

MnO₂ Nanoflower Grown on a Polypropylene Separator as Both Barrier and Accelerator of polysulfides for High-performance Li–S Batteries

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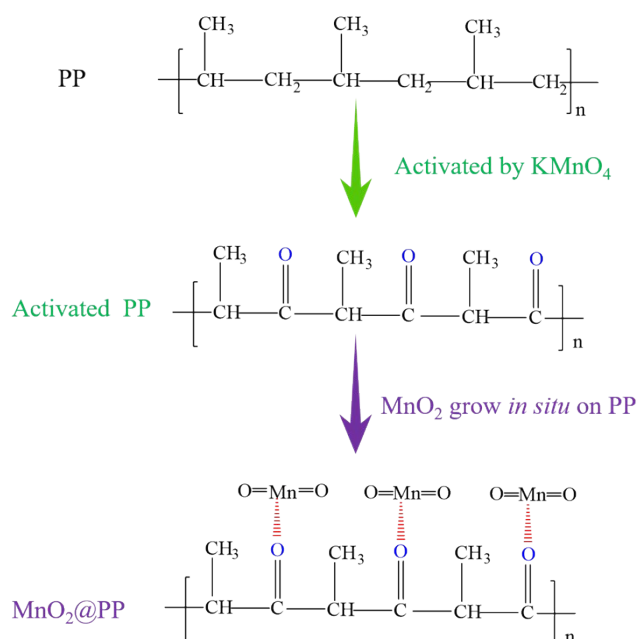


Figure S1. Schematic illustration of growth mechanism for the MnO₂@PP separator.

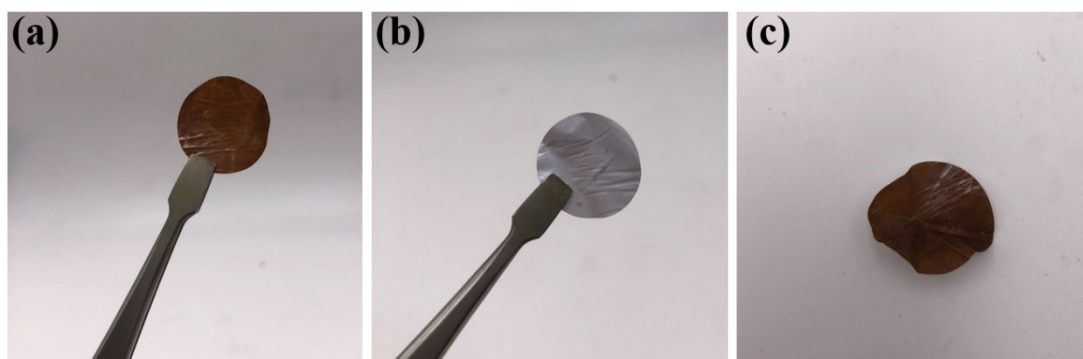


Figure S2. The digital photograph of the front side and reverse side of $\text{MnO}_2@\text{PP}$ separator and the kneading/spreading test of the $\text{MnO}_2@\text{PP}$ separator.

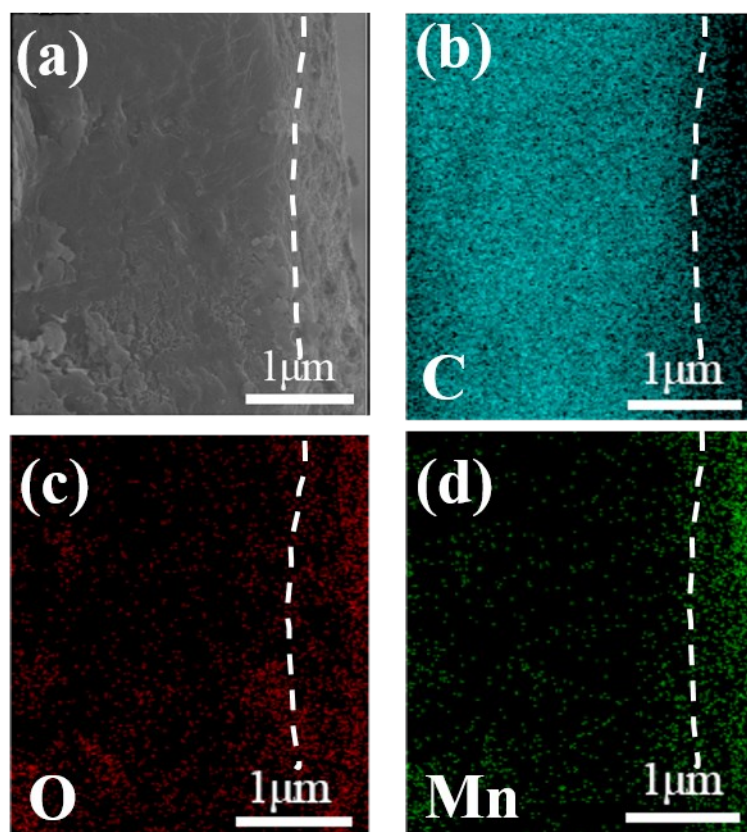


Figure S3. (a) Cross-sectional morphologies of $\text{MnO}_2@\text{PP}$ separator, and corresponding elemental mapping images of (b) C, (c) O, (d) Mn.

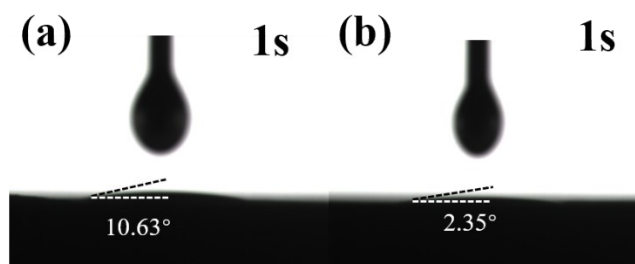


Figure S4. Contact angle measurements of (a) pristine separator; and (b) MnO_2/PP separator for the electrolyte.

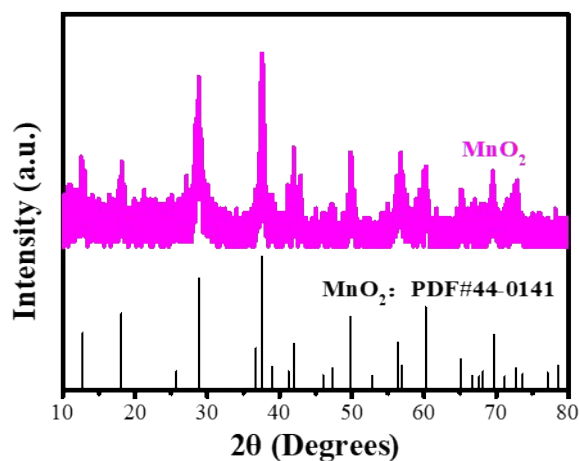


Figure S5. The XRD pattern of the MnO_2 powders stripped from the $\text{MnO}_2@\text{PP}$ separator.

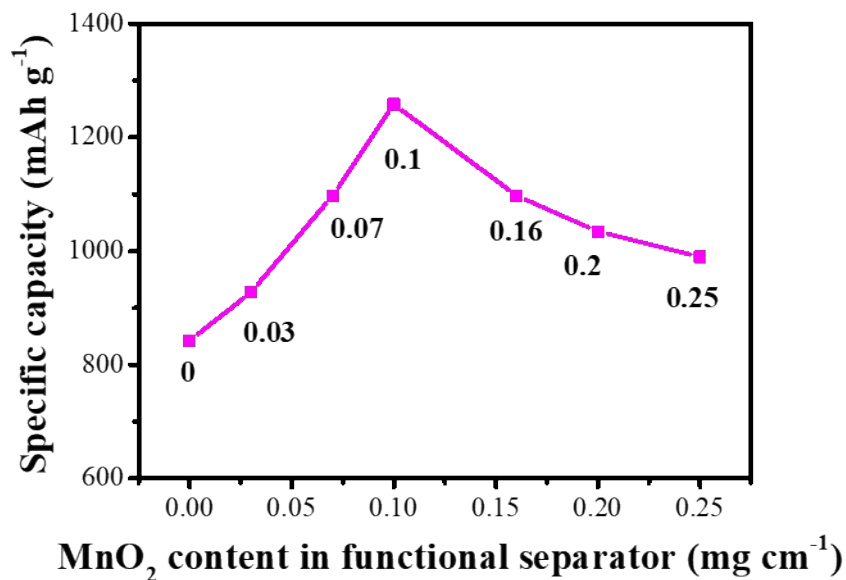


Figure S6. Capacity optimization of MnO_2 content in the $\text{MnO}_2@\text{PP}$ separator.

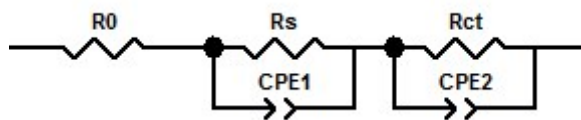


Figure S7. The equivalent circuit diagram of the Nyquist plots.

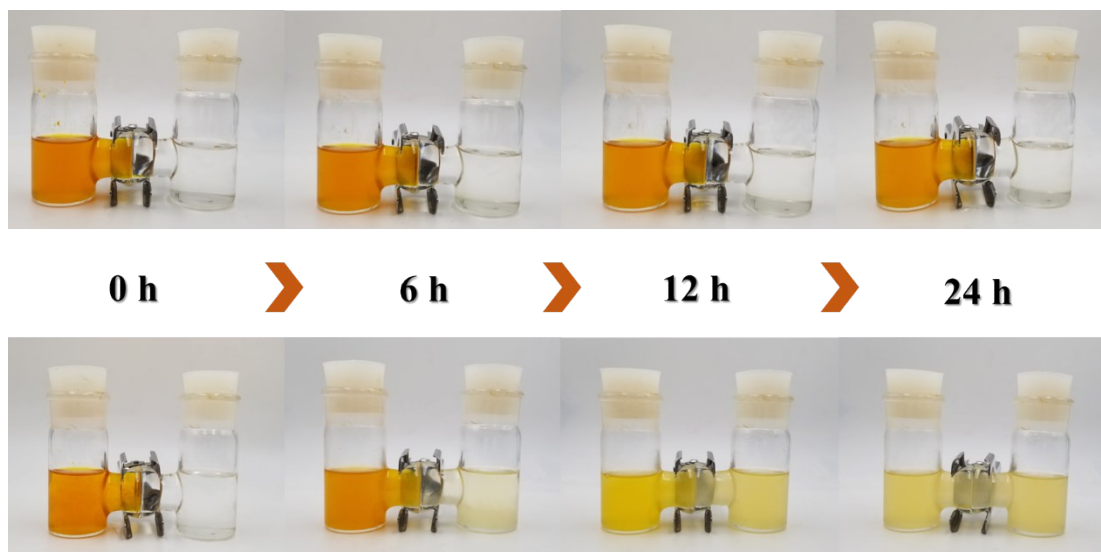


Figure S8. Digital photographs of the Li_2S_6 diffusion tests for the $\text{MnO}_2@\text{PP}$ separator (top) and PP separator (bottom)

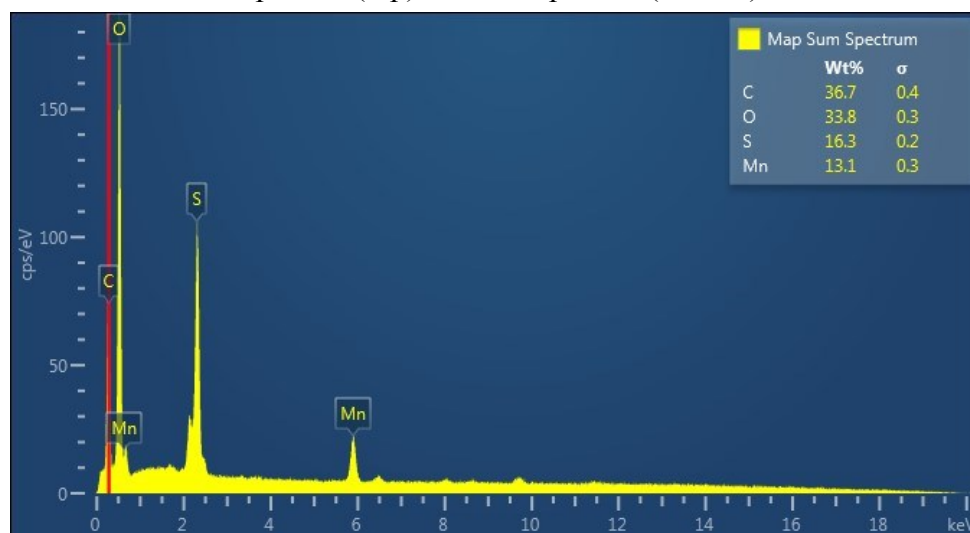


Figure S9. EDX spectra of $\text{MnO}_2@\text{PP}$ separator after cycling.

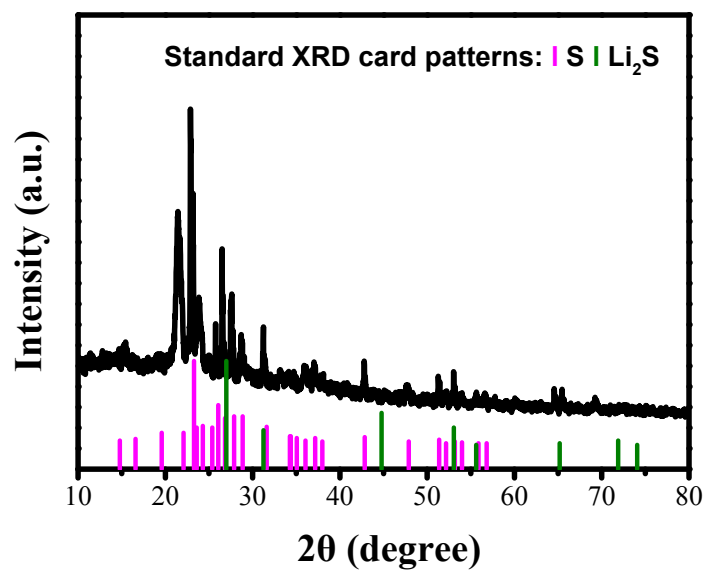


Figure S10. XRD patterns of MnO₂@PP separator after cycling and standard XRD patterns sulfur and Li₂S powder.

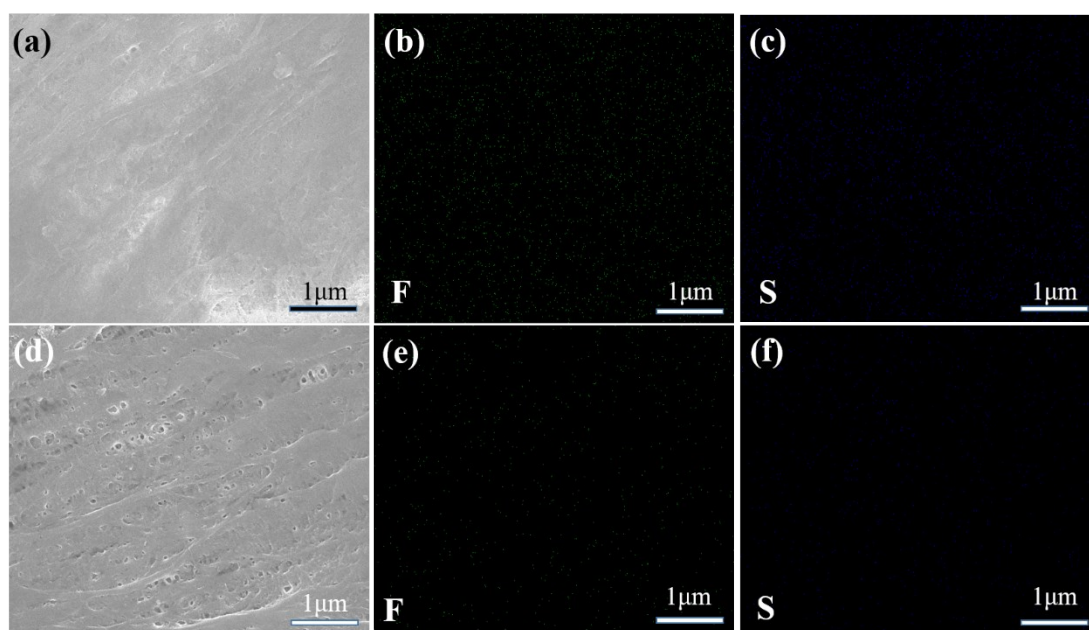


Figure S11. The SEM images and corresponding elemental mapping images of (a,b,c) PP and (d,e,f) MnO₂@PP separator after cycling.

Table S1. Comparison of electrochemical properties functional separators in Li–S cells.

Coating or interlayer	Thickness	Sulfur loading	Sulfur content	Cathode	Discharge Capacity	Areal capacity (mAh)	E/S ratio	Ref
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cm ²)								
MoO ₃ @CNT	N/A	1.0	60%	Super P/S	~755 mAh g ⁻¹ , 200 th , 0.3 C	<2.0	N/A	S1
EUC-CNF	N/A	1.5	70%	Super P/S	1038 mAh g ⁻¹ , 50 th , 0.2 C	<2.0	N/A	S2
SSNS/CNT	10μm	1.0	65%	KB/S	680 mAh g ⁻¹ , 100 th , 0.2 C	<2.0	N/A	S3
GO@MoS ₂	8μm	3.64	70%	CB/S	~600 mAh g ⁻¹ , 95 th , 0.2 C	2.2	14	S4
TiO ₂ /C	80μm	1.1	54%	AB/S	1000 mAh g ⁻¹ , 60 th , 0.1 C	<2.0	36	S5
CNF@ZrO ₂	N/A	2.7	70%	CB/S	800 mAh g ⁻¹ , 60 th , 0.2 C	~2.1	40	S6
rGO@SL	0.8nm	3.8	75%	CB/S	700 mAh g ⁻¹ , 50 th , 0.05 C	2.7	8	S7
TiN	25μm	1.3	70%	Super P/S	744 mAh g ⁻¹ , 200 th , 0.5 C	<2.0	46	S8
MnO ₂	380nm	1.5-2.5	66%	KB/S	~603 mAh g ⁻¹ , 500 th , 0.5 C	<2.0	8.8	S9
MnO ₂ @PP	500nm	6	70%	CB/S	~747 mAh g ⁻¹ , 150 th , 0.2 C	~6	~6.6	This work

References

- [S1] L. Y. Luo, X. Y. Qin, J. X. Wu, G. M. Liang, Q. Li, M. Liu, F. Y. Kang, G. H. Chen, B. H. Li, An interwoven MoO₃@CNT scaffold interlayer for high-performance lithium-sulfur batteries, *J. Mater. Chem. A*, 2018, **6**, 8612-8619.
- [S2] K. S. Wu, Y. Hu, Z. Shen, R. Z. Chen, X. He, Z. L. Cheng and P. Pan, Highly efficient and green fabrication of a modified C nanofiber interlayer for high-performance Li-S batteries, *J. Mater. Chem. A*, 2018, **6**, 2693-2699.
- [S3] S. S. Yao, J. C. J. Q. Huang, Z. H. Lu, Y. Deng, W. G. Chong, J. X. Wu, M. Haq, F. Ciucci and J. K. Kim, Novel 2D Sb₂S₃ nanosheet/CNT coupling layer for exceptional polysulfide recycling performance, *Adv. Energy Mater.*, 2018, 1800710.
- [S4] L. Tan, X. H. Li, Z. X. Wang, H. J. Guo, J. X. Wang, Lightweight reduced graphene oxide@MoS₂ interlayer as polysulfide barrier for high-performance lithium-sulfur batteries, *ACS Appl. Mater. Interfaces*, 2018, **10**, 3707-3713.
- [S5] S. Y. Liu, C. Y. Fan, Y. H. Shi, H. C. Wang, X. L. Wu, J. P. Zhang, Effective cathode design of three-layered configuration for high-energy Li-S batteries, *ACS Appl. Mater. Interfaces*, 2018, **10**, 509-516.
- [S6] Y. Li, J. Zhu, R. Shi, M. Dirican, P. Zhu, C. Yan, H. Jia, J. Zang, J. He, X. Zhang, Ultrafine and polar ZrO₂-inlaid porous nitrogen-doped carbon nanofiber as efficient polysulfide absorbent for high-performance lithium-sulfur batteries with long lifespan, *Chem. Eng. J.*, 2018, **349**, 376-387.

- [S7] Z. Z. Du, C. K. Guo, L. J. Wang, A. J. Hu, S. Jin, T. M. Zhang, H.C. Jin, Z. K. Qi, S. Xin, X. H. Kong, Y. G. Guo, H. X. Ji, L. J. Wan, Atom-Thick Interlayer Made of CVD-Grown Graphene Film on Separator for Advanced Lithium–Sulfur Batteries, *ACS Appl. Mater. Interfaces*, 2017, **9**, 43696–43703.
- [S8] B. Y. Hao, H. Li, W. Lv, Y. B. Zhang, S. Z. Niu, Q. Qi, S. J. Xiao, J. Li, F. Y. Kang, Q. H. Yang, Reviving catalytic activity of nitrides by the doping of the inert surface layer to promote polysulfide conversion in lithium-sulfur batteries, *Nano Energy*, 2019, **60**, 305-311.
- [S9] X. Song, G. P. Chen, S. Q. Wang, Y. P. Huang, Z. Y. Jiang, L. X. Ding, H. H. Wang, Self-Assembled Close-Packed MnO₂ Nanoparticles Anchored on a Polyethylene Separator for Lithium–Sulfur Batteries, *ACS Appl. Mater. Interfaces*, 2018, **10**, 26274-26282.