Supporting Information

Au-nanocrystals-decorated δ-MnO_2 as efficient catalytic cathode for high-performance Li–O_2 batteries

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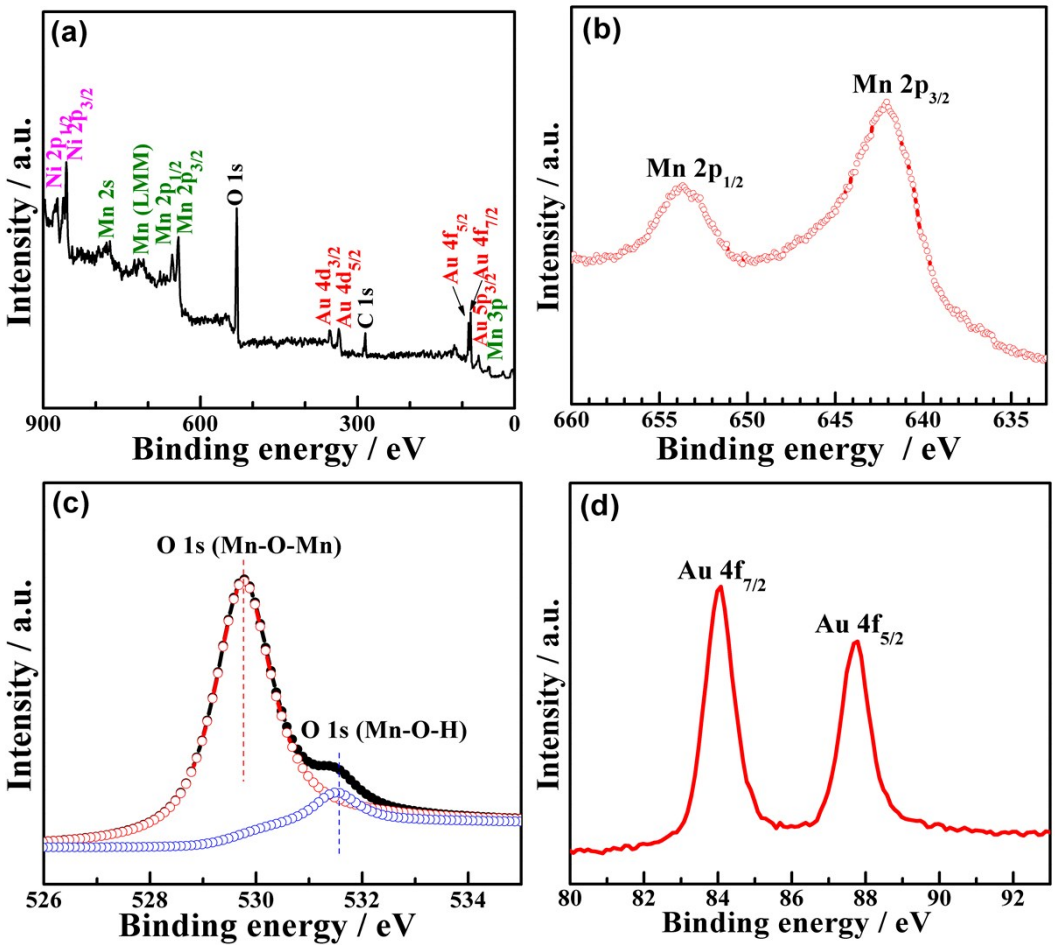

Fig. S1 (a) XPS survey of Au/δ-MnO_2 on graphene-coated Ni foam, (b) Mn2p XPS, (c) O1s XPS, and (d) Au4f XPS.

XPS survey in Fig. S1a reveals the expected elements of Au/δ-MnO_2 on the graphene-coated Ni foam. In Fig. S1b, two bands at 641.8 and 653.4 eV correspond to binding energy of $Mn2p_{3/2}$ and $Mn2p_{1/2}$ of MnO_2.[1] In Fig. S1c, two bands located at 529.8 and 531.6 eV are related to O1s binding energy in anhydrous (Mn-O-Mn) and hydrated (Mn-O-H) manganese oxides.[2] In Fig. S1d, two peaks at 84.0 and 87.8 eV correspond to binding energy of $Au4f_{7/2}$ and $Au4f_{5/2}$ of Au.[3]

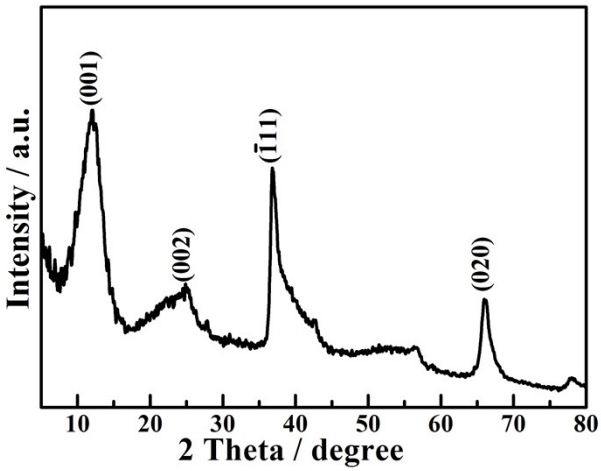

Fig. S2 XRD patterns of δ-MnO_2.

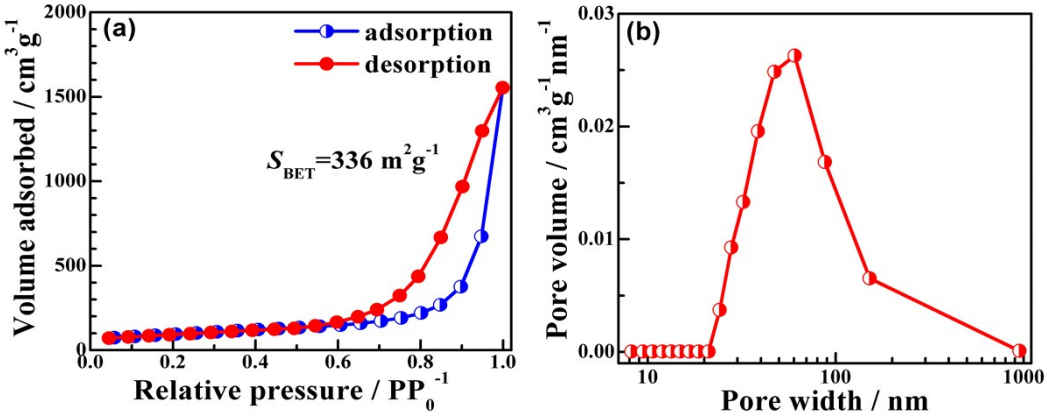

Fig. S3 (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of Au/δ-MnO_2 on graphene-coated Ni foam.

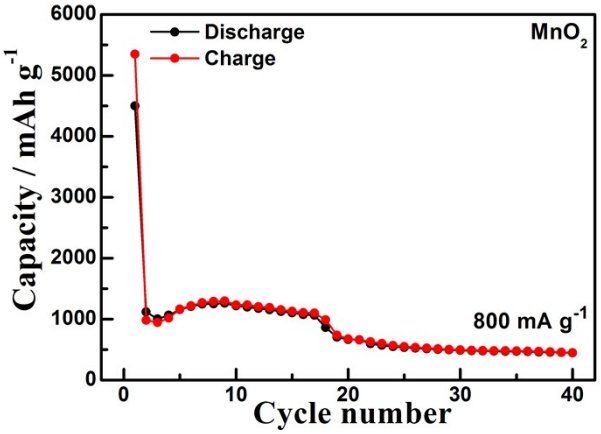

Fig. S4 Cycling performance of the Li–O_2 battery using δ-MnO_2 catalyst at 800 mA g^{-1} between 2 and 4.5 V without limiting the capacity.

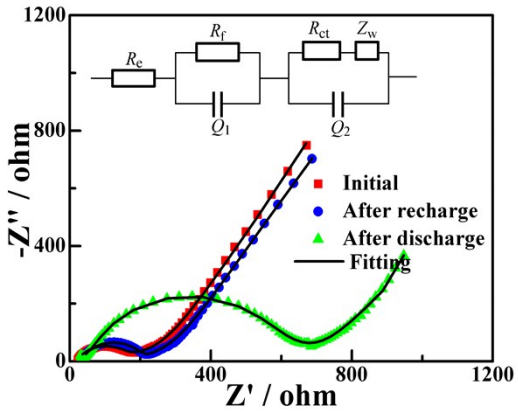

Fig. S5 EIS of Li–O_2 battery with Au/δ-MnO_2 catalyst at different charge and discharge states. The inset gives the equivalent circuit for fitting the plots.

In the equivalent circuit of Fig. S5, R_e represents electrolyte and ohm resistance, R_f and Q_1 represent surface film resistance and the relax capacitance, R_{ct} and Q_2 represent the charge transfer resistance and the double layer capacitance, and Z_w is the oxygen diffusion resistance. The fitting results are summarized in Table S1.

Table S1 Fitting results using the equivalent circuit.

Sample	R_e [Ω]	R_f [Ω]	Q_1		R_{ct} [Ω]	Q_2	
			Y [F]	n		Y [F]	n
Initial	19.4	120.8	2.2×10^{-3}	0.44	140.8	1.1×10^{-5}	0.75
After discharge	30.0	150.2	6.1×10^{-4}	0.39	437.2	7.6×10^{-6}	0.90
After charge	31.9	84.2	2.4×10^{-3}	0.56	175.3	4.4×10^{-6}	0.80

Table S2 Summary of electrochemical performance of Li–O_2 batteries with manganese or noble metal based catalysts.

Sample/electrode preparation method	Current density	Terminal voltage [V]	Charge/ discharge mode	Specific capacity [mAh $g_{total\ catalyst}^{-1}$]	Cycle number	Reference
Au/δ-MnO_2 Direct growth and binder free	**0.2 mA cm^{-2}/400 $g_{total\ catalyst}^{-1}$**	**2.5–4.1/2.1–4.3**	**Capacity limited**	**500**	**100/165**	**This work**
	0.4 mA cm^{-2}/800 $g_{total\ catalyst}^{-1}$	**2.0–4.5**	**Capacity unlimited**	**3012 (50th cycle)**	**50**	**This work**
porous Au free standing	500 mA $g_{total\ catalyst}^{-}$	2.2–4.0	Capacity unlimited	~300 (100th cycle)	100	[4]
MnO_x/Pd paste coating	100 mA $g_{total\ catalyst}^{-1}$	2.0–4.15	Capacity limited	400	50	[5]
$La_{0.75}Sr_{0.25}MnO_3$ paste coating	0.15 mA cm^{-2}	2.2–4.4	Capacity limited	667	124	[6]
α-MnO_2/G paste coating	0.09 mA cm^{-2}	2.8–4.0	Capacity limited	580	25	[7]
α-MnO_2/C paste coating	0.06 mA cm^{-2}	2.2–4.3	Capacity limited	500	60	[8]

References

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