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Electronic Supplementary Information (ESI) for

Metal glycerolate complex-derived Co@NC as highly efficient bifunctional oxygen electrocatalyst

Ying Wang*, Hongjie Yuan, Fan Liu, Tianjun Hu*

School of Chemistry and Material Science, Shanxi Normal University, Linfen 041004, China. E-mail: wangyinghc@sxnu.edu.cn; hutj@sxnu.edu.cn.

Catalyst preparation

The Co-gly was syntheized according to the previous report1.[1] Typically, 2.5 mmol $Co(CH_3COO)_2 \cdot 4H_2O$ and 3 g melamine were added into the 20 mL glycerol. After a 2-h continuous stirring, the mixture was poured into Teflon autoclave and heated at 180 ºC for 1.5 h. After washing and dry overnight at 60 ºC, the powders were calcined under nitrogen atmosphere at 550 ºC for 2 h, followed by heating for 2 h at the temperature of 600, 700, 800 and 900 º C, respectively (2 ºC min^{-1}). Afterwards, the solids were dispersed in 0.5 M HCl for 12 h. Then the powders were collected, washed with water and dried overnight. The above samples are named as Co@NC/NCNS-600, Co@NC/NCNS-700, Co@NC/NCNS-800 and Co@NC/NCNS-900, respectively.

Physical characterization

The structure of samples was analyzed by X-ray diffraction (XRD) using Rigaku ultima Ⅳ diffractometer. The composition and valence state of elements were tested by X-ray photoelectron spectroscopy (XPS) analysis using Thermo VG ESCALAB210 spectrometer. Raman spectroscopy was studied using inVia-Reflex microscopic confocal Raman spectrometer (Renishaw, UK) to investigate the graphitization degree. The morphology of samples was measured by transmission electron microscope (TEM) and high-resolution TEM using JEM-2100 instrument.

Electrochemical measurement

The electrochemical performance was tested on CHI660E electrochemical workstation using a three-electrode system in 0.1 M KOH solution. The Pt wire and Hg/HgO electrode were utilized as counter and reference electrodes, respectively. The rotating disk electrode (RDE, 0.126 cm^2) with catalyst loading of 0.2 mg cm^{-2} was used as the working electrode. The linear sweep voltammetry (LSV) curves for ORR and OER were recorded with a scan rate of 10 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 0.01 Hz to 100 KHz with an amplitude of 5 mV. The electrochemically active surface area (ECSA) of samples was calculated by double layer capacitance (C_{dl}) which was tested by cyclic voltammogram (CV) at different scan rate. The double layer current *I* is linearly proportional to the scan rate (ν), and the capacitance C_{dl} is given by the equation: $I = C_{dl}\nu$. The ECSA was obtained using the equation: ECSA = C_{dl}/C_s, where C_s is the specific capacitance of sample or the capacitance of an atomically smooth surface of the material with unit area.

The electron transfer number can be calculated based on the Koutecky-Levich equation:

$$J^{-1} = J_k^{-1} + J_d^{-1} = J_k^{-1} + (B\omega^{1/2})^{-1} \qquad (1)$$

$$B=0.62nFcD^{2/3}\nu^{-1/6} \qquad (2)$$

Where J is the measured current density, J_k and J_d are the kinetic and diffusion limited current densities, respectively; F is the Faraday constant (96485 C mol^{-1}), n is transferred electron number, c is the saturated concentration of oxygen (1.2×10^{-6} mol cm^{-3}), D is the diffusion coefficient of oxygen (1.9×10^{-5} cm^2 s^{-1}) and ν is kinematic viscosity of the electrolyte (0.01 cm^2 s^{-1}).

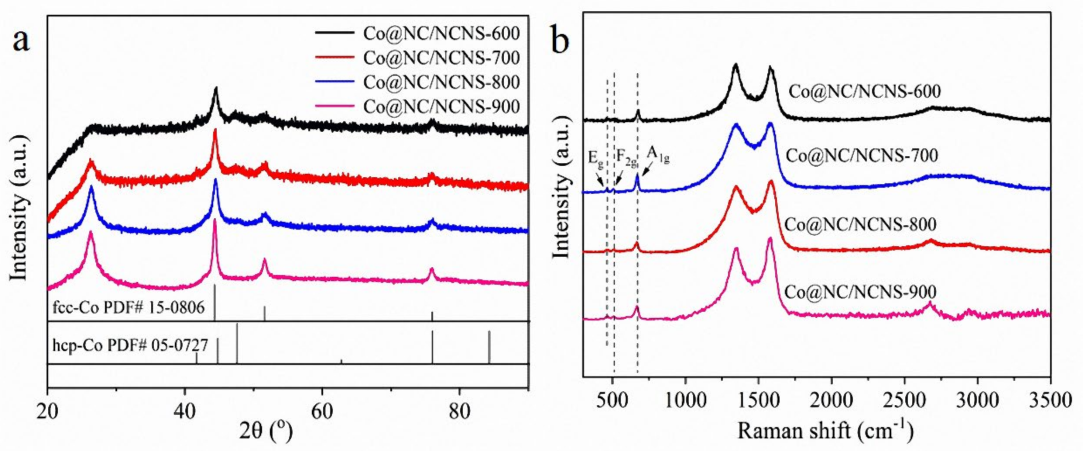

Fig. S1. XRD patterns (a) and Raman spectra (b) of Co@NC/NCNS samples.

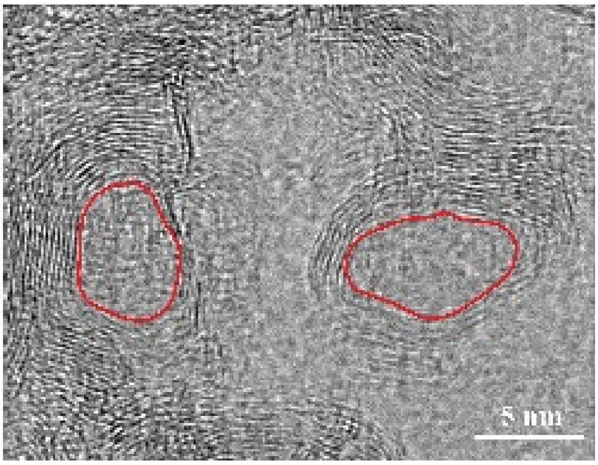

Fig. S2. The TEM image of Co@NC/NCNS-800.

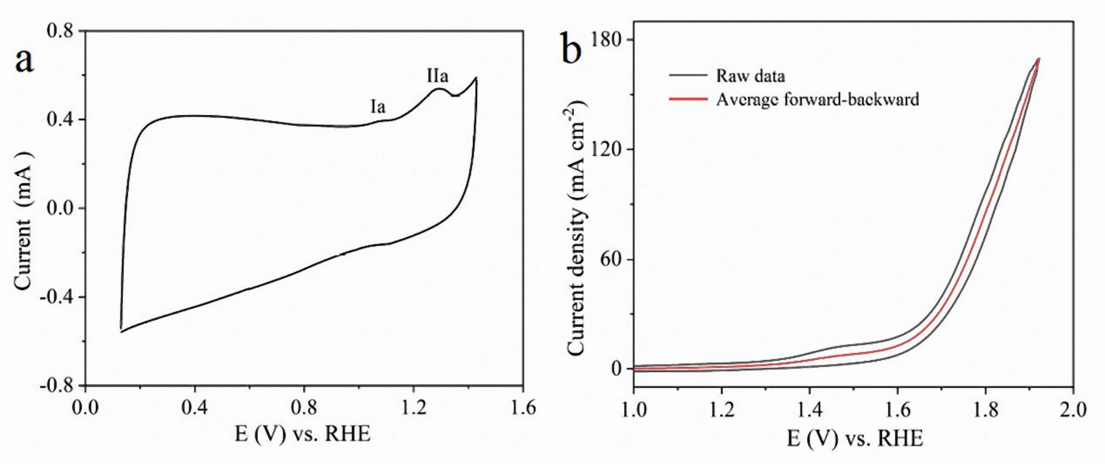

Fig. S3. CV curve for Co@NC/NCNS-800 in N_2 saturated 0.1 M KOH solution (a); CV cureve of OER for Co@NC/NCNS-800 in 0.1 M KOH solution (b).

The peaks Ia and IIa are attributed to the electrochemical transition involved Co^{2+}/Co_3O_4 and $Co_3O_4/CoOOH$ species, respectively. The peak at 1.45 V is attributed to the oxidation of CoOOH to CoO_2. The OER activity is capacity-corrected by taking an average of forward and backward scans.

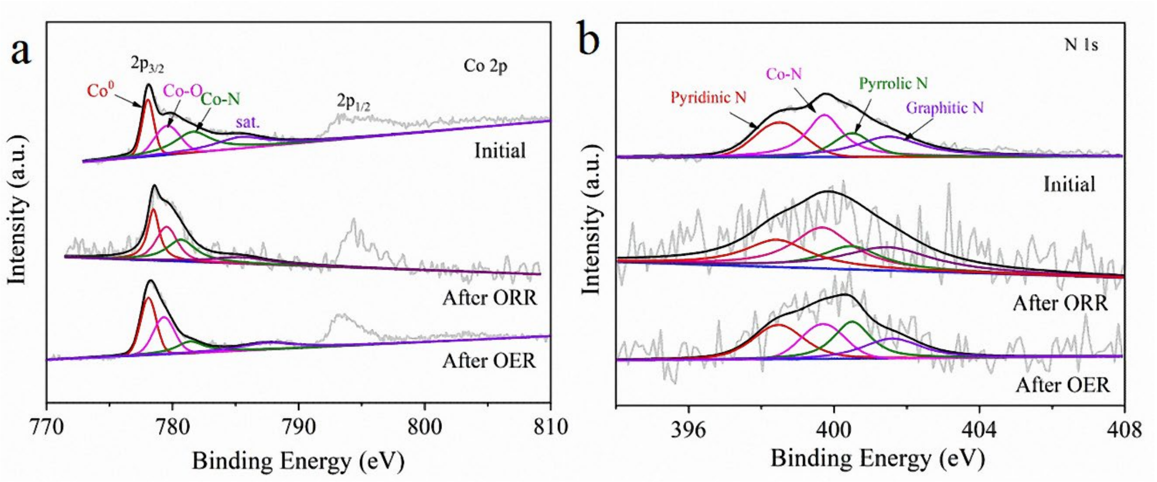

Fig. S4. Co 2p (a) and N 1s (b) spectra of Co@NC/NCNS-800 before and after OER stability test.

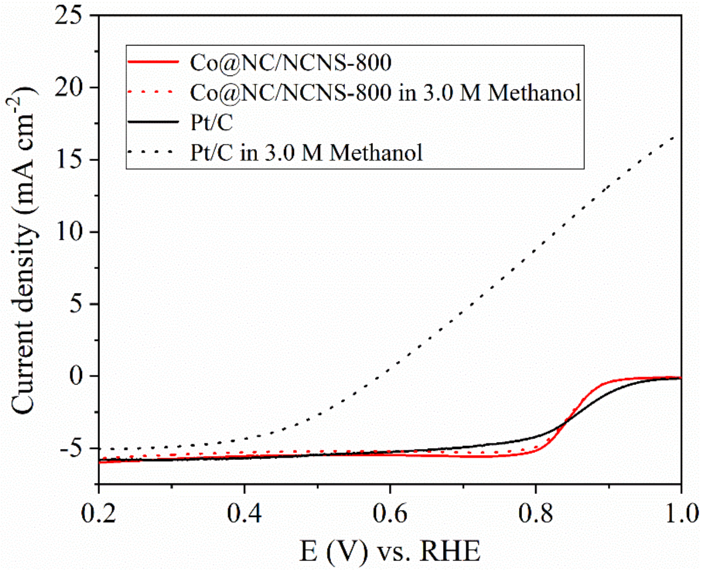

Fig. S5. LSV curves of Co@NC/NCNS-800 in O_2-saturated 0.1 M KOH solution with or without 3.0 M methanol solution.

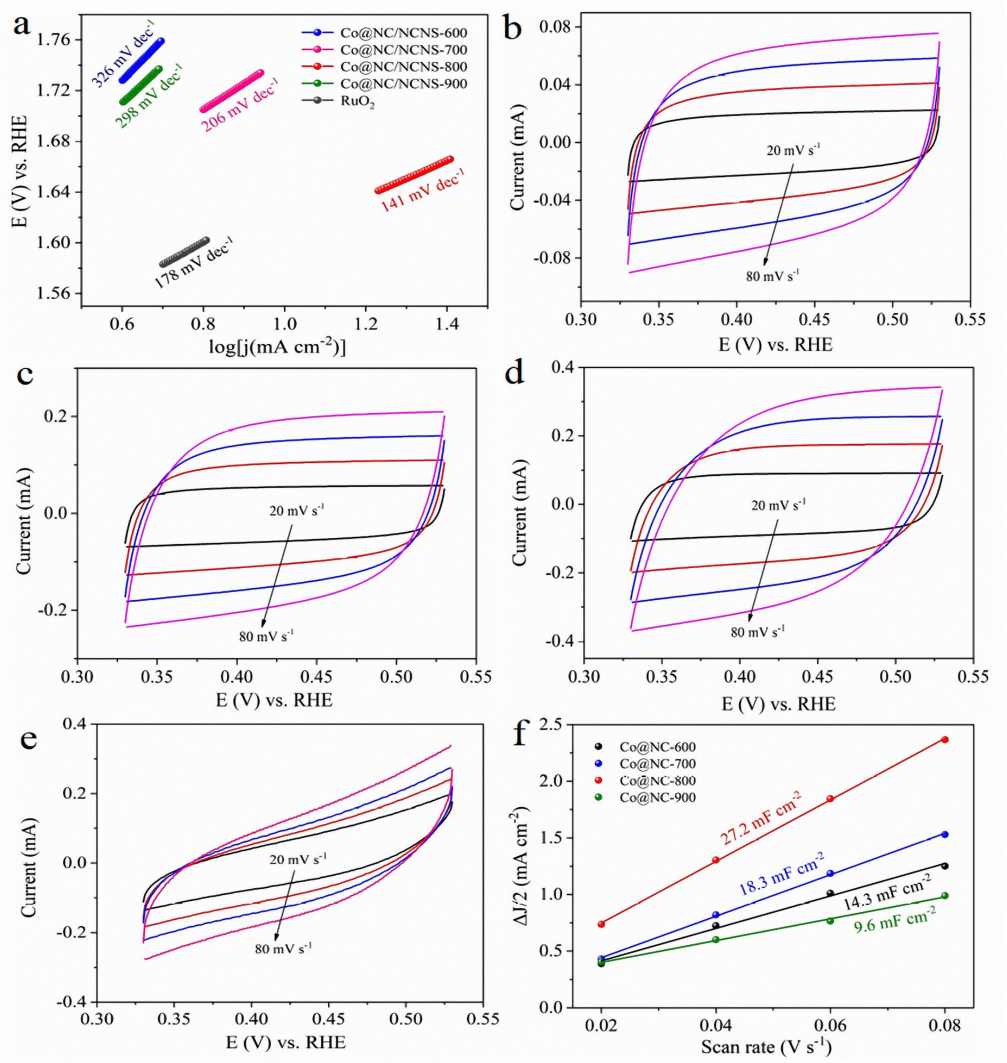

Fig. S6. The OER Tafel slopes of Co@NC/NCN samples (a); Cyclic voltammetry curves at different scan rate for Co@NC/NCNS-600 (b), Co@NC/NCNS-700 (c), Co@NC/NCNS-800 (d) and Co@NC/NCNS-900 (e); Capacitive currents as 0.44 V as a function of scan rate ($\Delta J = J_a$-J_c) (f).

Table S1 The surface chemical composition content of Co@NC/NCNS obtained by XPS

Sample	Surface composition (at. %)								
	C	O	Co	N[a]					
				Total	N1	N2	N3	N4	N4/N1
Co@NC/NCNS-600	82.4	8.4	0.8	8.4	47.5	15.1	20.2	17.2	0.36
Co@NC/NCNS-700	84.2	8.1	1.1	6.6	30.5	23.1	27.1	19.4	0.64
Co@NC/NCNS-800	86.1	7.6	1.0	5.3	26.4	31.6	16.4	25.6	0.97
Co@NC/NCNS-900	87.4	7.1	0.9	4.6	24.1	18.9	20.1	36.9	1.53

[a] N1: pyridinic N; N2: Co-N; N3: pyrrolic N; N4: graphitic N.

Table S2 Comparison in the ORR activities

Catalyst material	$E_{j=1/2}$ (V)	Reference
Co@NC/NCNS-800	0.84	This work
Fe/Fe_5C_2@N-C-1000	0.85	2
Co3O_{4-x}/NG	0.84	3
FeCo@NCNS	0.83	4
CoFe/NH-C NS	0.84	5
Ni_3Fe/N-C sheets	0.78	6
FeNiCo@NC-P	0.84	7
C-MOF-C2-900	0.82	8
NiCo-0.8@N-CNFs-800	0.82	9
Co@Co_3O_4/N-C	0.81	10
Co@C@NC	0.83	11

Table S3 Comparison in the OER activities

Catalyst material	$E_{j=10}$ (V)	Reference
Co@NC/NCNS-800	1.62 ($E_{j=15}$)	This work
(Cu, Co)$_3$OS$_3$@CNT-CN	1.66	12
FeP/Fe$_2$O$_3$@NPCA	1.63	13
FeN/SNC-900-3	1.63	14
CoNC-NB2	1.58	15
Co$_2$P/NPG	1.55	16
NGC@Co$_4$S$_3$/Ni$_x$S$_6$/NiOOH	1.59	17
Co$_9$S$_8$-NSHPCNF	1.58	18
In-CoO/CoP FNS	1.60	19
Co@CNT/MSC	1.62	20

Table S4 Comparison in the oxygen electrode activities

Catalyst material	$E_{j=1/2}$ (V)	$E_{j=10}$ (V)	ΔE (V)	Reference
Co@NC/NCNS-800	0.84	1.62 ($E_{j=15}$)	0.78	This work
Co-Co_3O_4@NAC	0.80	1.61	0.81	21
Ni-$CNNs_{-0.7}$	0.765	1.62	0.855	22
Co@CNT/MSC	0.84	1.62	0.78	20
FeCo@NCNS	0.83	1.60	0.77	4
Co/NGC-3	0.85	1.63	0.78	5
Ni_3Fe/N-C sheets	0.78	1.62	0.84	6
FeCo/FeCoNi@NCNTs-HF	0.85	1.61	0.76	23
FeNiCo@NC-P	0.84	1.54	0.70	7
DAP-DAB-$C_4H_6O_4 \cdot Co \cdot 4H_2O$	0.88	1.60	0.72	24
H-Co@FeCo/N/C	0.91	1.61	0.70	25
C-MOF-C2-900	0.82	1.58	0.76	8
Co/N-$HPC_{150/800}$	0.85	1.70	0.85	26
NiCo-0.8@N-CNFs-800	0.82	1.61	0.79	9
Co@Co_3O_4/N-C	0.81	1.62	0.81	10
FeNi/N-CPCF-950	0.87	1.59	0.72	27
ZOMC	0.85	1.56	0.71	28

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