

Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information

Improved structural design of single- and double-wall MnCo₂O₄ nanotube cathodes for long-life Li-O₂ batteries

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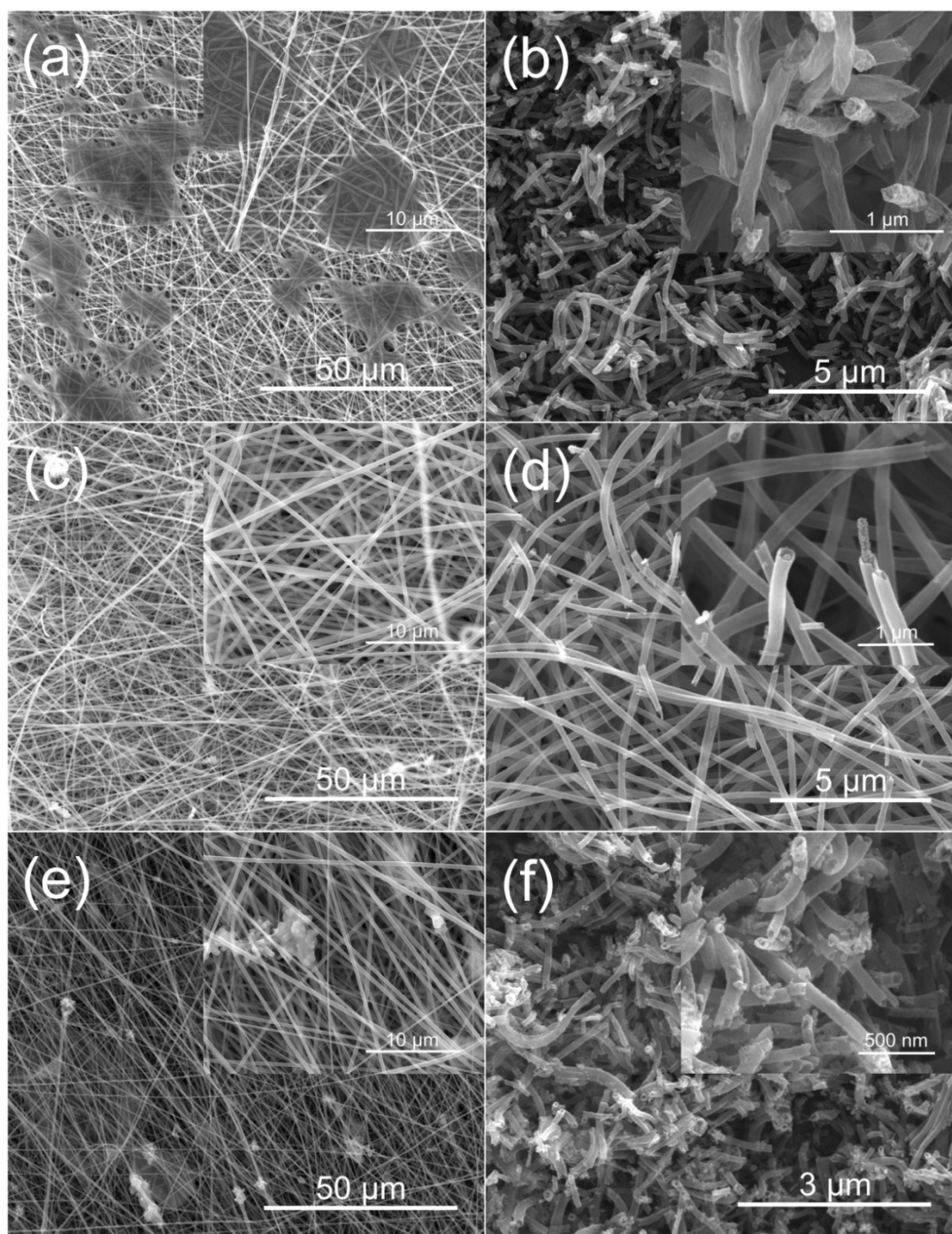


Fig. S1 Low- and high-magnification SEM images of the as-electrospun precursor nanofibers with M:PVP=0.59:1 (a), M:PVP=0.92:1 (b), and M:PVP=1.12:1 (c) before calcination, and the corresponding nanostructures (d), (e), and (f) after calcination in air, respectively.

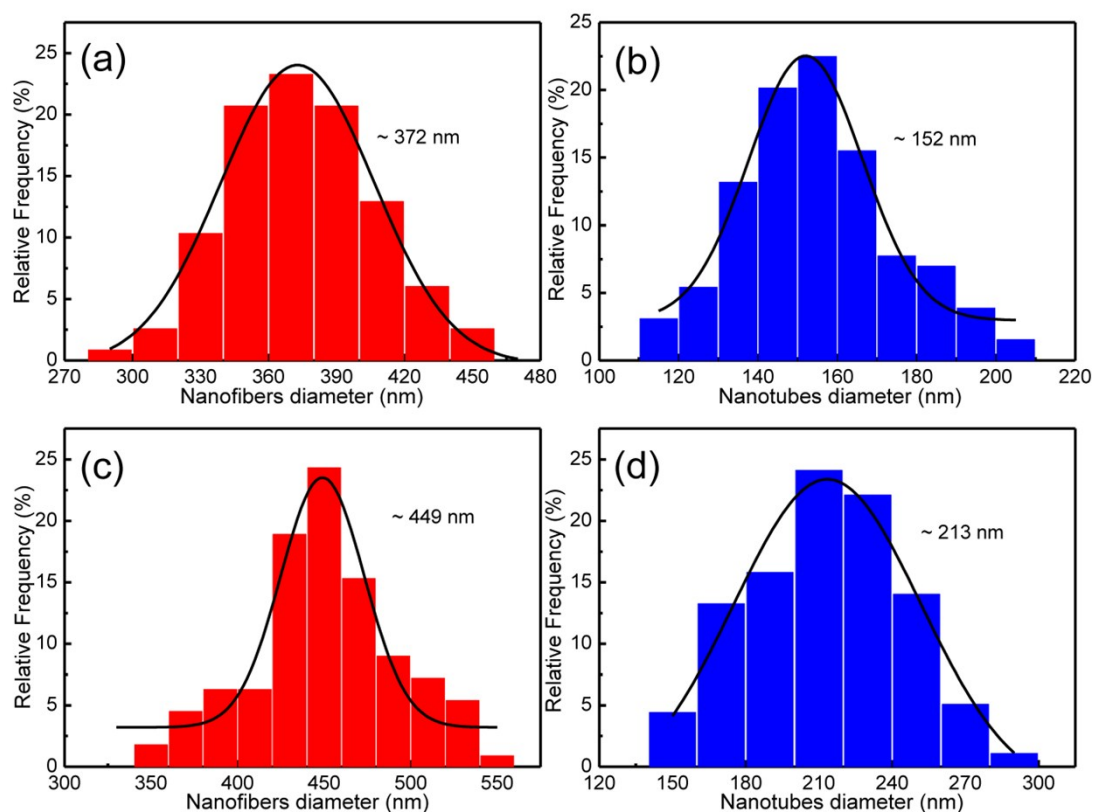


Fig. S2 Diameter distribution histograms of the as-electrospun nanofibers with M:PVP=1.01:1 (a) and M:PVP=0.74:1 (c) before calcination, and the corresponding SW-MCO-NT (b) and DW-MCO-NT (d) after calcination in air, respectively.

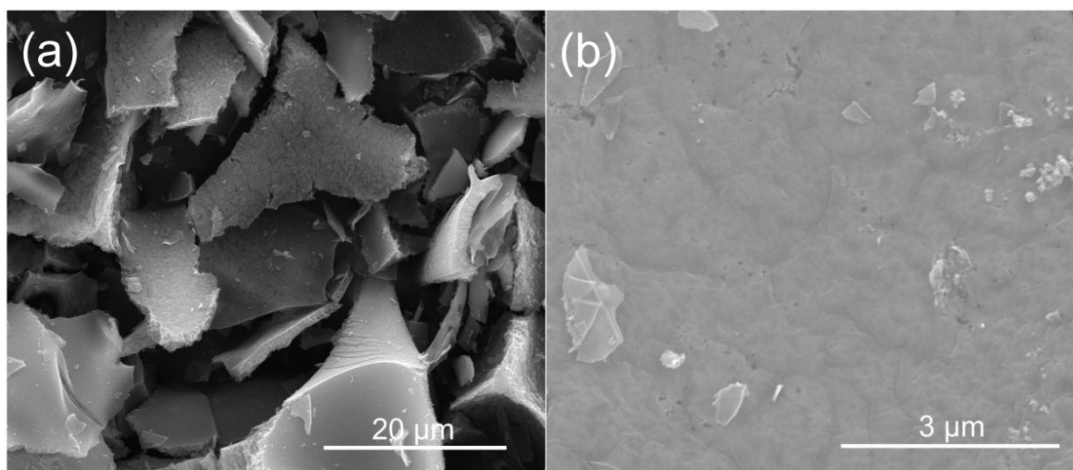


Fig. S3 SEM images of the B-MCO synthesized by a sol-gel method.

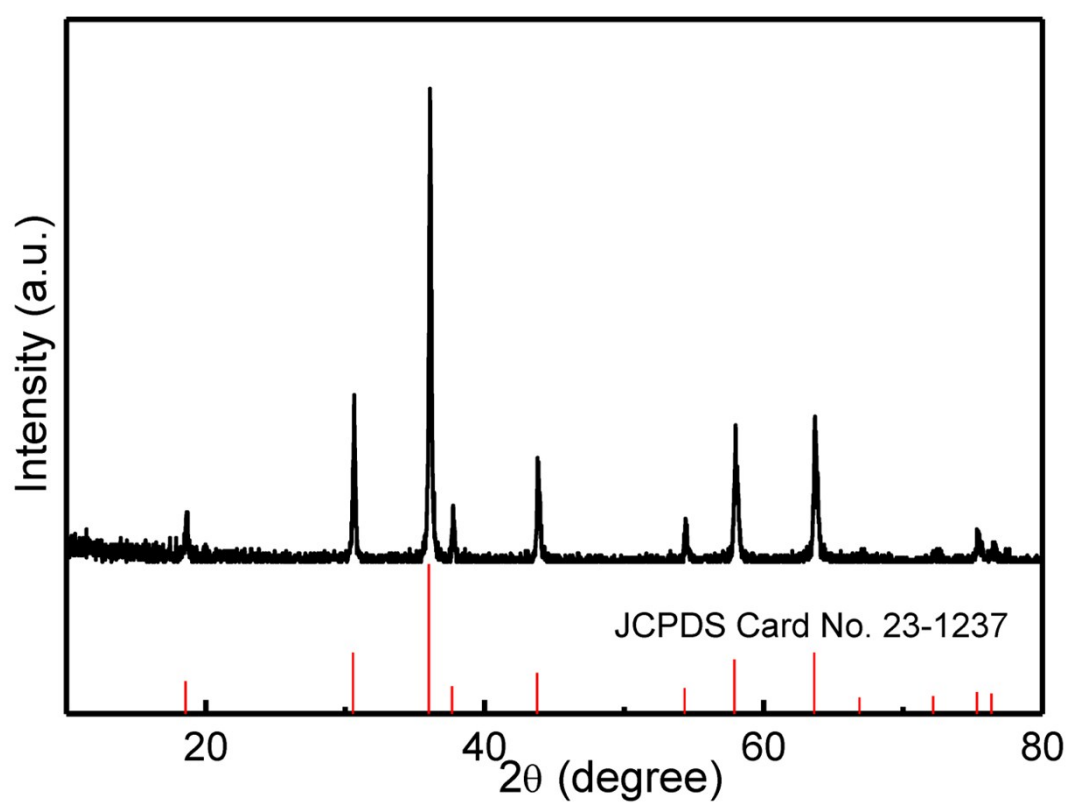


Fig. S4 XRD patterns of the B-MCO sample.

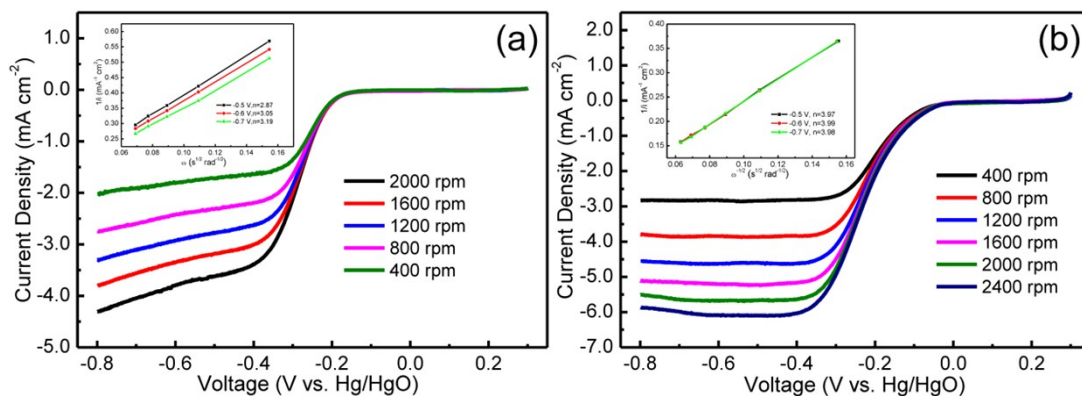


Fig. S5 Rotating disk voltammograms of B-MCO (a) and SW-MCO-NT (b) under different rotating speeds, and corresponding K-L plots at different potentials (inset).

Table S1. Comparison of the CV, ORR, and OER of the MnCo_2O_4 samples, commercial Pt/C and RuO_2 catalysts in alkaline solution.

Catalyst	CV		ORR		OER	
	E_{peak} (V)	I_{peak} (mA cm^{-2})	E_{onset} (V)	I_{limiting} (mA cm^{-2})	$E_{\text{half-wave}}$ (V)	I_{max} (mA cm^{-2})
Pt/C	-	-	0.021	-5.50	-	-
DW-MCO-NT	-0.134	-0.53	0.020	-5.12	0.830	23.56
SW-MCO-NT	-0.153	-0.47	-0.019	-5.11	0.846	21.75
B-MCO	-0.201	-0.21	-0.156	-3.76	-	6.65
RuO_2	-	-	-	-	0.794	22.80

E_{onset} (V) at $I = -0.07 \text{ mA cm}^{-2}$

I_{limiting} at $E = -0.8 \text{ V}$

I_{max} at $E = 1.0 \text{ V}$

$E_{\text{half-wave}}$ (V) at $I = 10 \text{ mA cm}^{-2}$

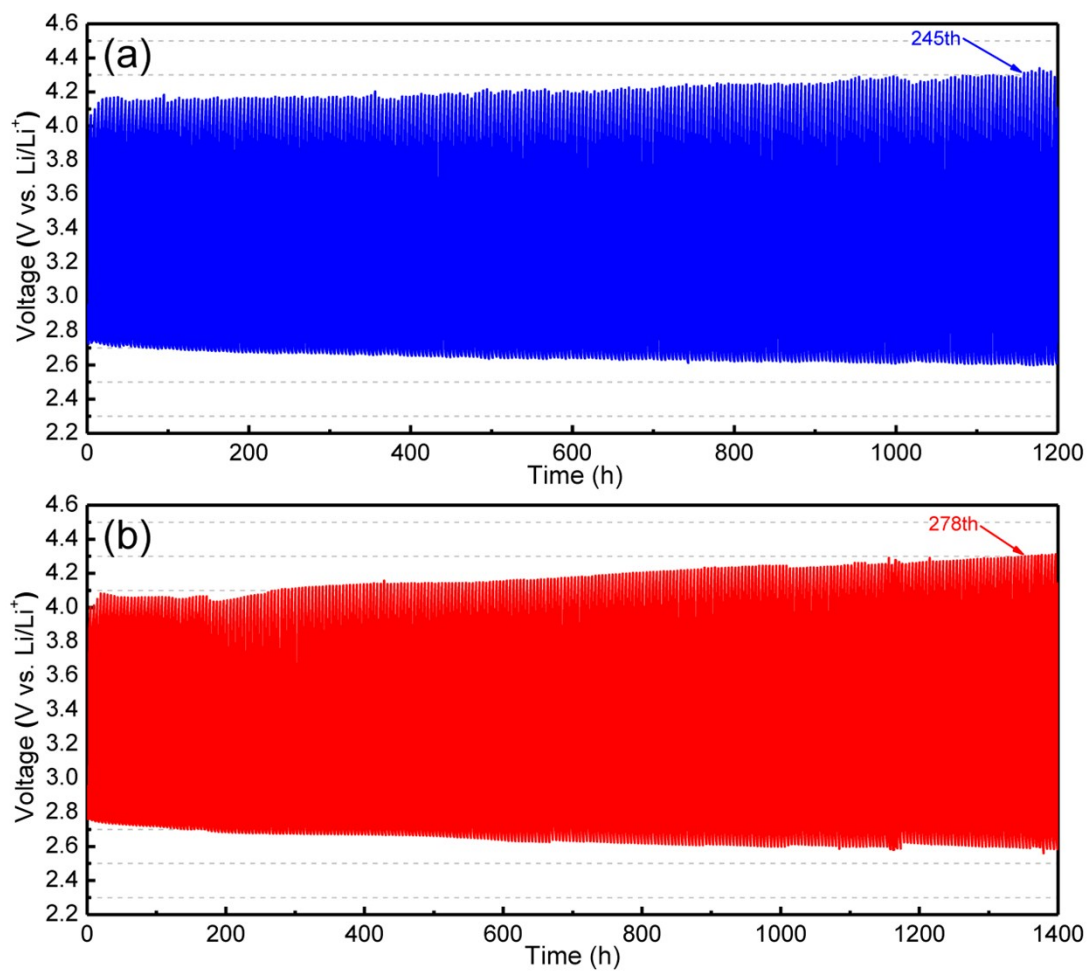


Fig. S6 Discharge/charge voltage profiles of the (a) SW-MCO-NT and (b) DW-MCO-NT electrode with a capacity limitation of 1000 mAh g⁻¹ at 400 mA g⁻¹ within 2.6–4.3 V.

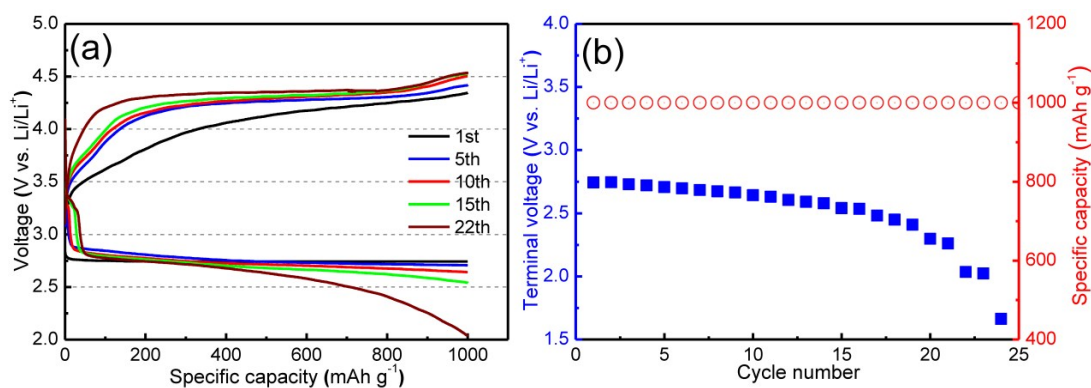


Fig. S7 (a) Discharge/charge curves of the Li-O₂ cell with the B-MCO electrode with a capacity limitation of 1000 mAh g⁻¹ at 400 mA g⁻¹. (b) The corresponding terminal discharge voltage vs. the cycle number.

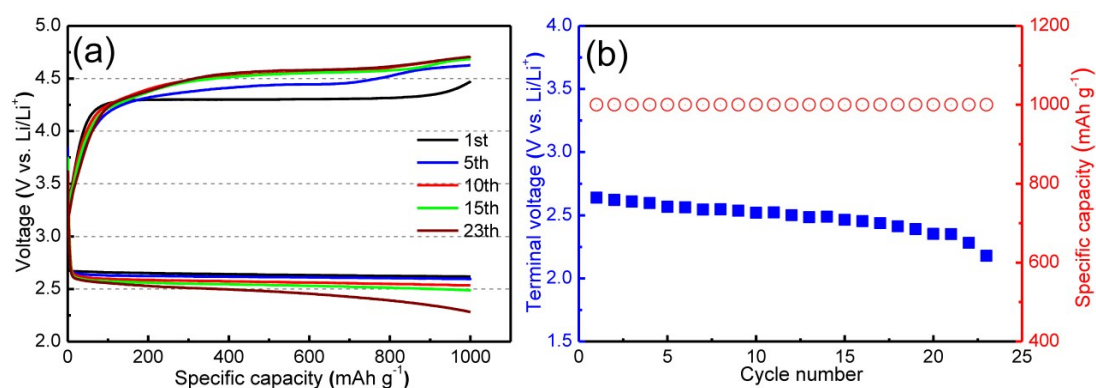


Fig. S8 (a) Discharge/charge curves of the Li-O₂ cell with the pure Super P based electrode under a limited capacity of 1000 mAh g⁻¹ at 400 mA g⁻¹. (b) The corresponding terminal discharge voltage vs. the cycle number.

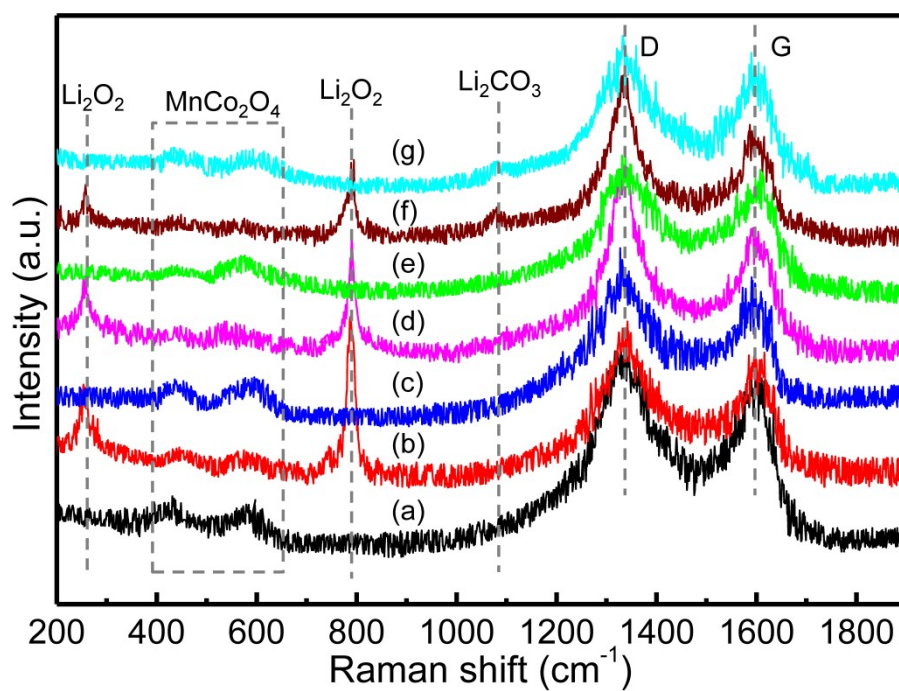


Fig. S9 Raman spectra of the DW-MCO-NT electrode: pristine electrode (a), 1st discharge (b), 1st charge (c), 100th discharge (d), 100th charge (e), 230th discharge (f), and 230th charge (g).

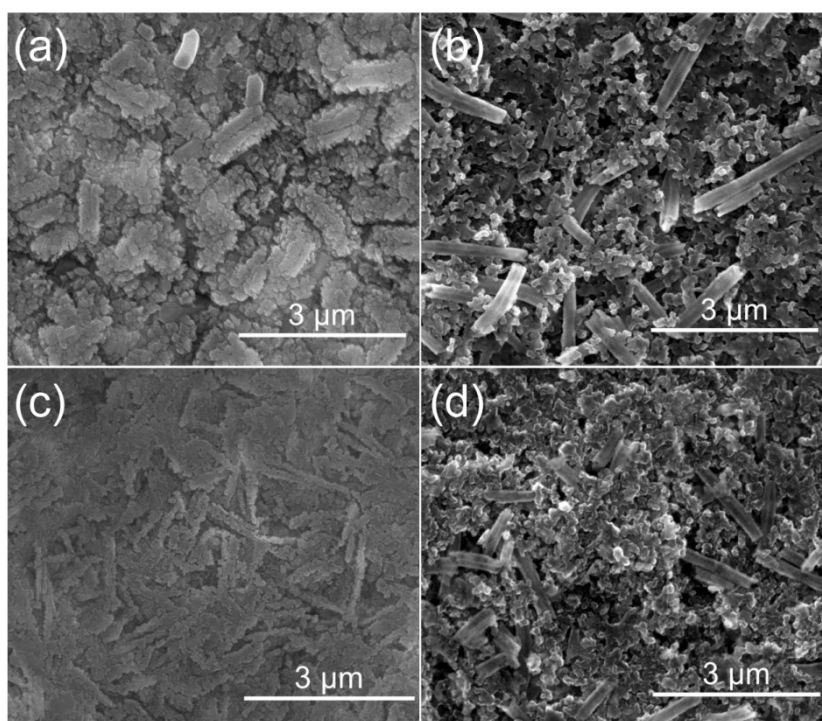


Fig. S10 SEM images of the DW-MCO-NT electrode after 100th discharge (a), 100th recharge (b), 230th discharge (c), and 230th recharged (d).

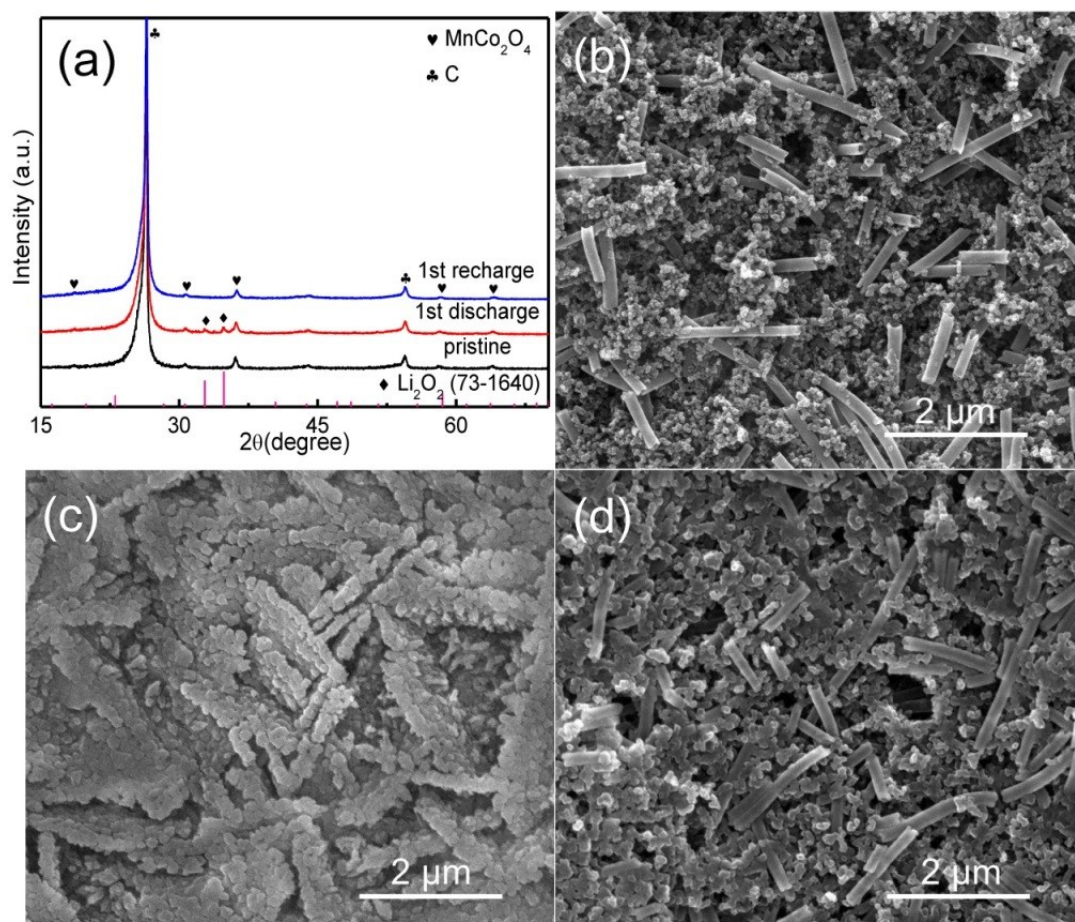


Fig. S11 (a) XRD patterns of the SW-MCO-NT electrode at different discharge/charge states. SEM images of the SW-MCO-NT electrode before discharge (b), after 1st discharge (c), and 1st recharged (d).

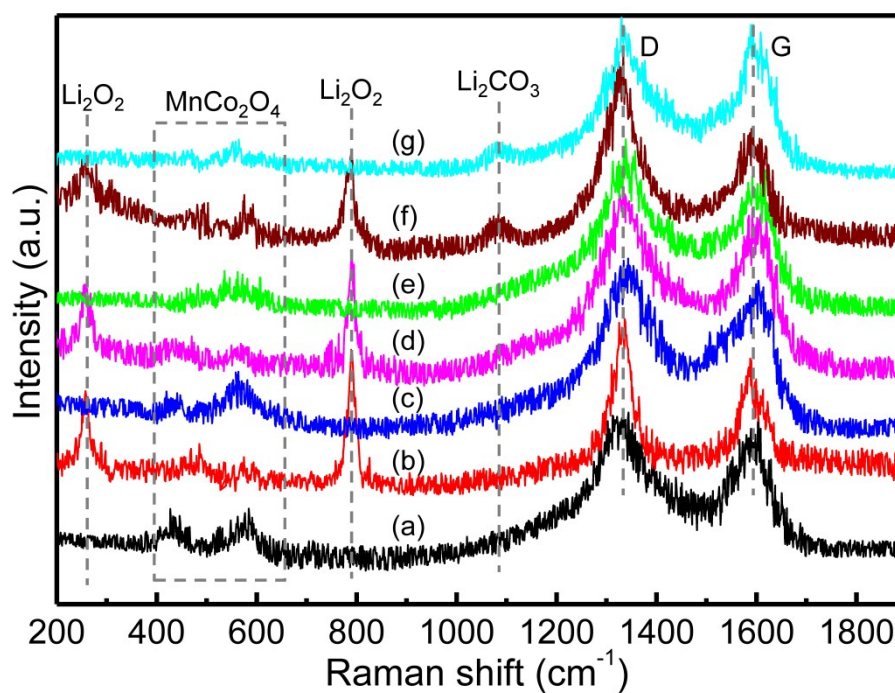


Fig. S12 Raman spectra of the SW-MCO-NT electrode: pristine electrode (a), 1st discharge (b), 1st charge (c), 100th discharge (d), 100th charge (e), 230th discharge (f), and 230th charge (g).

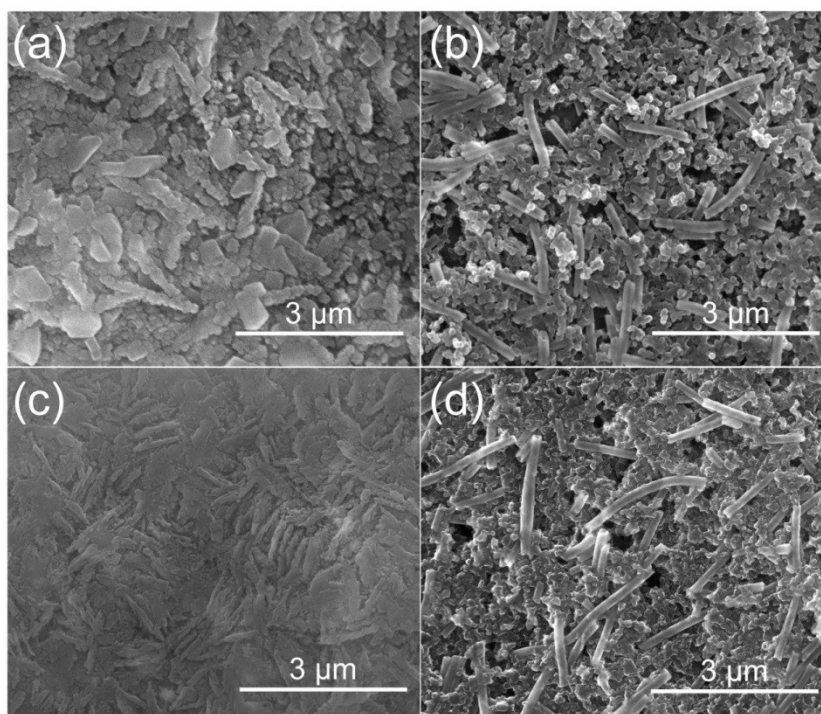


Fig. S13 SEM images of the SW-MCO-NT electrode after 100th discharge (a), 100th recharge (b), 230th discharge (c), and 230th recharged (d).

Table S2. Summary of electrochemical performances of Li-O₂ batteries with transition-metal oxides based catalysts.

Catalyst	Maximum capacity (current density)	Cycle (upper-limited capacity, current density)	Cyclic cut-off voltage	Electrolyte	Ref.
RuO ₂ @ La _{0.6} Sr _{0.4} Co _{0.8} Mn _{0.2} O ₃ nanofibers	12742 mAh g ⁻¹ (50 mA g ⁻¹)	100 (500 mAh g ⁻¹ , 50 mA g ⁻¹)	~2.6–4.3 V	1 M LiTFSI /TEGDME	[1]
NiCo ₂ O ₄ @Co ₃ O ₄ hybrid	4386 mAh g ⁻¹ (100 mA g ⁻¹)	60 (500 mAh g ⁻¹ , 100 mA g ⁻¹)	~2.0–4.3 V	1 M LiTFSI /TEGDME	[2]
NiMn ₂ O ₄ -FT particles	9440 mAh g ⁻¹ (150 mA g ⁻¹)	50 (900 mAh g ⁻¹ , 150 mA g ⁻¹)	~2.0–4.5 V	1 M LiTFSI /TEGDME	[3]
Yolk-shell Co ₂ CrO ₄ nanospheres	6260 mAh g ⁻¹ (200 mA g ⁻¹)	236 (1000 mAh g ⁻¹ , 200 mA g ⁻¹)	~2.0–4.5 V	1 M LiTFSI /TEGDME	[4]
3D ordered macroporous CoFe ₂ O ₄	4663 mAh g ⁻¹ (200 mA g ⁻¹)	47 (500 mAh g ⁻¹ , 200 mA g ⁻¹)	~2.3–4.5 V	1 M LiTFSI /TEGDME	[5]
Yolk-shell Co ₃ O ₄ @Co ₃ O ₄ /Ag	12000 mAh g ⁻¹ (200 mA g ⁻¹)	80 (1000 mAh g ⁻¹ , 200 mA g ⁻¹)	~2.3–4.5 V	1 M LiTFSI /TEGDME	[6]
MnCoO-CNT composite microspheres	37142 mAh g ⁻¹ (200 mA g ⁻¹)	245 (500 mAh g ⁻¹ , 200 mA g ⁻¹)	~2.0–4.35 V	Mixture ^[a]	[7]
NiFe ₂ O ₄ /C nanofibers	5.5 mAh (0.1 mA cm ⁻²)	40 (0.5 mAh, 0.1 mA cm ⁻²)	~2.4–4.5 V	1 M LiTFSI /TEGDME	[8]
MnCo ₂ O ₄ - graphene hybrid	3784 mAh g ⁻¹ (100 mA g ⁻¹)	40 (1000 mAh g ⁻¹ , 100 mA g ⁻¹)	~2.5–4.3 V	1 M LiClO ₄ /PC	[9]
MnCo ₂ O ₄ Microspheres	4861 mAh g ⁻¹ (200 mA g ⁻¹)	50 (1000 mAh g ⁻¹ , 250 mA g ⁻¹)	~2.5–4.4 V	1 M LiTFSI /TEGDME	[10]

Bio MnCo ₂ O ₄ nanowires	7076 mAh g ⁻¹ (~220 mA g ⁻¹)	16 (200 mAh g ⁻¹ , 100 mA g ⁻¹)	~2.0–4.3 V	0.1 M LiClO ₄ /DME	[11]
MnCo ₂ O ₄ nanowires /RGO	11092.1 mAh g ⁻¹ (200 mA g ⁻¹)	35 (1000 mAh g ⁻¹ , 200 mA g ⁻¹)	~2.3–4.3 V	1 M LiPF ₆ /TEGDME	[12]
MnCo ₂ O ₄ / P-doped porous carbon	13150 mAh g ⁻¹ (200 mA g ⁻¹)	200 (1000 mAh g ⁻¹ , 200 mA g ⁻¹)	~2.6–4.4 V	1 M LiTFSI /TEGDME	[13]
MnCo ₂ O ₄ hollow nanocages	2050 mAh g ⁻¹ (50 mA g ⁻¹)	70 (600 mAh g ⁻¹ , 400 mA g ⁻¹)	~2.1–4.5 V	1 M LiTFSI /TEGDME	[14]
MnCo ₂ O ₄ nanowire bundles/ Ni foam	12919 mAh g ⁻¹ (0.1 mA cm ⁻²)	144 (1000 mAh g ⁻¹ , 0.1 mA cm ⁻²)	~2.2–4.4 V	1 M LiClO ₄ /DMSO	[15]
MnCo ₂ O ₄ nanorods /Ni foam	10520 mAh g ⁻¹ (100 mA g ⁻¹)	119 (1000 mAh g ⁻¹ , 500 mA g ⁻¹)	~2.0–4.2 V	1 M LiTFSI /TEGDME	[16]
SW-MCO-NT	6360 mAh g ⁻¹ (200 mA g ⁻¹)	245 (1000 mAh g ⁻¹ , 400 mA g ⁻¹)	~2.6–4.3 V	1 M LiTFSI /TEGDME	This work
DW-MCO-NT	7501 mAh g ⁻¹ (200 mA g ⁻¹)	278 (1000 mAh g ⁻¹ , 400 mA g ⁻¹)	~2.6–4.3 V	1 M LiTFSI /TEGDME	This work

Mixture^[a]: 0.5 M LiTFSI, 0.5 M LiNO₃, and 0.05 M LiI /TEGDME.

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