Supplementary information

Porous calcium-manganese oxide/carbon nanotube microspheres as efficient oxygen reduction catalysts for rechargeable zinc air batteries

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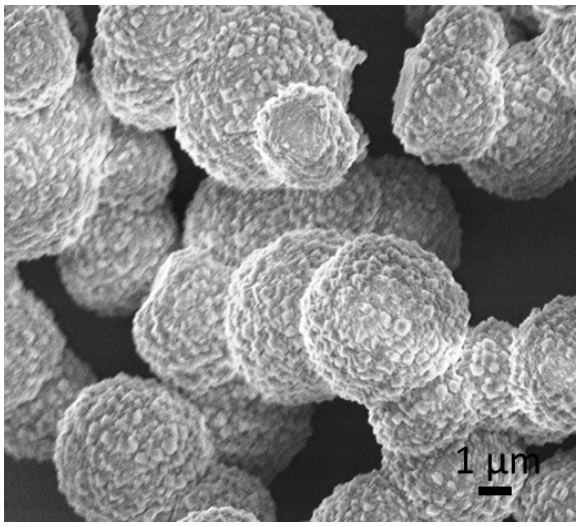

Fig. S1 SEM image of the carbonate precursor, $CaMn(CO_3)_2$.

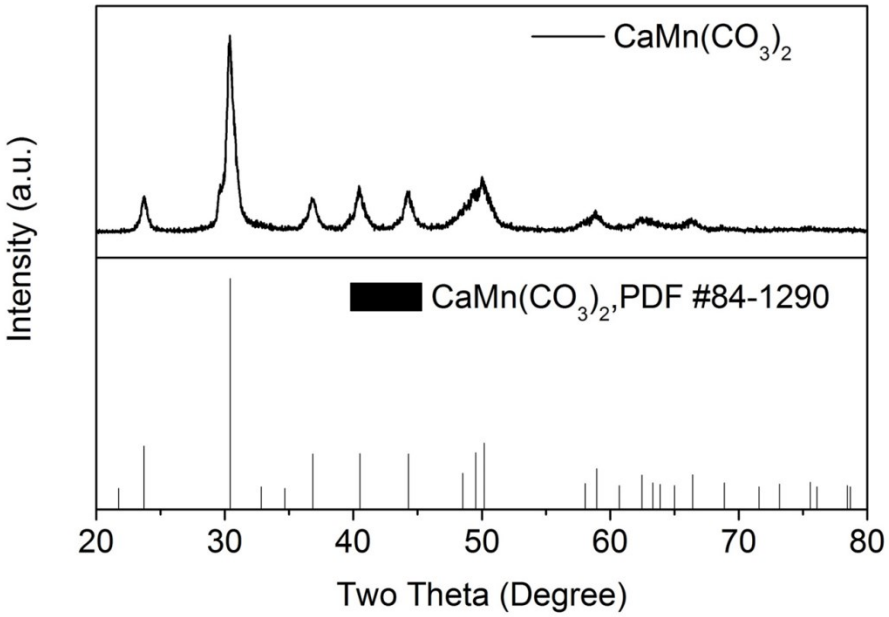

Fig. S2 XRD pattern of $CaMn(CO_3)_2$ and its standard, PDF #84-1290

The presence of $CaMn(CO_3)_2$ is further confirmed by XRD which corresponds to the standard (PDF #84-1290).

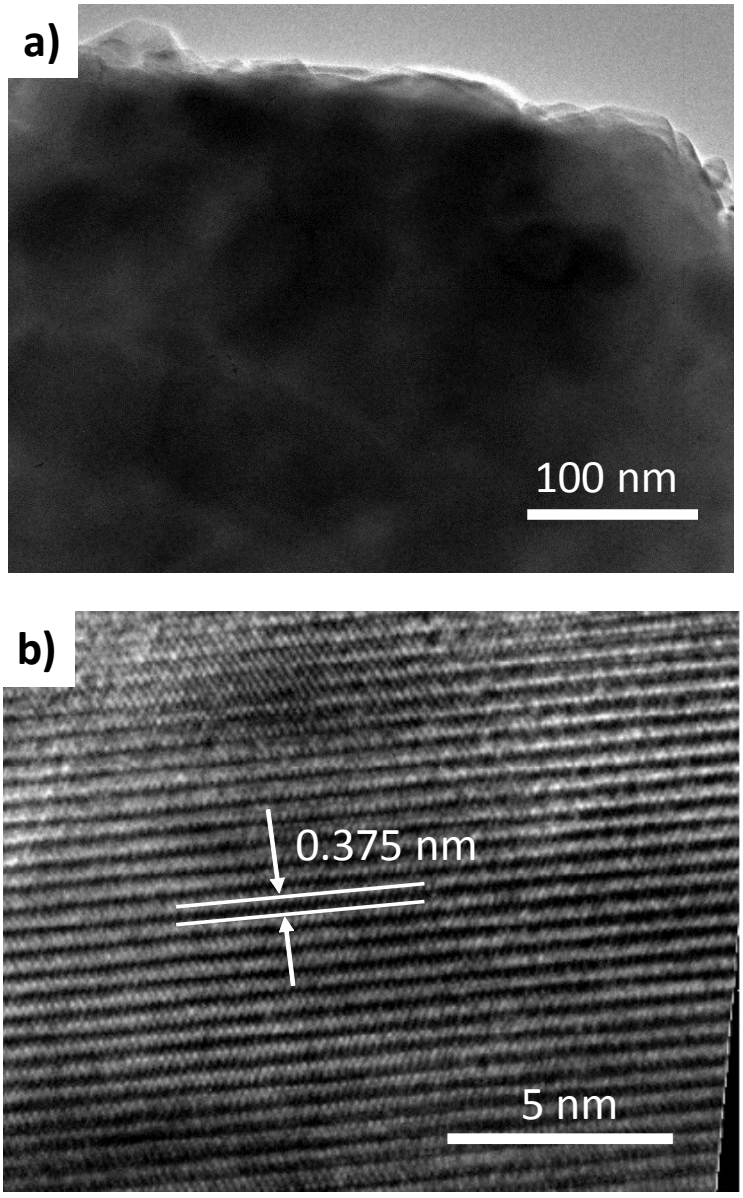

Fig. S3 TEM (a) and high-resolution TEM (b) images of $CaMnO_3$.

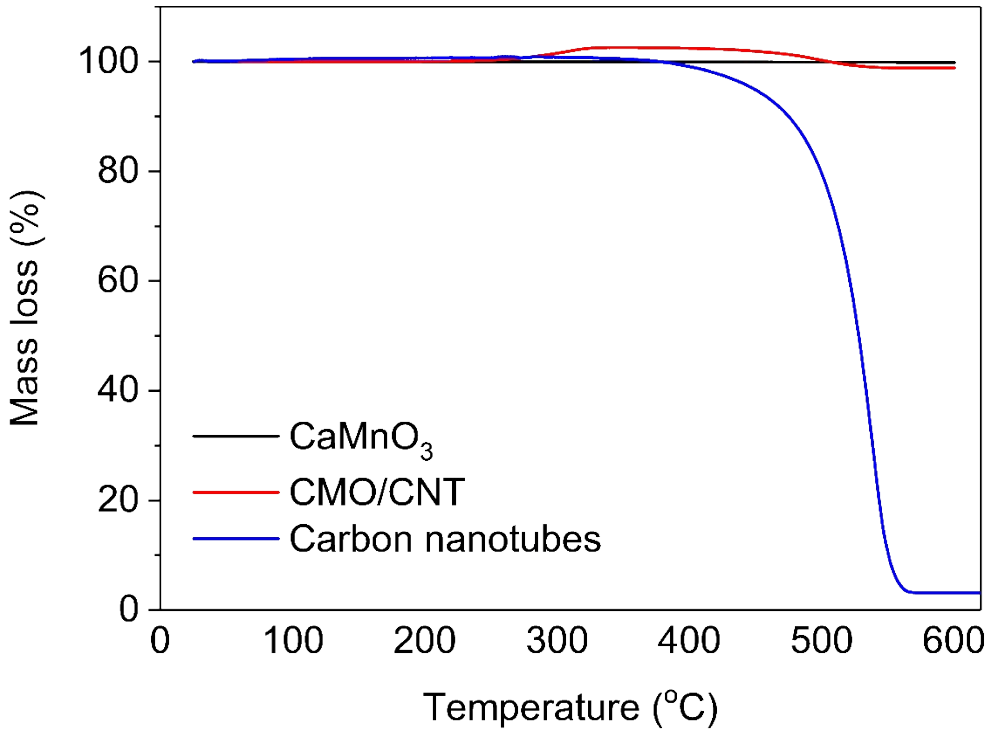

Fig. S4 TGA profile of $CaMnO_3$, CMO/CNT and carbon nanotubes in air. CMO/CNT (red) shows re-oxidation to stoichiometric $CaMnO_3$ (black), where no mass gain is observed in $CaMnO_3$. Pure carbon nanotubes (blue) burn off occurs above 350 °C and corresponds to the weight loss of carbon nanotubes in CMO/CNT.

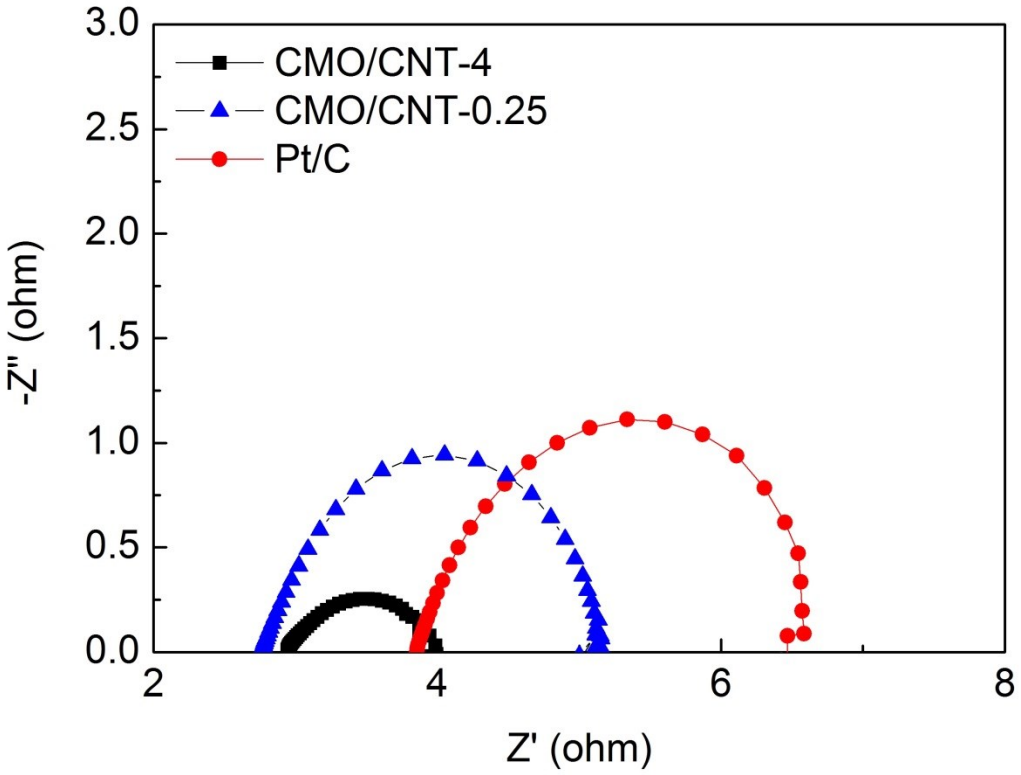

Fig. S5 Nyquist plot of zinc-air batteries with CMO/CNT-4, CMO/CNT-0.25 and Pt/C.

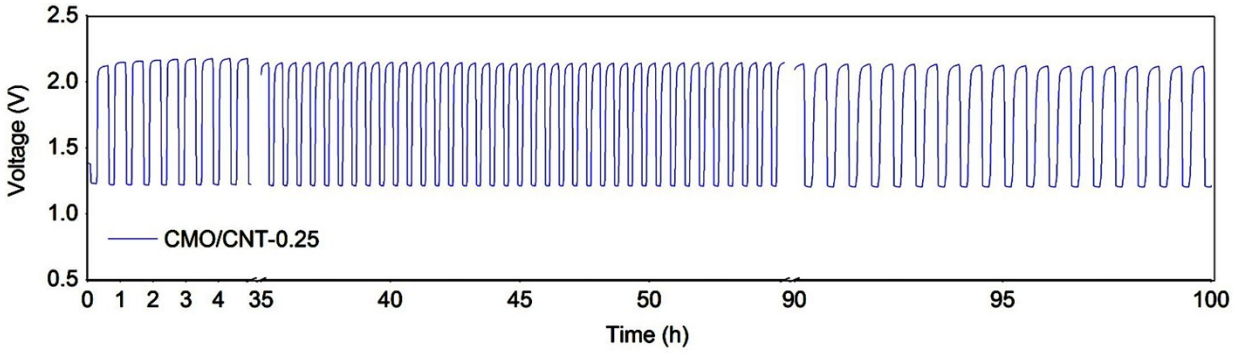

Fig. S6 Cycling stability performance of CMO/CNT-0.25 during galvanostatic recurrent pulse cycling test (discharging at 5 mA cm^{-2} for 10 min and charging at 2.5 mA cm^{-2} for 20 min in each cycle).

Table S1. Chemical states of Mn and O in $CaMnO_{3-\delta}$ and CMO/CNT.

	Mn $2p_{3/2}$			O 1s		
	Mn^{3+}	Mn^{4+}	Mn^{3+} content	lattice oxygen	adsorbed oxygen	lattice oxygen content
	(eV)	(eV)	(%)	(eV)	(eV)	(%)
$CaMnO_{3-\delta}$	642.0	642.8	34.8	529.0	532.1	42.2
CMO/CNT	641.7	642.5	33.6	529.4	531.0	41.3

Table S2 Tabulated data for oxygen reduction reaction of the various electrocatalysts, with Pt/C as the benchmark

Catalyst	Oxygen reduction reaction activity	
	Onset potential at tangent (V, vs RHE)	Current density at 0.2 V (vs RHE) (mA cm^{-2})
$CaMnO_3$	0.76	-2.47
CMO/CNT	0.84	-4.27
Carbon nanotubes	0.72	-2.83
20 % Pt/C	0.89	-5.34