Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary information

A General Approach for the Direct Fabrication of Metal Oxide-Based Electrocatalysts for Efficient Bifunctional Oxygen Electrodes

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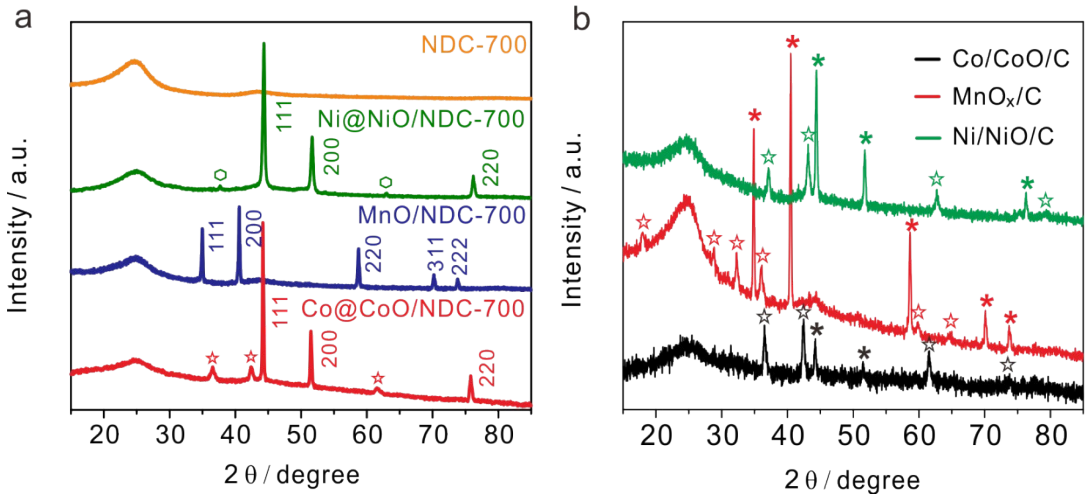

Fig. S1 (a) XRD pattern of Co@CoO/NDC-700, MnO/NDC-700, Ni@NiO/NDC-700 and NDC-700 catalysts; (b) XRD pattern of Co/CoO/C, MnO_x/C and Ni/NiO/C catalysts.

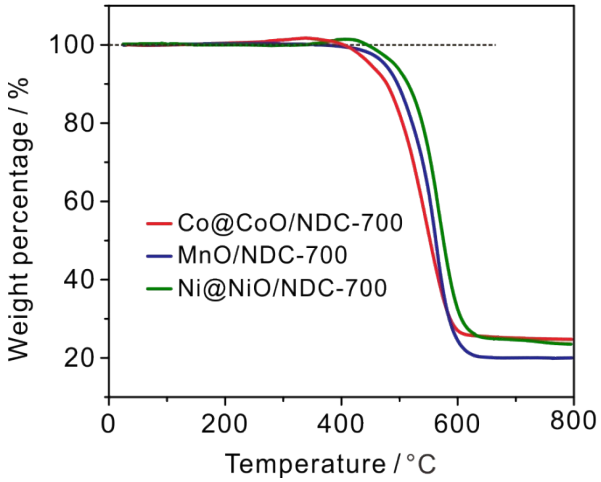

Fig. S2 Thermogravimetric Analysis (TGA) of Co@CoO/NDC-700, MnO/NDC-700 and Ni@NiO/NDC-700 catalysts.

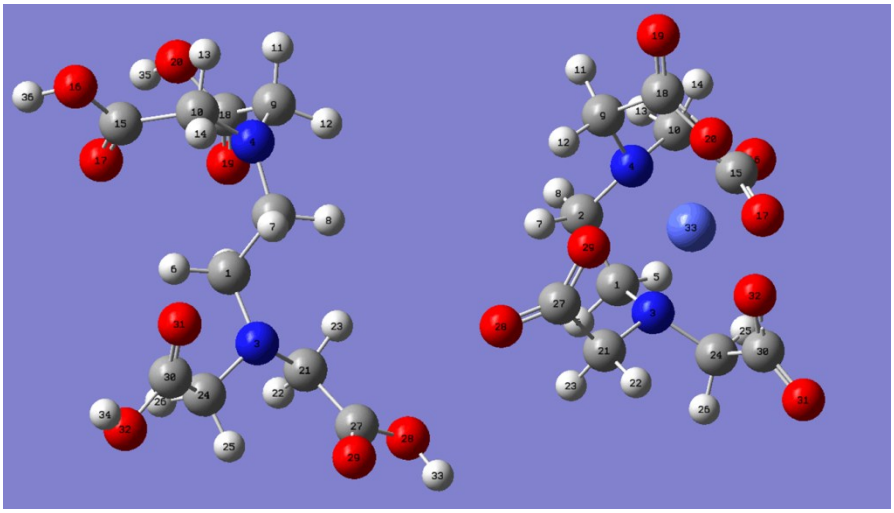

Fig. S3 Stick models of EDTA molecular and EDTA-Co chelating agent.

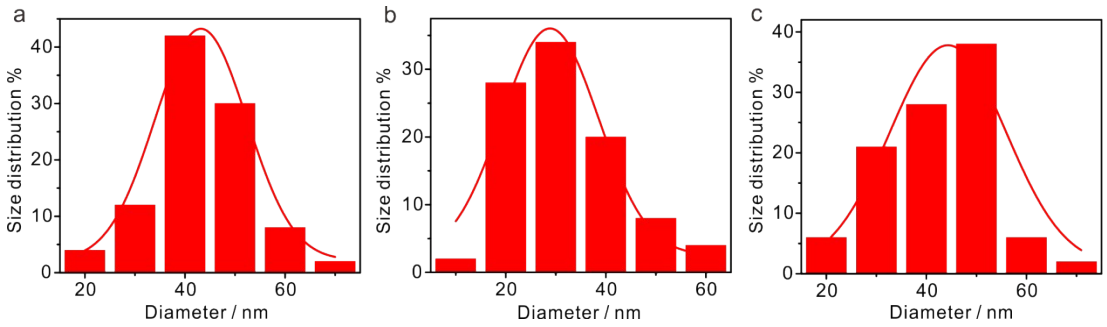

Fig. S4 Particle size distribution of Co@CoO/NDC-700 (a), Ni@NiO/NDC-700 (b) and MnO/NDC-700 (c) catalysts.

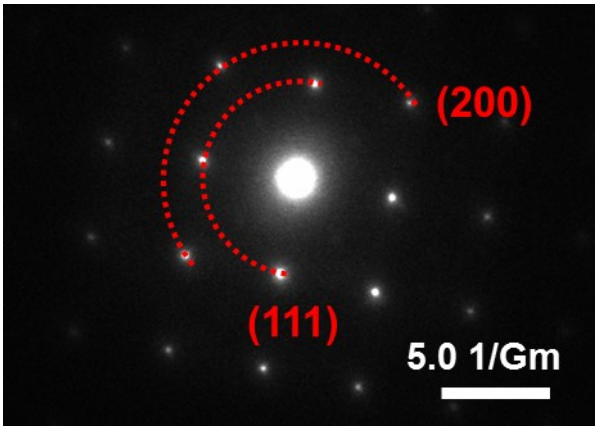

Fig. S5 Selected area electron diffraction (SAED) pattern of MnO/NDC-700 catalyst.

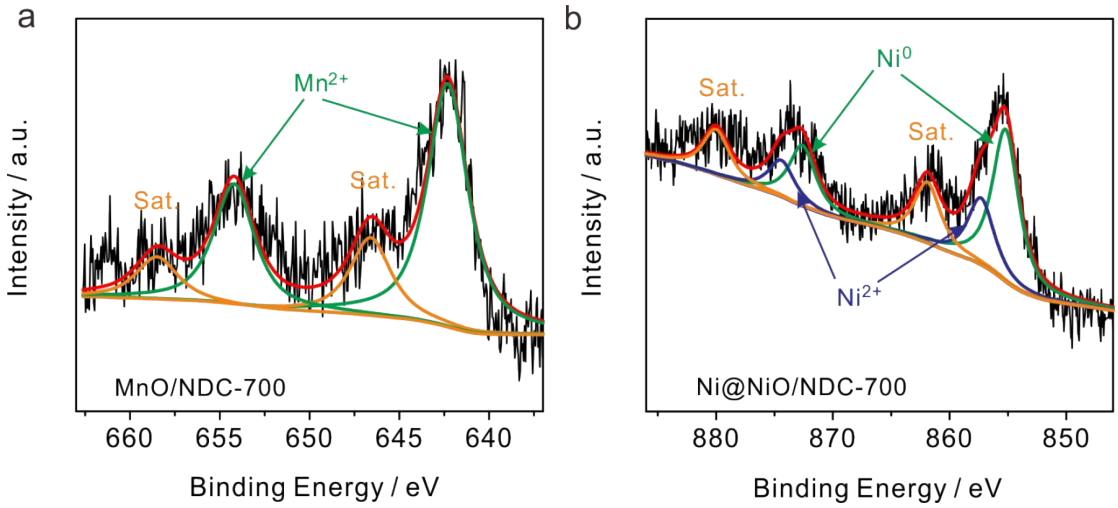

Fig. S6 High-resolution XPS spectra of Mn 2p (a) and Ni 2p (b).

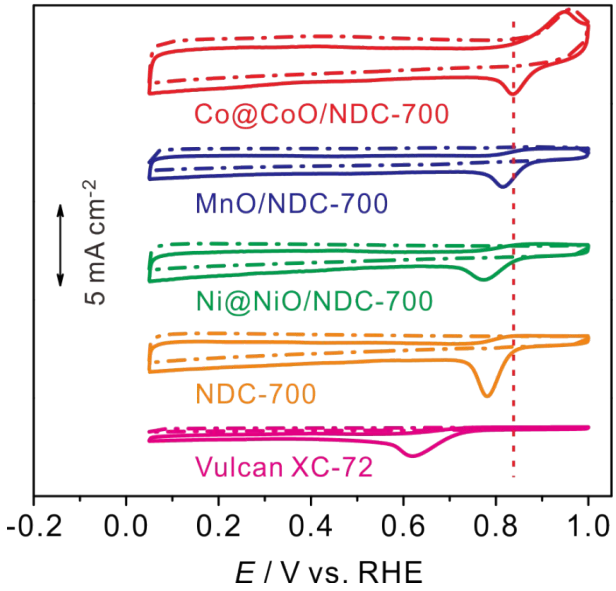

Fig. S7 Cyclic voltammetry comparison of Co@CoO/NDC-700, MnO/NDC-700, Ni@NiO/NDC-700, NDC-700 and Vulcan XC-72 at a scan rate of 50 mV s^{-1} in N_2- and O_2- saturated 1 M KOH solution.

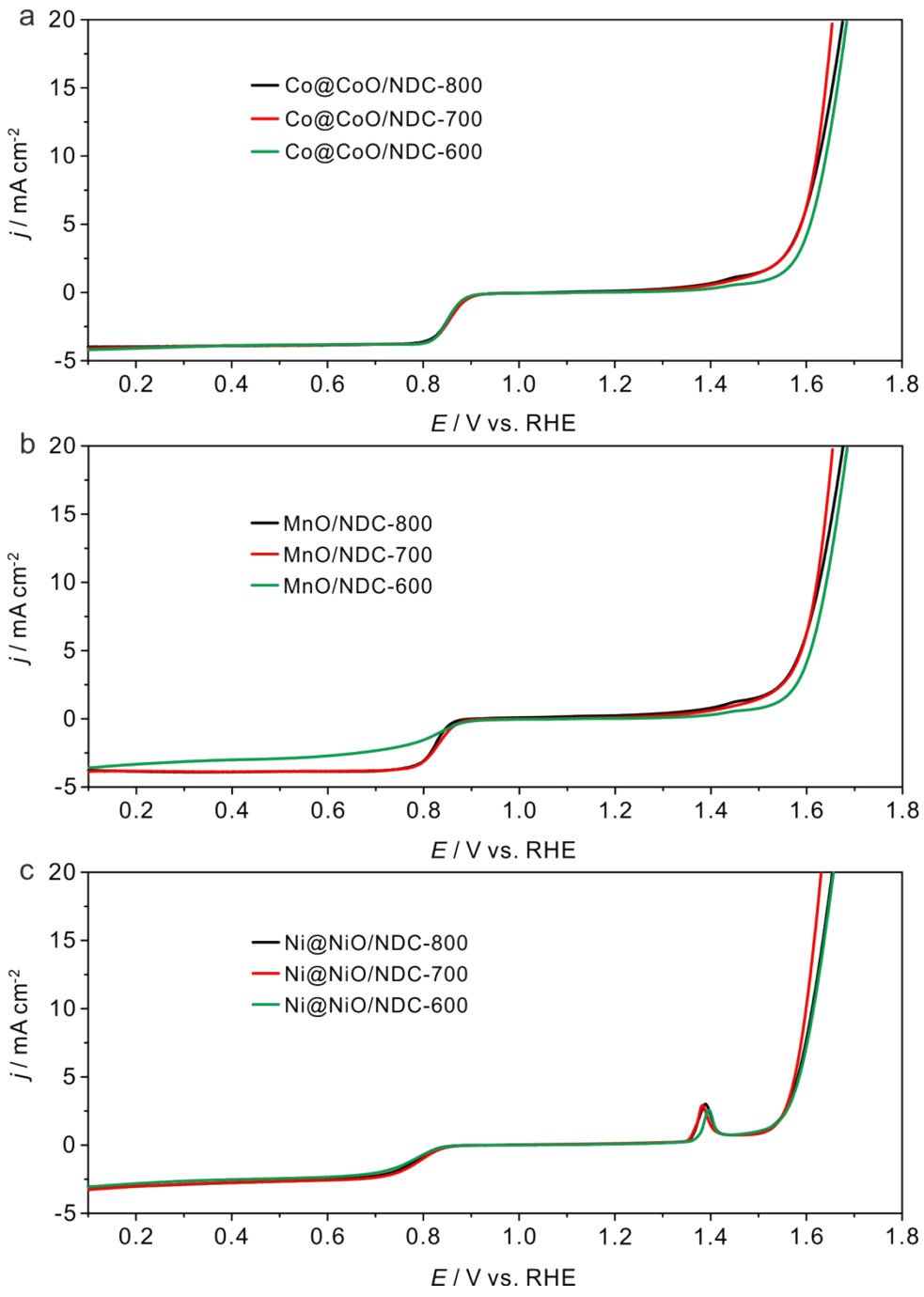

Fig. S8 (a) Bifunctional catalytic comparison of Co@CoO/NDC-600, Co@CoO/NDC-700 and Co@CoO/NDC-800; (b) Bifunctional catalytic comparison of MnO/NDC-600, MnO/NDC-700 and MnO/NDC-800; (c) Bifunctional catalytic comparison of Ni@NiO/NDC-600, Ni@NiO/NDC-700 and Ni@NiO/NDC-800 in O_2- saturated 1 M KOH solution.

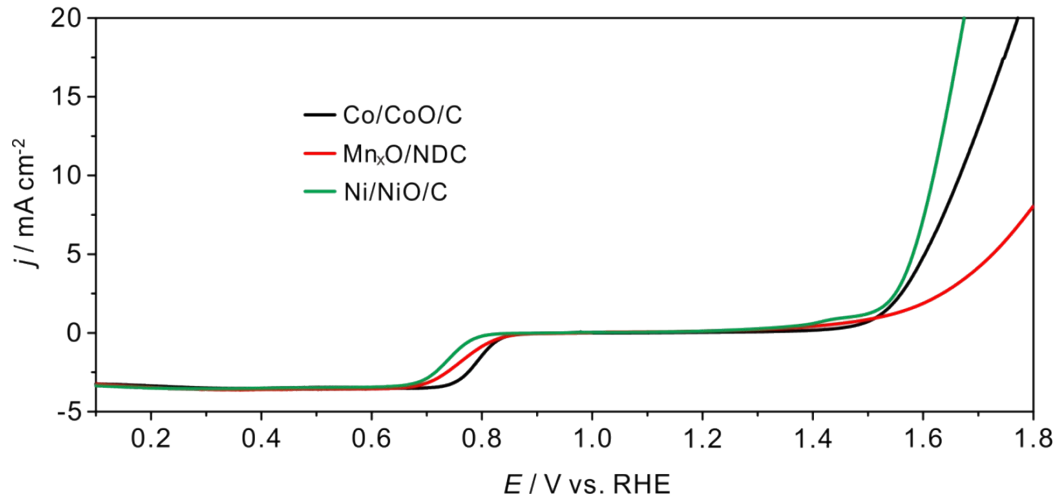

Fig. S9 Bifunctional catalytic comparison of Co/CoO/C, MnO_x/C and Ni/NiO/C in O_2-saturated 1 M KOH solution.

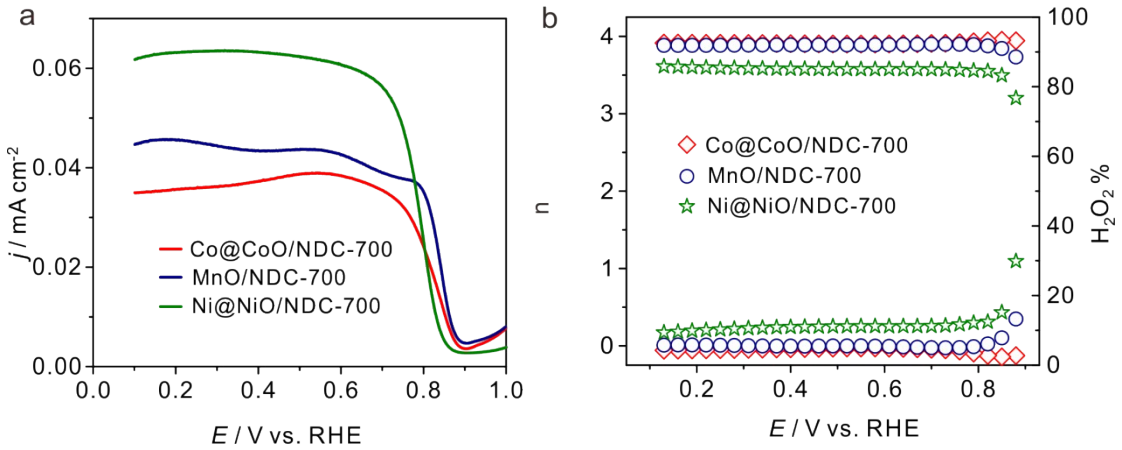

Fig. S10 (a) polarization curves of the ring current density on Ni/NDC-700, MnO/NDC-700 and Co@CoO/NDC-700 (The ring potential was 1.2 V). (b) The electron-transfer number n and H_2O_2 yield on Ni/NDC-700, MnO/NDC-700 and Co@CoO/NDC-700 catalysts.

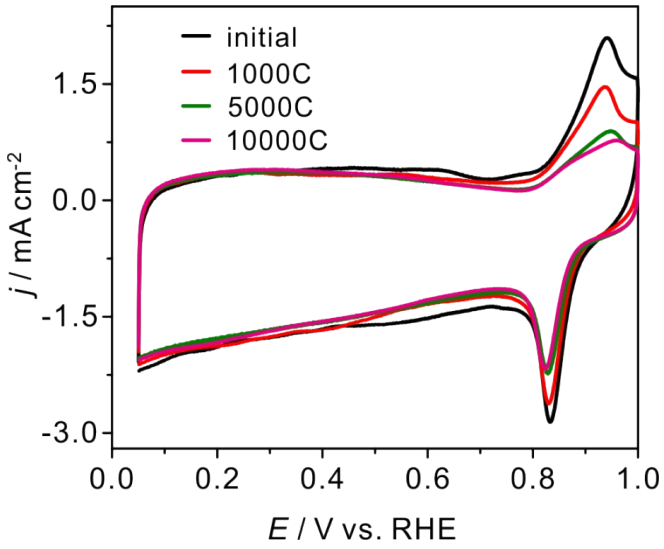

Fig. S11 Cyclic voltammetry curves of Co@CoO/NDC-700 in O_2-purged 1 M KOH solution at room temperature for various numbers of potential cycles.

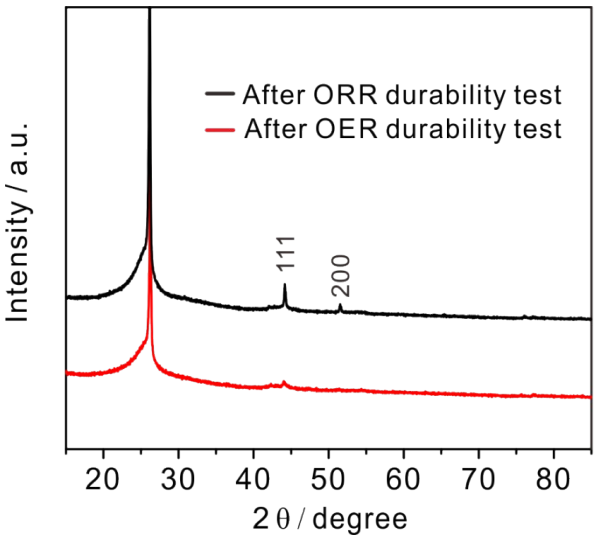

Fig. S12 XRD patterns of Co@CoO/NDC-700 after chronoamperometric stability measurement and chronopotentiometry stability measurement.

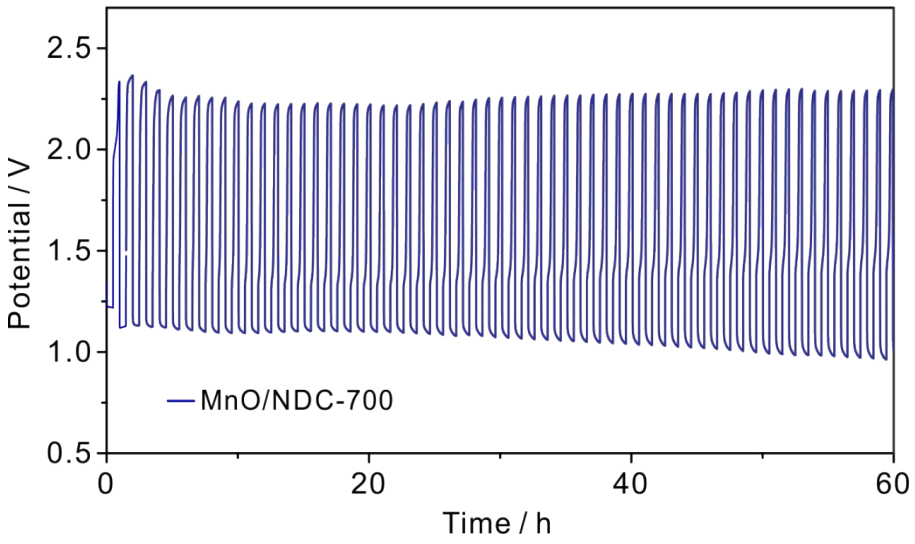

Fig. S13 Discharge/charge cycling curves of MnO/NDC-700 at current density of 10 mA cm^{-2}.

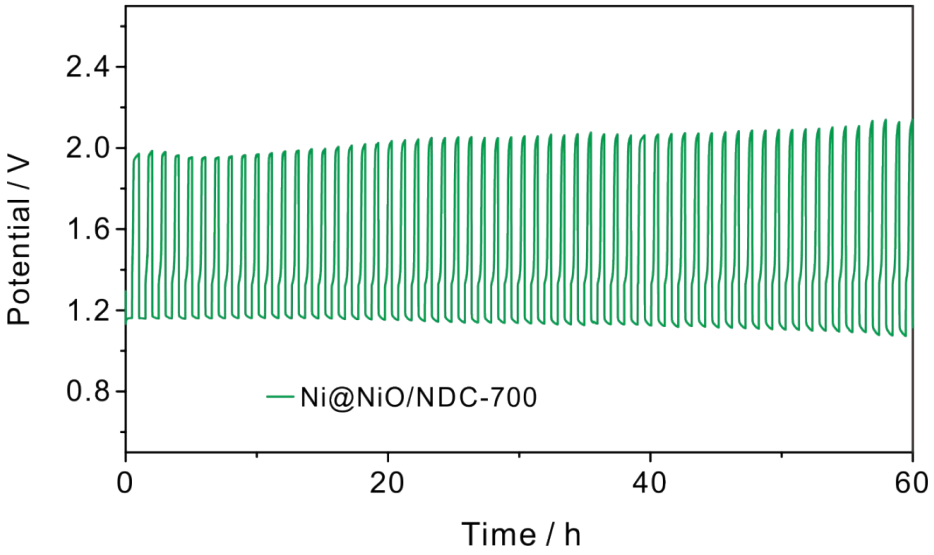

Fig. S14 Discharge/charge cycling curves of Ni@NiO/NDC-700 at current density of 10 mA cm^{-2}.

Table S1 Comparison of Mulliken atomic charges for EDTA and EDTA-Co (The red rows are corresponding to the bonding atoms).

Atom Number	Atom	EDTA	EDTA-Co
1	C	-0.105	-0.0237
2	C	-0.0909	-0.0239
3	N	-0.447	-0.434
4	N	-0.456	-0.433
9	C	-0.175	-0.109
10	C	-0.148	-0.110
15	C	0.497	0.543
16	O	-0.415	-0.562
17	O	-0.555	-0.498
18	C	0.516	0.535
19	O	-0.419	-0.570
20	O	-0.555	-0.493
21	C	-0.109	-0.109
24	C	-0.190	-0.109
27	C	0.498	0.535
28	O	-0.416	-0.571
29	O	-0.553	-0.570
30	C	0.482	0.535
31	O	-0.422	-0.571
32	O	-0.553	-0.493
33	Co	—	0.390

Table S2 Elemental composition by XPS (at. %)

Sample	**C 1s**	**N 1s**	**O 1s**	**M 2p (M = Co, Mn, Ni)**
Co@CoO/NDC-700	92	3.4	3.2	1.4
MnO/NDC-700	97.3	1.2	1.2	0.3
Ni@NiO/NDC-700	91	2.1	6.6	0.8
NDC-700	97.4	1.5	1.1	—

Table S3 Comparison of key performance parameters for rechargeable Zn-air batteries extracted from literature.

Catalysts	Loading (mg cm^{-2})	Peak power density	Voltage gap	Electrolyte	Refs
N-GRW	0.5	65 mW cm^{-2}	0.91 V @ 2 mA cm^{-2}	6 M KOH + 0.2 M $ZnCl_2$	1
CoO/N-CNT+NiFe LDH/CNT	1.0	265 mW cm^{-2}	0.70 V @ 10 mA cm^{-2}	6 M KOH + 0.2 M zinc acetate	2
NCNF-1000	2.0	185 mW cm^{-2}	0.73 V @ 10 mA cm^{-2}	6 M KOH + 0.2 M zinc acetate	3
Co@NG-acid	1.0	350 mW cm^{-2}	—	6 M KOH	4
CuPt-NC	2.0	250 mW cm^{-2}	—	6 M KOH	5
MnO_2/Co_3O_4	2.0	33 mW cm^{-2}	0.90 V @ 15 mA cm^{-2}	6 M KOH	6
FeCo@NC-750	1.0	132 mW cm^{-2}	0.74 V @ 10 mA cm^{-2}	6 M KOH + 0.2 M zinc acetate	7
$Pb_2Ru_2O_{6.5}$	—	195 mW cm^{-2}	0.77 V @ 10 mA cm^{-2}	6 M KOH + 0.2 M ZnO	8
NiFe@NCX	1.0	83 mW cm^{-2}	0.78 V @ 50 mA cm^{-2}	6 M KOH	9
P,S-CNS	0.5	198 mW cm^{-2}	1.04 V @ 25 mA cm^{-2}	6 M KOH	10
C–CoPAN900	1.0	125 mW cm^{-2}	0.90 V @ 2 mA cm^{-2}	6 M KOH + 0.2 M $ZnCl_2$	11
A-EPC-900	—	—	0.85 V @ 5 mA cm^{-2}	6 M KOH + 0.2 M $ZnCl_2$	12
COMT@Ni	1.0	—	0.70 V @ 10 mA cm^{-2}	6 M KOH + 0.2 M $ZnCl_2$	13
HMC	0.1	—	0.81 V @ 2 mA cm^{-2}	6 M KOH + 2% ZnO	14
Co-PDA-C	1.0	—	0.94 V @ 2 mA cm^{-2}	6 M KOH + 0.2 M $ZnCl_2$	15
CoFe@NCNTs	1.0	150 mW cm^{-2}	0.75 V @ 10 mA cm^{-2}	6 M KOH + 0.2 M zinc acetate	16
BNPC-1100	2.0	—	1.06 V @ 2 mA cm^{-2}	6 M KOH + 0.2 M $ZnCl_2$	17
α-MnO_2/CNT10	—	66.3 mW cm^{-2}	0.86 V @ 10 mA cm^{-2}	6 M KOH + 0.2 M zinc acetate	18
MnO_2-2h/KB	1.0	133.17 mW cm^{-2}	—	6 M KOH	19

NCNT/$Co_xMn_{1-x}O$	0.5	—	0.57 V @ 7 mA cm^{-2}	6 M KOH + 2% ZnO	20
S-DGF	—	300 mW cm^{-2}	0.78 V @ 2 mA cm^{-2}	6 M KOH + 0.2 M $ZnCl_2$	21
$NiCo_2S_4$/N-CNT	1.0	147 mW cm^{-2}	0.63 V @ 10 mA cm^{-2}	6 M KOH + 0.2 M $ZnCl_2$	22
Ni_3Fe/N-C sheets	—	—	0.78 V @ 10 mA cm^{-2}	6 M KOH	23
egg-CMS	3.2	—	0.51 V @ 10 mA cm^{-2}	6 M KOH	24
CuFe alloy		212	—	6 M KOH	25
Co@CoO/NDC-700	1.0	192.1	0.68 V @ 10 mA cm^{-2}	6 M KOH + 0.2 M zinc acetate	This work
MnO/NDC-700	1.0	130.2	1.15 V @ 10 mA cm^{-2}	6 M KOH + 0.2 M zinc acetate	This work
Ni@NiO/NDC-700	1.0	109.5	0.77 V @ 10 mA cm^{-2}	6 M KOH + 0.2 M zinc acetate	This work

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