

## Supporting Information

### Interface-tuned Mo-based nanospheres for efficient oxygen reduction and hydrogen evolution catalysis

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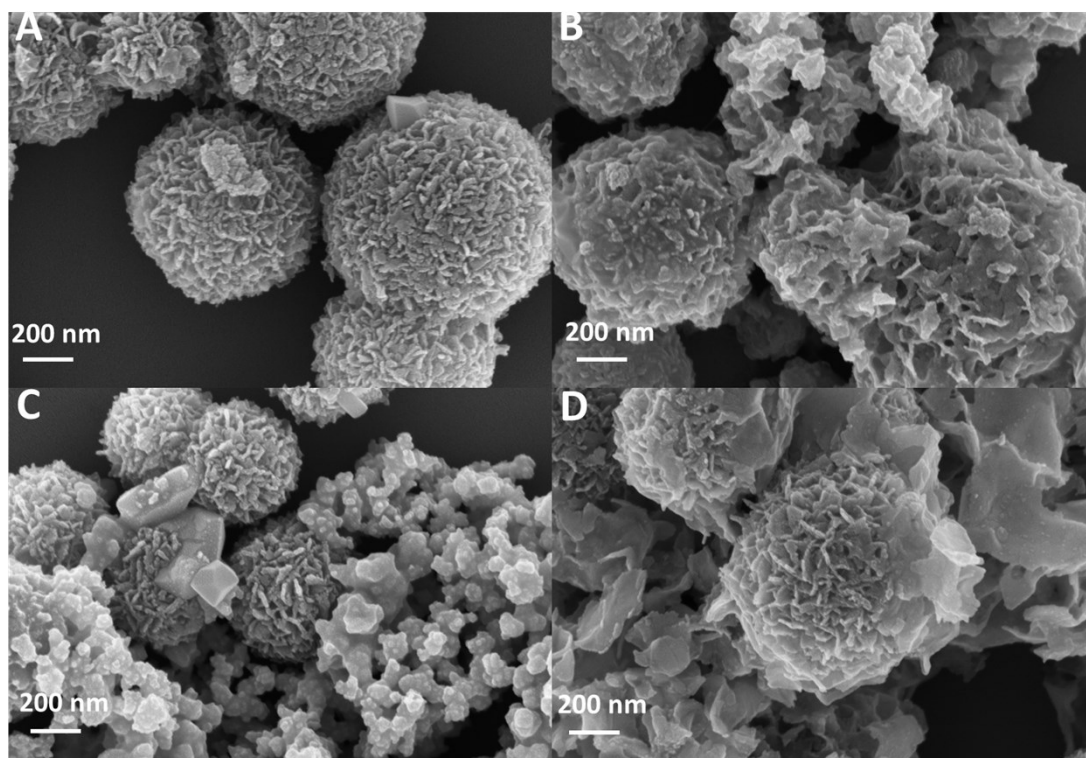


Figure S1 SEM images of (A) HNs-Co-2, (B) HNs-Co-6, (C) HNs-Co-10, and (D) HNs-Co-12 catalysts.

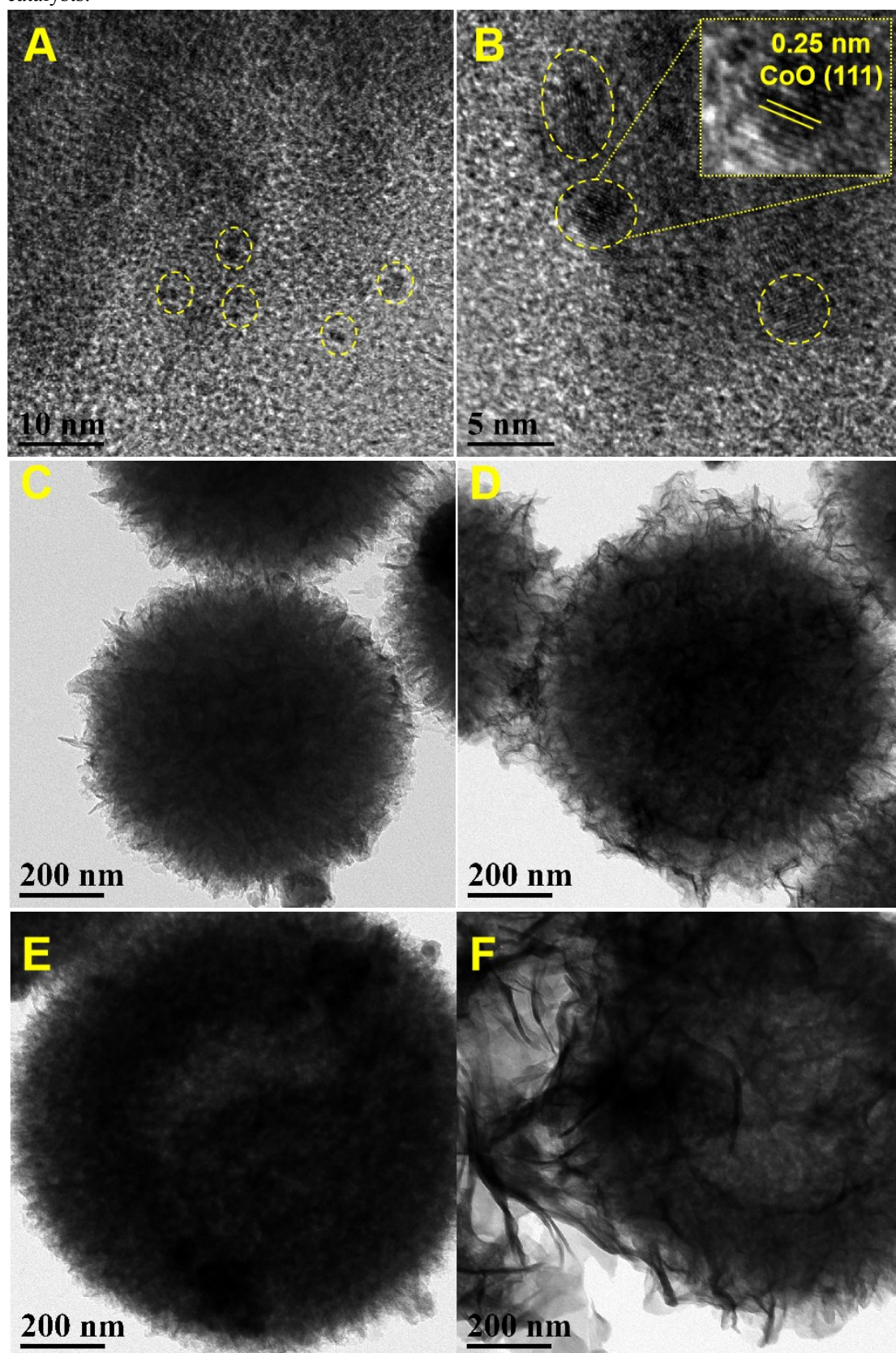


Figure S2 (A,B) High-resolution TEM images of (A) HNs and (B) HNs-Co; (C-F) HRTEM images of (C) HNs-Co-2, (D) HNs-Co-6, (E) HNs-Co-10, and (F) HNs-Co-12 catalysts.

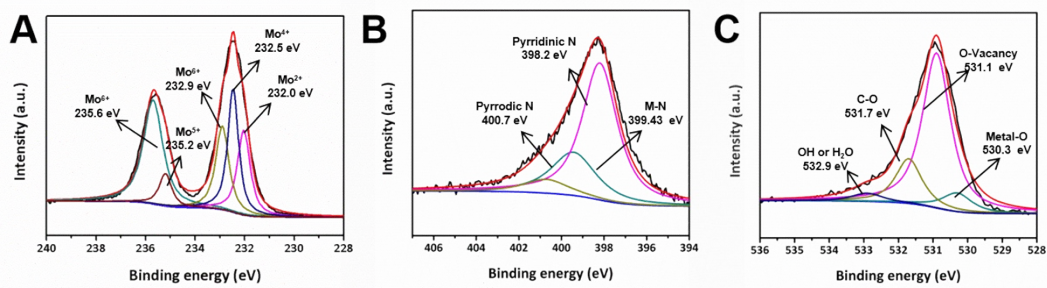


Figure S3 High-resolution (A) Mo 3d, (B) N 1s, and (C) O 1s XPS spectra of HNs.

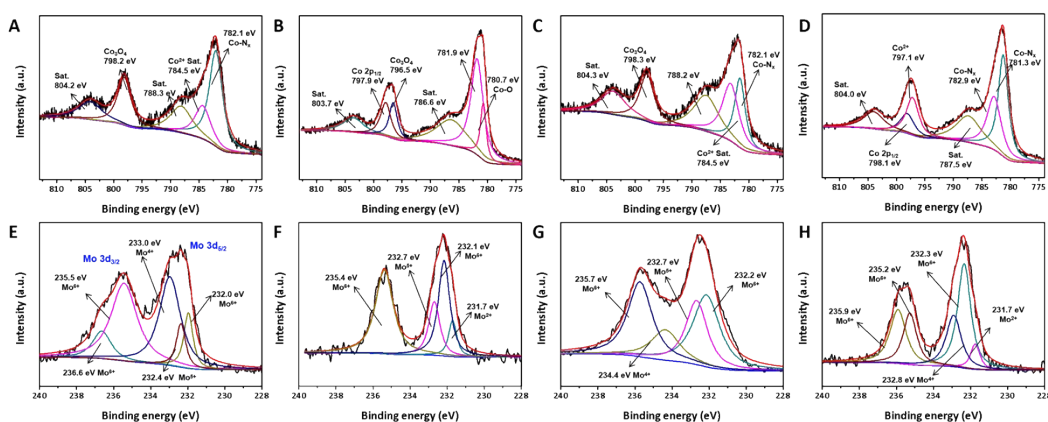


Figure S4 High resolution Co 2p and Mo 3d XPS spectra of (A, F) HNs-Co-2, (B, G) HNs-Co-6, (C, H) HNs-Co-10, and (E) HNs-Co-12 catalysts.

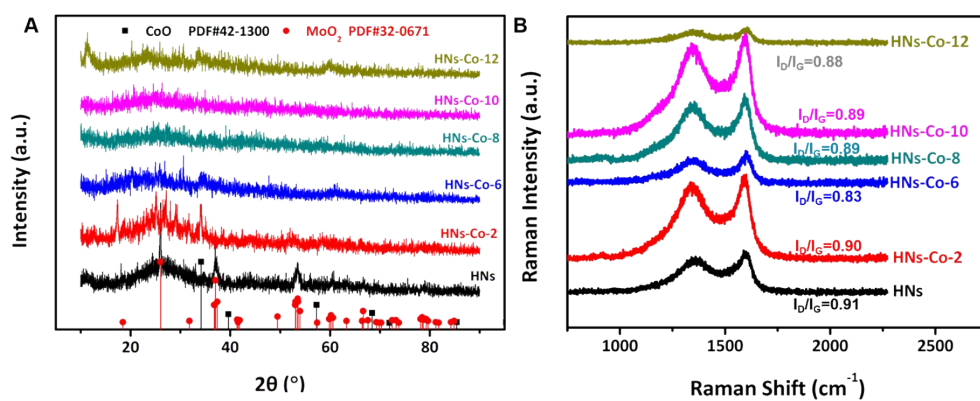


Figure S5 (A) XRD patterns and (B) Raman spectra of HNs and HNs-Co-X with different Co contents.

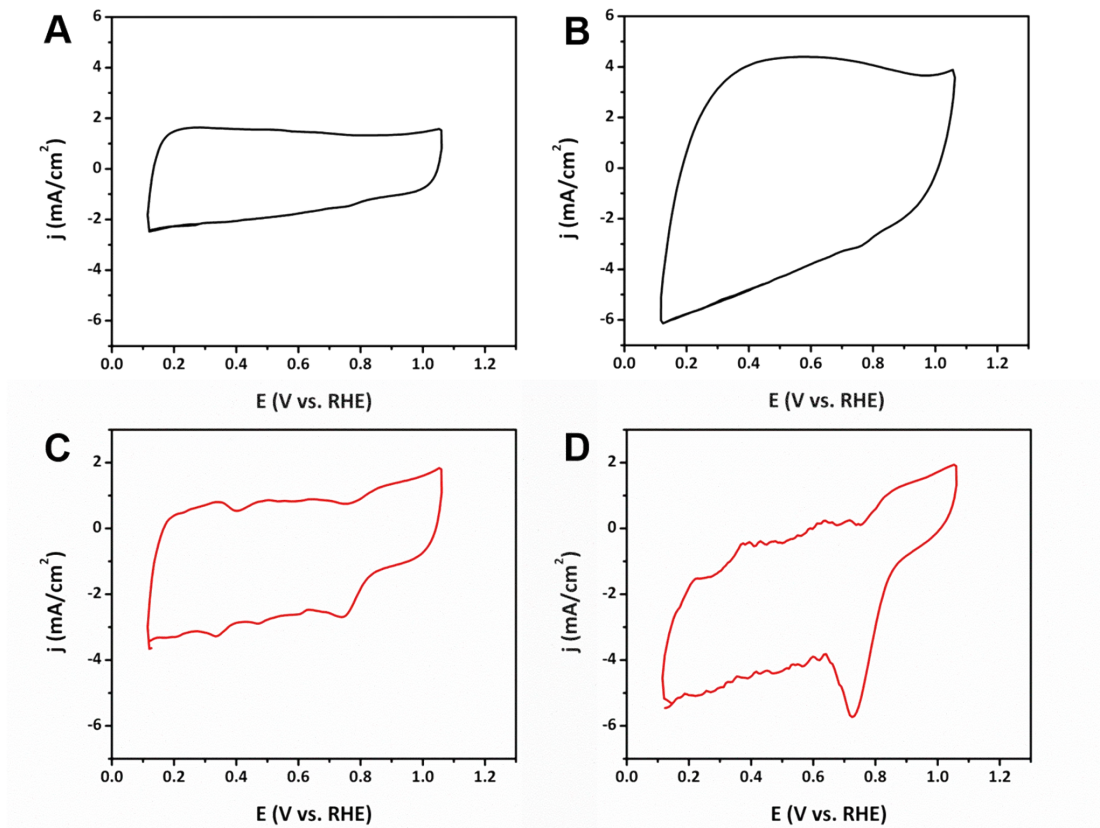


Figure S6 (A, C) CV curves of HNs and (B, D) HNs-Co catalysts in  $N_2$  and  $O_2$ -saturated 0.1 M KOH solution.

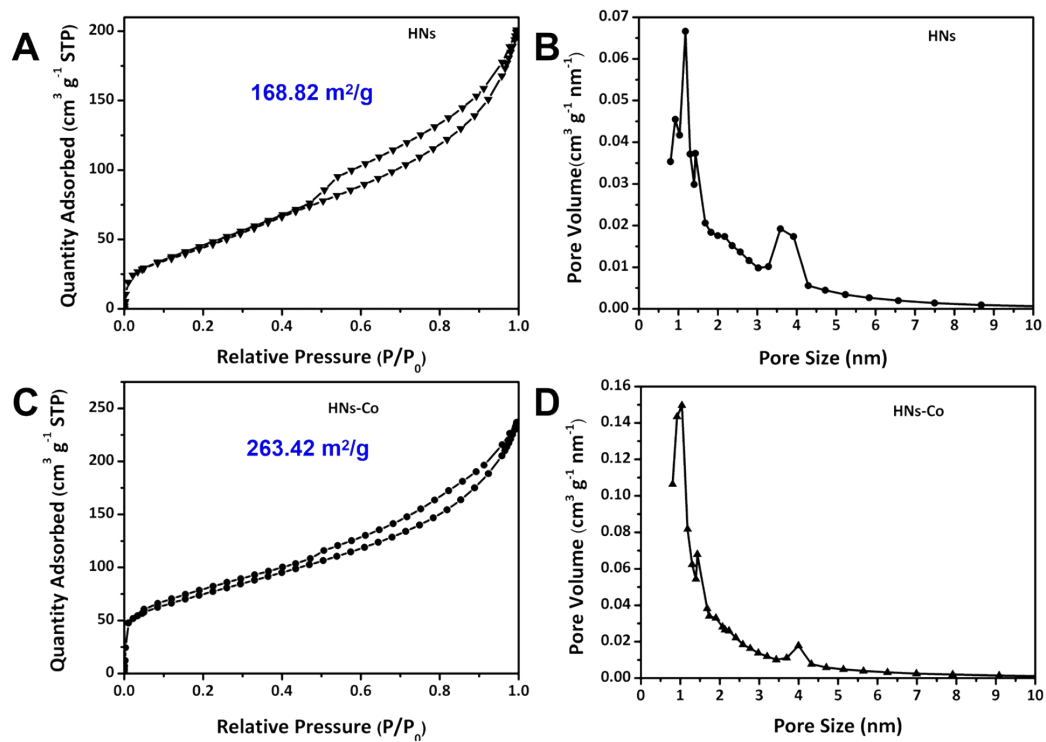


Figure S7 N<sub>2</sub> adsorption–desorption isotherms and pore size distributions of HNs (A, C) and HNs-Co (B, D) catalysts.

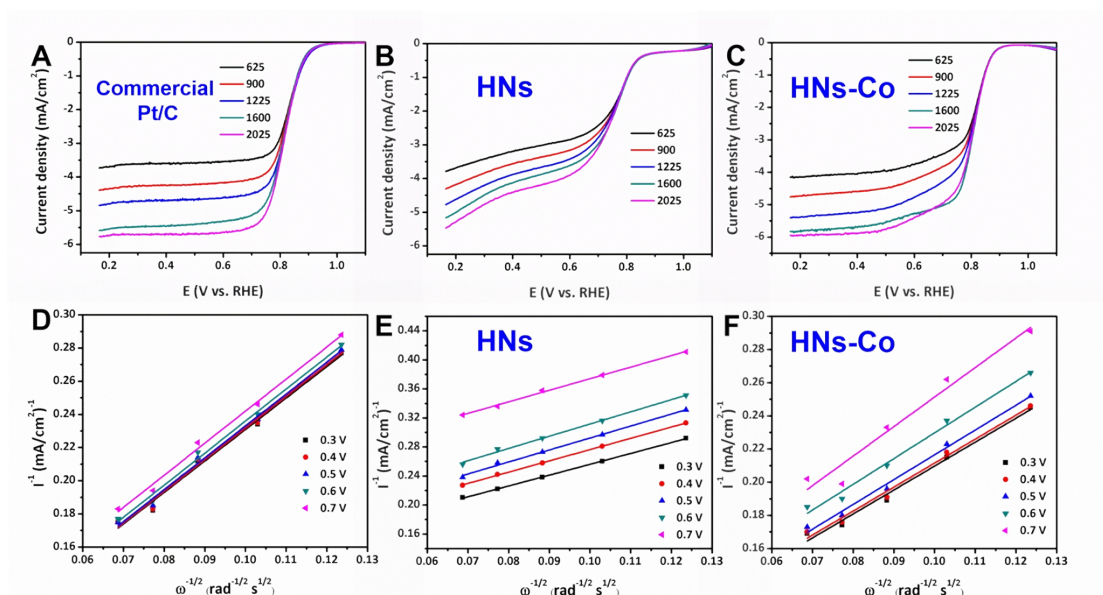


Figure S8 LSV curves in O<sub>2</sub>-saturated 0.1 M KOH solution and the corresponding Koutecky–Levich plots of commercial Pt/C (A, D), HNs (B, E), and HNs-Co (C, F) catalysts.

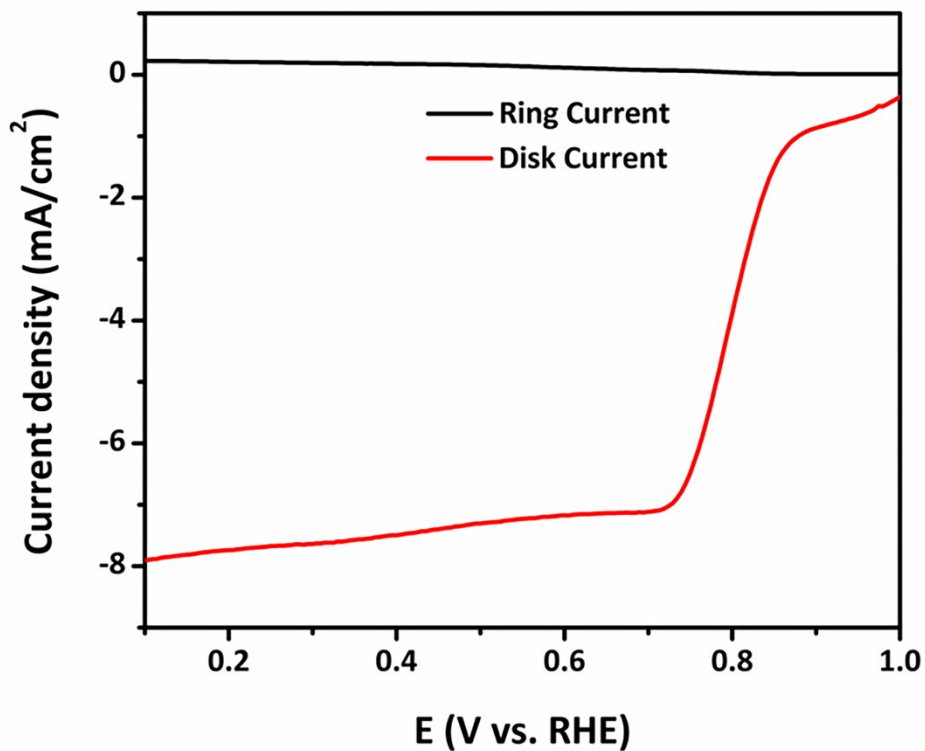
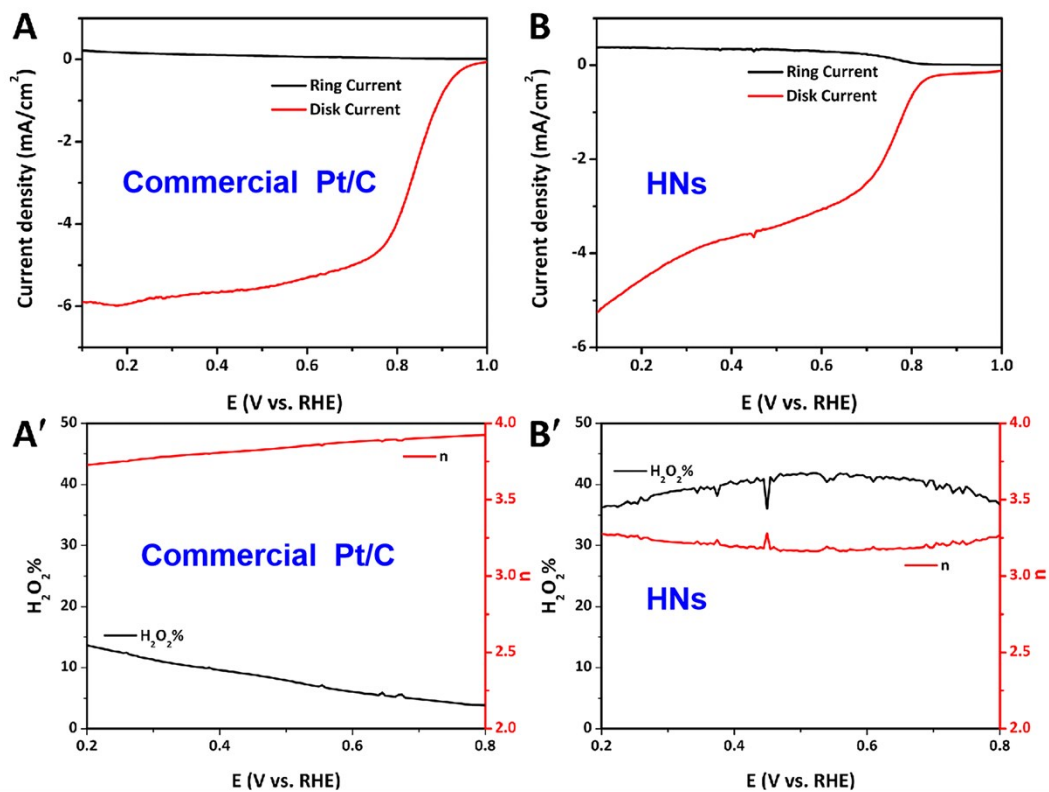


Figure S9 RRDE curve of HNs-Co catalyst.



FigureS 10 RRDE curves of commercial JM Pt/C (A, A') and HNs (B, B') catalysts.

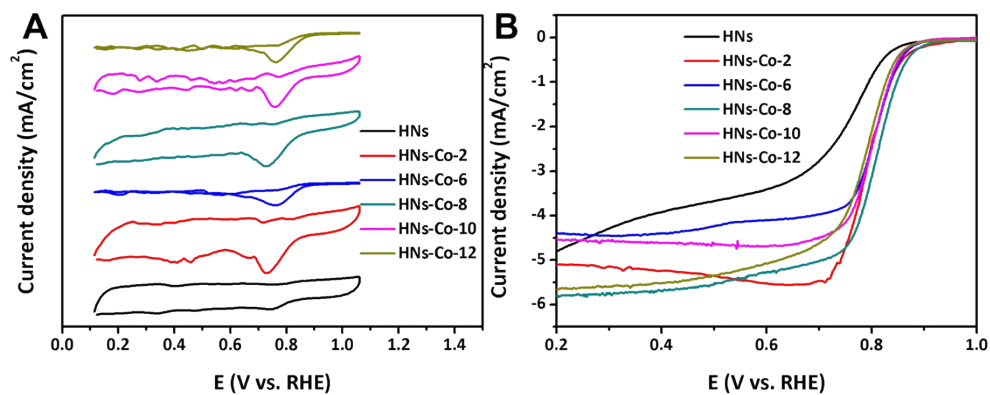


Figure S11 (A) CV and (B) LSV curves of HNs and HNs-Co-X catalysts with different Co contents.

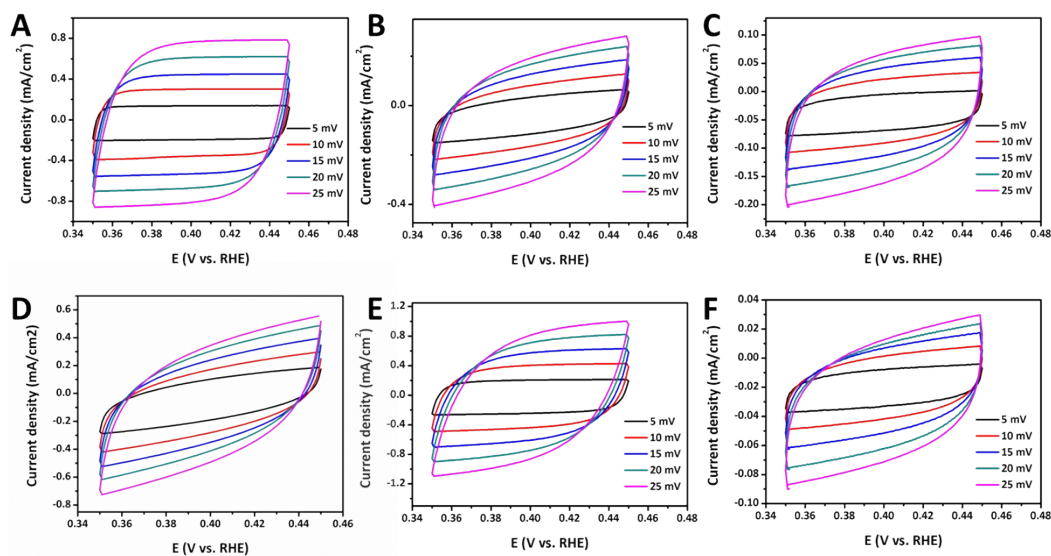


Figure S12 CV curves of (A) HNs, (B) HNs-Co-2, (C) HNs-Co-6, (D) HNs-Co-8, (E) HNs-Co-10, and (F) HNs-Co-12 catalysts at different scan rates between 0.35 V and 0.45 V.

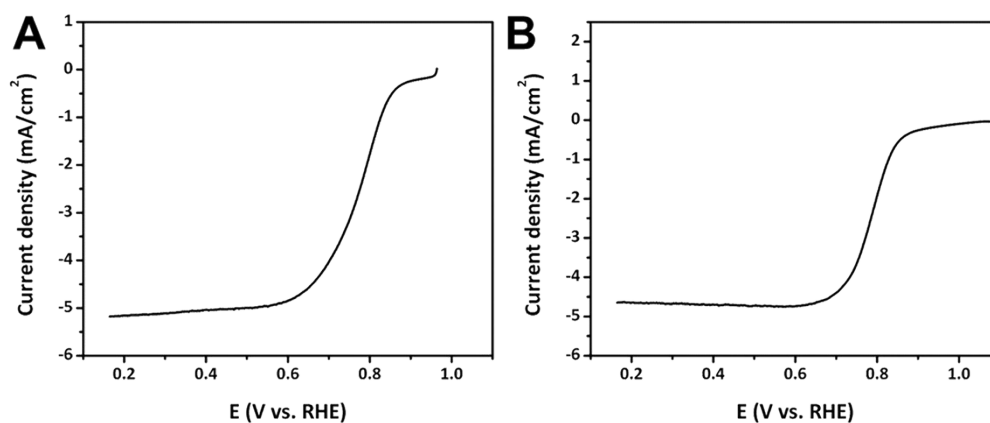


Figure S13 LSV curves of (A) CNN and (B) CNN-Co for ORR.

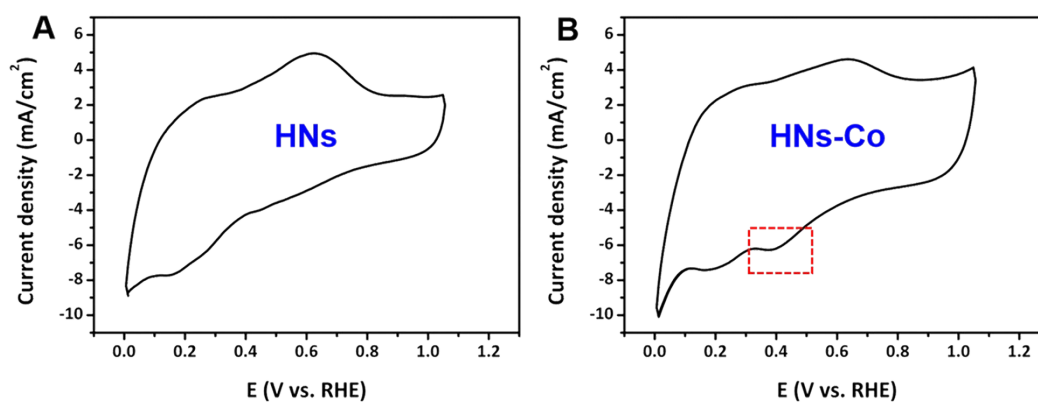


Figure S14 CV curves of (A) HNs and (B) HNs-Co catalysts recorded in 0.1 M  $\text{HClO}_4$  aqueous solution.

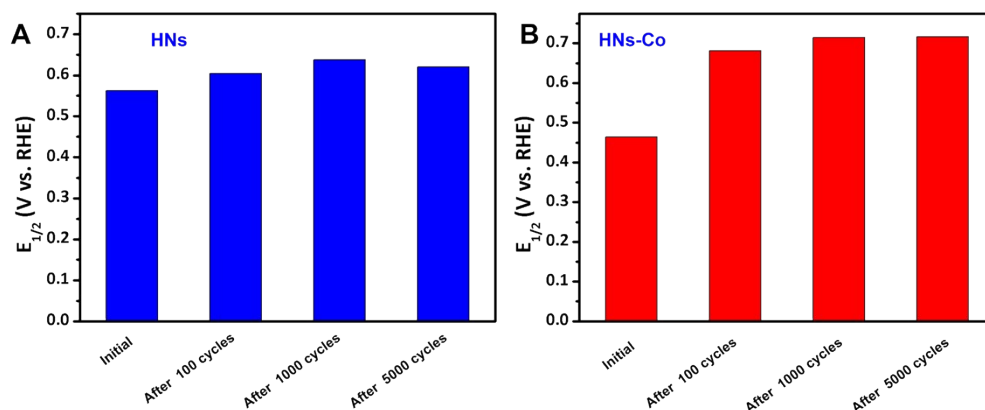


Figure S15  $E_{1/2}$  comparison of (A) HNs and (B) HNs-Co catalysts before and after potential cycling in 0.1 M  $\text{HClO}_4$  aqueous solution.

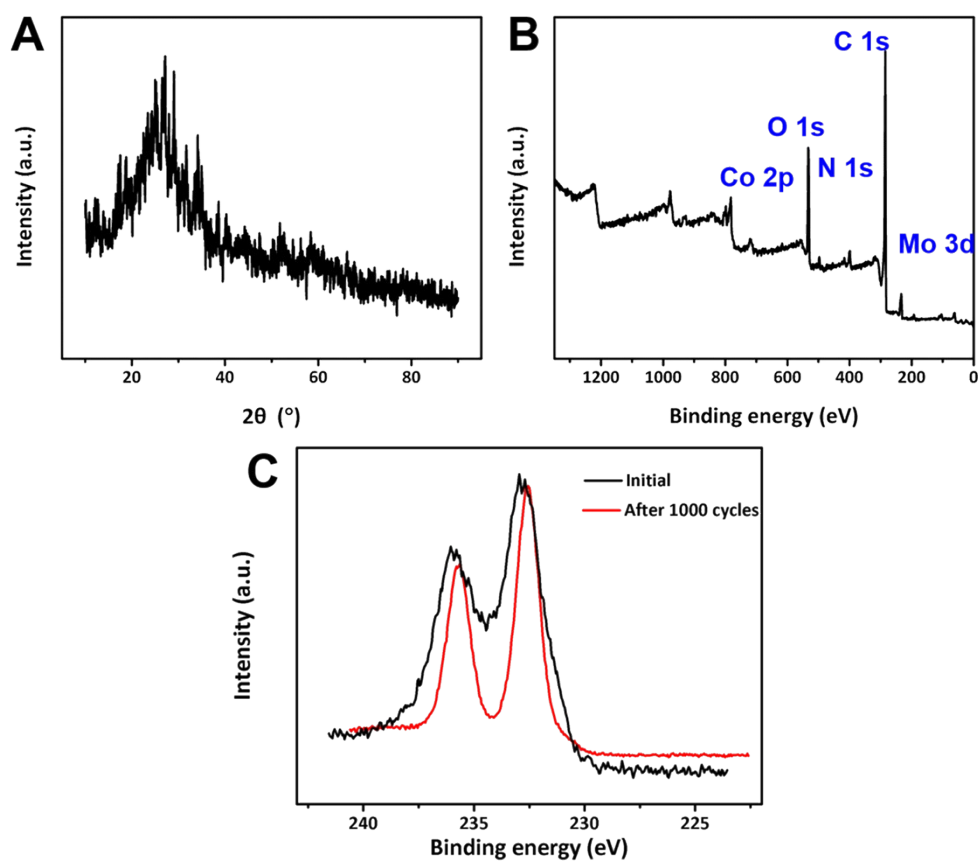


Figure S16 (A) XRD pattern, (B) XPS survey, and (C) high resolution Mo 3d XPS spectra of HNs-Co after 1000 cycles in acidic medium.



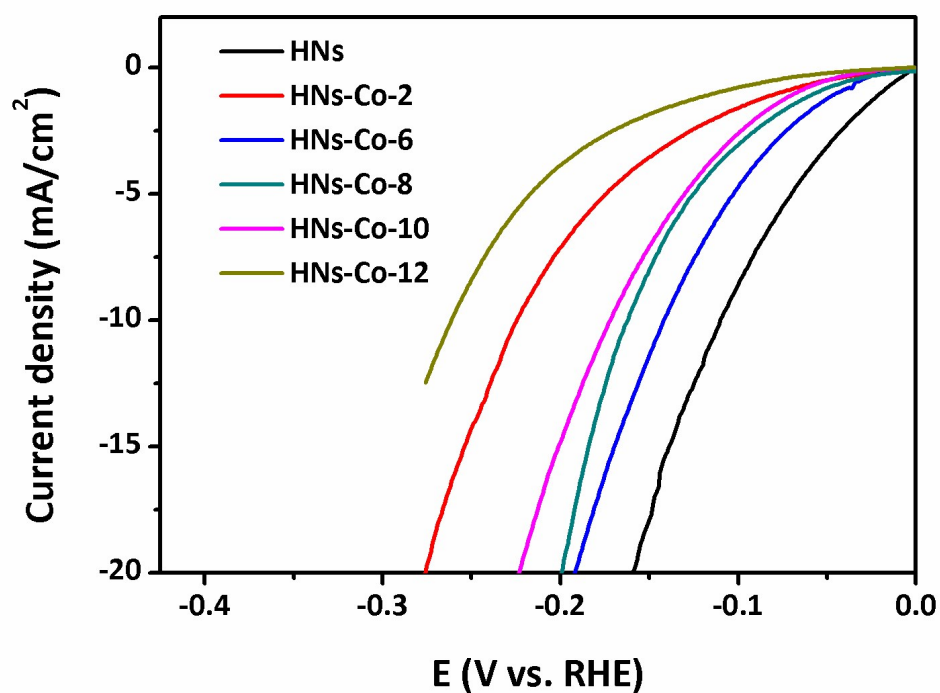


Figure S17 HER LSV curves of HNs, and HNs-Co-X with different Co contents in 1 M KOH aqueous solution.

Table S1 Surface compositions of HNs and HNs-Co-X catalysts measured by XPS.

Catalysts	C	N	O	Mo	Co
HNs	67.06	13.18	14.26	5.17	0
HNs-Co-2	77.11	4.25	15.05	0.96	2.63
HNs-Co-6	59.82	3.1	30.63	0.69	5.77
HNs-Co-8	82.54	4.15	10.73	0.59	1.98
HNs-Co-10	67.65	7.87	18.79	2.44	3.25
HNs-Co-12	53.78	2.68	33.75	0.74	9.05

Table S2 Electrical conductive information of the all samples.

Samples	Resistivity ( $\Omega \cdot \text{cm}$ )	Conductivity ( $\text{s/cm}$ )
HNs	0.15	$6.67 \cdot 10^{-3}$
HNs-Co-2	0.12	$8.33 \cdot 10^{-3}$
HNs-Co-6	0.09	$1.11 \cdot 10^{-3}$
HNs-Co-8	0.06	$1.67 \cdot 10^{-3}$
HNs-Co-10	0.07	$1.43 \cdot 10^{-3}$
HNs-Co-12	0.08	$1.25 \cdot 10^{-3}$

Table S3 ORR catalysis comparison of HNs-Co and reported Mo-based catalysts in 0.1 M KOH solution.

Catalyst	$E_{1/2}$ (mV)	Reference
<b>HNs-Co</b>	<b>0.81</b>	<b>This work</b>
Mo <sub>2</sub> C-GNR	0.80	1
V-MoS <sub>2</sub> -15	0.73	2
Mo <sub>2</sub> C-C-5	0.71	3
Mo-N/C@MoS <sub>2</sub>	0.81	4
MoO <sub>2</sub> -G-20 h	about 0.66	5
rGMS-600	0.70	6

Table S4 ORR catalysis comparison of HNs-Co and reported Mo-based catalysts in acidic medium.

Catalyst	$E_{1/2}$ (mV)	Electrolyte	Reference
<b>HNs-Co</b>	<b>720</b>	<b>0.1 M HClO<sub>4</sub></b>	<b>This work</b>
Co <sub>0.6</sub> Mo <sub>1.4</sub> N <sub>2</sub>	about 500	0.1 M HClO <sub>4</sub>	7
MoN	About 325	0.1 M HClO <sub>4</sub>	8
Co <sub>0.50</sub> Mo <sub>0.50</sub> N <sub>y</sub> /NCNC	about 560	0.5 M H <sub>2</sub> SO <sub>4</sub>	9
(Fe <sub>3</sub> Mo)-N/C-3	674	0.5 M H <sub>2</sub> SO <sub>4</sub>	10
Mo <sub>2</sub> C-GNR	600	0.5 M H <sub>2</sub> SO <sub>4</sub>	1

Table S5 HER catalysis comparison of HNs, HNs-Co, and reported Mo-based catalysts in 1 M KOH solution.

Catalyst	Overpotential (mV)	Reference
<b>HNs</b>	<b>111</b>	<b>This work</b>
<b>HNs-Co</b>	<b>163</b>	<b>This work</b>
MoO <sub>2</sub> -Ni NWs	58.4	11
MoO <sub>2</sub> /PDDA-rGO	57	12
MoSe <sub>2</sub> /MoO <sub>2</sub>	142	13
porous MoO <sub>2</sub>	27	14
Mo <sub>2</sub> C/C hybrids	140	15

## Reference

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