Supporting Information

Cation Exchange Synthesis of $Ni_xCo_{(3-x)}O_4$ (x=1.25) Nanoparticles on Aminated Carbon Nanotubes with High Catalytic Bifunctionality for Oxygen Reduction/Evolution Reaction toward Efficient Zn-Air Batteries

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This PDF file includes:

Experimental section.

Figures. S1 to S8

Tables S1-S3

Experimental section.

Synthesis of the cp-$Ni_xCo_{(3-x)}O_4$/NH_2-CNTs: 20 mg of $Co(Ac)_2 \cdot 6H_2O$ and 10 mg of $Ni(Ac)_2 \cdot 4H_2O$ and 15 mg of NH_2-CNTs were dispersed in 50 mL of dimethylformamide (DMF) and ethanol (EtOH) with a volume ratio 8:2 by magnetic stirring for 10 h at 80 °C, followed by the addition of 0.50 mL of NH_4OH (30% solution). Then the solution was transferred to 100 mL of Teflon-lined autoclave and maintained at 160 °C for 6 h. After cooling, the product was separated by centrifugation, washed with deionized water and ethanol, and dried in an oven at 60 °C.

Synthesis of the NiO/NH_2-CNTs: 10 mg of $Ni(Ac)_2 \cdot 4H_2O$ and 15 mg of NH_2-CNTs were dispersed in 50 mL mixed solution of DMF and EtOH with a volume ratio 8:2 by magnetic stirring for 10 h at 80 °C, followed by the addition of 0.50 mL of NH_4OH (30% solution). Then the solution was transferred to 100 mL of Teflon-lined autoclave and maintained at 160 °C for 6 h. After cooling, the product was separated by centrifugation, washed with deionized water and ethanol, and dried in an oven at 60 °C.

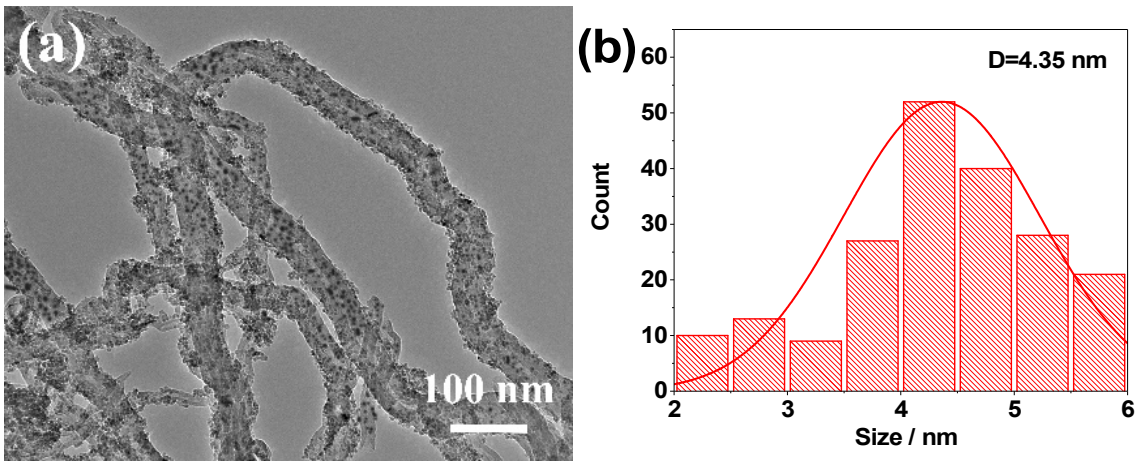

Figure S1. (a) TEM image of the Co_3O_4/NH_2-CNTs. (b) Size distribution histogram of the Co_3O_4 NPs in the Co_3O_4/NH_2-CNTs.

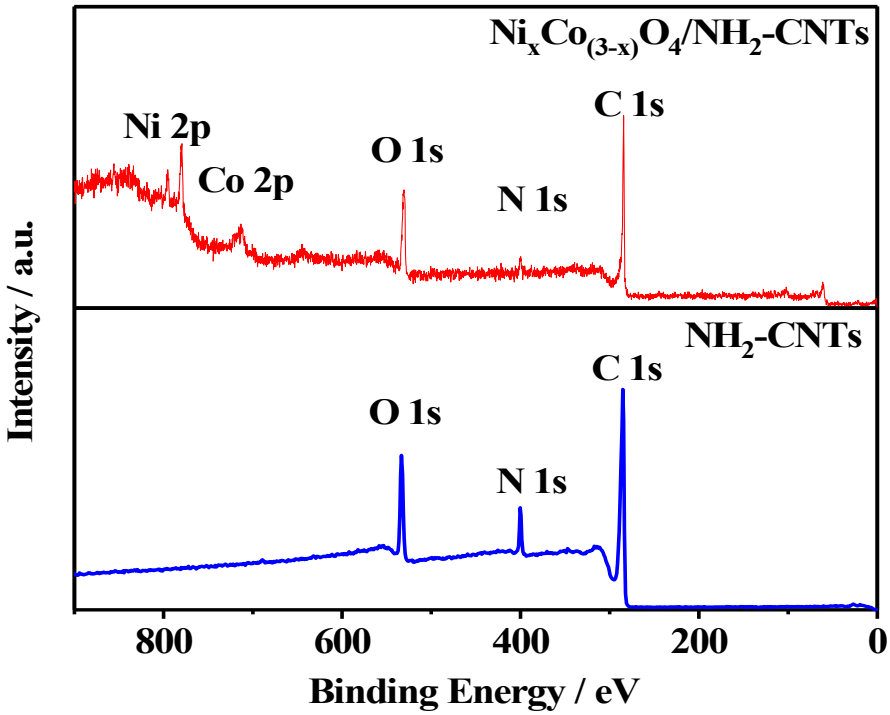

Figure S2. XPS survey spectra of the $Ni_xCo_{(3-x)}O_4/NH_2$-CNTs and the NH_2-CNTs.

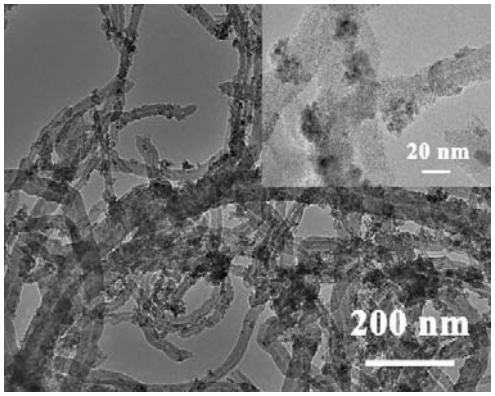

Figure S3. TEM image of the Co_3O_4/CNTs. The inset shows a magnified TEM image of the Co_3O_4/CNTs.

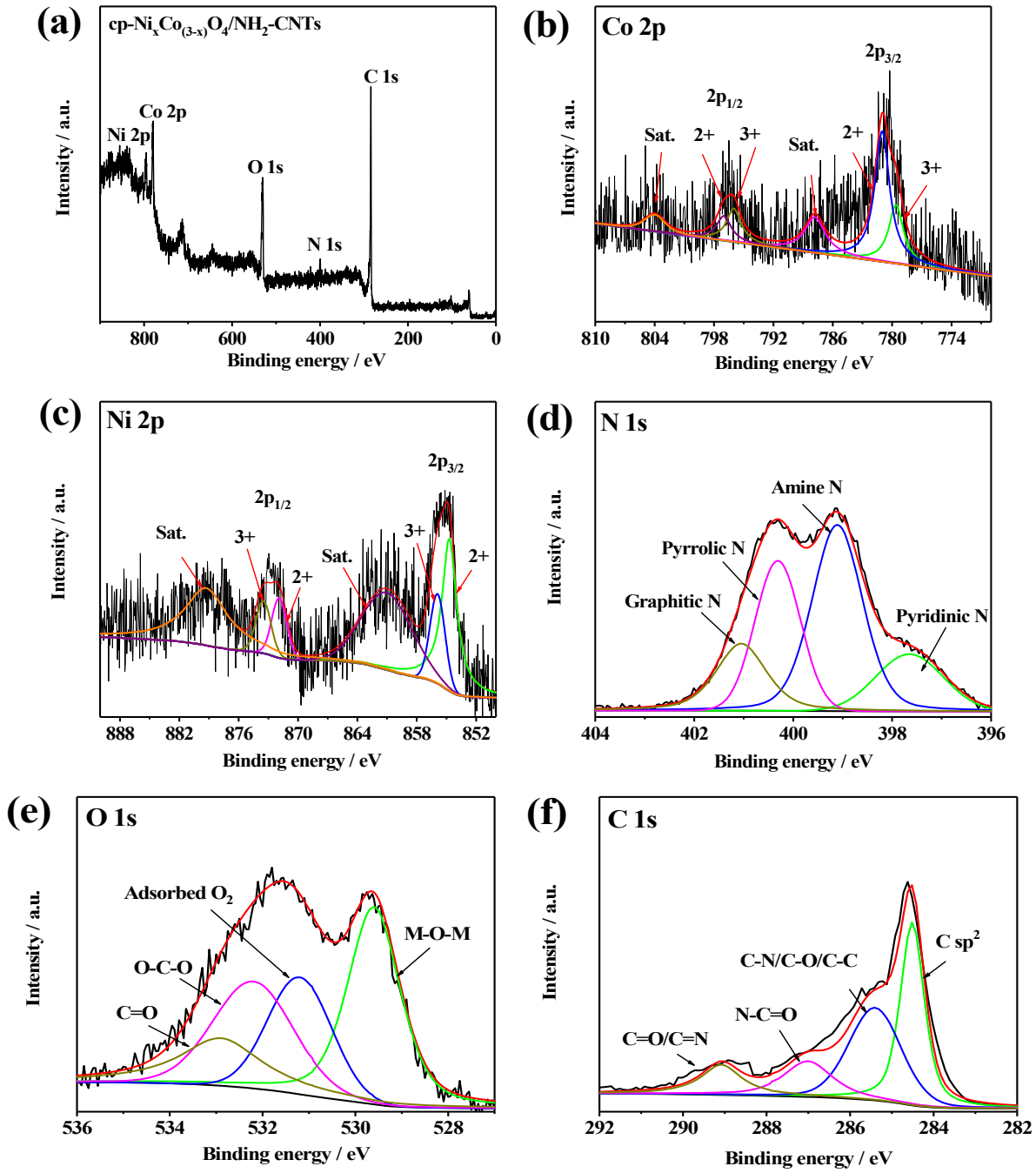

Figure S4. (a) XPS survey spectra of the cp-Ni$_x$Co$_{(3-x)}$O$_4$/NH$_2$-CNTs. High-resolution XPS spectra of (b) Co 2p, (c) Ni 2p, (d) N 1s, (e) O 1s and (f) C 1s.

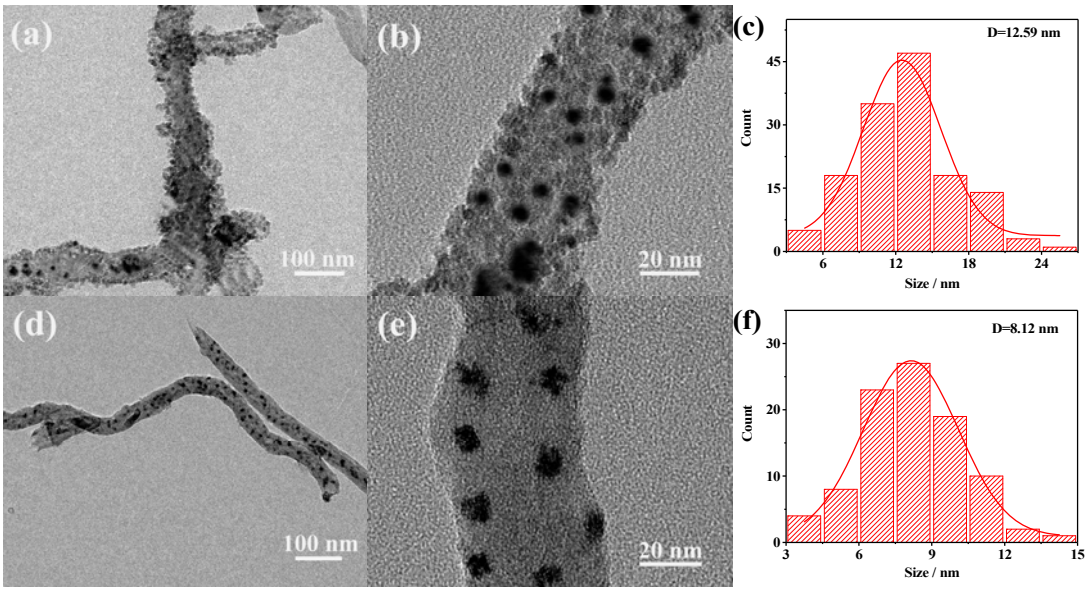

Figure S5. TEM images of the cp-$Ni_xCo_{(3-x)}O_4/NH_2$-CNTs obtained from the direct co-precipitation at (a) the low and (b) high magnifications. (c) Size distribution histogram of the $Ni_xCo_{(3-x)}O_4$ NPs in the cp-$Ni_xCo_{(3-x)}O_4/NH_2$-CNTs. TEM images of the NiO/NH_2-CNTs obtained from the direct co-precipitation at (d) the low and (e) high magnifications. (f) Size distribution histogram of the NiO NPs in the NiO/NH_2-CNTs.

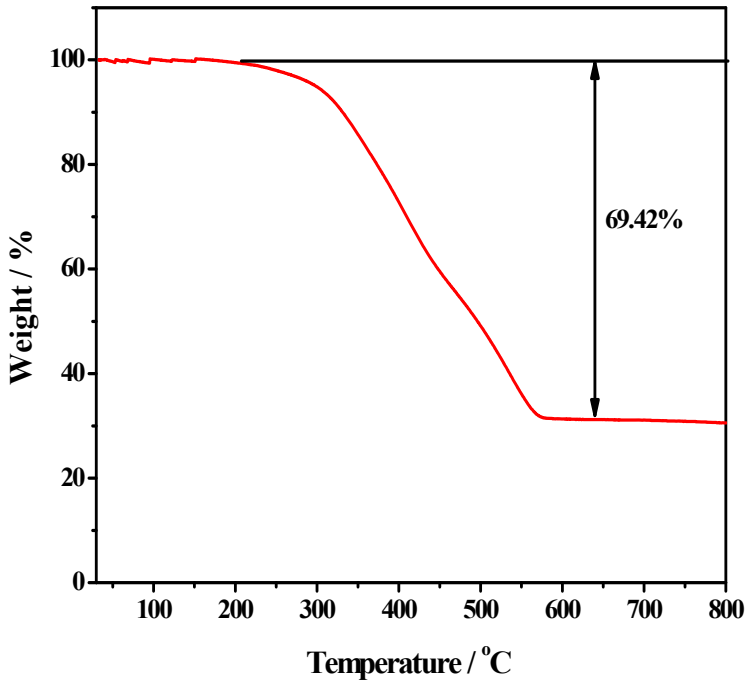

Figure S6. TGA curve of the cp-$Ni_xCo_{(3-x)}O_4/NH_2$-CNTs.

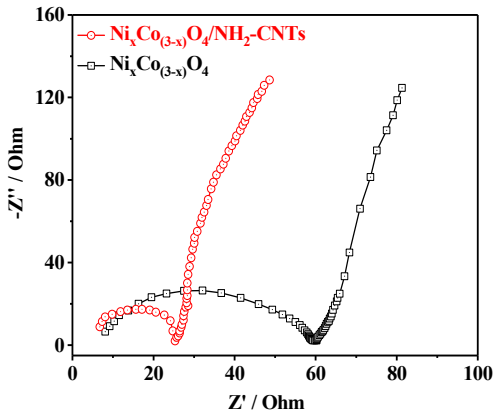

Figure S7. Electrochemical impedance spectra of the $Ni_xCo_{(3-x)}O_4/NH_2$-CNTs and the $Ni_xCo_{(3-x)}O_4$.

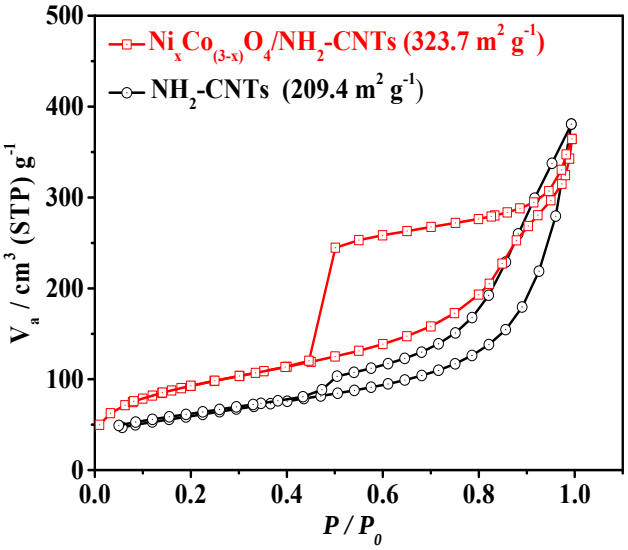

Figure S8. N_2 adsorption-desorption isotherms of $Ni_xCo_{(3-x)}O_4/NH_2$-CNTs and NH_2-CNTs.

Table S1. Relative percentages of the atoms in the $Ni_xCo_{(3-x)}O_4/NH_2$-CNTs and NH_2-CNTs based on the XPS results.

Sample	C	N	O	Ni	Co
$Ni_xCo_{(3-x)}O_4/NH_2$-CNTs	59.09	4.67	24.55	4.77	6.92
NH_2-CNTs	69.82	8.56	21.62	-	-

Table S2. Relative percentages of the C, O, and N containing components in the NH_2-CNTs and $Ni_xCo_{(3-x)}O_4/NH_2$-CNTs estimated based on the XPS spectra deconvolution.

sample	element	Assignment	Binding energy /eV	percentage / %
NH_2-CNTs	C	C sp^2	284.8	38.72
		C-C/C-N/C-O	285.6	20.33
		N-C=N/C=O	287.2	30.42
		O-C=O/C=N	289.7	10.53
	O	O-C-O	531.9	59.23
		C=O	533.2	40.77
	N	Pyridinic N	398.9	12.76
		Amine (-NH_2)	399.3	29.08
		Pyrrolic N	400.5	49.43
		Graphitic N	401.3	8.73
$Ni_xCo_{(3-x)}O_4/NH_2$-CNTs	C	C sp^2	284.6	38.54
		C-C/C-N/C-O	285.4	20.53
		N-C=N/C=O	287.0	30.32
		O-C=O/C=N	289.5	10.61
	O	O-C-O	531.8	23.69
		C=O	533.0	16.30
		M-O-M	529.9	25.71
		Adsorbed O_2	531.0	34.30
	N	pyridinic N	398.6	12.87
		amine (-NH_2)	399.1	23.17
		pyrrolic N	400.4	55.43
		graphitic N	401.0	8.53

Table S3. Comparison of the catalytic bifunctionality of the $Ni_xCo_{(3-x)}O_4/NH_2$-CNTs with those reported.

Bifunctional Catalyst	Mass Loading / mg cm^{-2}	E_{ORR} at onset potential / V	E_{ORR} at the current density of -3 mA cm^{-2}) / V	E_{OER} at onset potential / V	E_{OER} at the current density of -10 mA cm^{-2}) / V	ΔE= (OER-ORR) vs. RHE /V	Ref.
$Ni_xCo_{(3-x)}O_4/NH_2$-CNTs	0.12	0.948	0.851	1.479	1.615	0.764	This work
$MnCo_2O_4$/CNT	0.1	0.88	0.75	1.49	1.62	0.86	[1]
Co_3O_4/N-rGO	0.11	0.89	0.80	1.54	1.81	1.01	[2]
Co_9S_8/NSC	0.12	0.90	0.82	1.52	1.65	0.89	[3]
$NiFe_2O_4$/MWCNT	0.64	0.91	0.81	1.49	1.61	0.80	[4]
$NiCo_2O_4$	0.22	0.93	0.78	1.51	1.62	0.84	[5]
$NiCo_2O_4$/G	0.41	0.92	0.62	1.52	1.62	0.94	[6]
$CoFe_2O_4$/CNTs	1.0	0.904	0.75	1.55	1.65	0.90	[7]
$Fe_{0.1}Ni_{0.9}Co_2O$	0.2	0.825	0.2	1.503	1.65	1.45	[8]
$NiCo_2O_4$/C	0.19	0.87	0.72	1.52	1.65	0.93	[9]
$NiCo_2O_4$@Co_3O_4	0.23	0.82	0.68	1.55	1.68	1.0	[10]
$FeCo_2O_4$/hollow graphene(HG)	1.0	0.92	0.82	1.54	1.65	0.83	[11]
$ZnCo_2O_4$/NCNT	0.2	0.88	0.80	1.56	1.65	0.85	[12]
Co_3O_4@Co/NCNT	0.21	0.88	0.72	1.52	1.62	0.89	[13]
NiCo/PFC aerogels	0.2	0.86	0.79	1.54	1.63	0.84	[14]

Reference

1. X. Ge, Y. Liu, F. W. Goh, T. S. Hor, Y. Zong, P. Xiao, Z. Zhang, S. H. Lim, B. Li and X. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 12684-12691.
2. T. Zhang, C. He, F. Sun, Y. Ding, M. Wang, P. Lin, J. Wang and Y. Lin, *Sci. Rep.*, 2017, **7**, 43638-43645.
3. H.-x. Zhong, K. Li, Q. Zhang, J. Wang, F.-l. Meng, Z.-j. Wu, J.-m. Yan and X.-b. Zhang, *NPG Asia Mater.*, 2016, **8**, 308-308.
4. P. Li, R. Ma, Y. Zhou, Y. Chen, Q. Liu, G. Peng, Z. Liang and J. Wang, *RSC Adv.*, 2015, **5**, 73834-73841.
5. M. Prabu, K. Ketpang and S. Shanmugam, *Nanoscale*, 2014, **6**, 3173-3181.
6. D. U. Lee, B. J. Kim and Z. Chen, *J. Mater. Chem. A*, 2013, **1**, 4754-4762.
7. W. Yan, W. Bian, C. Jin, J. H. Tian and R. Yang, *Electrochim. Acta*, 2015, **177**, 65-72.
8. Y. T. Lu, Y. J. Chien, C. F. Liu, T. H. You and C. C. Hu, *J. Mater. Chem. A*, 2017, **5**, 21016-21026.
9. J. Wang, Z. Wu, L. Han, R. Lin, H. L. Xin and D. Wang, *Chemcatchem*, 2016, **8**, 736-742.
10. P. Sennu, H. S. Park, K. U. Park, V. Aravindan, K. S. Nahm and Y. S. Lee, *J. Catal.*, 2017, **349**, 175-182.
11. W. Yan, Z. Yang, W. Bian and R. Yang, *Carbon*, 2015, **92**, 74-83.
12. B. Y. Xia, Y. Yan, N. Li, H. B. Wu, X. W. Lou and X. Wang, *Nat. Energy*, 2016, **1**, 15006-15011.
13. N. Sikdar, B. Konkena, J. Masa, W. Schuhmann and T. K. Maji, *Chemistry*, 2017.
14. G. Fu, Y. Chen, Z. Cui, Y. Li, W. Zhou, S. Xin, Y. Tang and J. B. Goodenough, *Nano Lett.*, 2016, **16**, 6516-6522.