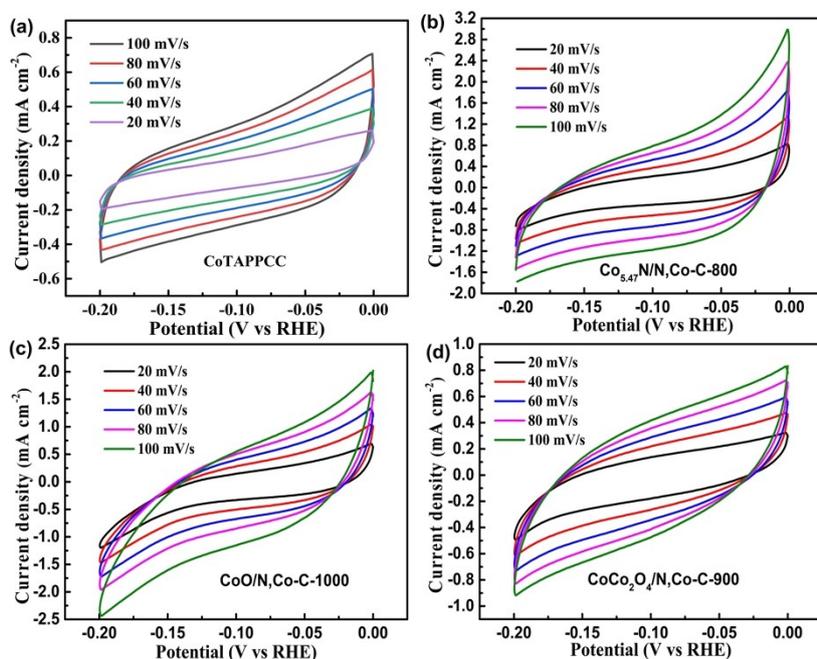


Figure S4. CV curves for the as-prepared samples at different scan rates: (a) CoTAPPCC, (b)  $\text{Co}_{5.47}\text{N}/\text{N},\text{Co-C-800}$ , (c)  $\text{CoO}/\text{N},\text{Co-C-1000}$ , and (d)  $\text{CoCo}_2\text{O}_4/\text{N},\text{Co-C-900}$ .

**Table S1.** Comparison of HER performance of Co<sub>5.47</sub>N/N,Co-C-800 with some other reported electrocatalysts at 10 mA cm<sup>-2</sup>.

Electrocatalysts	Overpotential (mV@10 mA cm <sup>-2</sup> )	Refs.
Co <sub>5.47</sub> N NP@N-PC	149 (1.0 M KOH)	1
Co <sub>5.47</sub> N@N-rGO-750	190 (1.0 M KOH)	2
Co <sub>5.47</sub> N-WO <sub>2</sub> @C/NF	36 (1.0 M KOH)	3
Co-Mo-N /NF	82 (1.0 M KOH)	4
CoFeN-NCNTs//CCM	151 (1 M KOH)	5
Co <sub>5.47</sub> N/Mo <sub>5</sub> N <sub>6</sub>	44 (1 M KOH)	6
Fe, Ni-Co <sub>5.47</sub> N@N-VrGO-2	121 (0.5 M H <sub>2</sub> SO <sub>4</sub> )	7
Co <sub>5.47</sub> N/rGO@NF	123 (1.0 M KOH)	8
Mo <sub>2</sub> C@NCs	110 (1.0 M KOH)	9
C, N, S-doped C	180 (0.5 M H <sub>2</sub> SO <sub>4</sub> )	10
CoP-nph-CMP-800	360 (1.0 M KOH)	11
P@pCoPc-1/Co <sub>3</sub> O <sub>4</sub>  CC	120 (1.0 M KOH)	12
MoP/NF	114 (1.0 M KOH)	13
MoS <sub>2</sub> -MoP/C	102 (1.0 M KOH)	14
phosphosulfide (MoPS)	170 (1.0 M KOH)	15
MoP@NCHSs-900	92 (1.0 M KOH)	16
Ni, Co-doped MoP	102 (0.5 M H <sub>2</sub> SO <sub>4</sub> )	17
CoP <sub>2</sub> /RGO	88 (1.0 M KOH)	18
CoNi(1:1)-TB-800N <sub>2</sub>	114 (1.0 M KOH)	19
Co <sub>9</sub> S <sub>8</sub> -40/CC	100 (1.0 M KOH)	20
Co-Ni <sub>3</sub> N	225 (1.0 M KOH)	21
N-doped Mo <sub>2</sub> C	99 (1.0 M KOH)	22
Ni/Mo <sub>2</sub> C(1:2)-NCNFs	143 (1.0 M KOH)	23
Co <sub>5</sub> Mo <sub>1.0</sub> P NSs@NF	173	24
Ni@Ni-Mo	> 190	25
Co <sub>0.75</sub> Ni <sub>0.25</sub> /CC	108	26
<b>Co<sub>5.47</sub>N/N,Co-C-800</b>	<b>76 (1.0 M KOH)</b>	<b>This work</b>

**Table S2.** Comparison of HER performance of Co<sub>5.47</sub>N/N,Co-C-800 with some other reported electrocatalysts at 100 mA cm<sup>-2</sup>.

Electrocatalysts	Overpotential (mV@100 mA cm <sup>-2</sup> )	Refs.
Co <sub>5.47</sub> N@N-rGO-750	~320 (1 M KOH)	2
Co <sub>5</sub> Mo <sub>1.0</sub> P NSs@NF	~300 (1 M KOH)	24
Ni@Ni-Mo	276 (1 M KOH)	25
Co <sub>0.75</sub> Ni <sub>0.25</sub> /CC	237 (1 M KOH)	26
F-CTF-1-AA	> 430 (1.0 M KOH)	27
Co-NCNTFs	~300 (1 M KOH)	28
Co <sub>2</sub> P@C	~350 (0.5 M H <sub>2</sub> SO <sub>4</sub> )	29
Co(OH) <sub>2</sub> @PANI	~250 (0.5 M H <sub>2</sub> SO <sub>4</sub> )	30
MoSe <sub>2</sub> -Mo <sub>2</sub> C	~250 (0.5 M H <sub>2</sub> SO <sub>4</sub> )	31
graphene-Mo <sub>2</sub> C	~370 (0.5 M H <sub>2</sub> SO <sub>4</sub> )	32
Pd-PHE MA/NF-5000	~350 (1 M KOH)	33
CoFeCo PBA	~320 (1 M KOH)	34
Ni(OH) <sub>2</sub> -Fe <sub>2</sub> P/Ti mesh	252 (1 M KOH)	35
<b>Co<sub>5.47</sub>N/N,Co-C-800</b>	<b>229 (1.0 M KOH)</b>	<b>This work</b>

**Table S3.** Comparison of the XPS data of Co<sub>5.47</sub>N/N,Co-C-800 before and after the electrolysis.

Species	Peak positions before electrolysis (eV)	Peak positions after electrolysis (eV)
Co <sup>2+</sup> ions	781.5/796.6	781.3/796.5
Co-N bonds	779.9/794.8	779.8/794.9
N 1s	398.2/398.9/400.7/401.9	397.5/398.7/400.6/402.6
C 1s	284.6/285.1/286.3/289.2	284.5/285.0/286.5/288.8
O 1s	529.9/531.4/532.5	530.3/531.2/532.3

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