† Electronic Supplementary Information

Multiple Active Components Synergistically Driven Cobalt and Nitrogen Co-Doped Porous Carbon as High-performance Oxygen Reduction Electrocatalyst

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Table. S1 The raw materials for the preparation of the C@N and Co@C-N catalysts.

Samples	Amount of $g\text{-}C_3N_4$ (g)	Molar Quantity of Co-source (mmol)	Amount of D-glucose (g)	Hydrothermal Temperature (℃)	Thermalysis Temperature (℃)	Atmosphere
C@N	0.5	--	2.16	120	900	Ar
Co@C-N-120-900	0.5	1	2.16	120	900	Ar
Co@C-N-140-900	0.5	1	2.16	140	900	Ar
Co@C-N-160-900	0.5	1	2.16	160	900	Ar

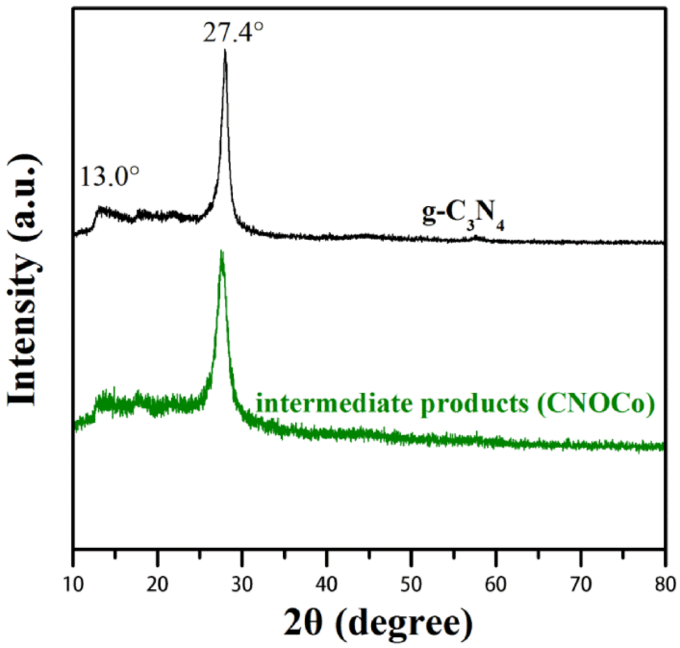

Figure S1 XRD patterns of as-prepared porous g-C_3N_4 and intermediate products (CNOCo) under ST 120 ℃.

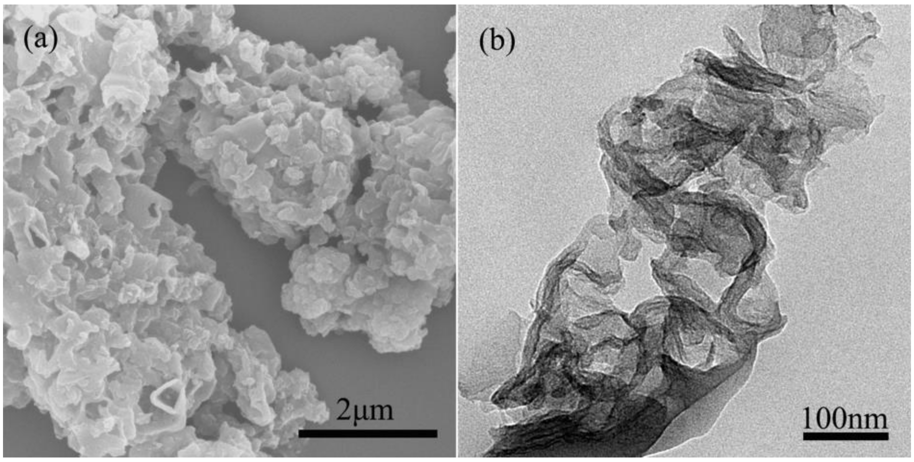

Figure S2 The SEM image (a) and TEM image (b) of porous g-C_3N_4.

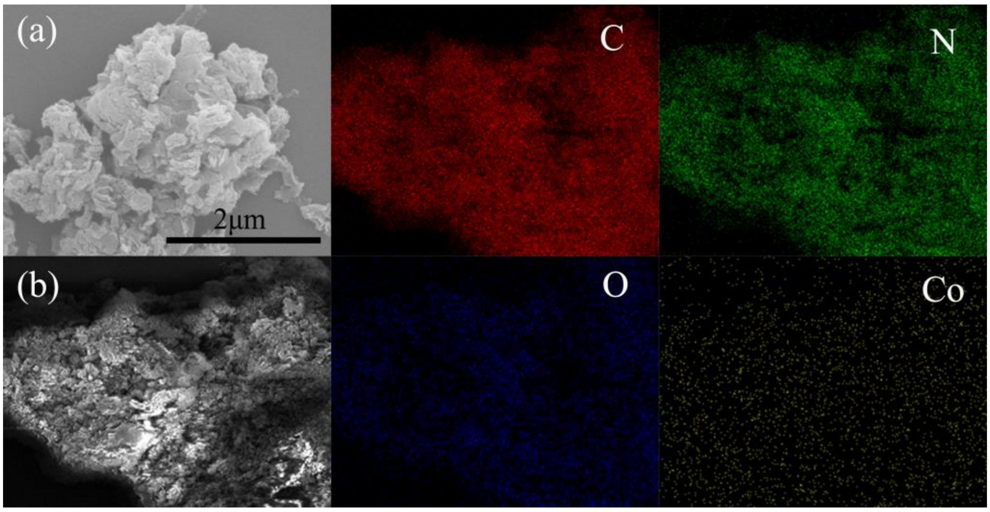

Figure S3 The SEM images (a and b) of intermediate products (CNOCo) under ST 120 ℃ and the corresponding EDS mapping elements C, N, O and Co for the boxed area of image (b).

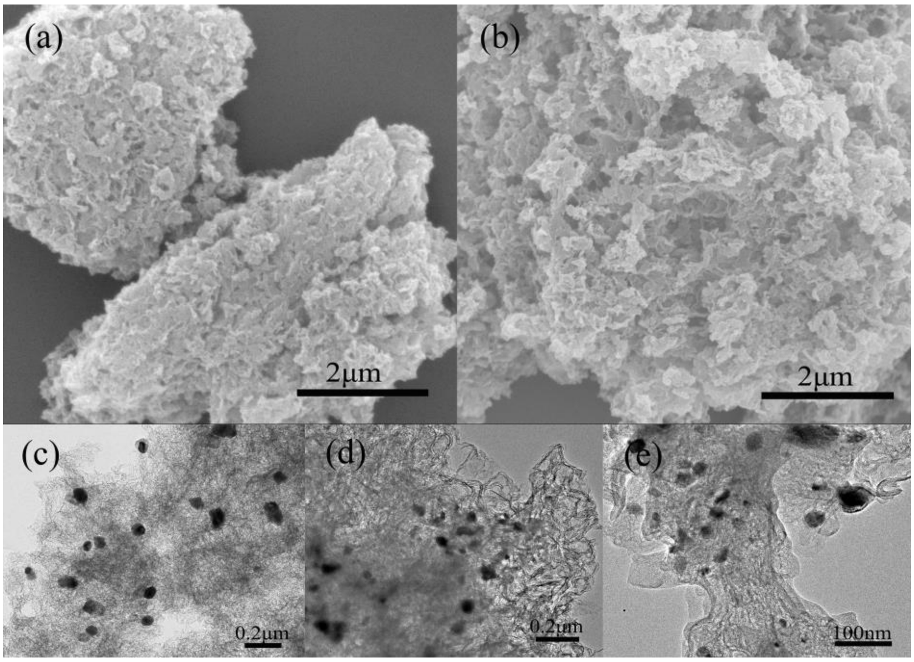

Figure S4 SEM images of (a) C@N and (b) Co@C-N-120-900, TEM images of (c) Co@C-N-120-900, (d) Co@C-N-140-900 and (e) Co@C-N-160-900 catalysts.

Table. S2 The relative percentage in C@N and Co@C-N catalysts from detailed deconvolution of XPS N1s spectra.

Samples	Pyridinic-N	Pyrrolic-N	Graphitic- N	Oxidized-N
C@N	68.07%	19.73%	8.72%	3.48%
Co@C-N-120-900	74.39%	17.96%	6.50%	1.15%
Co@C-N-140-900	62.42%	29.49%	1.8%	6.29%
Co@C-N-160-900	42%	49.64%	1.52%	6.83%

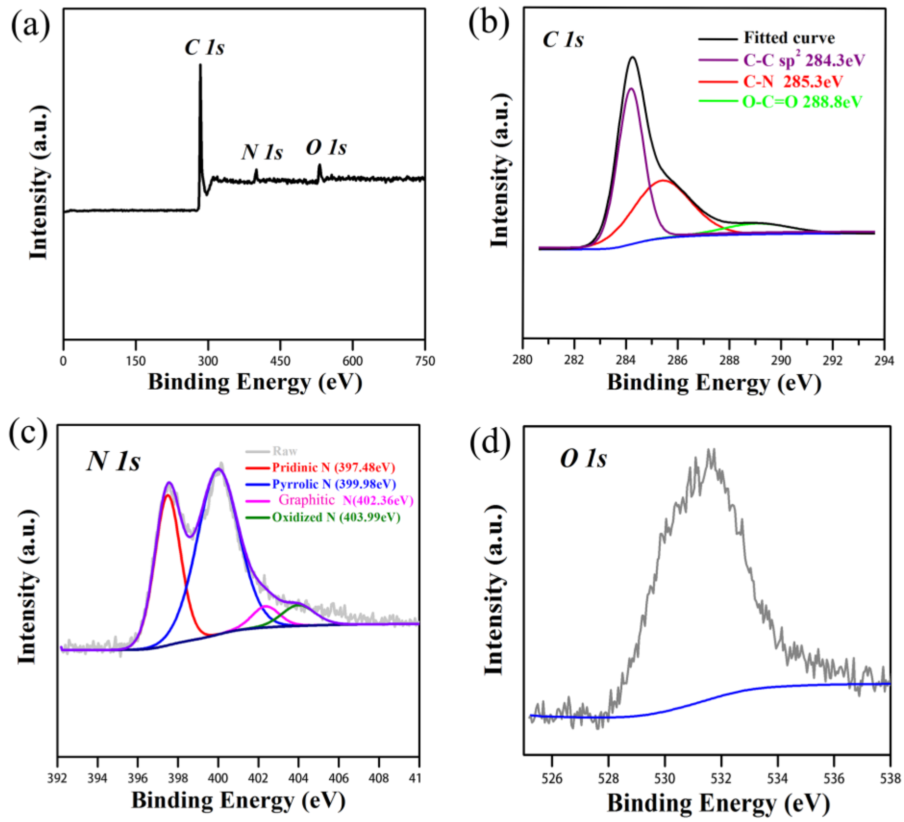

Figure S5 (a) X-ray photoelectron spectroscopy (XPS) survey spectrum of C@N; (b, c and d) C 1s, N1s and Co2p high resolution spectrum of the C@N catalyst.

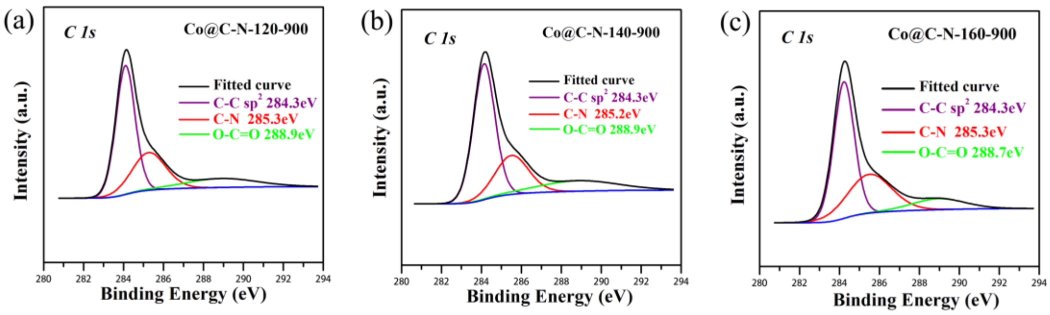

Figure S6 (a, b and c) C 1s high resolution spectrum of the Co@C-N-120-900, Co@C-N-140-900 and Co@C-N-160-900 catalysts, respectively.

Table. S3 The relative percentage in C@N and Co@C-N catalysts from detailed deconvolution of XPS C1s spectra.

Samples	**C-C sp^2**	**C-N**	**O-C=O**
C@N	67.55%	25.07%	7.38%
Co@C-N-120-900	67.02%	20.58%	12.4%
Co@C-N-140-900	66.88%	15.66%	17.45%
Co@C-N-160-900	65.49%	15.59%	18.91%

Table. S4 The summary for BET special surface area and pore volume (pore distribution) of Co@C-N-120-900, Co@C-N-140-900 and Co@C-N-160-900 catalysts.

Samples	**BET special surface area (SSA)**	**Pore volume**	**Pore diameter**
C@N	1108 m^2 g^{-1}	2.876 cm^3 g^{-1}	ca. 3.031 nm
Co@C-N-120-900	1080 m^2 g^{-1}	2.463cm^3 g^{-1}	ca. 3.031 nm
Co@C-N-140-900	785 m^2 g^{-1}	1.432 cm^3 g^{-1}	ca. 3.032 nm
Co@C-N-160-900	436 m^2 g^{-1}	0.734 cm^3 g^{-1}	ca. 4.957 nm

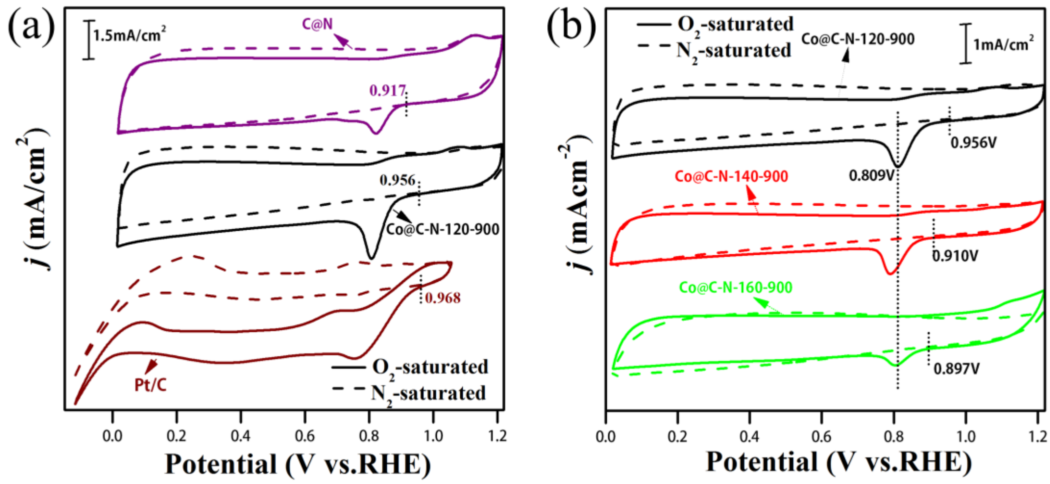

Figure S7 (a) Cycle voltammograms of C@N, Co@C-N-120-900 and Pt/C recorded by purging the electrolyte with O_2-saturated and N_2-saturated sweeping the potential at a scan rate of 50mV s^{-1}; (b) Cycle voltammograms of Co@C-N-120-900, Co@C-N-140-900 and Co@C-N-160-900 recorded by purging the electrolyte with O_2-saturated and N_2-saturated sweeping the potential at a scan rate of 50mV s^{-1}.

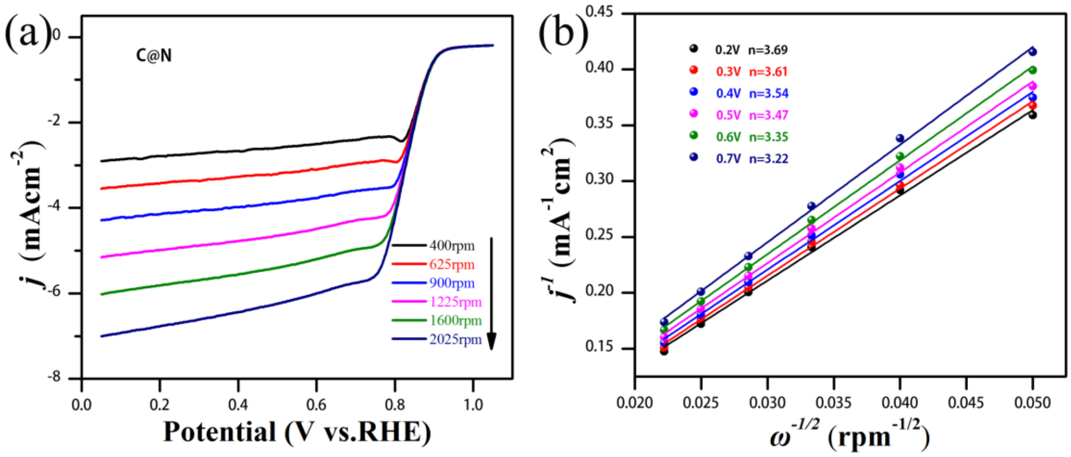

Figure S8 (a and b) RDE voltammograms of the C@N recorded at different RDE rotation rates from 400 to 2025rpm and the corresponding K-L plots.

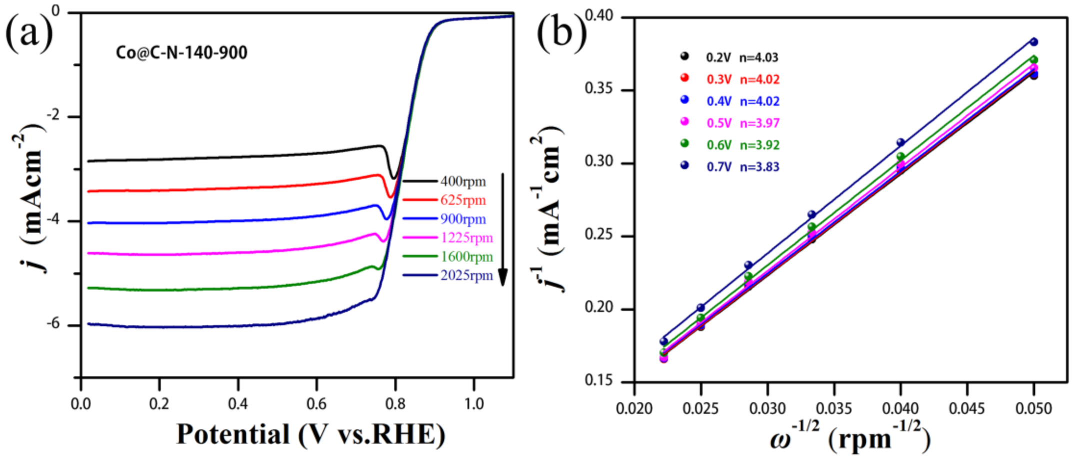

Figure S9 (a and b) RDE voltammograms of the Co@C-N-140-900 recorded at different RDE rotation rates from 400 to 2025rpm and the corresponding K-L plots.

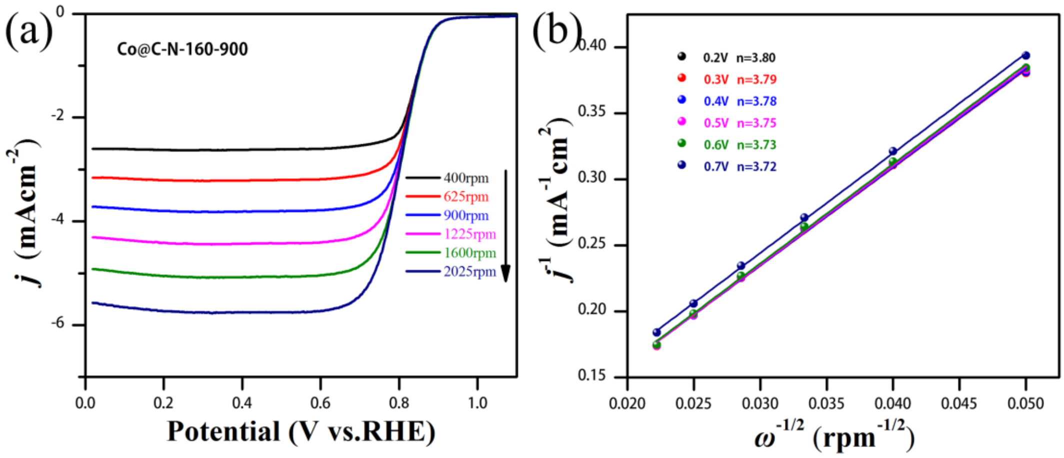

Figure S10 (a and b) RDE voltammograms of the Co@C-N-160-900 recorded at different RDE rotation rates from 400 to 2025rpm and the corresponding K-L plots.

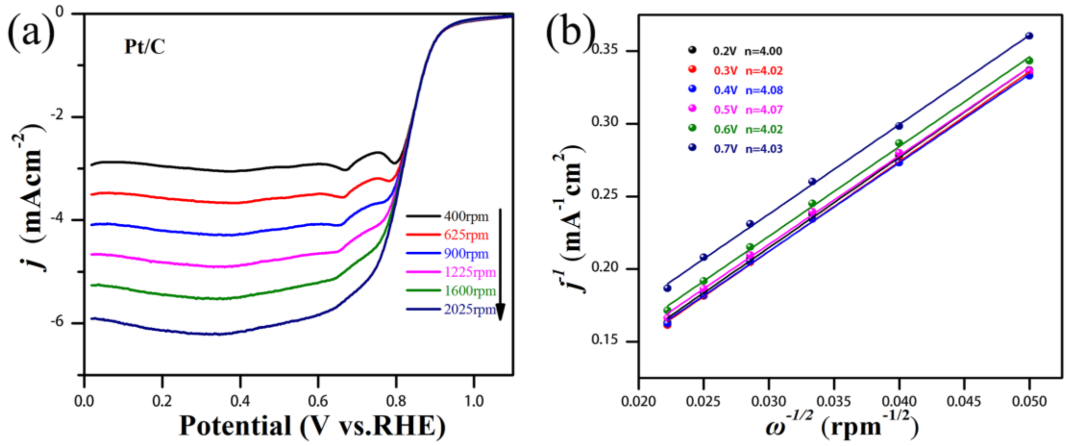

Figure S11 (a and b) RDE voltammograms of the Pt/C recorded at different RDE rotation rates from 400 to 2025rpm and the corresponding K-L plots.

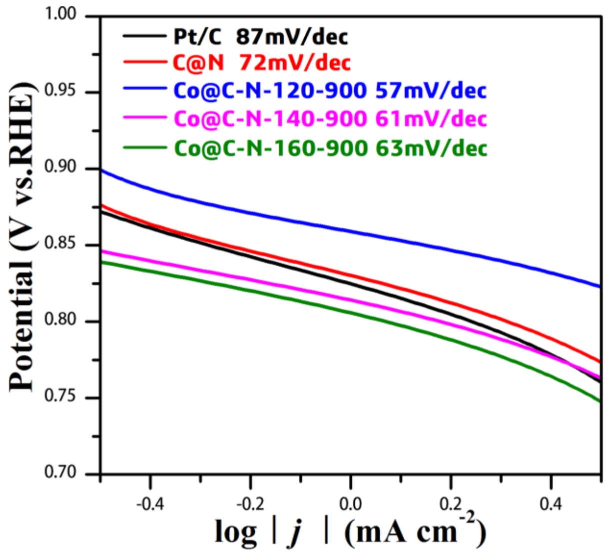

Figure S12 Tafel plots of Pt/C, C@N and Co@C-N catalysts.

Table. S5 The comparison of the ORR performances of the Co@C-N-120-900 and some other Co, N co-doped carbon catalysts.

catalysts	*Catalysts loading (mg/cm²)*	*E_{onset} (V)*	*$E_{1/2}$ (V)*	*J_k (mA/cm²)*	*n*	*references*
Co N-doped carbon	*0.407*	*0.89 vs. RHE*	*0.70 vs.RHE*	*~4.6*	*3.7*	*[1]*
Cobalt and nitrogen-cofunctionalized graphene	*0.1*	*-0.098 vs. Ag/AgCl*	*-0.162 vs. Ag/AgCl*	*4.120 (-0.5V vs.Ag/Agcl)*	*3.72*	*[2]*
Co-N onion-like carbon	*0.1529*	*-0.13 vs. Ag/AgCl*	*-0.19 vs. Ag/AgCl*	*3.98 (-0.4V vs. Ag/Agcl)*	*3.93*	*[3]*
Co-N-CNTs	*0.1*	*-0.138 vs. Ag/AgCl*	*~*	*5*	*4*	*[4]*
Co-N_x/C	*0.4*	*0.93(vs. RHE)*	*~*	*5.49*	*3.97*	*[5]*
Co-N-PGCS	*0.25*	*-0.075 vs. Ag/AgCl*	*-0.151 vs. Ag/AgCl*	*~6(-0.4V vs. Ag/AgCl)*	*3.97*	*[6]*
Co-CNF	*0.498*	*~*	*0.832 vs.RHE*	*~5*	*3.8*	*[7]*
Co SAs/N-C	*~*	*0.982 vs.RHE*	*0.881 vs.RHE*	*~5.5*	*~*	*[8]*
Co-N doped carbon	*0.283*	*0.940 vs.RHE*	*0.851 vs.RHE*	*~4.8*	*3.7*	*[9]*
Co@N-CNTs	*0.6*	*0.929 vs.RHE*	*0.849 vs.RHE*	*6*	*~*	*[10]*
Co,N-CNF	*~*	*-0.082 vs. Ag/AgCl*	*-0.155 vs.Ag/AgCl*	*5.71*	*~*	*[11]*
Co-NpGr	*~*	*0.93V vs.RHE*	*~*	*~4*	*4.1*	*[12]*
Co@C-N-120-900	*0.2*	*0.956 vs.RHE*	*0.851 vs.RHE*	*5.6*	*3.99-4.04*	*This work*

- E_{onset} , $E_{1/2}$ and n represent the onset potential, the half-wave potential and the transfer electron numbers of electrocatalysts, respectively.

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