# Supporting Information (SI) for:

# Co,Fe,N-Modified Carbon Composites for Excellent Catalytic Performances toward Electrochemical Reduction Reaction

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**Calculation details**

Koutecky–Levich equation:

$$\frac{1}{I} = \frac{1}{I_K} + \frac{1}{I_d} = \frac{1}{nFAkC^0} - \frac{1}{0.62nFAD_{O_2}^{2/3}\nu^{-1/6}C^0\omega^{1/2}} \qquad \text{(equation S1)}$$

where $I$ is the measured current density, $I_k$ is the kinetic current density, $I_d$ is the diffusion-limiting current density, $\omega$ is the angular velocity ($\omega = 2\pi N$, N is the rotation speed), $F$ is the Faraday constant (96 485 C mol$^{-1}$), $A$ is the geometric electrode area (cm$^2$), $k$ is the rate constant of the reaction, $C^o$ is the bulk concentration of $O_2$ ($1.2\times 10^{-6}$ mol cm$^{-3}$), $D_{O_2}$ is the diffusion coefficient of $O_2$ ($1.9\times 10^{-6}$ cm$^2$ s$^{-1}$) and $n$ is the kinematic viscosity of the electrolyte (0.01 cm$^2$ s$^{-1}$). For RRDEs, the electron transfer number ($n$) and percentage of peroxide species ($y_{peroxide}$) relative to the total products were determined by the following equations:

$$n = \frac{4NI_d}{NI_d + I_r} \qquad \text{(equation S2)}$$

$$y_{peroxide} = \frac{200I_r}{NI_d + I_r} \qquad \text{(equation S3)}$$

where $I_d$, $I_r$ and $N$ are the disk current, the ring current, and the current collection efficiency of the RRDE, respectively. Here, $N = 0.38$.

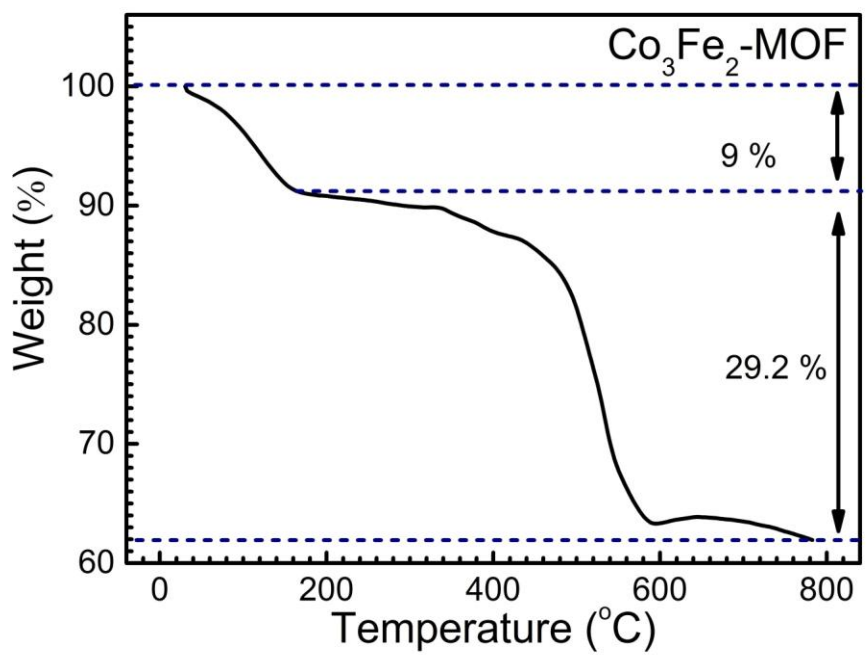


**Figure S1.** Thermogravimetric analysis (TGA) of $Co_3Fe_2$-MOF precursor under Ar.

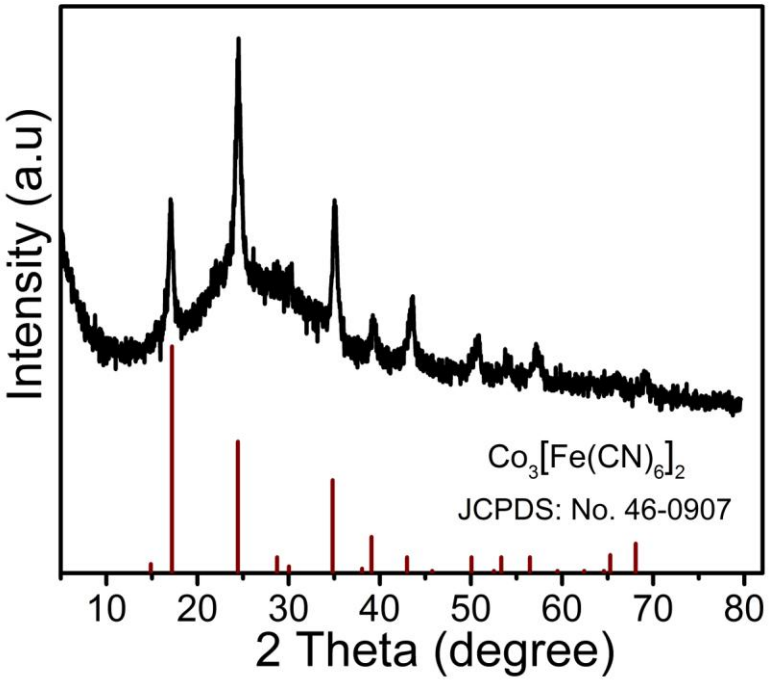


**Figure S2.** XRD pattern of $Co_3Fe_2$-MOF precursor.

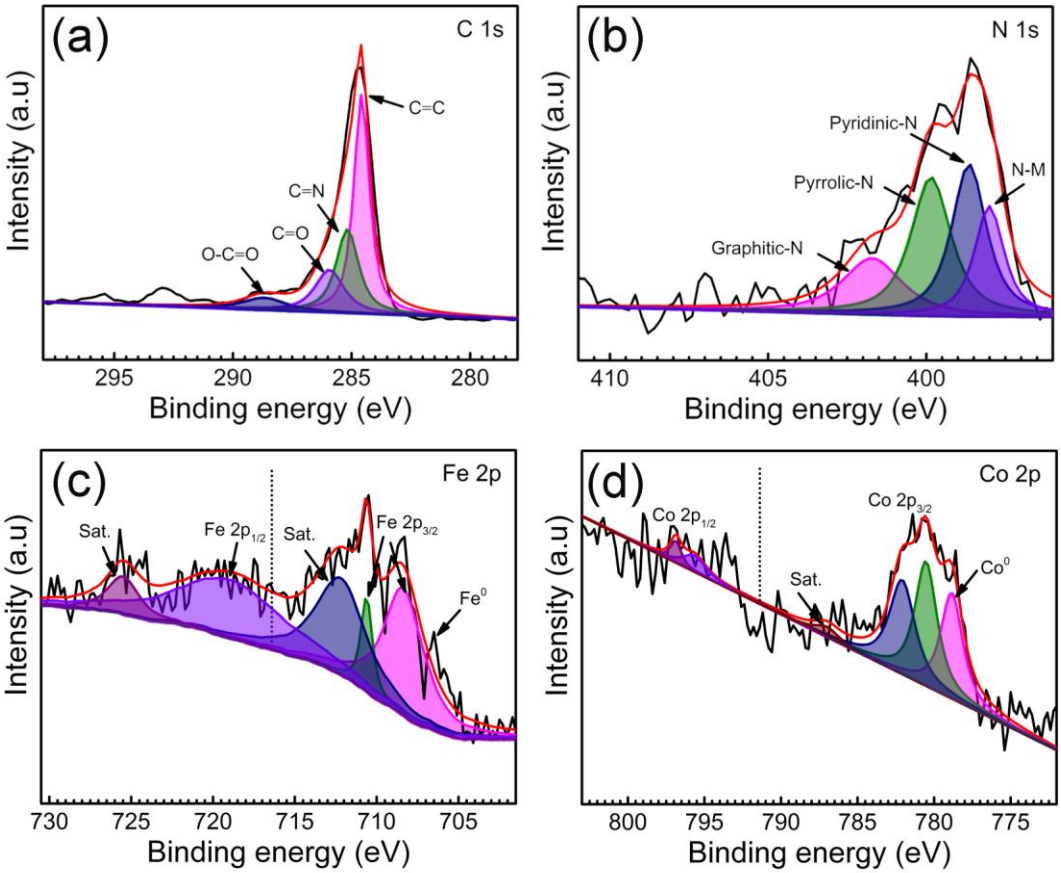


**Figure S3.** High resolution XPS spectra of (a) C 1s, (b) N 1s, (c) Fe 2p and (d) Co 2p of the CMS-2.

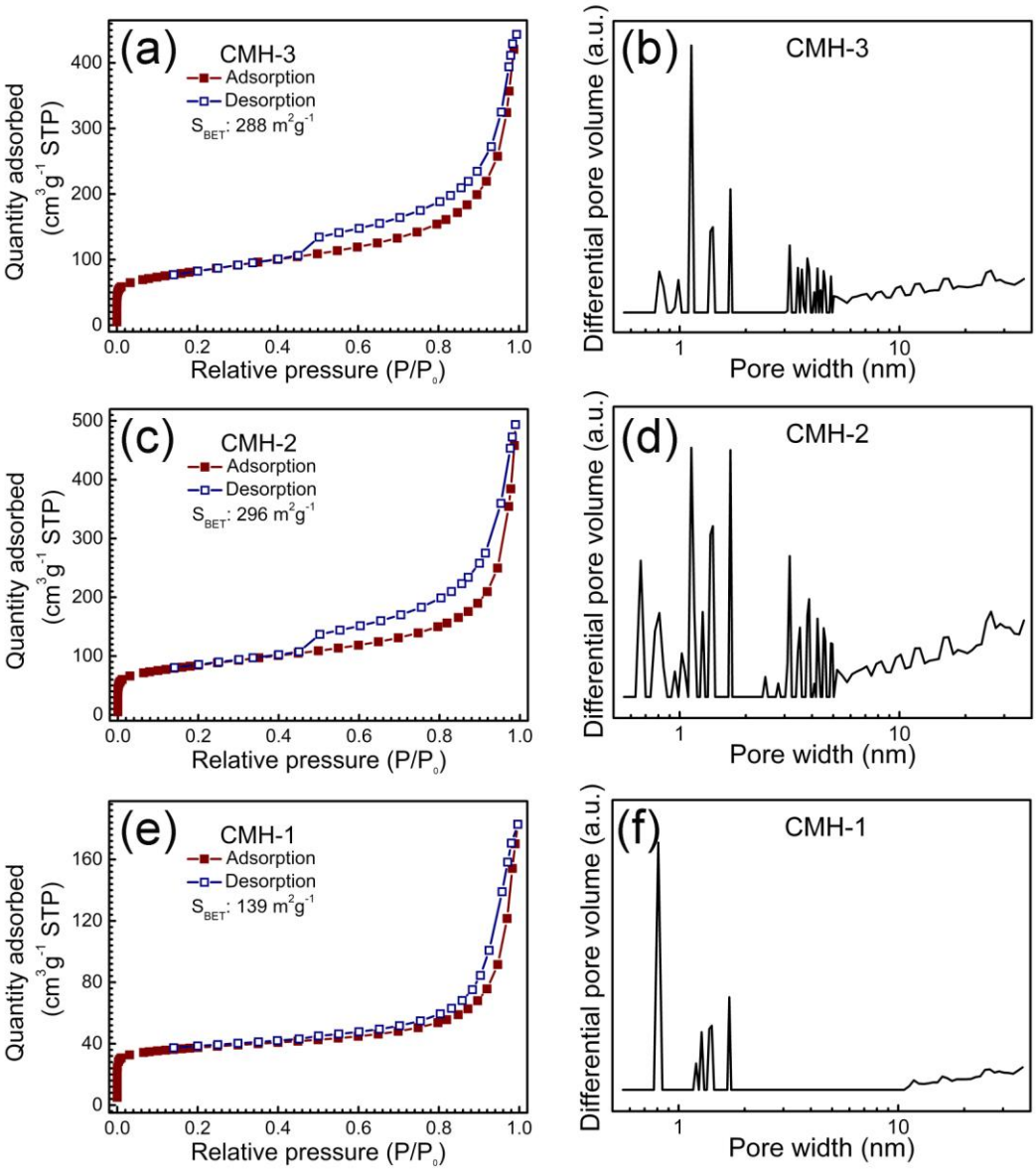


**Figure S4.** $N_2$-sorption isotherms and pore size distribution from the NLDFT model of catalysts (a, b) CMH-3, (c, d) CMH-2, and (e, f) CMH-1, respectively.

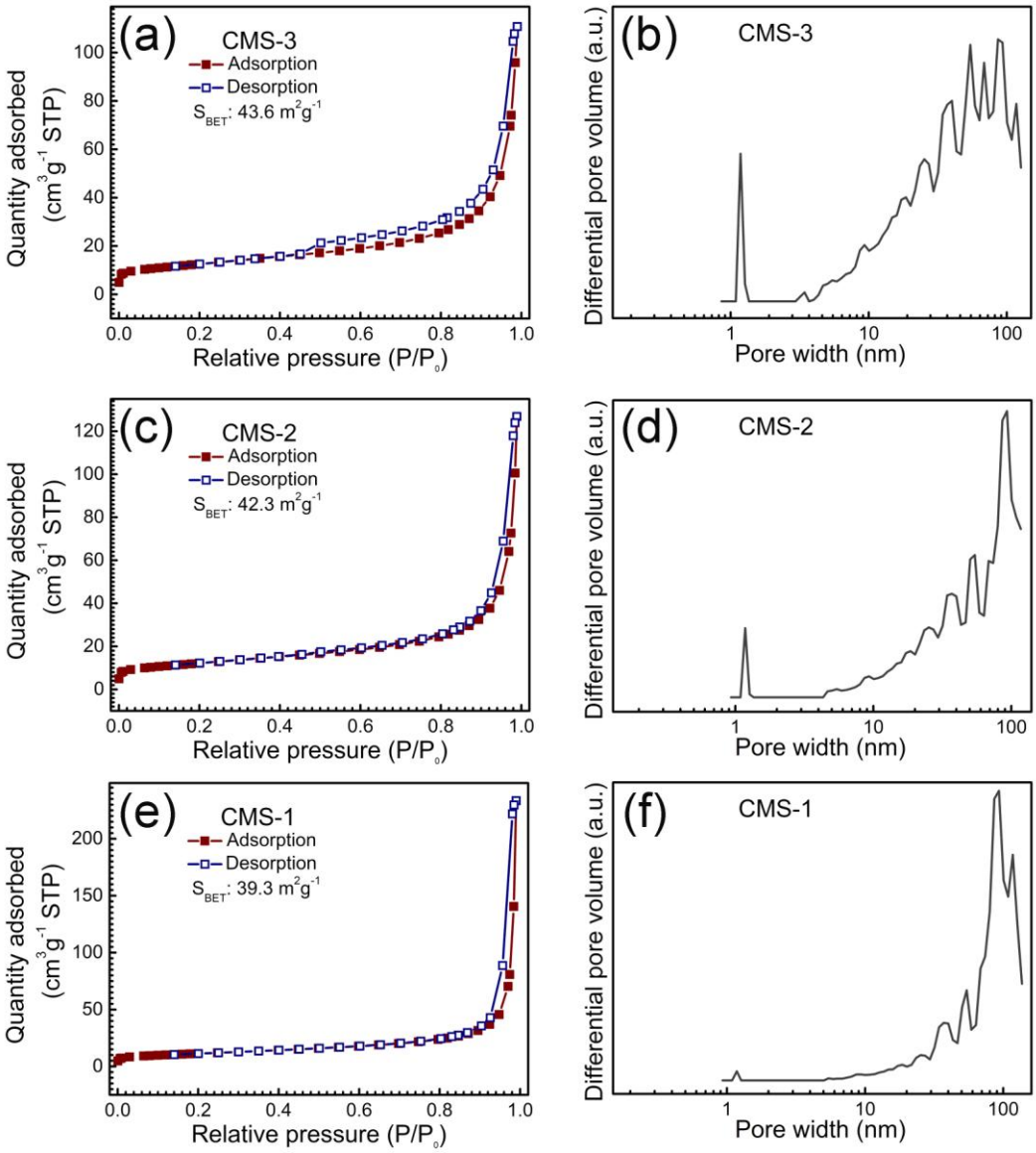


**Figure S5.** $N_2$-sorption isotherms and pore size distribution from the NLDFT model of catalysts (a, b) CMS-3, (c, d) CMS-2, and (e, f) CMS-1, respectively.

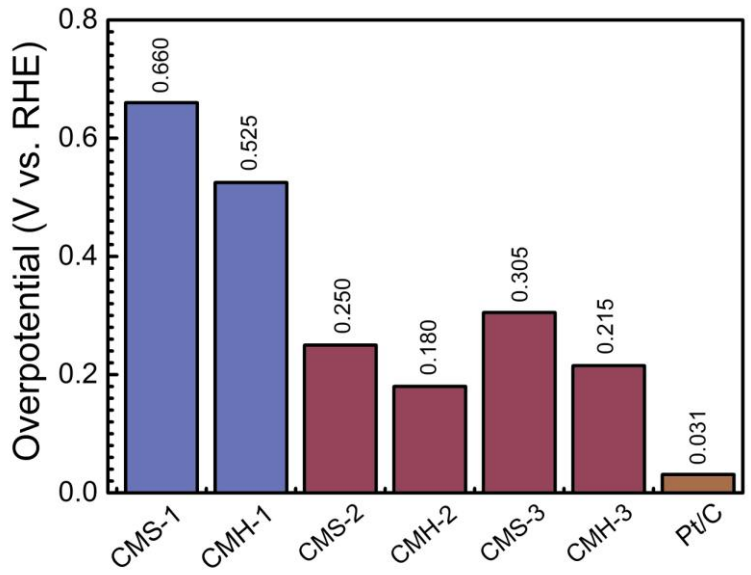


**Figure S6.** Overpotential histogram tested in HER under 10 mA·cm$^{-2}$.

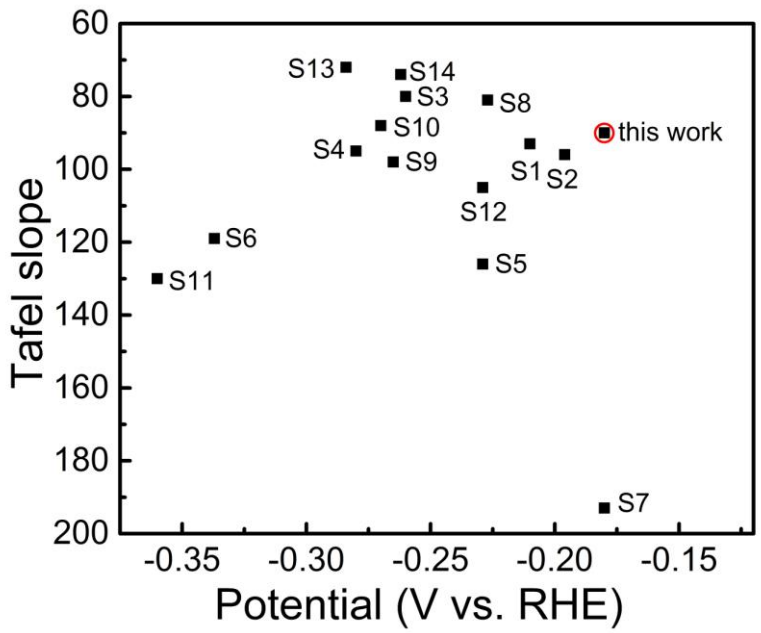


**Figure S7.** Compare the relationship between overpotential and Tafel slope of HER from different catalysts in 0.5 M $H_2SO_4$.

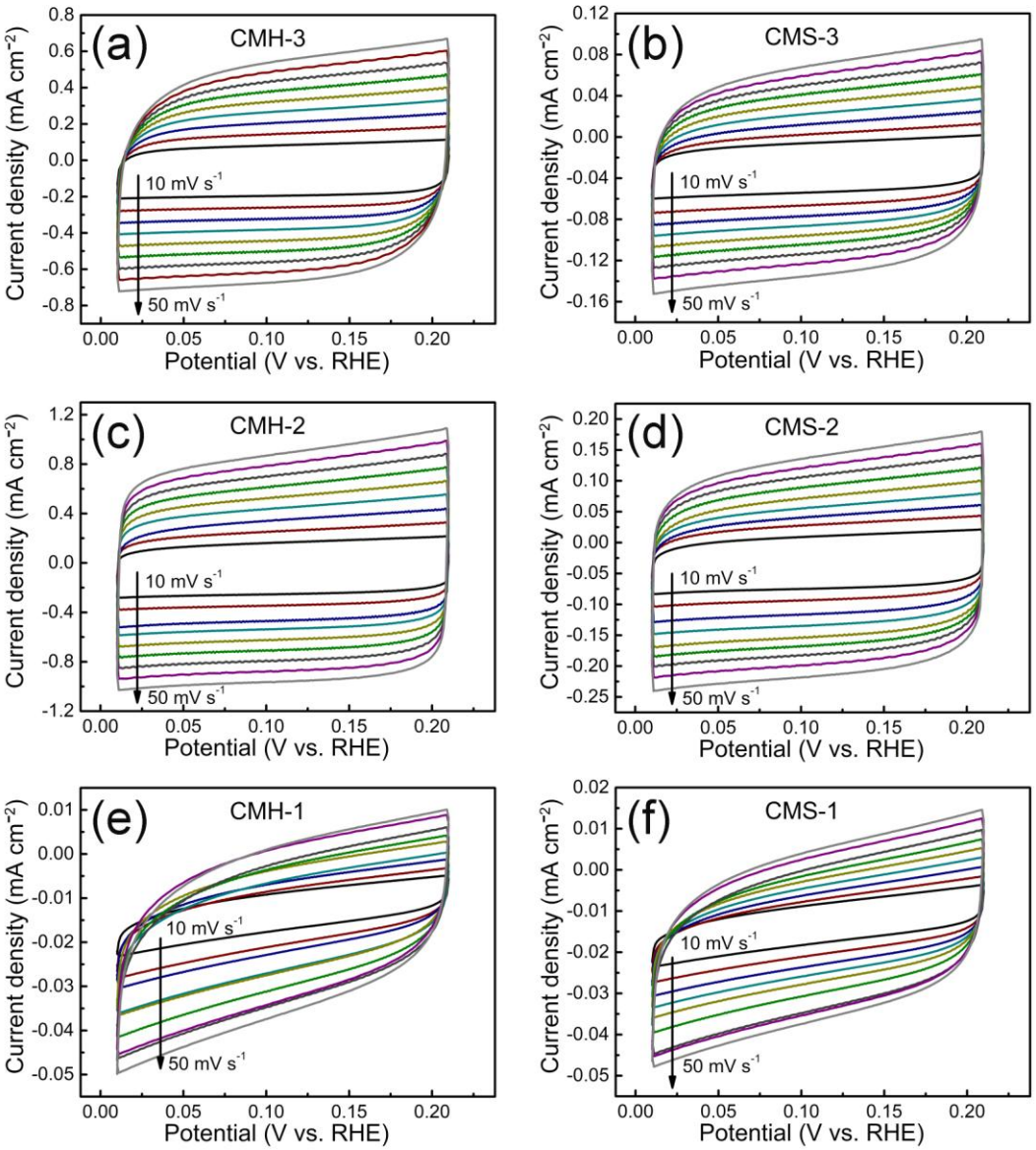


**Figure S8.** Cyclic voltammograms (CV) were taken in a potential window without faradaic processes (a) CMH-3, (b) CMS-3, (c) CMH-2, (d) CMS-2, (e) CMH-1 and (f) CMS-1 in 0.5 M $H_2SO_4$.

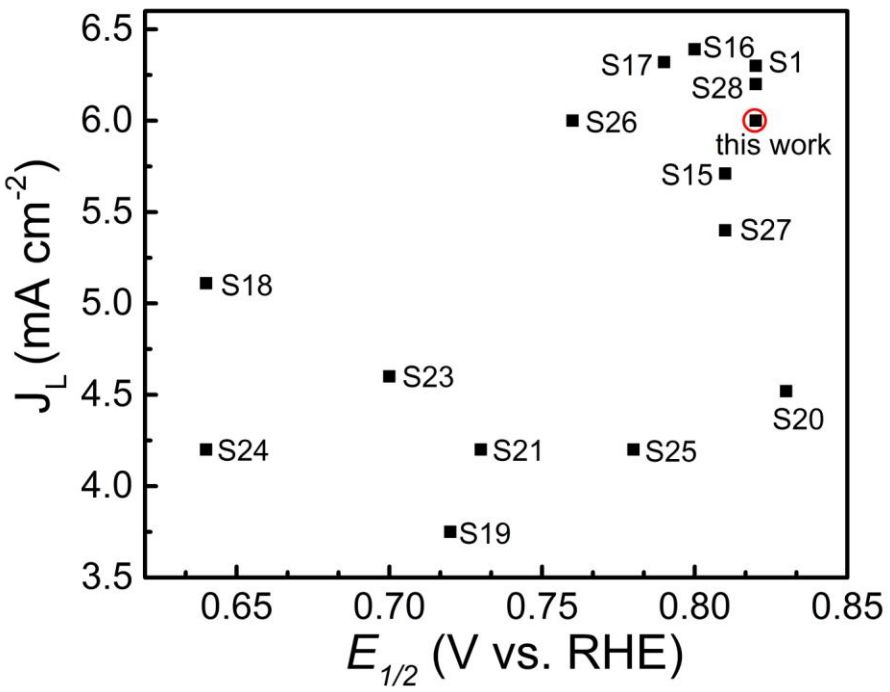


**Figure S9.** Compare the relationship between half-wave potential and limiting current of ORR from different catalysts in 0.1 M KOH.

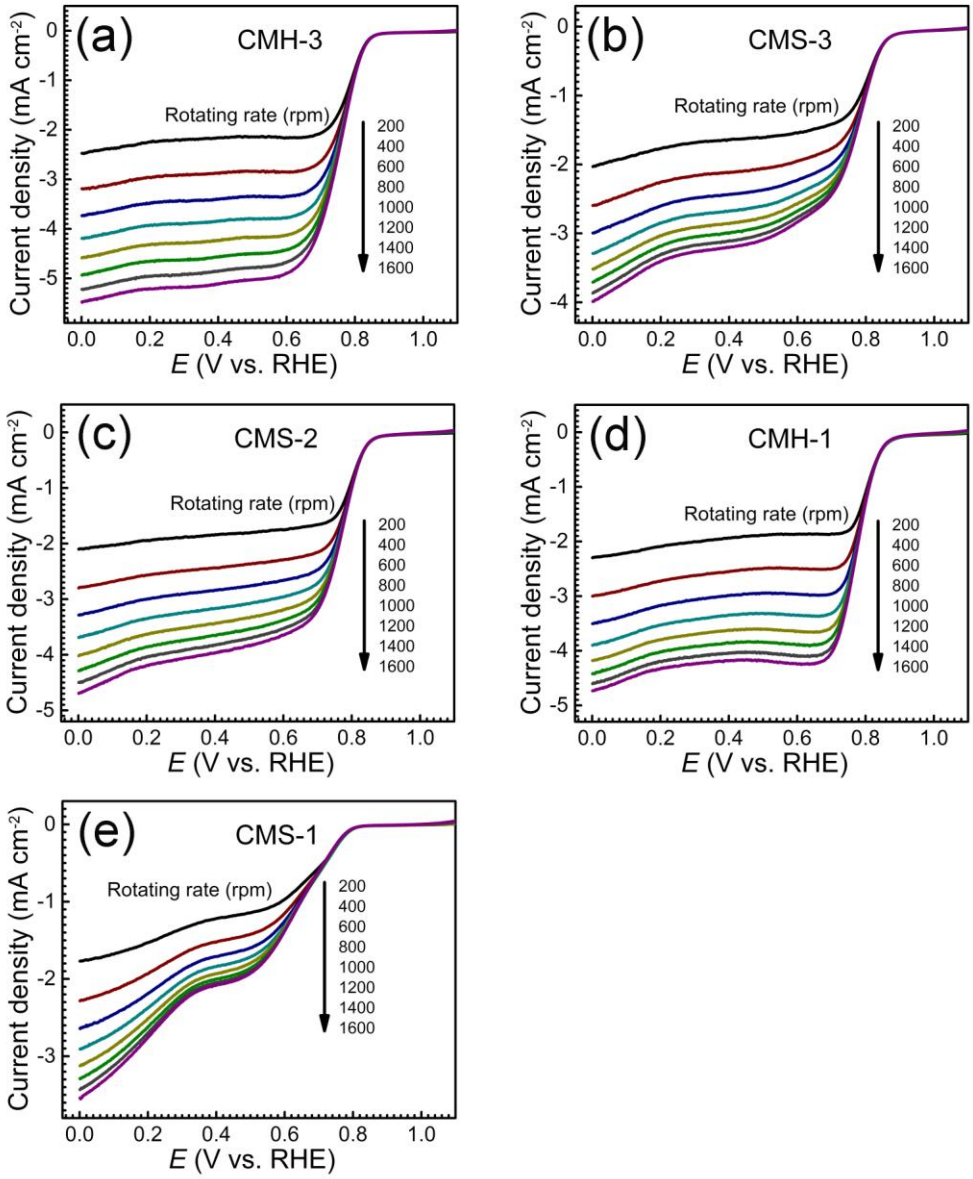


**Figure S10.** The polarization curves obtained for CMH-3, CMS-3, CMS-2, CMH-1 and CMS-1 in a 0.1 M KOH solution with a sweep rate of 5 mV $s^{-1}$ at different rotating rates.

**Table S1.** Comparison of the HER performance from different catalysts in 0.5 M $H_2SO_4$ unless stated otherwise.

| Author | Catalysts | $\eta_{10}$ [mV] | Tafel slope [mV $dec^{-1}$] |
|---|---|---|---|
| **This work** | **$Co_2FeC_xN_y$** | **180** | **90** |
| E. Zhang[S1] | Co@NCNT | 210 | 93 |
| H. Su[S2] | Co@CNF-700 | 196 | 96 |
| X. Zou[S3] | Co-NRCNTs | 260 | 80 |
| Y. Feng[S4] | Co–P-300 | 280 | 95 |
| Y. Hou[S5] | N/Co-doped PCP//NRGO | 229 | 126 |
| F. Zheng[S6] | Co in N-doped carbon | 337 | 119 |
| Z. C. Xing[S7] | Co-entrapped N-doped carbon nanotubes | 180 | 193 |
| Y. H[S8] | $Fe_xP$@NPC | 227 | 81 |
| H. Fei[S9] | Co nanoparticles embedded in N-doped carbon | 265 | 98 |
| Z. Zhang[S10] | Co/N co-doped porous carbon | 270 | 88 |
| M. Ledendecker[S11] | MnNi (0.1M $H_2SO_4$) | 360 | - |
| J. Deng[S12] | CoNi alloy in N-doped graphene shells (0.1 M $H_2SO_4$) | 229 | 105 |
| J. Deng[S13] | FeCo alloy in N-doped carbon nanotube | 284 | 72 |
| Y. Yang[S14] | FeCo in N-doped graphene | 262 | 74 |

**Table S2.** Comparison of the ORR performance from different catalysts in 0.1 M KOH.

| Author | Catalysts | $E_o$ [V *vs.* RHE] | $E_{1/2}$ [V *vs.* RHE] | $J_L$ [mA cm$^{-2}$] |
|---|---|---|---|---|
| **This work** | **$Co_2FeC_xN_y$** | **0.92** | **0.82** | **6.0** |
| L. Shang[S15] | Co,N-CNF | 0.91 | 0.81 | 5.71 |
| X. X. Ma[S16] | $Co_3C$/Co-N-C/G | 0.99 | 0.80 | 6.39 |
| W. X. Yang[S17] | Co-N/C-800 | 0.85 | 0.79 | 6.32 |
| Yiligum[S18] | $CoO_x$/NC | 0.84 | 0.64 | 5.11 |
| Y. L. Niu[S19] | $Fe_3C$@Fe/N -graphene | 0.93 | 0.72 | 3.75 |
| E. Zhang[S1] | Co@NCNT | 1.03 | 0.82 | 6.3 |
| D. X. Ji[S20] | Fe-CACNFs | 0.96 | 0.83 | 4.52 |
| Y. Hu[S21] | $Fe_3C$/C-700 | 0.90 | 0.73 | 4.20 |
| L. Shang[S22] | Co,N-CNF | 0.9 | 0.81 | 5.71 |
| P. Zhang[S23] | Carbon-L | 0.86 | 0.70 | 4.6 |
| T. R. Zhan[S24] | NiFe-LDH/rGO | 0.80 | 0.64 | 4.20 |
| X. J. Fan[S25] | Fe3C-GNRs | 0.94 | 0.78 | 4.20 |
| S. Yasuda[S26] | Fe–N–C/VA -CNT | 0.89 | 0.76 | 6.00 |
| W. Xia[S27] | Co@Co3O4@ C-CM | 0.9 | 0.81 | 5.4 |
| J. Zhang[S28] | Fe/Co/WC @NC | 0.91 | 0.82 | 6.2 |

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