Supporting Information

Synthesis of hierarchical porous δ-MnO_2 nanoboxes as an efficient catalyst for rechargeable Li–O_2 battery

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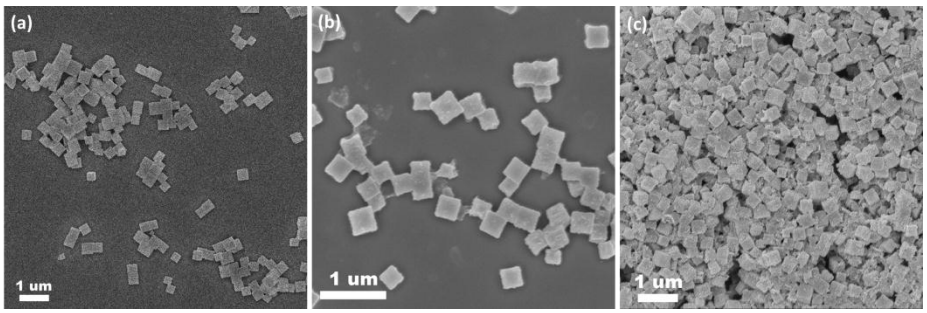

Fig. S1. SEM images of the obtained (a) nanocube-like PBAs precursors, (b) porous Mn_3O_4 nanoboxes and (c) hierarchical porous δ-MnO_2 nanoboxes.

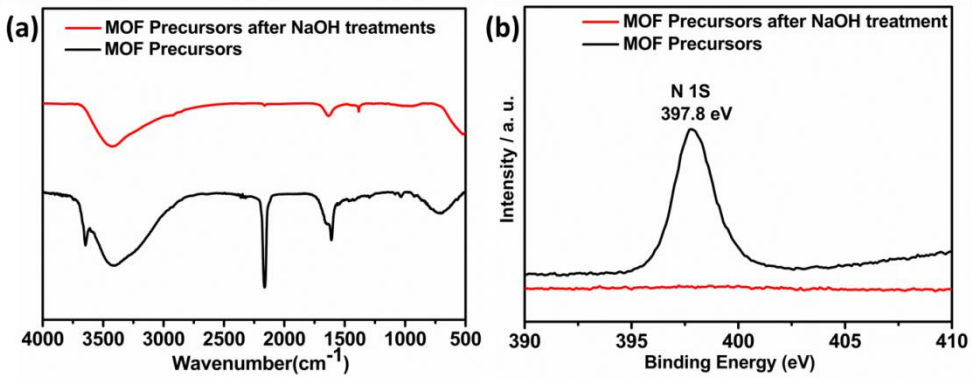

Fig. S2. (a) FT-IR and (b) N 1s XPS spectra of the PBAs precursor before (black) and after (red) NaOH treatment.

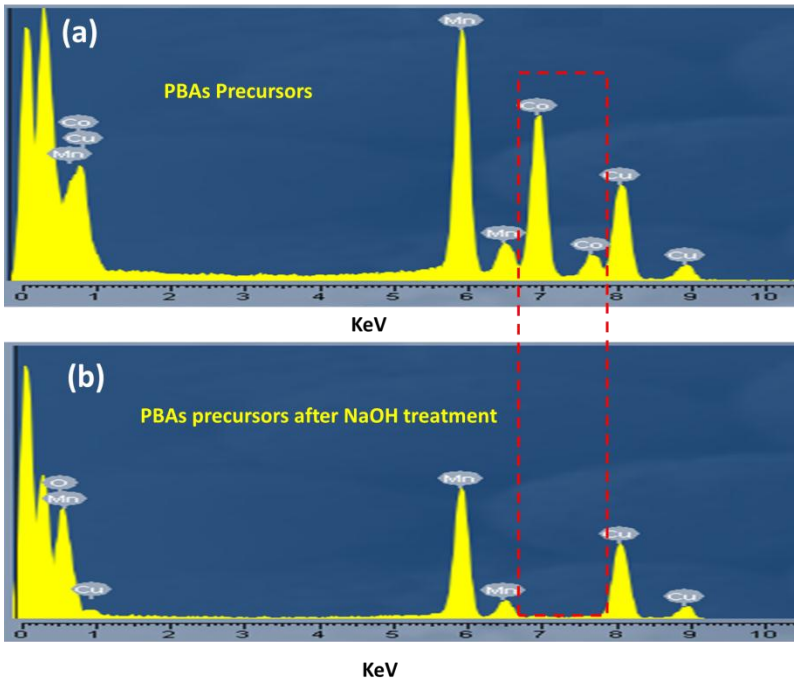

Fig. S3. EDX spectra of the PBAs precursors (a) before and (b) after the NaOH treatment.

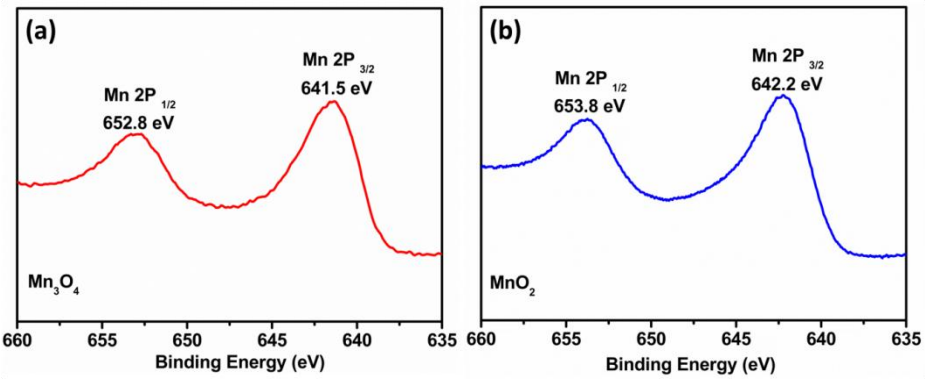

Fig. S4. XPS survey of (a) porous Mn_3O_4 nanoboxes and (b) hierarchical porous δ-MnO_2 nanoboxes.

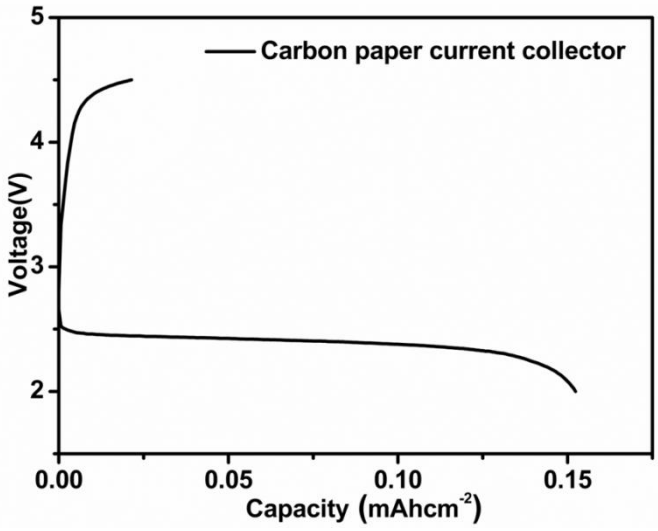

Fig. S5. Discharge–charge curves of Li–O_2 batteries with blank carbon paper current collector.

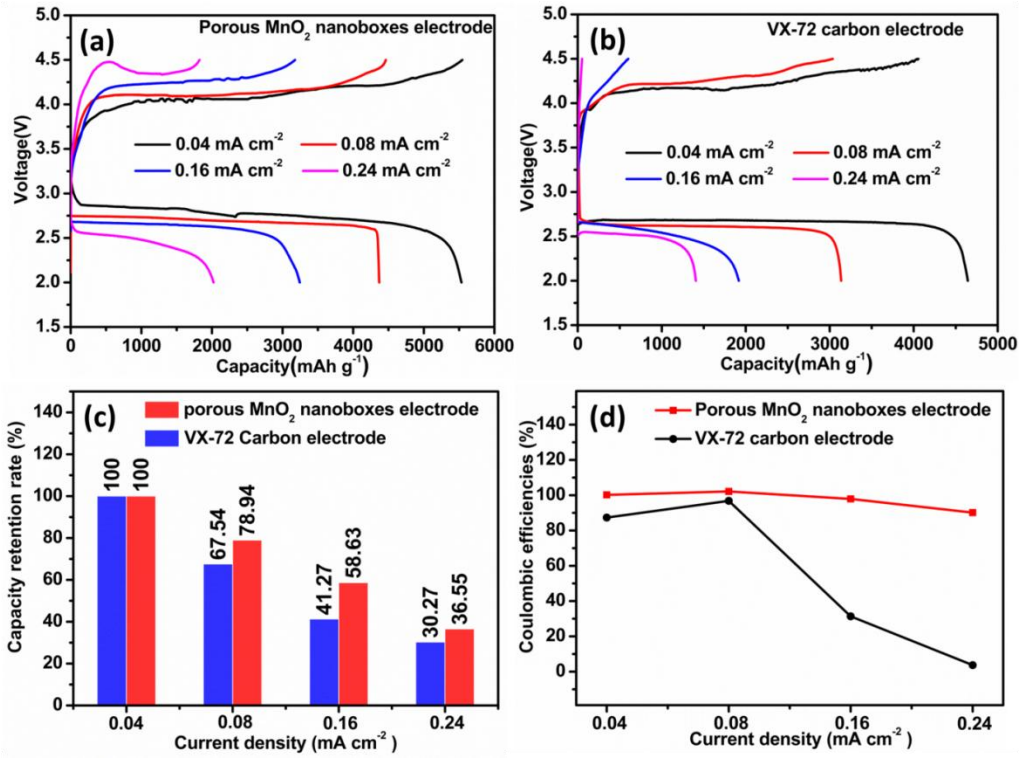

Fig. S6. First discharge-charge curves of Li-O_2 batteries with (a) hierarchical porous δ-MnO_2 nanoboxes and (b) VX-72 carbon electrodes at various current densities; (c) Discharge capacity retention of Li–O_2 battery cells with different electrodes at various current densities; (d) Coulombic efficiency of Li–O_2 batteries with different electrodes at various current density.

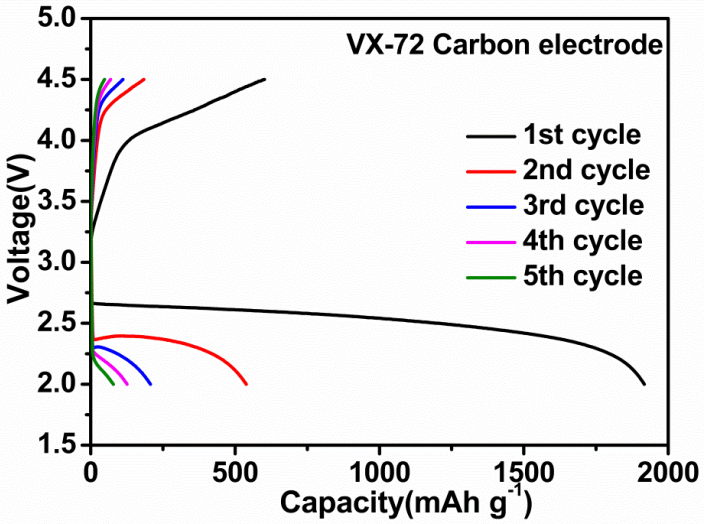

Fig. S7. Discharge–charge curves of Li–O_2 batteries with VX-72 carbon electrode at 0.16 mA cm^{-2}.

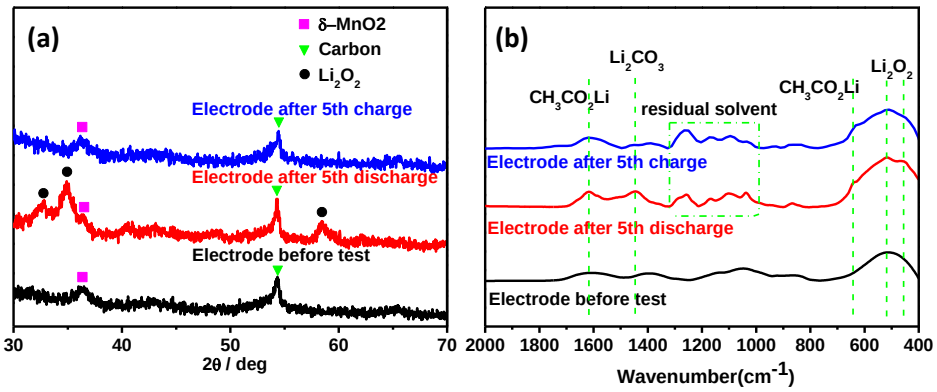

Fig. S8. (a) XRD pattern and (b) FTIR spectrum of the electrode at different states.

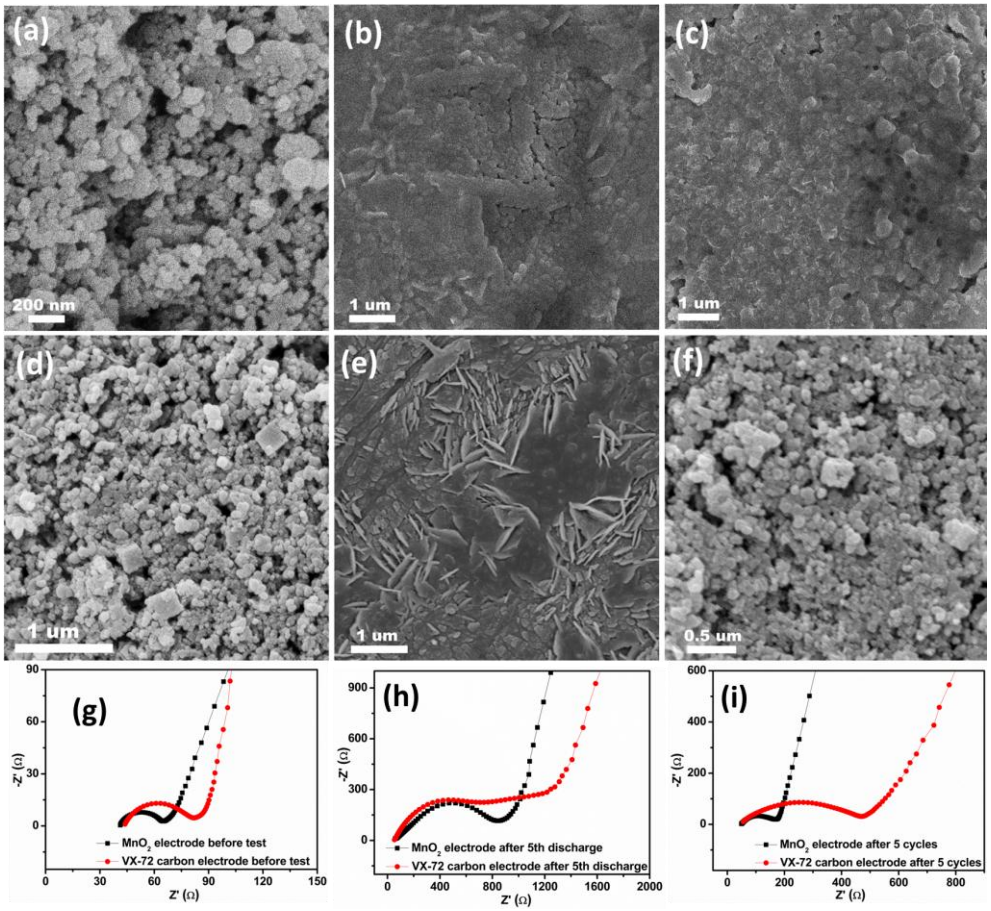

Fig. S9. SEM images of the VX-72 carbon electrode (a, b, c) and hierarchical porous δ-MnO_2 nanoboxes electrode (d, e, f), before test (a, d), after 5th discharge (b, e) and after 5th charge (c, f); (g), (h), (i) electrochemical impedance spectra of Li–O_2 batteries with the hierarchical porous δ-MnO_2 nanoboxes and VX-72 carbon electrodes at different discharge–charge states.

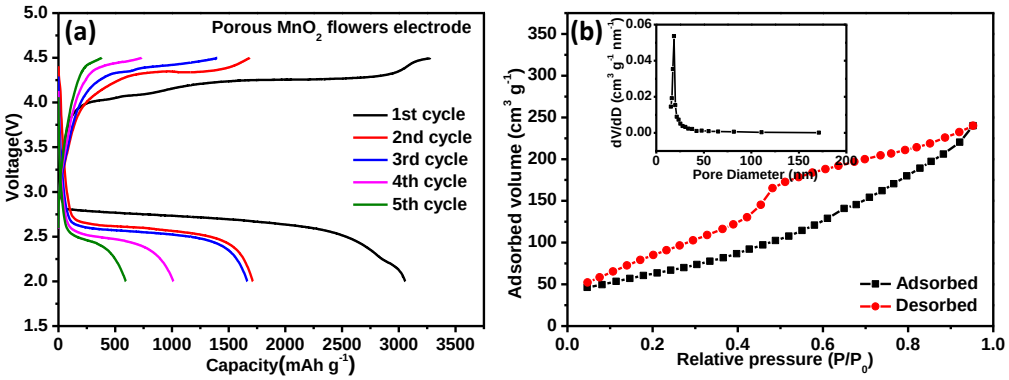

Fig. S10. (a) Discharge–charge curves of Li–O_2 batteries with hierarchical porous δ-MnO_2 nanoboxes electrode at 0.16 mA cm^{-2}; (b) Nitrogen adsorption–desorption isotherms and pore size distribution (inset) of the flower-like δ-MnO_2. The BET surface area is about 229.6 m^2 g^{-1} and the pore volume is 0.340 cm^3 g^{-1}

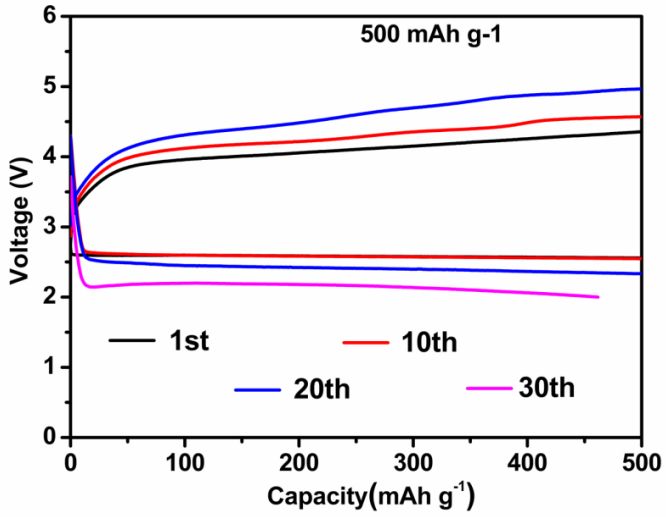

Fig. S11. Cyclic performance of the VX-72 carbon electrode at 0.16 mA cm^{-2} with limited capacity of 500 mAh g^{-1}.

Table S1. Summary of surface area of manganese-based catalysts and their related Li-O_2 batteries performance.

Catalyst	BET surface area ($m^2 g^{-1}$)	Overpotential (V)	Maximum capacity based on total mass ($mAh g^{-1}$)	Rate capacity ($mAh g^{-1}$)	Cycle performance	Ref.
α-MnO_2	--	1.4 at 70 mA g^{-1}	730 at 70 mA g^{-1}	--	--	[1]
δ-MnO_2/3-D graphene	108	1.4 V at 0.083 mA cm^{-2}	3660 at 48 mA g^{-1}	700 at 387 mA g^{-1}	132 cycles at 1000 mA g^{-1}	[2]
α-MnO_2 /graphene	71	0.99 at 0.06 mA cm^{-2}	2304 at 100mA g^{-1}	--	25cycles at 3000 mA g^{-1}	[3]
α-MnO_2/porous carbon	70	1.38 at 100 mA g^{-1}	1400 at 100mA g^{-1}	--	60 cycles at 500 mA g^{-1}	[4]
ε-MnO_2/Ni foam	125.57	1.25 at 10 mA g^{-1}	7000 at 100mA g^{-1}	6300 at 500 mA g^{-1}	120 cycles at 1000 mA g^{-1}	[5]
Our sample	249.3	1.36 at 0.08 mA cm^{-2}	5533 at 50 mA g^{-1}	2022 at 200 mA g^{-1}	248 cycles at 500 mAh g^{-1} 113 cycles at 1000 mAh g^{-1}	

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