

Electronic Supplementary Information

**Self-assembly Co-doped MnO₂ nanorods networks with
abundant oxygen vacancies modified separators for high-
performance Li-S batteries**

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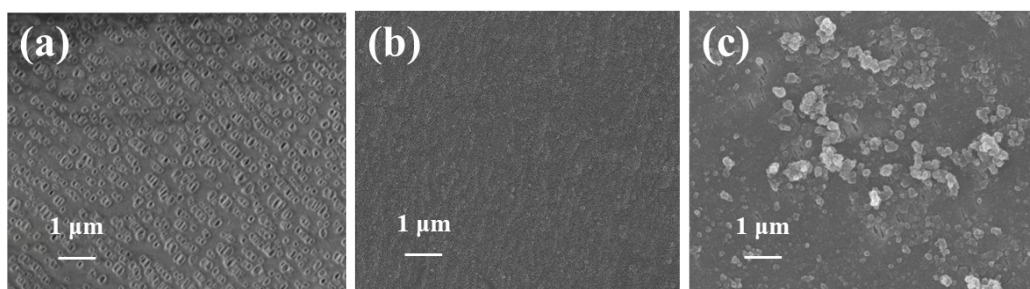


Fig. S1. SEM images of (a) PP separator, (b) Co-MnO_x@PP separator, and (c) MnO₂@PP separator.

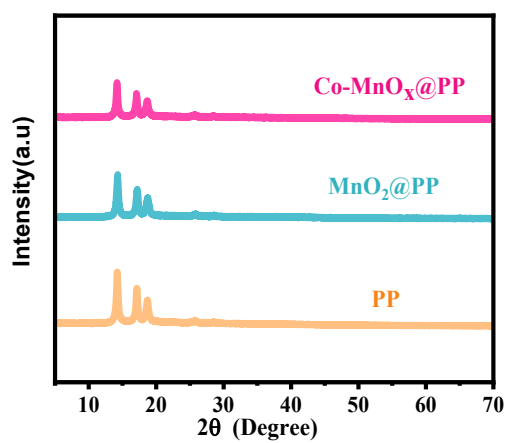


Fig. S2. XRD patterns of Co-MnO_x@PP, MnO₂@PP and PP separators.

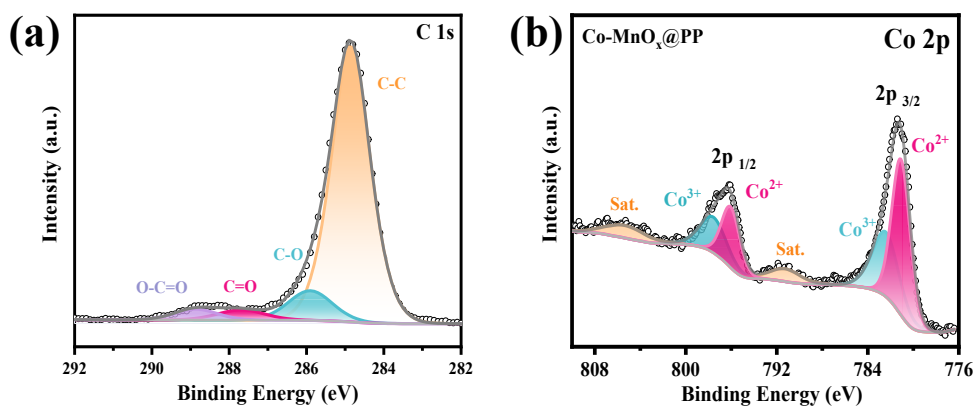


Fig. S3. XPS spectra of (a) C 1s, (b) Co 2p for Co-MnO_x@PP separators.

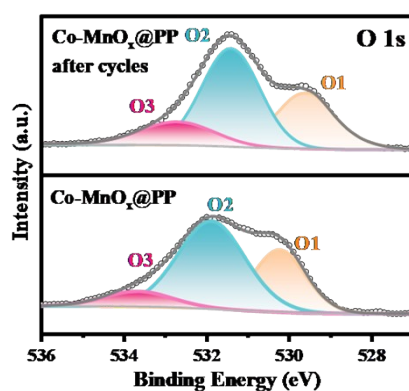


Fig. S4. XPS spectra of O 1s for Co-MnO_x@PP separators after cycles.

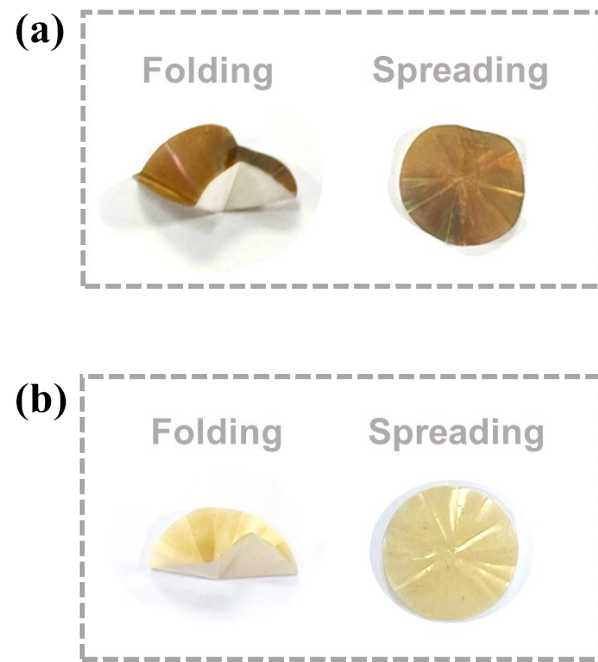


Fig. S5. Digital photographs of the folding and spreading test of (a) Co-MnO_x@PP and (b) MnO₂@PP separators.

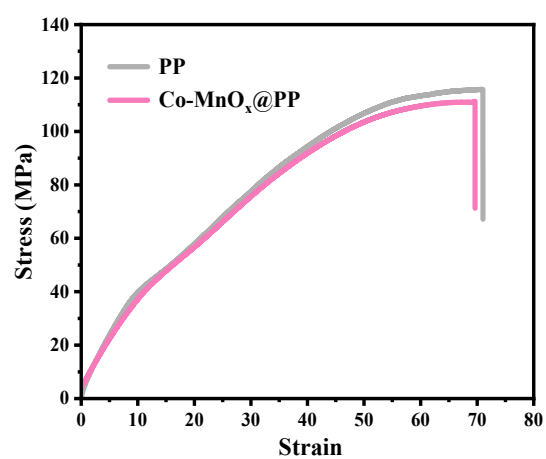


Fig. S6. Typical tensile stress-strain curves of commercial PP and Co-MnO_x@PP separators.

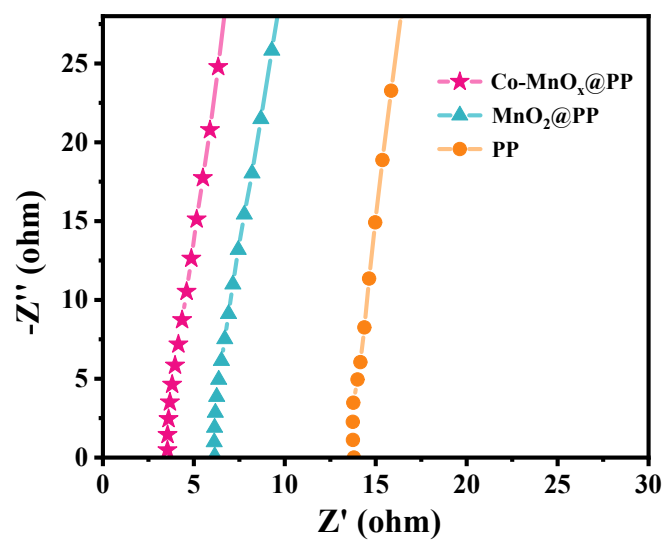


Fig. S7. EIS of the lithium symmetric cells with Co-MnO_x@PP, MnO₂@PP and PP separators.

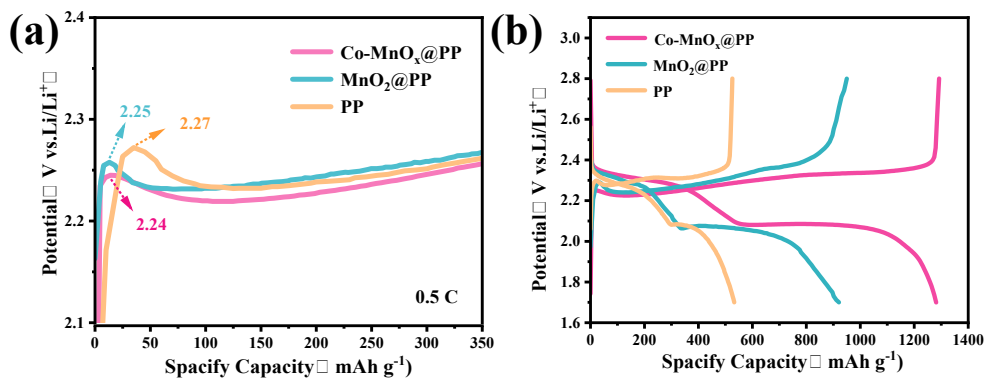


Fig. S8. (a) Initial and (b) whole charge/discharge curves of Li-S cells with Co-MnO_x@PP, MnO₂@PP and PP separators at 0.5 C.

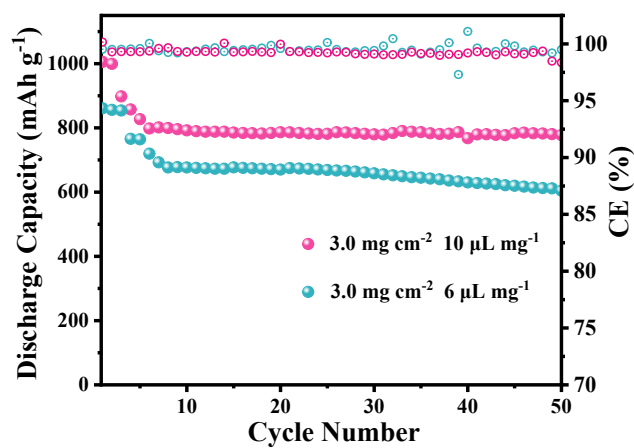


Fig. S9. The cycle of Co-MnO_x@PP modified separator under high sulfur loading and low E/S ratio

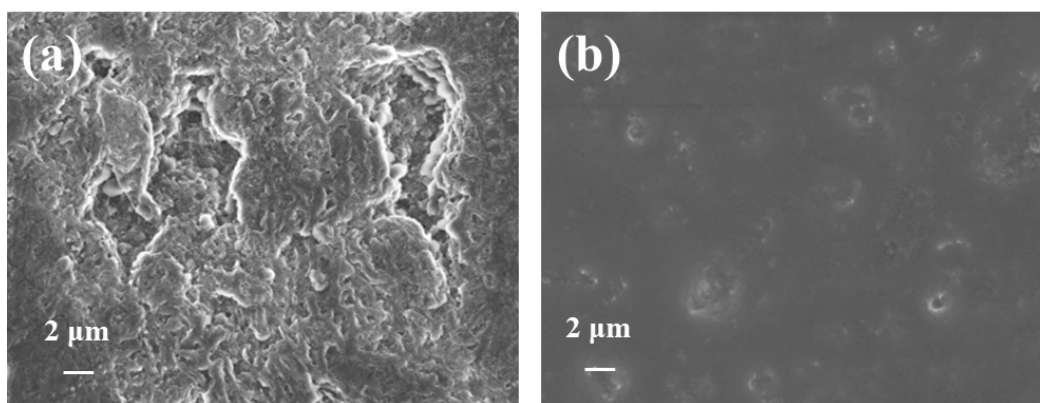


Fig. S10. SEM images of Li anode in contact with (a) PP and (b) Co-MnO_x@PP separators after 100 cycles.

Table S1. Summary of electrochemical performance of Li-S batteries configured with different modified separators and interlayers.

Modified separator	S loading (mg cm ⁻²)	Reversible capacity (mAh g ⁻¹)	Capacity retention /cycle number/Rate	Ref.
MnO ₂ @PE	1.5	603	65 %/500/0.5 C	[1]
Fe ₃ O ₄ /RGO//PP	0.7-1.0	728	60%/400/1.8 C	[2]
Co ₃ O ₄ @GC/N-CNT NF-coated separator	2.0	389	59 %/500/0.5 C	[3]
MnO-OVs/NCNTs/PP	1.5	618	66 %/500/1 C	[4]
MnO ₂ separator	1-1.2	494	71 %/500/0.5 C	[5]
Mn/Co-N-C separator	1.0	522	64 %/1000/2 C	[6]
NiCo ₂ O _{4-x} modified separator	1.5	327	53 %/500/2.5 C	[7]
CSUST1/CNT_x0002 coated separator	2.0	708	58 %/600/1 C	[8]
Co-MnO _x @PP	1.6	902	84.4 %/200/0.5 C	This work
	1.6	715	65.3 %/500/3 C	
	3.0	777	78.8 %/50/0.5 C	

References

1. Song, X.; Chen, G.; Wang, S.; Huang, Y.; Jiang, Z.; Ding, L. X.; Wang, H. Self-Assembled Close-Packed MnO₂ Nanoparticles Anchored on a Polyethylene Separator for Lithium-Sulfur Batteries. *ACS Appl. Mater. Interfaces* 2018, 10 (31), 26274-26282.
2. P. Cheng, P. Guo, D. Liu, Y. Wang, K. Sun, Y. Zhao, D. He, Fe₃O₄/RGO modified separators to suppress the shuttle effect for advanced lithium-sulfur batteries, *J. Alloys Compd.* 784 (2019) 149-156.
3. Saroha, R.; Oh, J. H.; Lee, J. S.; Kang, Y. C.; Jeong, S. M.; Kang, D.-W.; Cho, C.; Cho, J. S. Hierarchically porous nanofibers comprising multiple core-shell Co₃O₄@graphitic carbon nanoparticles grafted within N-doped CNTs as functional interlayers for excellent Li-S batteries. *Chem. Eng. J.* 2021, 426.
4. Yu, X.; Chen, W.; Cai, J.; Lu, X.; Sun, Z. Oxygen vacancy-rich MnO nanoflakes/N-doped carbon nanotubes modified separator enabling chemisorption and catalytic conversion of polysulfides for Li-S batteries. *J. Colloid Interface Sci.* 610(2022), 407-417
5. Wang, X.; Yang, L.; Wang, Y.; Li, Q.; Chen, C.; Zhong, B.; Chen, Y.; Guo, X.; Wu, Z.; Liu, Y.; Liu, Y.; Sun, Y. Novel functional separator with self-assembled MnO₂ layer via a simple and fast method in lithium-sulfur battery. *J. Colloid Interface Sci.* 606 (1) (2022), 666-676.
6. Qiao, S.; Wang, Q.; Lei, D.; Shi, X.; Zhang, Q.; Huang, C.; Liu, A.; He, G.; Zhang, F. Oxygen vacancy enabled fabrication of dual-atom Mn/Co catalysts for high-

- performance lithium-sulfur batteries. *J. Mater. Chem. A* 10 (21) (2022), 11702-11711.
7. Zhu, Y.; Zuo, Y.; Ye, F.; Zhou, J.; Tang, Y.; Chen, Y. Dual-regulation strategy to enhance electrochemical catalysis ability of NiCo₂O_{4-x} for polysulfides conversion in Li-S batteries. *Chem. Eng. J.* 2022, 428.
 8. Jin, H. G.; Wang, M.; Wen, J. X.; Han, S. H.; Hong, X. J.; Cai, Y. P.; Li, G.; Fan, J.; Chao, Z. S. Oxygen Vacancy-Rich Mixed-Valence Cerium MOF: An Efficient Separator Coating to High-Performance Lithium-Sulfur Batteries. *ACS Appl. Mater. Interfaces* 13 (3) (2021), 3899-3910.