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Supporting Information

Using confined carbonate crystals for the fabrication of nanosize metal oxide@carbon with superior lithium storage capacity

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Calculation of the volume expansion ratio (R).

Parameters used in the calculation model of the volume change in manganese oxide@C anode.

Component	ρ, Desity (g cm^{-3})	M_w, Molecular weight (g mol^{-1})
$MnCO_3$	3.125	114.95
MnO	5.45	70.94
Li_2O	2.013	29.88
Mn	7.44	54.94

The theoretical volume expansion ratio (R) of MnO is calculated using the following equation:

$$R = \frac{V_{Li_2O} + V_{Mn}}{V_{MnO}} = \frac{\frac{M_{Li_2O}}{\rho_{Li_2O}} + \frac{M_{Mn}}{\rho_{Mn}}}{\frac{M_{MnO}}{\rho_{MnO}}}$$

$$R = \frac{\frac{29.88}{2.013} + \frac{54.938}{7.44}}{\frac{70.94}{5.45}} \times 100\% = 171\%$$

The volume expansion ratio (R) that this structure can tolerate is calculated using the following equation:

$$R = \frac{V_{MnCO_3}}{V_{MnO}} = \frac{V_{MnCO_3}}{\frac{n_{MnO} \times M_{MnO}}{\rho_{MnO}}} = \frac{V_{MnCO_3} \times \rho_{MnO}}{\frac{m_{MnCO_3}}{M_{MnCO_3}} \times M_{MnO}} = \frac{M_{MnCO_3} \times \rho_{MnO}}{M_{MnO} \times \rho_{MnCO_3}}$$

$$R = \frac{114.95 \times 5.45}{70.94 \times 3.125} \times 100\% = 282\%$$

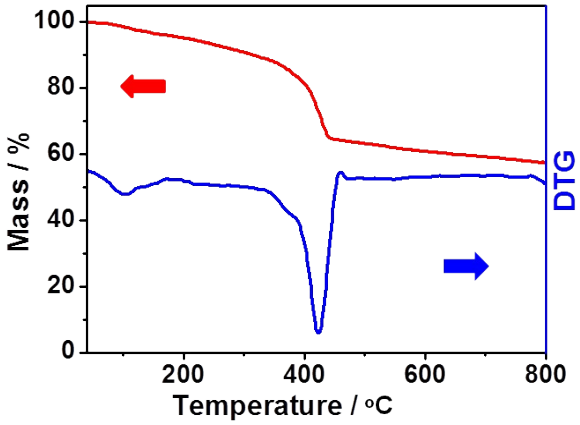

Fig. S1 TGA curve of the $MnCO_3$ cube after coating with a polymer layer produced from a dopamine precursor ($MnCO_3$@dopamine). The measurement was conducted at a heating rate of 10 °C min^{-1} in a nitrogen flow.

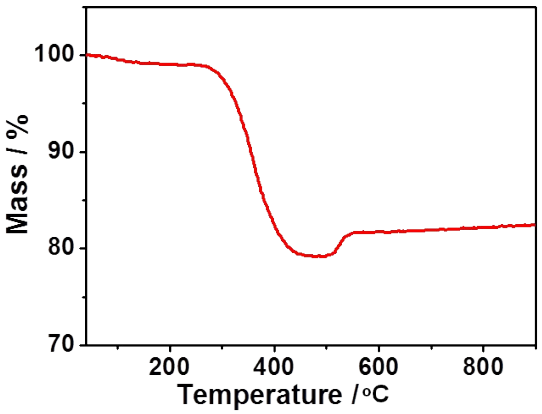

Fig. S2 TGA curve of the MnO@C hybrid. The measurement was conducted at a heating rate of 10 °C min^{-1} in an air flow.

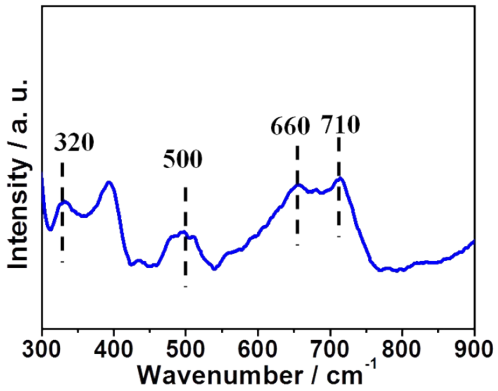

Fig. S3 Raman spectrum of the Fe_3O_4/γ-Fe_2O_3@C hybrid. One can see the peaks at ~660 and 320 cm^{-1} corresponding to the stoichiometric Fe_3O_4. The peaks at ~500 and 710 cm^{-1} can be ascribed to γ-Fe_2O_3.

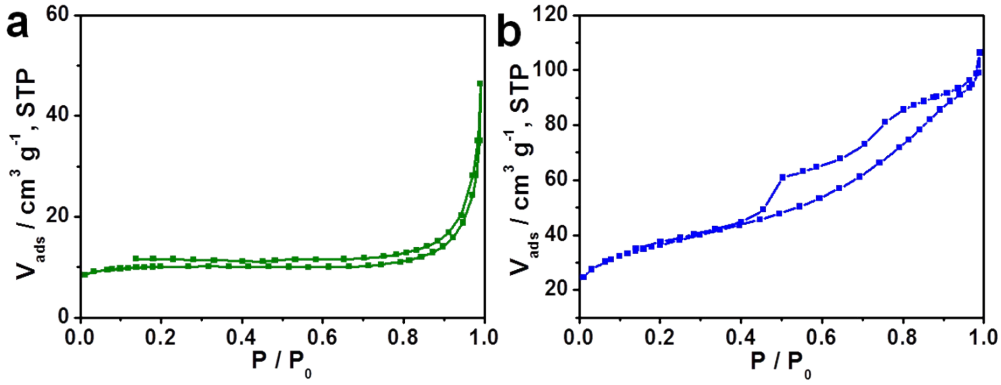

Fig. S4 (a) N_2 adsorption–desorption isotherm of the CoO/Co_3O_4@C hybrid, (b) N_2 adsorption–desorption isotherm of the Fe_3O_4/γ-Fe_2O_3@C hybrid.

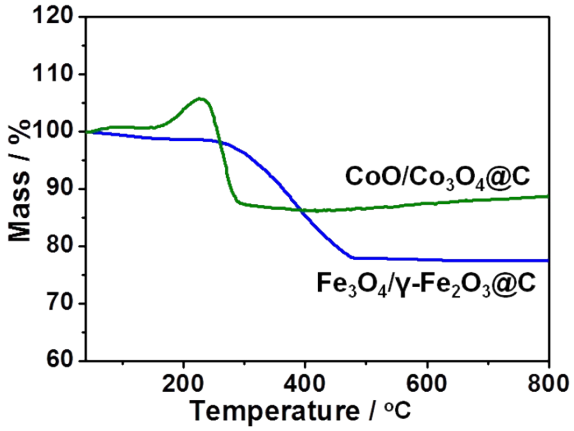

Fig. S5 TGA curves of the CoO/Co_3O_4@C and Fe_3O_4/γ-Fe_2O_3@C hybrids. The measurements were conducted at a heating rate of 10 °C min^{-1} in an air flow.

Table S1. The reported performances of MnO@C anodes for LIBs and the result in this study.

Sample	Initial coulombic efficiency	Cycle number	Capacity at 0.2 A g^{-1} (mA h g^{-1})	Rate capacity (mA h g^{-1})	Ref
Mesoporous MnO@C cube	71% (0.2 A g^{-1})	200	886	770 (2 A g^{-1}) (300 cycles)	This study
GNs/MnO nanowires	60.5% (0.1 A g^{-1})	200	723	285 (2.5 A g^{-1})	9
Hollow porous MnO/C microsphere	71% (0.1 A g^{-1})	50	600	315 (3 A g^{-1})	10
MnO/C nanorod	54.9% (0.1 A g^{-1})	100	721	371 (1.6 A g^{-1})	26
Microparticulate porous MnO@C	56% (0.1 A g^{-1})	100	479	238 (0.8 A g^{-1})	29
Nanosize MnO dispersed spherical carbon	76.5% (0.5 A g^{-1})	300	676	287 (2 A g^{-1})	30
MnO/C microsheets	62.9% (0.1 A g^{-1})	50	598	323 (2 A g^{-1})	31
Tube-like MnO/C	61.5% (0.2 A g^{-1})	60	610	350 (2 A g^{-1})	33