Supporting Information

Systematic Study of the Electronic, Carbon and N-doping Effects of CoMn Oxide Composites as Bifunctional Oxygen Electrocatalysts

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Synthesis of Co_3O_4.

In a typical synthesis, 6 mL of $Co(NO_3)_2$ solution (0.5 M) and 9 mL of ammonia (25 wt%) were slowly added into 6 mL DI water under constant stirring. The mixture was stirred for 60 min and then heated at 180 °C for 60 min. The final product was washed with deionized water and dried at 60 ºC overnight.

Synthesis of MnO_2

In a typical synthesis of MnO_2, 0.3951 g $KMnO_4$ was first dissolved in 35 mL deionized water under constant stirring. Then, 0.87 mL of concentrated HCl solution (37 wt%) was slowly added to the above $KMnO_4$ solution. The mixture was transferred into an autoclave (50 mL) and then heated at 140 °C for 12 h. $Mn_xCo_{2-x}O_2$ was synthesized using the same procedure by adding different amounts of $Co(Cl)_2$ solution.

Synthesis of Mn_2O_3:

A total of 25 mmol of $MnSO_4$ and 25 mmol of Na_2CO_3 were added to 30 mL deionized water under constant stirring. The resulting precipitate was calcined for 4 h at 600 °C.

Synthesis of Mn_3O_4:

$Mn(CH_3COO)_2$ (0.2541 g) was dissolved in 40 mL deionized water. NaOH solution (7.5 M) was slowly added under constant stirring. The mixture was transferred into an autoclave (50 mL) and then heated at 160 °C for 10 h. The resulting precipitate was

washed with deionized water, dried at 60 °C overnight, and finally calcined at 400 °C for 1 h in a muffle furnace.

Synthetic of $Co_{2.25}Mn_{0.75}O_4$/CNT-H (hydrothermal)

CNTs (0.0225 g) were dispersed in a mixture of 30 mL ethanol and 1.375 mL deionized water by ultrasonication for 20 min. A total of 0.51 mmol $Co(NO_3)_2$ and 0.17 mmol $Mn(NO_3)_3$ were dissolved into the above solution under constant stirring. Then, 0.625 mL ammonia (25 wt%) was dropped into the mixture. The resulting suspension was kept at 70 °C under magnetic stirring for 24 h. After that, the mixture was transferred into a 50 mL autoclave for hydrothermal reaction at 150 °C for 3 h. The resulting product was washed with deionized water and dried at 60 °C.

Synthesis of NCNTs

CNTs and melamine were mixed together by thorough grinding. NCNTs were prepared by pyrolyzing the CNT-melamine composite at 800 °C for 2 h in an Ar atmosphere.

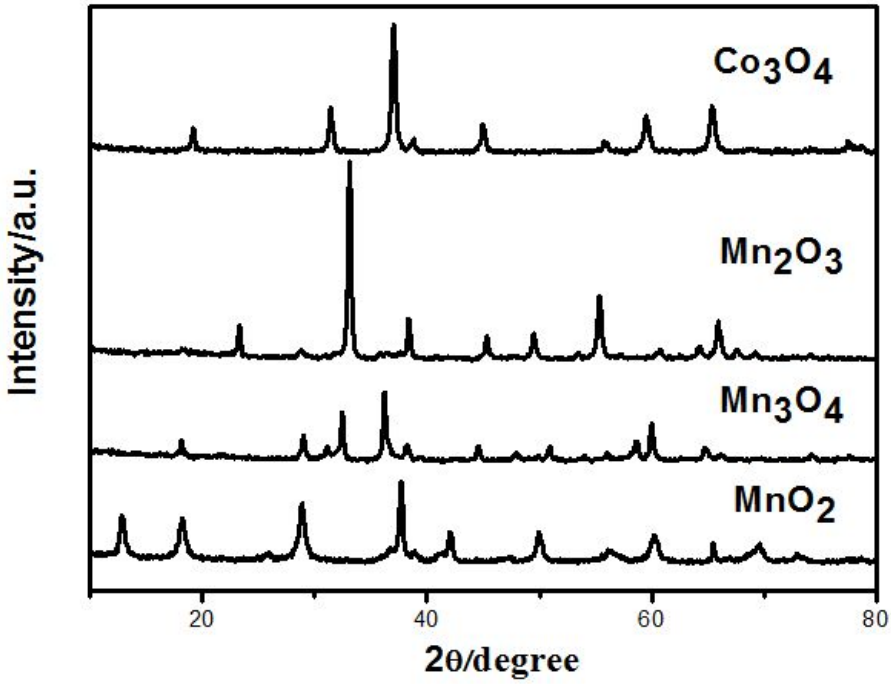

Figure S1. XRD patterns of Co_3O_4, Mn_3O_4, Mn_2O_3 and MnO_2

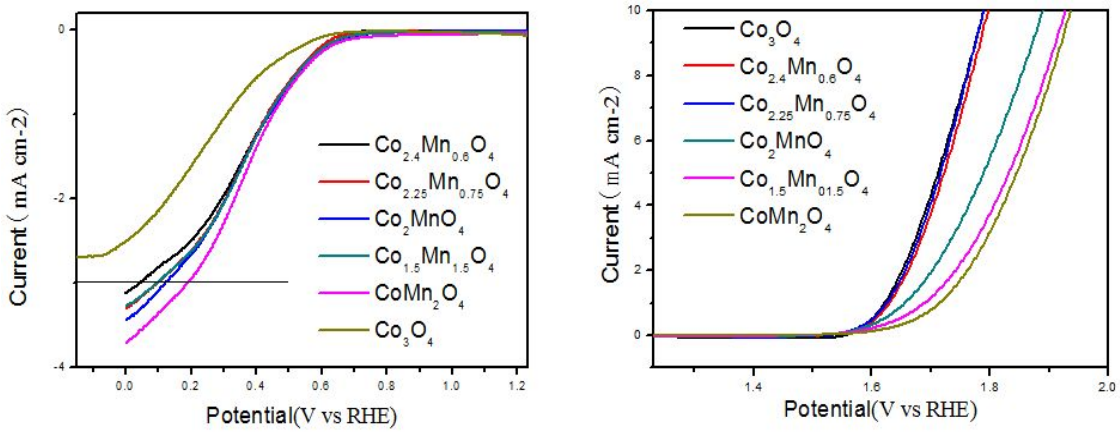

Figure S2. ORR and OER polarization curves of $Co_xMn_{3-x}O_4$ in 0.1 M O_2-saturated KOH solution at 900 rpm; the scan rate is 5 $mV \cdot s^{-1}$; the electrode loading for all samples is 250 $\mu gcat \cdot cm^{-2}$.

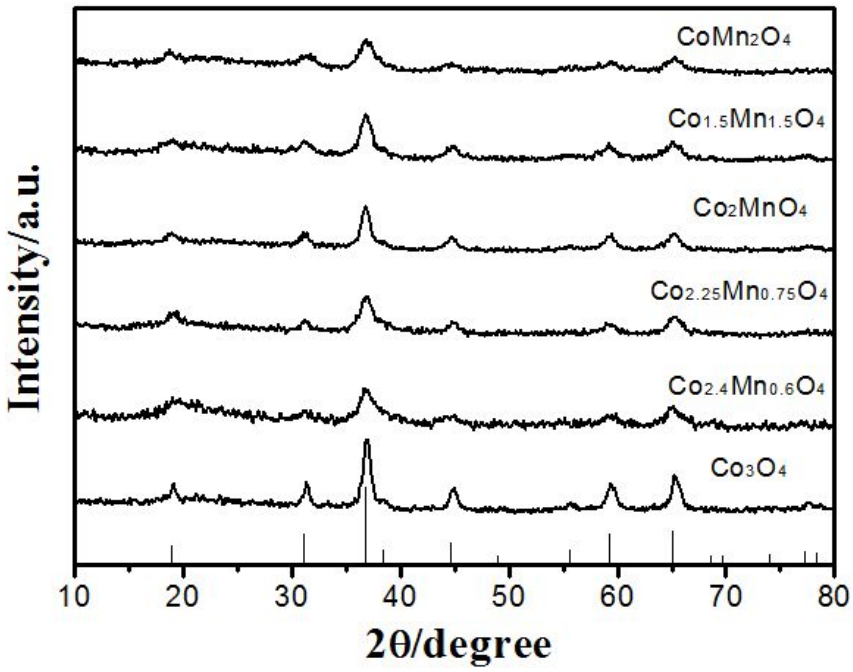

Figure S3. XRD patterns of $CoMn_2O_4$, $Co_{1.5}Mn_{1.5}O_4$, Co_2MnO_4, $Co_{2.25}Mn_{0.75}O_4$, $Co_{2.4}Mn_{0.6}O_4$ and Co_3O_4

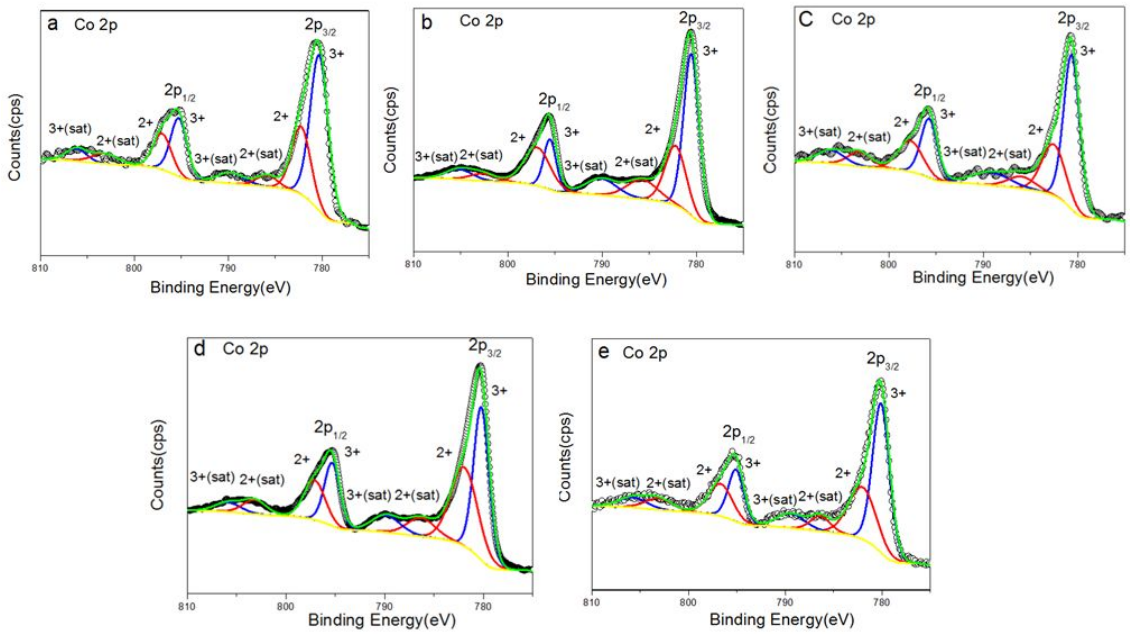

Figure S4. XPS Co 2p spectra of $Co_xMn_{3-x}O_4$: (a) Co_3O_4, (b) $Co_{2.4}Mn_{0.6}O_4$, (c) $Co_{2.25}Mn_{0.75}O_4$, (d) Co_2MnO_4, (e) $Co_{1.5}Mn_{1.5}O_4$

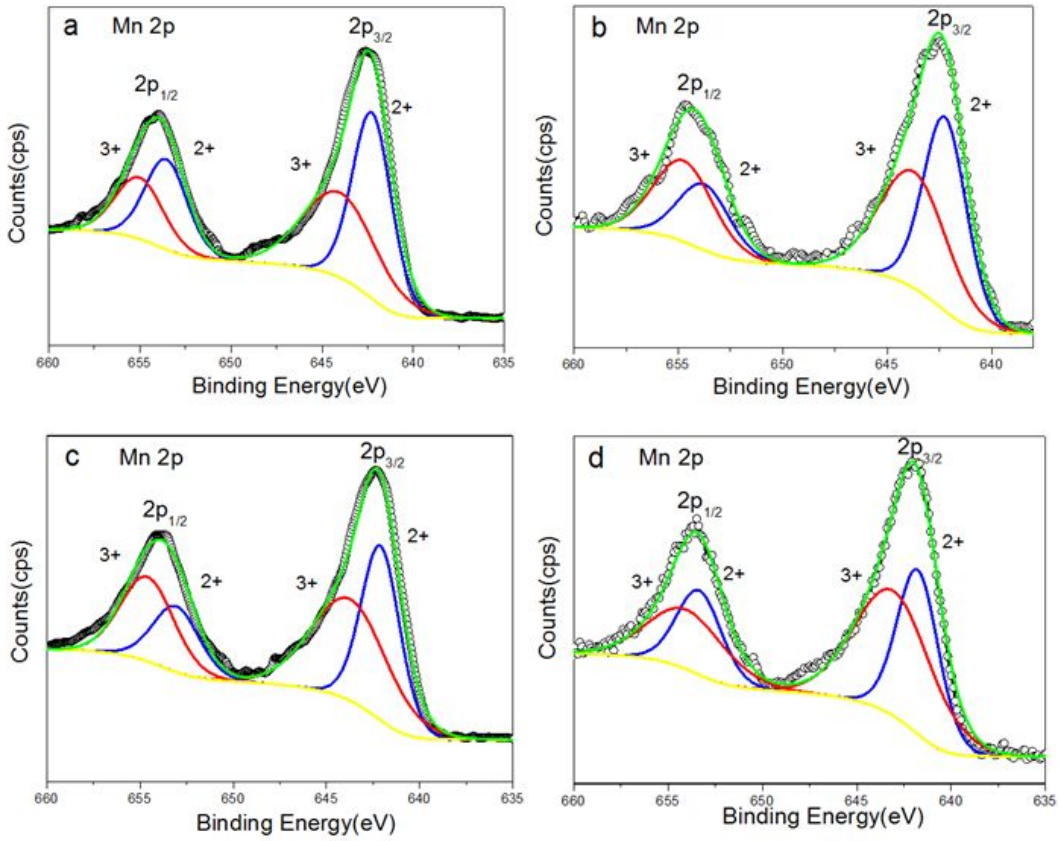

Figure S5. XPS Mn2p spectra of $Co_xMn_{3-x}O_4$: (a) $Co_{2.4}Mn_{0.6}O_4$, (b) $Co_{2.25}Mn_{0.75}O_4$, (c) Co_2MnO_4, (d) $Co_{1.5}Mn_{1.5}O_4$

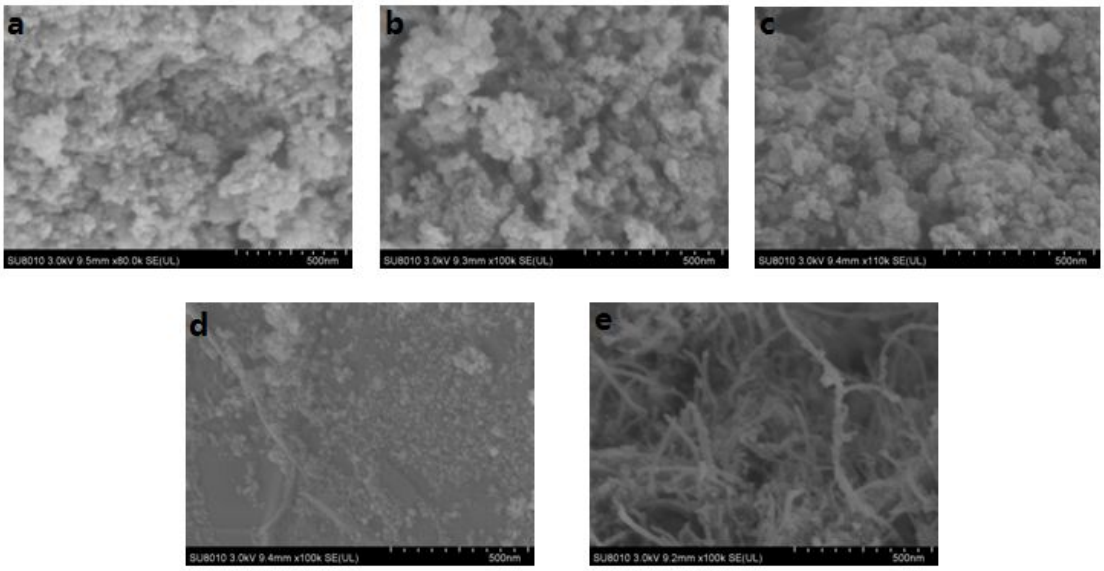

Figure S6. SEM images of $Co_{2.25}Mn_{0.75}O_4$/carbon: (a) EC-300，(b) EC-600JD，(c) Vulcan，(d) Graphene, and (e) CNTs

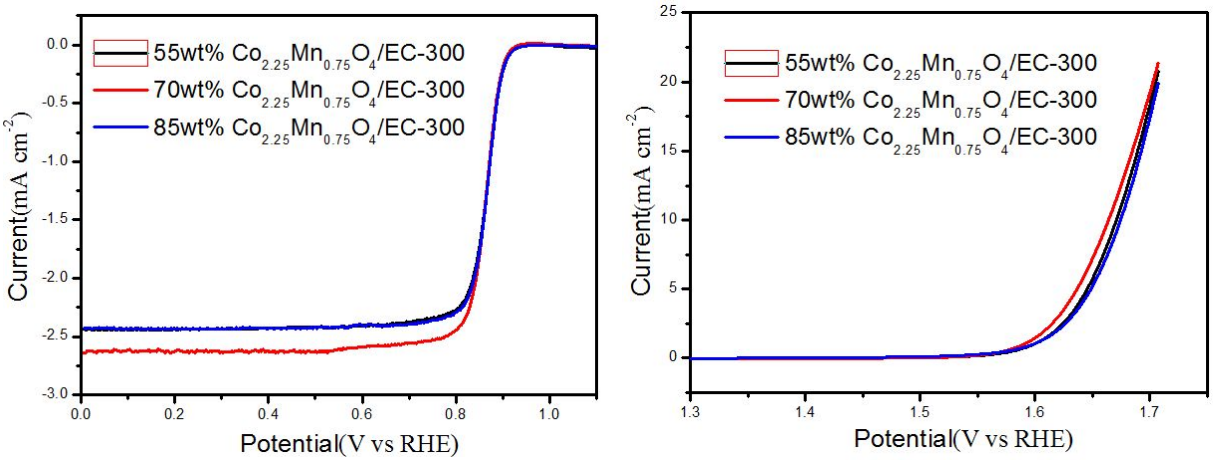

Figure S7. ORR and OER polarization curve of 55 wt% $Co_{2.25}Mn_{0.75}O_4$/EC-300, 70 wt% $Co_{2.25}Mn_{0.75}O_4$/EC-300 and 85 wt% $Co_{2.25}Mn_{0.75}O_4$/EC-300 in 1 M O_2-saturated KOH solution at 900 rpm; the scan rate is 5 $mV \cdot s^{-1}$; the electrode loading for all samples is 250 $\mu gcat \cdot cm^{-2}$.

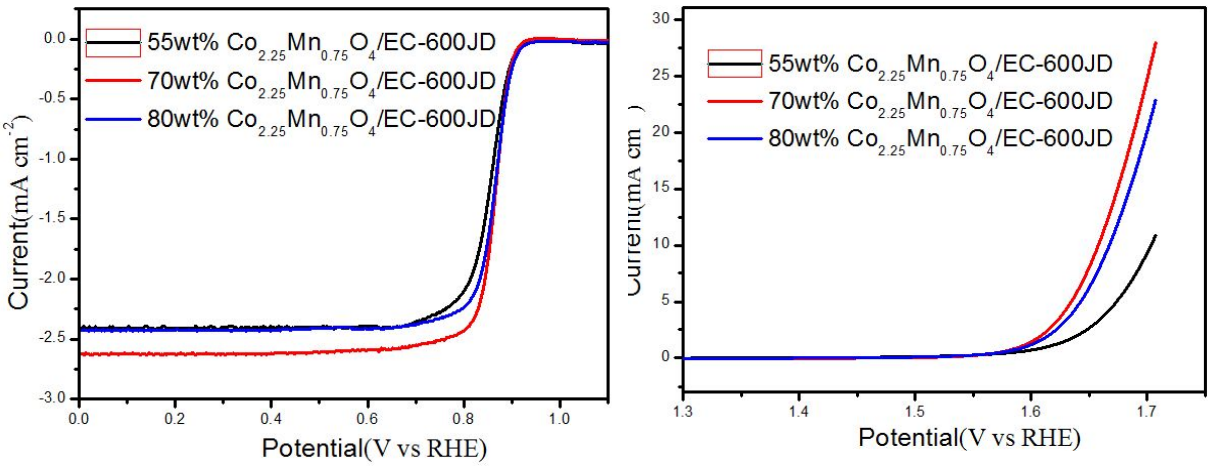

Figure S8. ORR and OER polarization curve of 55wt% $Co_{2.25}Mn_{0.75}O_4$/EC-600JD, 70wt% $Co_{2.25}Mn_{0.75}O_4$/EC-600JD and 85wt% $Co_{2.25}Mn_{0.75}O_4$/EC-600JD in 1 M O_2-saturated KOH solution at 900 rpm; the scan rate is 5 $mV \cdot s^{-1}$; the electrode loading for all samples is 250 $\mu gcat \cdot cm^{-2}$.

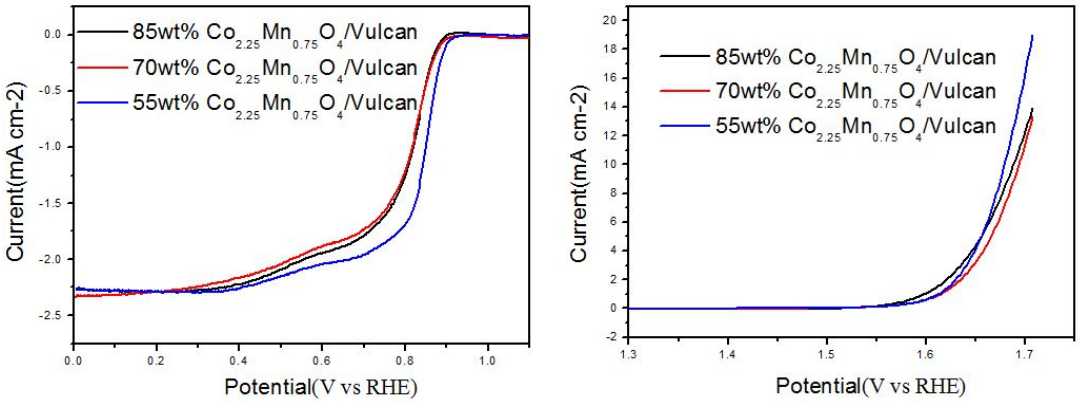

Figure S9. ORR and OER polarization curve of 55wt% $Co_{2.25}Mn_{0.75}O_4$/Vulcan, 70wt% $Co_{2.25}Mn_{0.75}O_4$/ Vulcan and 85wt% $Co_{2.25}Mn_{0.75}O_4$/Vulcan in 1 M O_2-saturated KOH solution at 900 rpm; the scan rate is 5 $mV \cdot s^{-1}$; the electrode loading for all samples is 250 $\mu gcat \cdot cm^{-2}$.

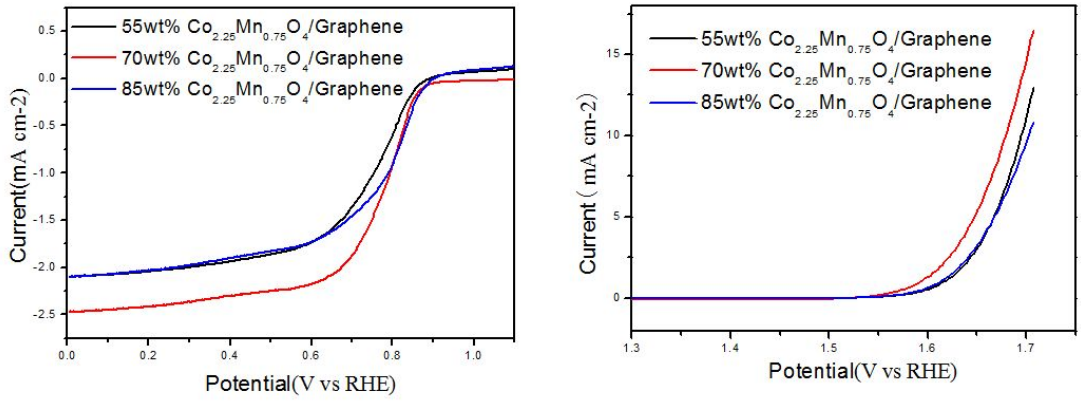

Figure S10. ORR and OER polarization curve of 55wt% $Co_{2.25}Mn_{0.75}O_4$/Graphene, 70wt% $Co_{2.25}Mn_{0.75}O_4$/ Graphene and 85wt% $Co_{2.25}Mn_{0.75}O_4$/ Graphene in 1 M O_2-saturated KOH solution at 900 rpm; the scan rate is 5 $mV \cdot s^{-1}$; the electrode loading for all samples is 250 $\mu gcat \cdot cm^{-2}$.

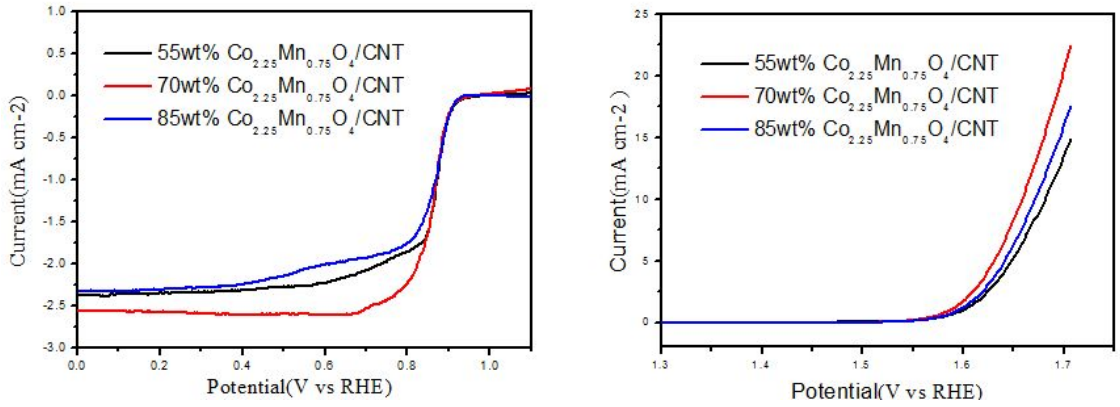

Figure S11. ORR and OER polarization curve of 55wt% $Co_{2.25}Mn_{0.75}O_4$/CNT, 70wt% $Co_{2.25}Mn_{0.75}O_4$/CNT and 85wt% $Co_{2.25}Mn_{0.75}O_4$/CNT in 1 M O_2-saturated KOH solution at 900 rpm; the scan rate is 5 $mV \cdot s^{-1}$; the electrode loading for all samples is 250 $\mu gcat \cdot cm^{-2}$.

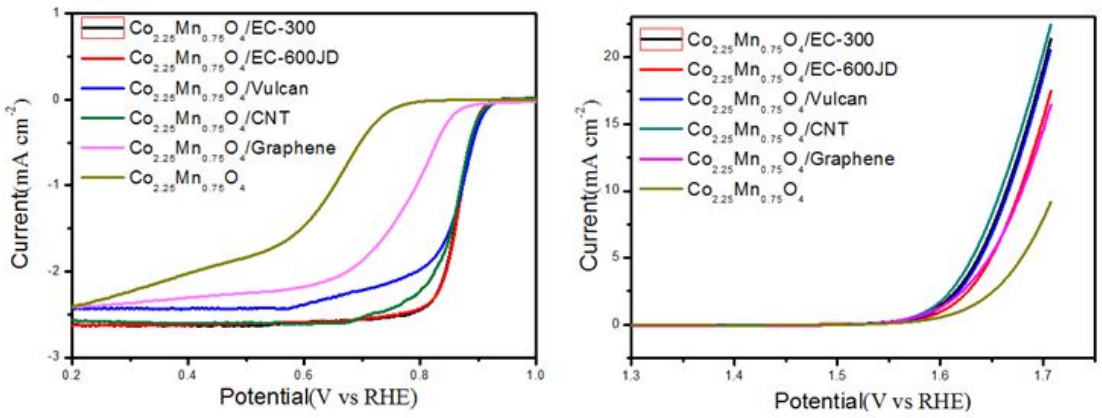

Figure S12. ORR and OER polarization curves of $Co_{2.25}Mn_{0.75}O_4$ /carbon (EC-300, EC-600JD, Vulcan, Graphene, CNT) with identical content of CoMn oxide (70%) in 1 M O_2-saturated KOH solution at 900 rpm; the scan rate is 5 $mV \cdot s^{-1}$; the electrode loading for all samples is 250 $\mu gcat \cdot cm^{-2}$.

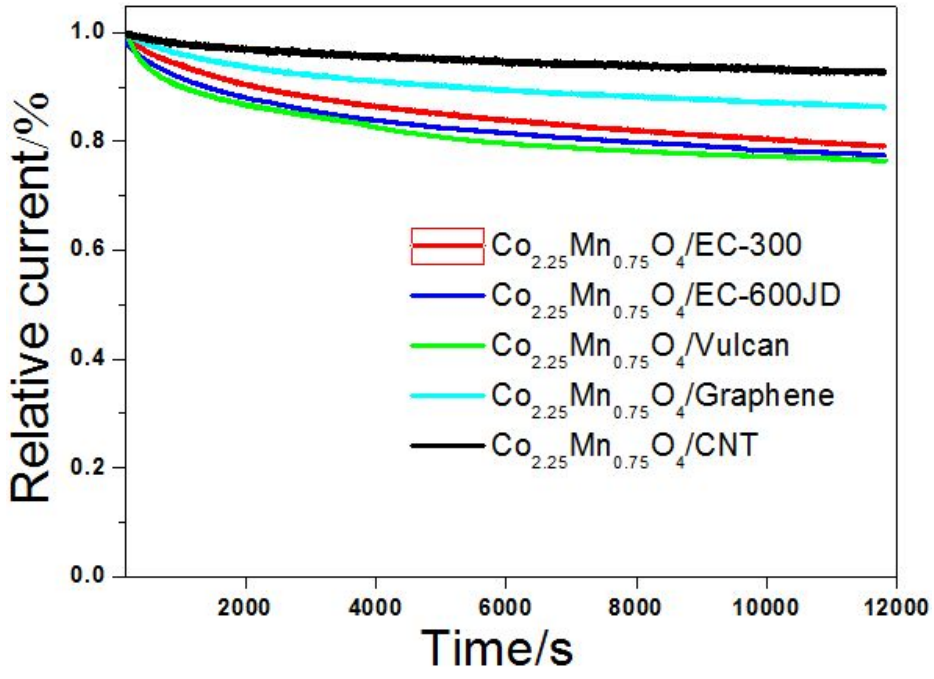

Figure S13. Chronoamperometric responses of $Co_{2.25}Mn_{0.75}O_4$/carbon (EC-300, EC-600JD, Vulcan, Graphene, CNT) based on the relative retained current (%) vs. time operated at 0.70 V in O_2-saturated 1 M KOH.

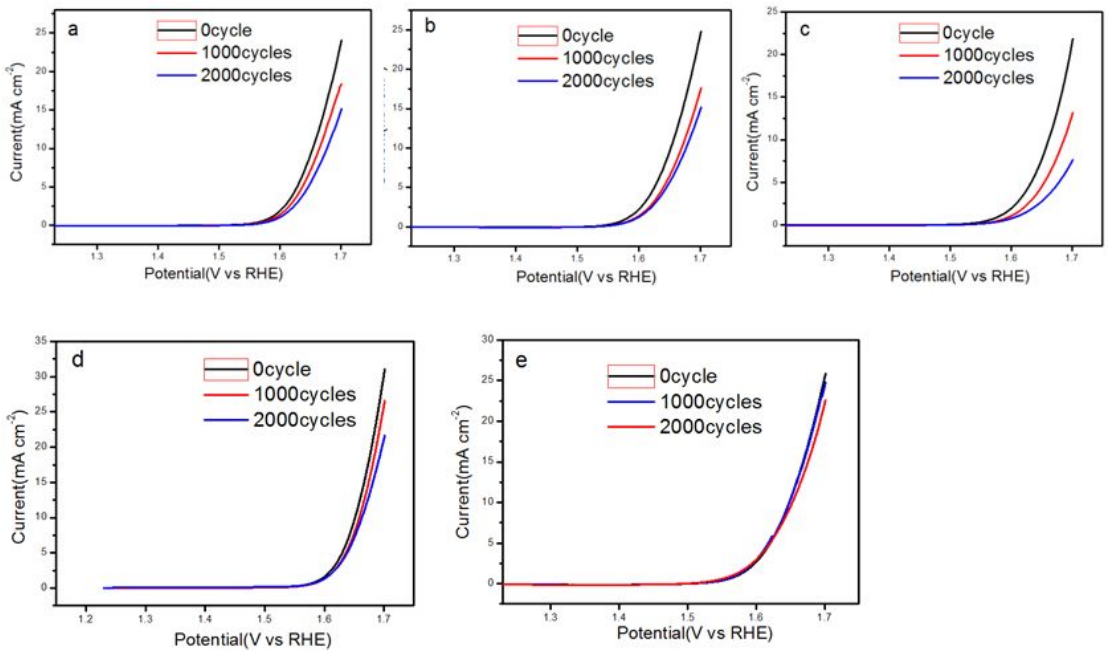

Figure S14. LSV curves of $Co_{2.25}Mn_{0.75}O_4$/carbon (EC-300, EC-600JD, Vulcan, Graphene, CNT) collected before and after 2000 cycles from 1.25 V to 1.65 V at 5 mV/s

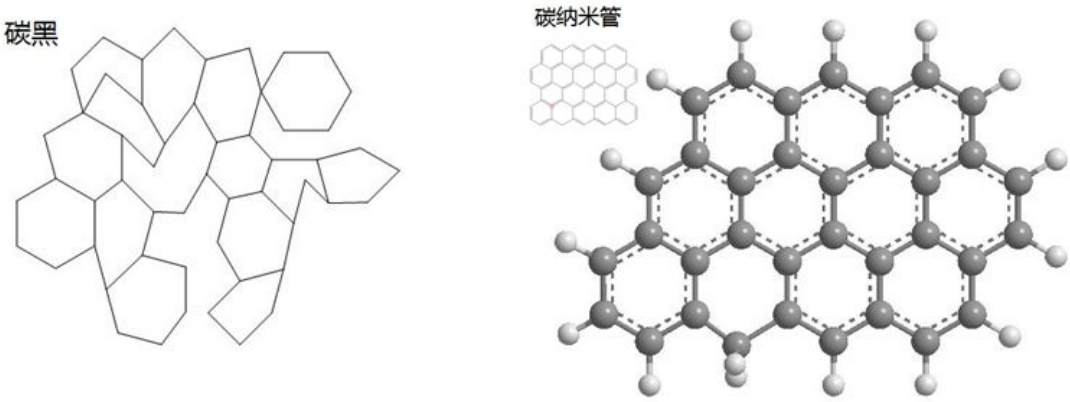

Figure S15. The structure of carbon black (EC-300) and carbon nanotube (CNT)

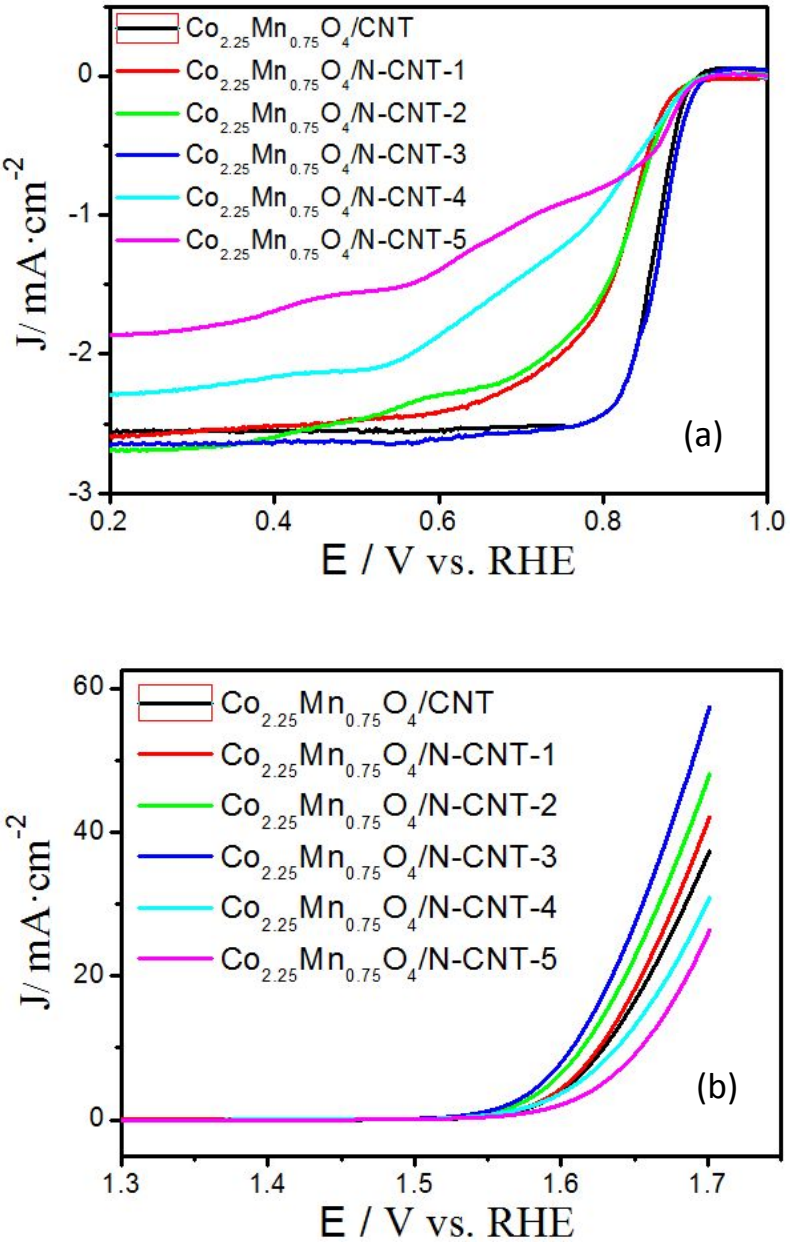

Figure S16. (a) ORR and (b) OER polarization curves for $Co_{2.25}Mn_{0.75}O_4$/CNT and different $Co_{2.25}Mn_{0.75}O_4$/NCNT samples in 1M O_2-saturated KOH solution at 900 rpm. The scan rate is 5 mV·s^{-1}. The loading for all catalysts is 250 μg cat ·cm^{-2}.

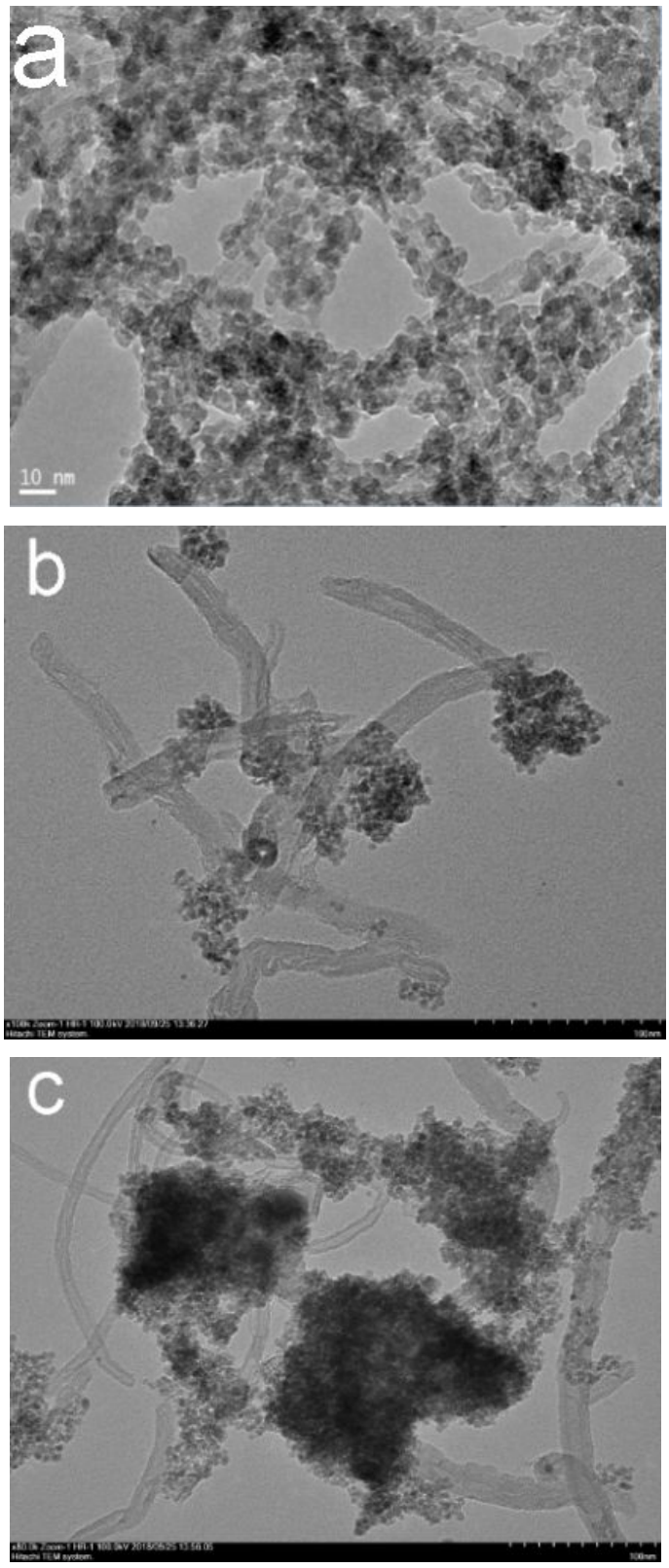

Figure S17. TEM pictures of $Co_{2.25}Mn_{0.75}O_4$/CNT-3(a) , $Co_{2.25}Mn_{0.75}O_4$/CNT-4 (b)and $Co_{2.25}Mn_{0.75}O_4$/CNT-5(c).

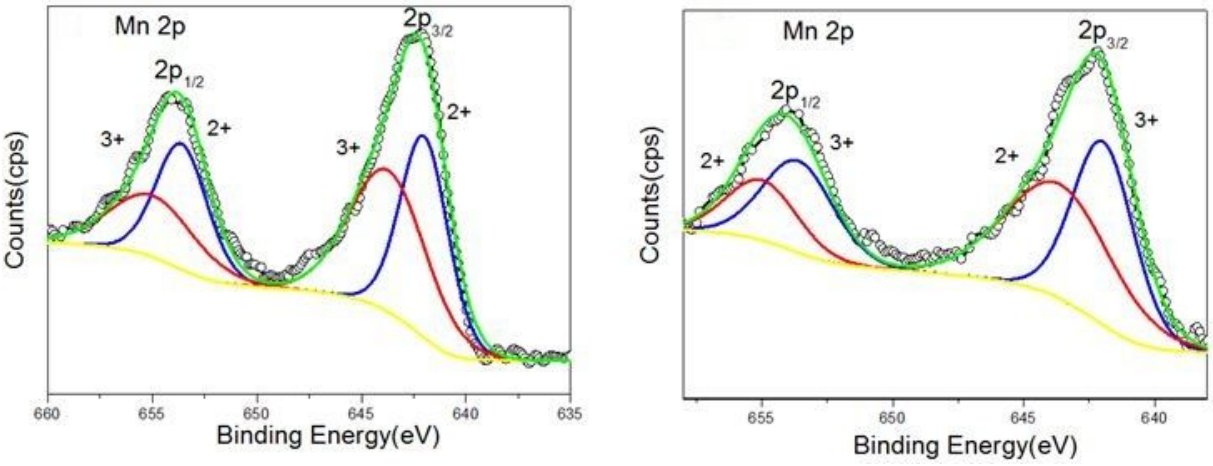

Figure S18. (a) XPS Mn 2p spectra of the $Co_{2.25}Mn_{0.75}O_4$/CNT, (b) XPS Mn 2p spectra of the $Co_{2.25}Mn_{0.75}O_4$/NCNT-3

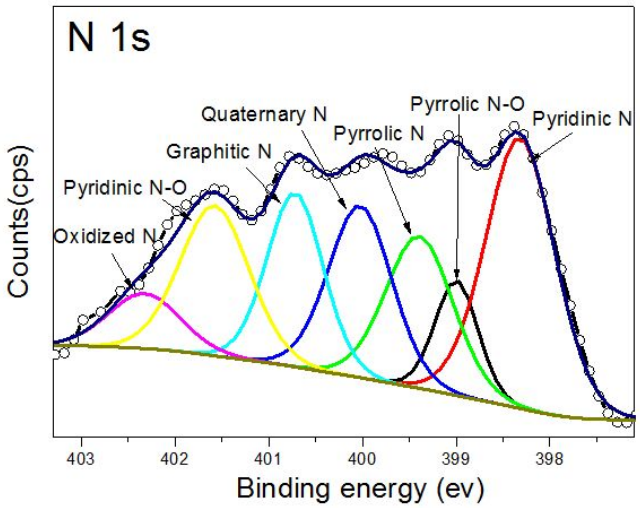

Figure S19. XPS N1s spectra of the $Co_{2.25}Mn_{0.75}O_4$/NCNT-3

Table S1. Crystal structure information of metal oxides

Material	Crystal phase	Space group	Lattice parameters（Å^3）
Co_3O_4	Cubic (FCC)	Fd3m（227）	8.0837*8.0837*8.0837
MnO_2	Tetragonal (BCC)	I4/m（87）	9.7847*9.7847*2.863
Mn_2O_3	Cubic (BCC)	Ia-3（206）	9.4091*9.4091*9.4091
Mn_3O_4	Tetragonal (BCC)	I41/amd（141）	5.78*5.78*9.33

Table S2. Changes of lattice parameters after Mn doping in Co_3O_4

Catalyst	Crystal phase	Space group	Lattice parameters	Cell volume
Co_3O_4	Cubic	Fd3m(227)	a=b=c=11.815Å	1649*A^{-3}
$Co_{2.4}Mn_{0.6}O_4$	Cubic	Fd3m(227)	a=b=c=11.825Å	1653*A^{-3}
$Co_{2.25}Mn_{0.75}O_4$	Cubic	Fd3m(227)	a=b=c=11.832Å	1656*A^{-3}
Co_2MnO_4	Cubic	Fd3m(227)	a=b=c=11.839Å	1659*A^{-3}
$Co_{1.5}Mn_{1.5}O_4$	Cubic	Fd3m(227)	a=b=c=11.861Å	1664*A^{-3}

Table S3. The valence states of Co and Mn sepecies in the samples

Sample	Co^{3+}/Co^{2+}	Mn^{3+}/Mn^{2+}
Co_3O_4	1.81	--
$Co_{2.4}Mn_{0.6}O_4$	1.61	0.76
$Co_{2.25}Mn_{0.75}O_4$	1.64	1.10
Co_2MnO_4	1.41	1.25
$Co_{1.5}Mn_{1.5}O_4$	1.07	1.35

Table S4. Summary of electric conductivity of Co_3O_4 and carbon (EC-300, EC-600JD, Vulcan, Graphene, CNT)

	Electric Resistivity (Ω·cm)	Surface area ($m^2 \cdot g^{-1}$)	Particle Size (nm)	Pore Volume (mL/100g)
Co_3O_4	$9.0*10^3$	--	--	--
EC-300	3.9	800	50	365
EC-600JD	6.5	1400	30	495
Vulcan	108	254	30	174
Graphene	0.6	500	D=0.3μm	--
CNT	0.1	490	L=5μm	OD=5nm

* D, diameter; L, length; OD, outer diameter.

Table S5. Summary of bifunctional catalytic performance of $Co_{2.25}Mn_{0.75}O_4$/Carbon (Carbon= EC-300, EC-600JD, Vulcan, Graphene, CNT)

Catalyst	OER (E_{10}, E_{onset})	ORR ($E_{1/2}$, J_{lim})	ΔE (E_{10}-$E_{1/2}$)
55 wt% $Co_{2.25}Mn_{0.75}O_4$ /EC-300	1.675 V, 1.57 V	0.86 V, 2.47 mA/cm^2	0.815 V
70 wt% $Co_{2.25}Mn_{0.75}O_4$ /EC-300	1.66 V, 1.57 V	0.86 V, 2.61 mA/cm^2	0.80 V
85 wt% $Co_{2.25}Mn_{0.75}O_4$ /EC-300	1.67 V, 1.57 V	0.86 V, 2.47 mA/cm^2	0.81 V
55 wt% $Co_{2.25}Mn_{0.75}O_4$	1.70 V, 1.61 V	0.84 V, 2.47	0.86 V

/EC-600JD		mA/cm^2	
70 wt% $Co_{2.25}Mn_{0.75}O_4$ /EC-600JD	1.67 V, 1.58 V	0.86 V, 2.61 mA/cm^2	0.81 V
85 wt% $Co_{2.25}Mn_{0.75}O_4$ /EC-600JD	1.68 V, 1.58 V	0.86 V, 2.47 mA/cm^2	0.82 V
55 wt% $Co_{2.25}Mn_{0.75}O_4$/Vulcan	1.68 V, 1.57 V	0.84 V, 2.25 mA/cm^2	0.84 V
70 wt% $Co_{2.25}Mn_{0.75}O_4$/Vulcan	1.67 V, 1.57 V	0.81 V, 2.25 mA/cm^2	0.86 V
85 wt% $Co_{2.25}Mn_{0.75}O_4$/Vulcan	1.69 V, 1.57 V	0.80 V, 2.25 mA/cm^2	0.89 V
55wt% $Co_{2.25}Mn_{0.75}O_4$/Graphene	1.70 V, 1.59 V	0.77 V, 2.08 mA/cm^2	0.93 V
70 wt% $Co_{2.25}Mn_{0.75}O_4$/Graphene	1.68 V, 1.57 V	0.76 V, 2.5 mA/cm^2	0.92 V
85 wt% $Co_{2.25}Mn_{0.75}O_4$/Graphene	1.69 V, 1.57 V	0.76 V, 2.08 mA/cm^2	0.93 V
55 wt% $Co_{2.25}Mn_{0.75}O_4$/CNT	1.68 V, 1.58 V	0.87 V, 2.47 mA/cm^2	0.81 V
70 wt% $Co_{2.25}Mn_{0.75}O_4$/CNT	1.66 V, 1.58 V	0.87 V, 2.61 mA/cm^2	0.79 V
85 wt% $Co_{2.25}Mn_{0.75}O_4$/CNT	1.67 V, 1.58 V	0.87 V, 2.45 mA/cm^2	0.80 V

Table S6. Summary of bifunctional catalytic performance of $Co_{2.25}Mn_{0.75}O_4$/CNT and different $Co_{2.25}Mn_{0.75}O_4$/NCNT samples

Catalyst	OER（E_{10}）	ORR（$E_{1/2}$）	ΔE（E_{10}-$E_{1/2}$）
$Co_{2.25}Mn_{0.75}O_4$/CNT	1.66 V	0.87 V	0.79 V
$Co_{2.25}Mn_{0.75}O_4$/CNT-1	1.62 V	0.80 V	0.82 V
$Co_{2.25}Mn_{0.75}O_4$/CNT-2	1.61 V	0.80 V	0.81 V
$Co_{2.25}Mn_{0.75}O_4$/CNT-3	1.60 V	0.88 V	0.72 V
$Co_{2.25}Mn_{0.75}O_4$/CNT-4	1.64 V	0.73 V	0.91 V
$Co_{2.25}Mn_{0.75}O_4$/CNT-5	1.66 V	0.69 V	0.97 V