

Experiment

Chemicals

Cobaltous nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Sigma-Aldrich Corp. Nafion (D520, 5 wt.%) was purchased from DuPont Corp. Polyvinyl pyrrolidone (PVP, K30), sodium chloride (NaCl), Potassium hydroxide (KOH), and ethanol ($\text{C}_2\text{H}_5\text{OH}$) were purchased from Shanghai Chemical Corp. Commercial platinum/carbon (Pt/C) catalyst and RuO_2 (99.9%) catalyst were purchased from JM. All these chemicals were used as purchased without any purification.

Electrochemical calculation

At various potentials, the electron transfer number (n) per oxygen molecule involved during ORR was computed based on the following Koutecky-Levich (K-L) equation:

$$J^{-1} = J_L^{-1} + J_K^{-1} = B^{-1} \omega^{-1/2} + J_K^{-1} \quad [1]$$

where J represents the measured current, J_k represents the kinetic-limiting current, and ω expresses the electrode rotation rate. A series of current values (J) were collected by changing the electrode rotation rate. The linear graph can then be obtained by plotting the relationship between J and ω . The electron transfer number (n) of per oxygen molecule involved could be computed by using the slope (B) of the linear graph and the following relationship:

$$B = 0.62nFC_{\text{O}_2}D_{\text{O}_2}^{2/3}v^{-1/6} \quad [2]$$

where n represents the electron transfer number of per oxygen molecule in the ORR process, F expresses the Faradaic constant (96485 C mol^{-1}), C_{O_2} is the concentration of O_2 in 0.1 M KOH ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$), D_{O_2} is the diffusion coefficient of O_2 in 0.1 M KOH ($1.90 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and v represents the kinematic viscosity of 0.1 M KOH ($0.01 \text{ cm}^2 \text{ s}^{-1}$).

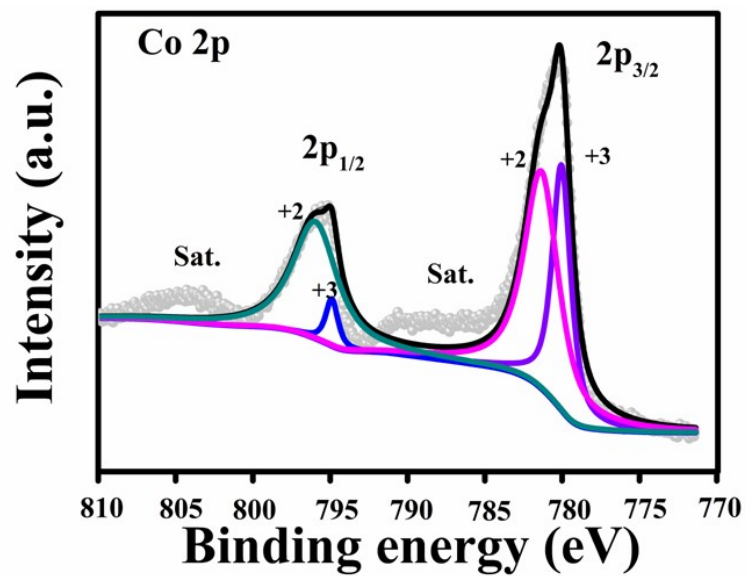


Fig. S1 The Co spectrum of Co₃O₄/C.

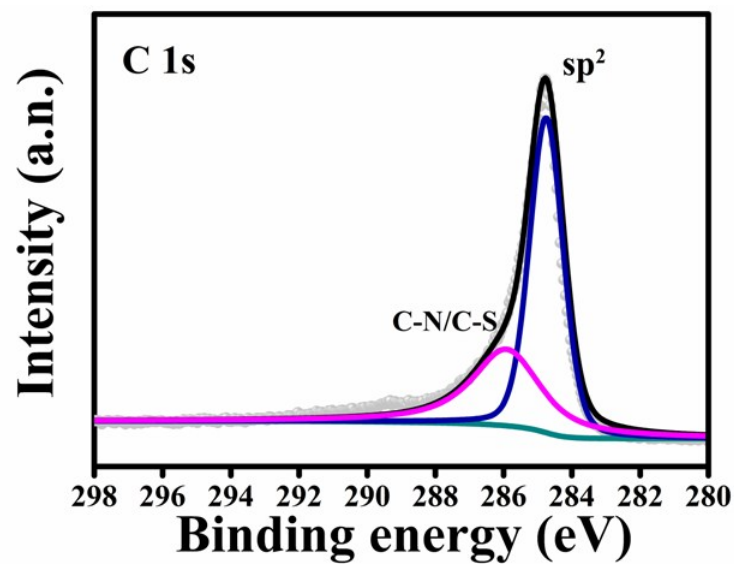


Fig. S2 The C spectrum of Co₉S₈/C.

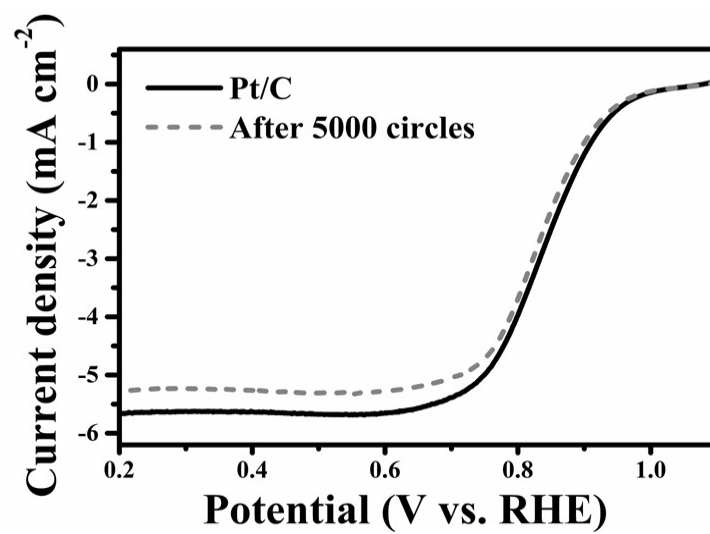
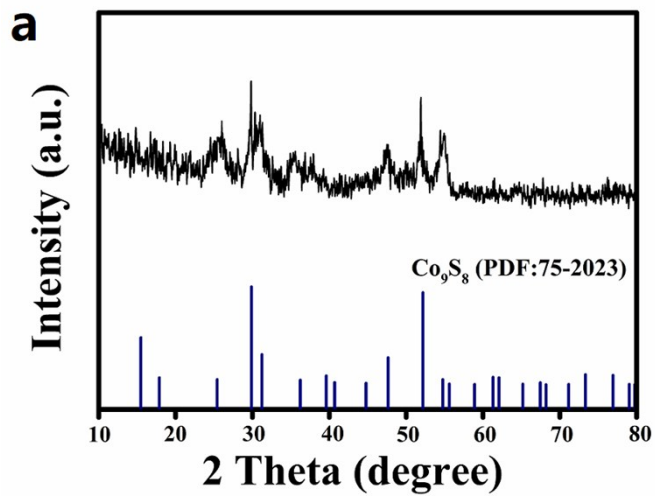


Fig. S3 Linear sweep voltammetry curves of the Pt/C catalyst before and after 5000 cycles.



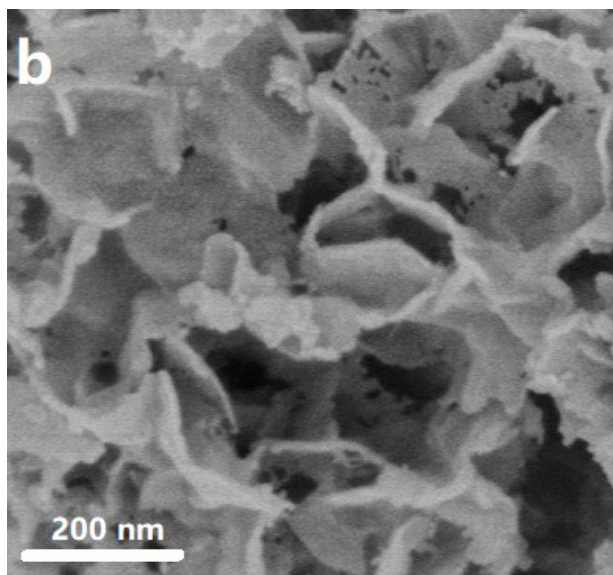


Fig. S4. the XRD (a) and SEM (b) pattern of the Co₉S₈/C after cycling testing

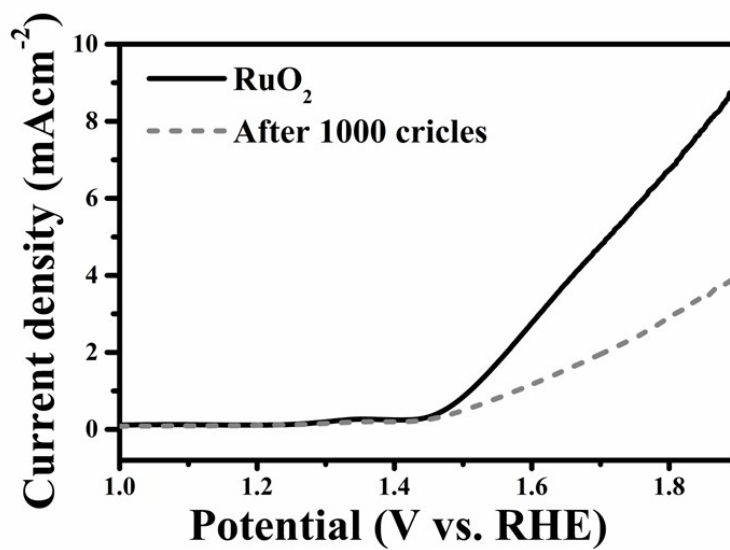


Fig. S5 Linear sweep voltammetry curves of the RuO₂ catalyst before and after 1000 cycles.

Table. S1 The E_{onset} and $E_{1/2}$ of $\text{Co}_9\text{S}_8/\text{C}$ and $\text{Co}_3\text{O}_4/\text{C}$.

Smamples	Co_9S_8	Co_3O_4
$E_{\text{onset}}/\text{V}$	0.892	0.780
$E_{1/2}/\text{V}$	0.778	0.652

Table. S2 The electrochemical performance of recently reported no-noble metal materials for the ORR and OER in an alkaline solution.

Catalysts	ORR		OER		Refs.
	$E_{\text{onset}} (\text{V})$	$E_{1/2} (\text{V})$	$E_{\text{onset}} (\text{V})$	Overpotential at $10 \text{ mA} \cdot \text{cm}^{-2}$ (V)	
$\text{Co}_9\text{S}_8/\text{C}$	0.892	0.778	1.500	0.434	This work
Co/C sphere	0.962		1.720		S1
S,N-Fe/N/C-CNT	0.850			0.370	S2
N-CCs		0.780		0.390	S3
NC/Co-NGC DSNC	0.920	0.820	1.640		S4
Co@NCNT HMS		0.871	1.552		S5
SWCNT@NPC		0.850		0.388	S6
egg-CMS	0.840	0.690	1.510		S7
Co@ $\text{Co}_3\text{O}_4/\text{NC}$		0.800	1.650		S8
P-Doped CoSe_2		0.870		0.230	S9

Reference

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