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Electronic Supplementary Information

Crab-shell induced synthesis of ordered macroporous carbon nanofiber arrays coupled with $MnCo_2O_4$ nanoparticles as bifunctional oxgen catalyst for rechargeable Zn-Air batteries

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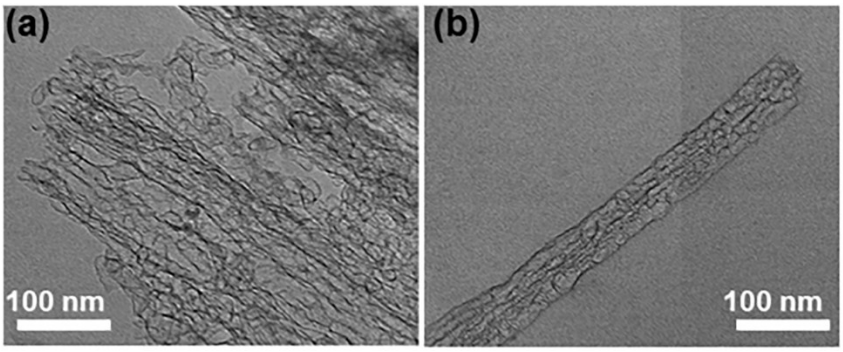

Figure S1 TEM images of pristine MCNA

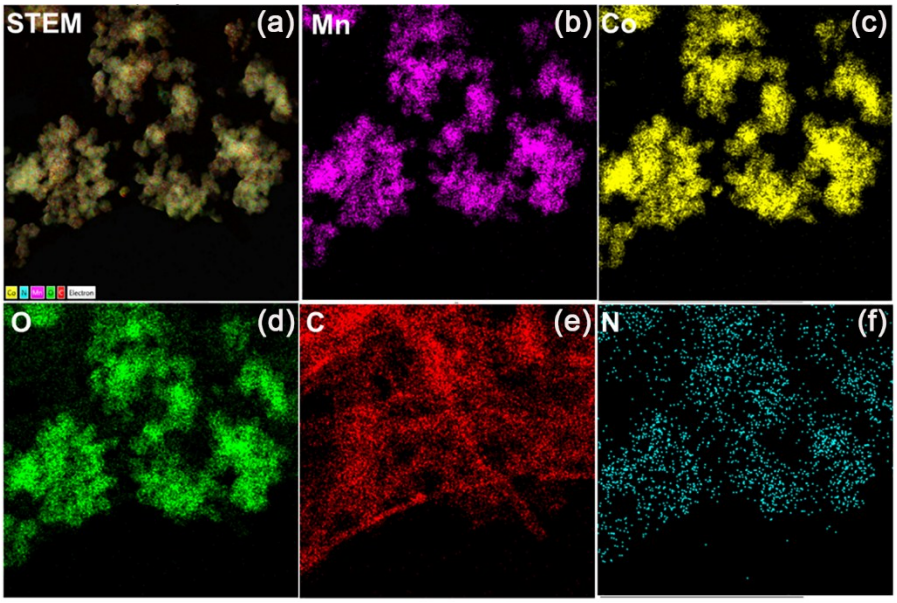

Figure S2 TEM elemental mapping of $MnCo_2O_4$/NMCNA hybird: (a) bright-field TEM image; (b) N-K edge; (d) Co-K edge; (e) Mn-K edge; and (f) O-K edge.

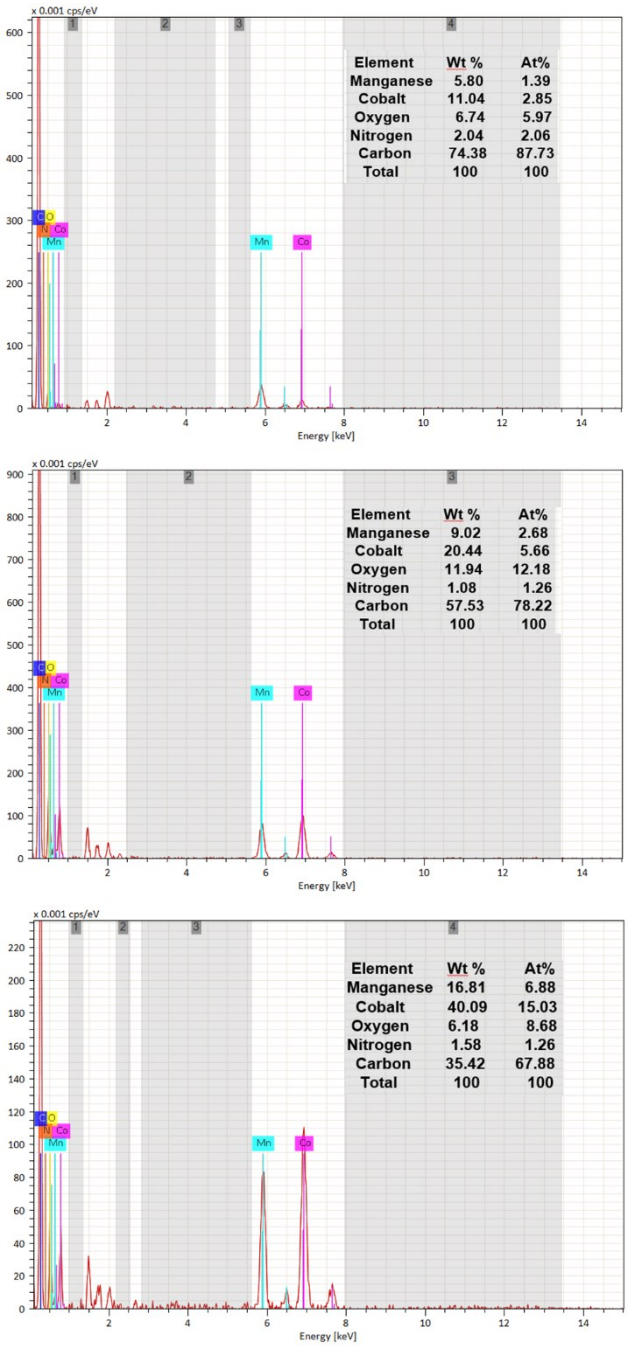

Figure S3 EDX spectrum of the $MnCo_2O_4$/NMCNA-30 % (a), $MnCo_2O_4$/NMCNA-50 % (b) and $MnCo_2O_4$/NMCNA-70 % (c) composites.

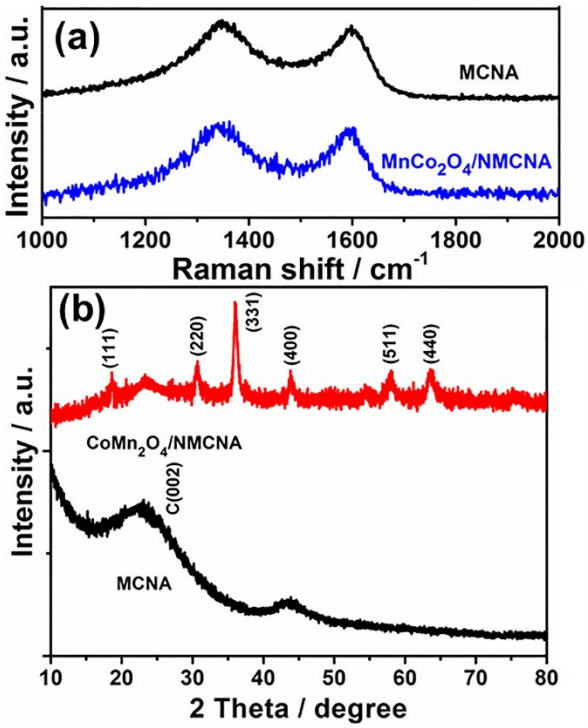

Figure S4 (a) Raman and (b) XRD patterns of MCNA and $MnCo_2O_4$/NMCNA samples

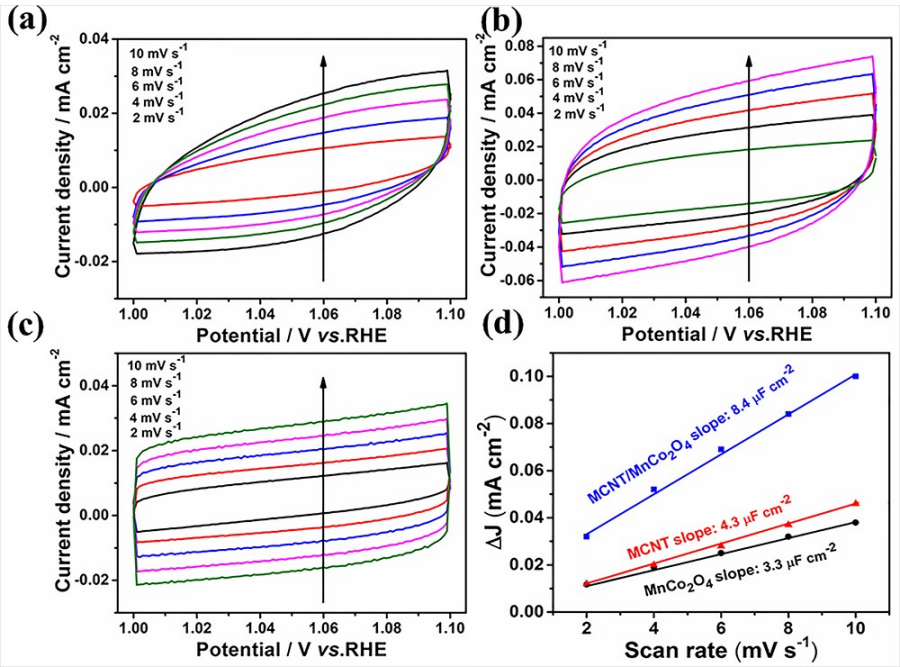

Figure S5 CVs of (c) $MnCo_2O_4$, (b) MCNA and (c) $MnCo_2O_4$/NMCNA at scan rates from 2 to 10 mV s^{-1}. (d) Scan rate dependence of the current densities of the three catalysts at 1.06 V vs RHE.

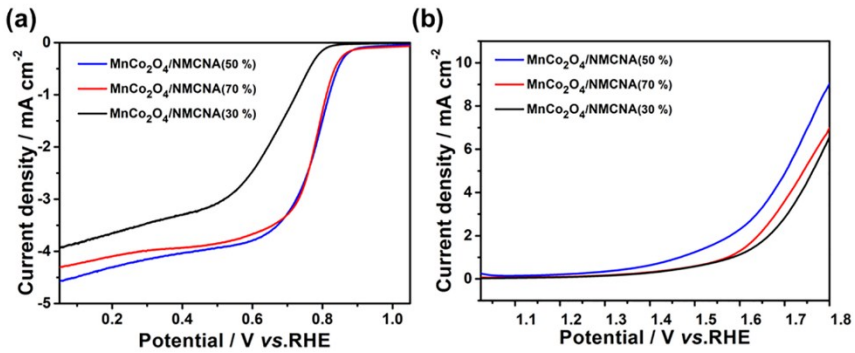

Figure S6 (a) ORR and (b) OER polarization curves of $MnCo_2O_4$/NMCNA-30%, $MnCo_2O_4$/NMCNA-50% and $MnCo_2O_4$/NMCNA-70% hybird in O_2-saturated 0.1 M KOH electrolyte.

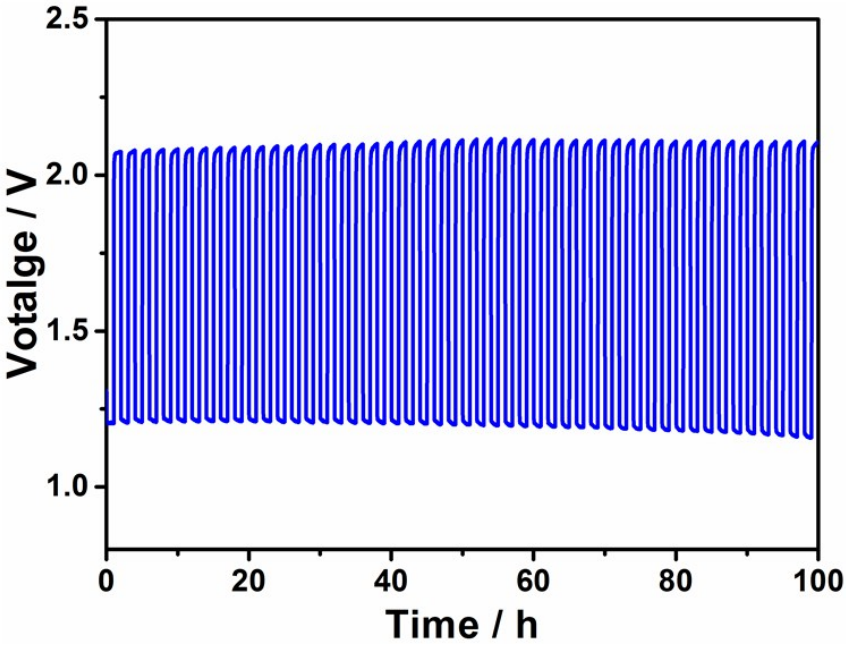

Figure S7. The repeated charge–discharge cycling curves of Zn-air batteries with $MnCo_2O_4$/MCNA catalyst at a current density of 10 mA cm^{-1} in which discharge and charge period was set to be 1 h.

Table S1 Comparison of the ORR activity for several recently reported metal-free catalysts.

Catalyst	Mass loading ($mg\ cm^{-2}$)	Electron transfer number	Onset potential (V. vs RHE)	Ref
Co_3O_4 /rmGO	0.1	3.9	0.88	[1]
$Co(OH)_x$NCNT	0.1	3.85	0.87	[2]
N-CG– CoO	/	~ 4	0.90	[3]
Fe_3O_4/N-GAs	0.1	3.72-3.95	0.77	[4]
Ni_3Fe/N-C sheets	0.13	3.82-3.89	0.90	[5]
egg-CMS	0.136	3.11	0.84	[6]
NCNT/CoO-NiO-NiCo	0.21	3.85	0.97	[7]
nanoporous Carbon-L	0.02	3.68	0.86	[8]
Co@Co_3O_4@C-CM	0.1	3.8-3.9	0.93	[9]
Co-600-800	/	3.84	0.85	[10]
$MnCo_2O_4$/NMCNA	0.1	3.9	0.90	This work

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