Supporting Information

Role of Cobalt Phthalocyanine on the Formation of High-Valent Cobalt Species Revealed by In situ Raman

Jinzhi Jia[a], Xiaohua Zhao[a,b], Wenhui Hu[c], Yantao Wang[a], Junfeng Huang[a], Jier Huang[c], Hua Li[a], Yong Peng[a], Haiyan Ma[a,*] and Cailing Xu[a,*]

[a] State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, College of Earth and Environmental Sciences, School of Materials and Energy, Lanzhou University, Lanzhou 730000, China.

[b] School of Chemical Engineering, Lanzhou University of Arts and Sciences, Lanzhou 730000, China.

[c] Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201, United States.

[*]Corresponding author.
E-mail address: mahy06@lzu.edu.cn (H. Ma), xucl@lzu.edu.cn (C. Xu)

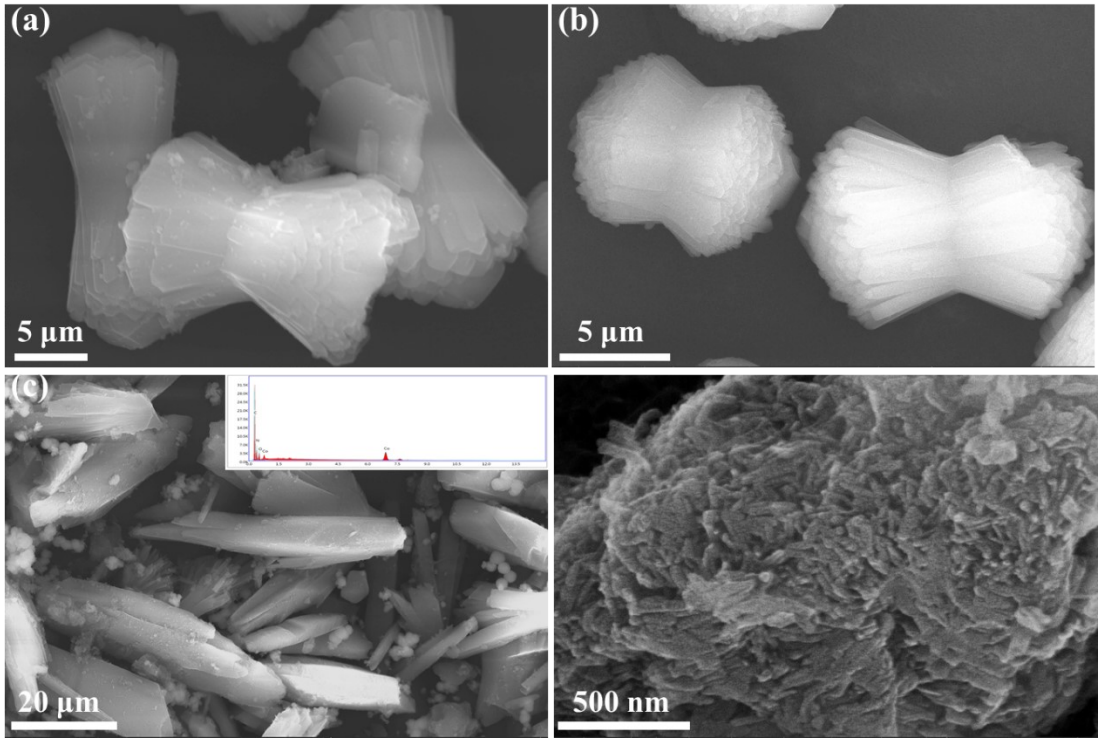

Fig. S1 SEM images of Co-MOF-74 (a), Co-MOF-74@CoPc (b), CoPc (c) and Pc (d).

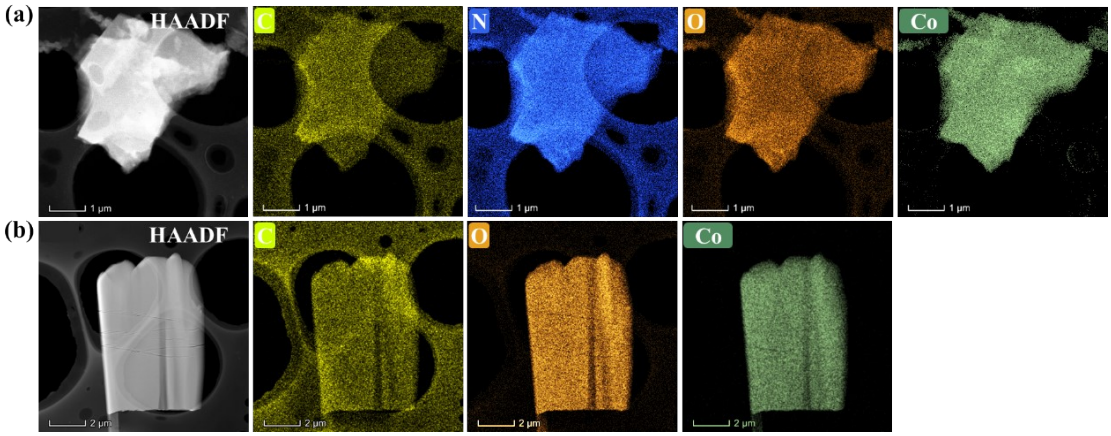

Fig. S2 The HAADF-STEM images and the corresponding EDS elemental mapping images of Co-MOF-74@CoPc (a) and Co-MOF-74 (b).

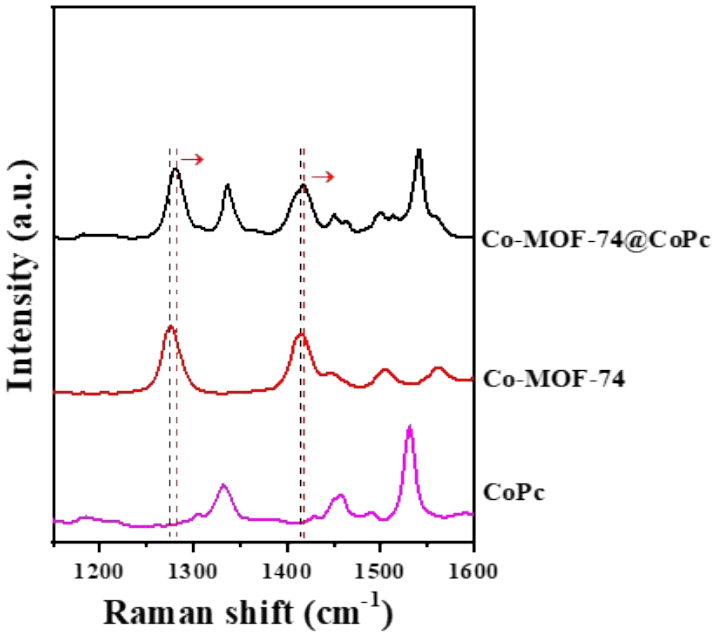

Fig. S3 Raman spectra of CoPc, Co-MOF-74 and Co-MOF-74@CoPc.

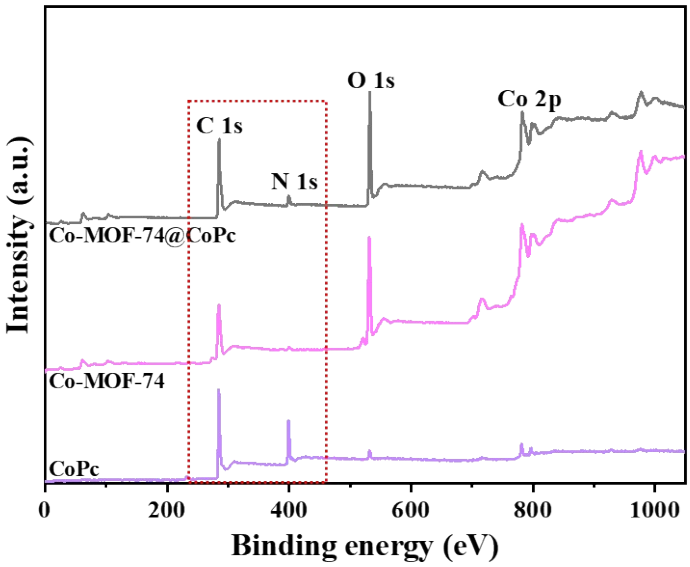

Fig. S4 The XPS survey spectra of CoPc, Co-MOF-74 and Co-MOF-74@CoPc.

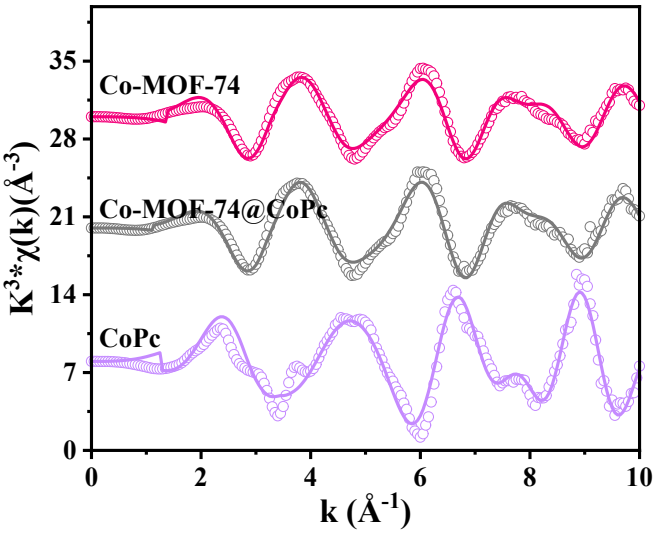

Fig. S5 The Co K-edge extended EXAFS oscillation functions of CoPc, Co-MOF-74 and Co-MOF-74@CoPc.

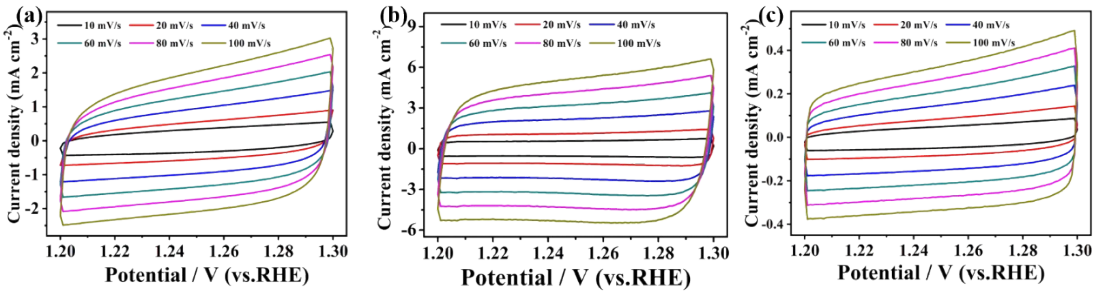

Fig. S6 Cyclic voltammetry curves of Co-MOF-74 (a), Co-MOF-74@CoPc (b) and CoPc (c) at different scanning rates from 10 - 100 mV s^{-1} in 1 M KOH solution.

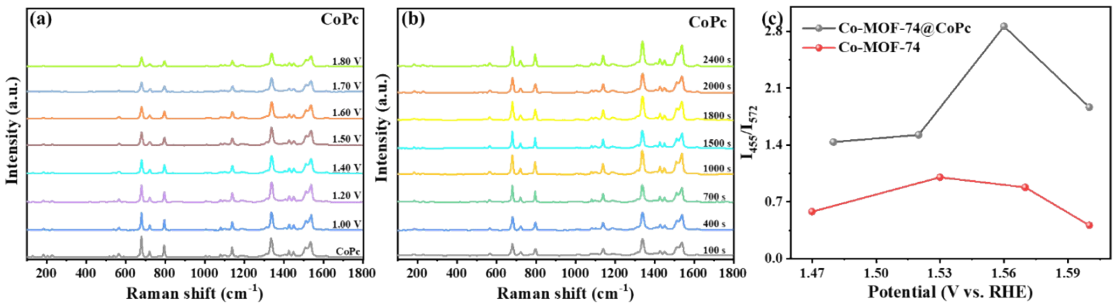

Fig. S7 Potential-dependent (a) and time-dependent (b) in-situ Raman spectra of CoPc during OER process. (c) The evolution of I_{455}/I_{572} versus potential of Co-MOF-74 and Co-MOF-74@CoPc during OER process.

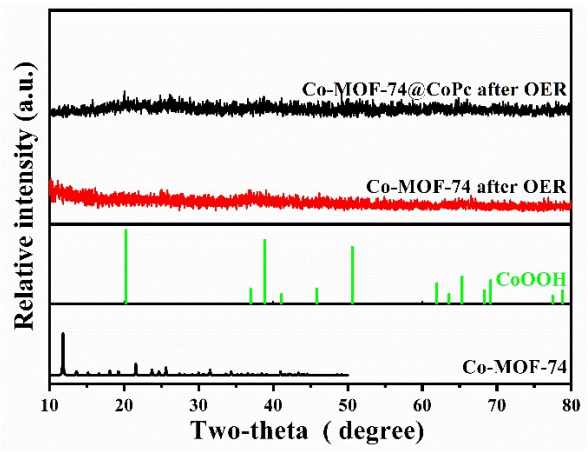

Fig. S8 The XRD patterns of Co-MOF-74 and Co-MOF-74@CoPc after the OER stability.

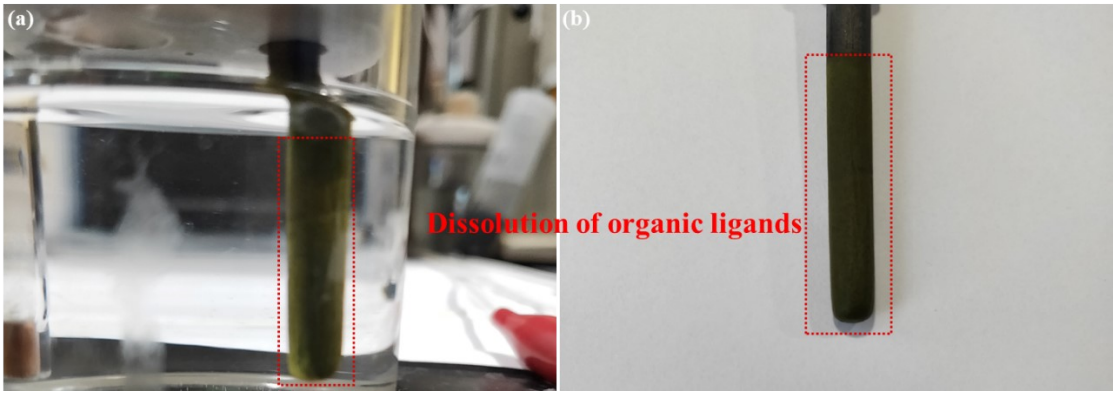

Fig. S9 (a, b) Optical microscopy images of the reference electrode after the OER stability.

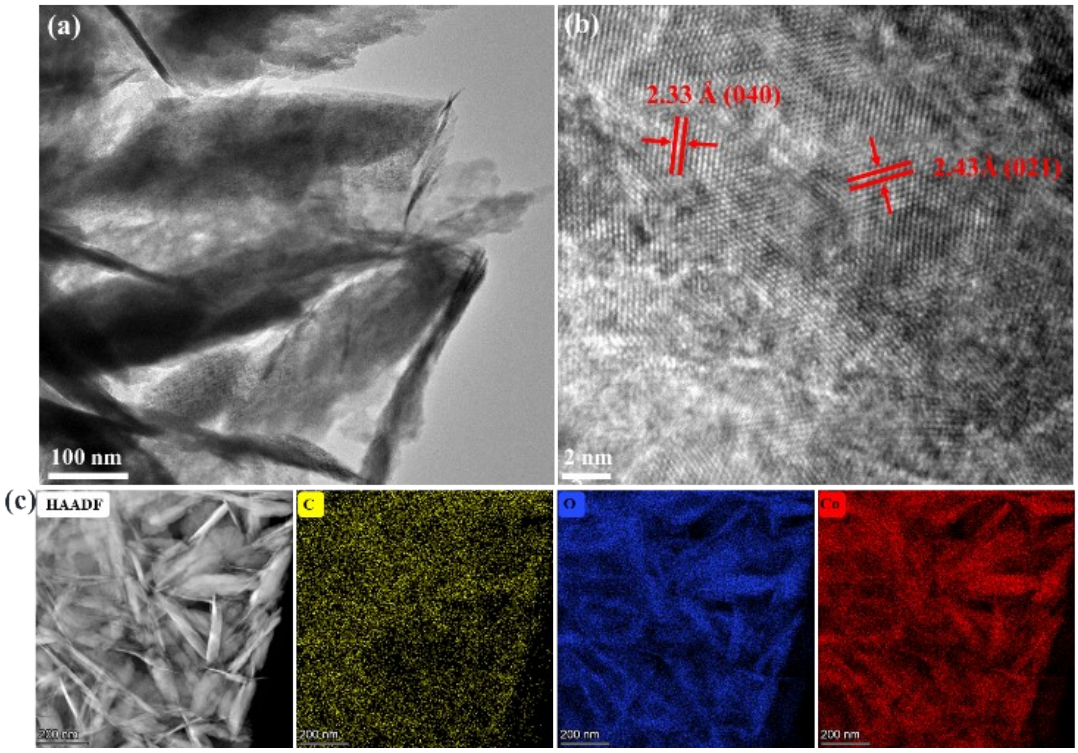

Fig. S10 (a) TEM image, (b) HRTEM image, (c) HAADF-STEM image and corresponding EDS elemental mapping images of the Co-MOF-74 after the OER stability.

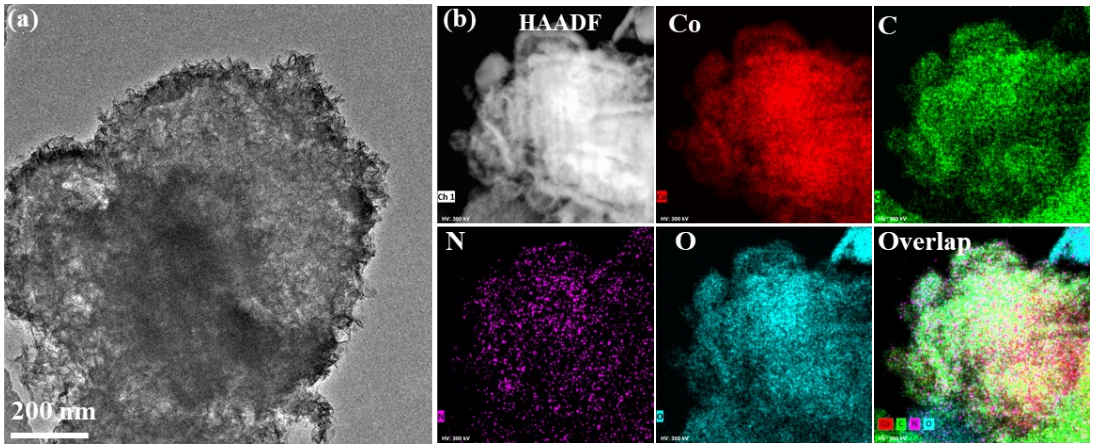

Fig. S11 (a) TEM image, (b) HAADF-STEM image and corresponding EDS elemental mapping images of the Co-MOF-74@CoPc after the OER stability.

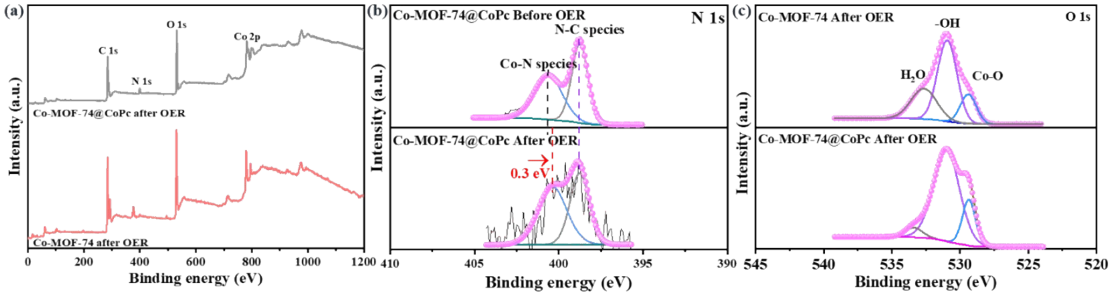

Fig. S12 Survey XPS spectra (a) and High-resolution O 1s XPS spectra (c) of the Co-MOF-74, Co-MOF-74@CoPc after the OER stability. (b) High-resolution N 1s XPS spectra of Co-MOF-74@CoPc and Co-MOF-74/CoPc after the OER stability.

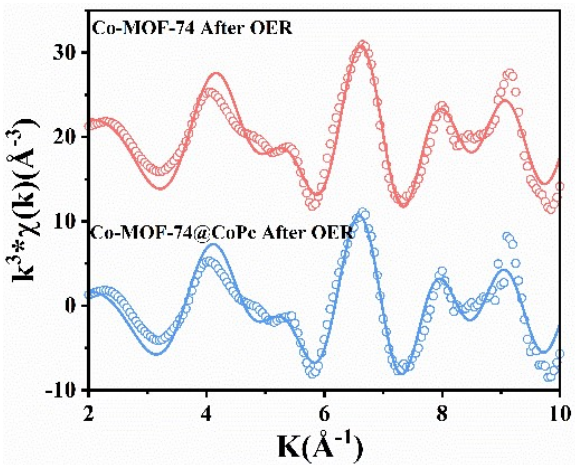

Fig. S13 (a) The Co K-edge extended EXAFS oscillation functions of Co-MOF-74 and Co-MOF-74@CoPc after the OER stability. The experimental spectra are represented by scatter points, and the theoretical fits are represented by the solid line.

Table S1. EXAFS Fitting parameters of Co R-space for Co-MOF-74 and Co-MOF-74@CoPc, respectively.

Samples	**Path**	**CN**	**S_0^2**	**ΔE_0 (eV)**	**σ^2 (Å^2)**	**R (Å)**
Co-MOF-74	Co-O_1	3	0.87	7.0	0.002	2.06
	Co-O_2	3			0.0095	2.24
	Co-C	3			0.010	3.20
	Co-Co	2			0.010	3.06
Co-MOF-74@CoPc	Co-O_1	3	0.85	4.7	0.0025	2.05
	Co-O_2	3			0.010	2.18
	Co-C	3			0.010	3.11
	Co-Co	2			0.010	3.06

Table S2. EXAFS Fitting parameters of Co R-space for Co-MOF-74 and Co-MOF-74@CoPc after the OER stability, respectively.

Samples	Path	CN	S_0^2	ΔE_0 (eV)	σ^2 (Å^2)	R (Å)
Co-MOF-74	Co-O_1	6	0.95	-3.3	0.0077	1.91
	Co-Co	6			0.0096	2.85
Co-MOF-74@CoPc	Co-O_1	6	0.95	-5.1	0.0076	1.91
	Co-Co	6			0.0097	2.85

CN: coordination numbers;

S_0^2: amplitude reduction factor, ($0.7<S_0^2<1.0$);

σ^2: Debye-Waller factors, ($\sigma^2<0.02$);

ΔE_0: the inner potential correction, ($-10<\Delta E_0<10$);

R: bond length, all the path distances discussed are apparent distances without phase correction.

Table S3. Comparison of OER catalytic activity of Co-MOF-74 and Co-MOF-74@CoPc with M-MOF-74 and Pc based catalysts in alkaline media.

Samples	Test Condition	Overpotential (mV@mA cm^{-2})	Tafel slope (mV dec^{-1})	Durability (h)	Substrate	References
Co-MOF-74@CoPc	1.0 M KOH	291@10	69	220	GC	This work
Co-MOF-74	1.0 M KOH	351@10	73	58	GC	This work
$Fe(OH)_3$@Co-MOF-74	1.0 M KOH	292@10	44	20	CP	[1]
Co-MOF-74	1.0 M KOH	389@10	80	20	CP	[1]
FeCo-MNS-1.0	0.1 M KOH	298@10	21.6	10000 s	GC	[2]
$Co_{0.6}Fe_{0.4}$-MOF-74	1.0 M KOH	280@10	56	12	GC	[3]
CoFe-MOF-74/Co/CC	1.0 M KOH	226@20	85.1	70	CC	[4]
Fe-MOF-74@NF	1.0 M KOH	207@10	41.1	72	NF	[5]
NiFe-MOF-74/NF	1.0 M KOH	223@10	71.6	65	NF	[6]
Co_3O_4@MOF-74	1.0 M KOH	285@50	43	12	NF	[7]
NiCoFe-MOF-74	1.0 M KOH	270@10	89	8	GC	[8]
$FeCo_2Ni$-MOF-74	1.0 M KOH	269@10	8.0	100	GC	[9]
NiPc-GO	1.0 M KOH	320@10	61	17	GC	[10]
FeCo-PPC	1.0 M KOH	254@10	42.86	24	NF	[11]
NiPc–$NiFe_{0.09}$	1.0 M KOH	300@10	55	1000 cycles	GC	[12]
pCoPc-1/CC	1.0 M KOH	382@10	102.9	12	CC	[13]
NiPc–MOF	1.0 M KOH	onset potential 250	74	50	FTO	[14]

CP: Carbon Paper

GC: Glassy Carbon

NF: Nickel Foam

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