

Hierarchical manganese valence gradient  $\text{MnO}_2$  via phosphorus doping for cathode materials

with improved stability

Limin Zhao\*, Zejuan Ni, Bo Ge, Chuanyu Jin, Hui Zhao, Wenzhi Li

School of Materials Science and Engineering, Liaocheng University, Liaocheng 252059, PR

China

\*Corresponding authors. E-mail: [zhaolimin@lcu.edu.cn](mailto:zhaolimin@lcu.edu.cn)

## **Table of Contents:**

**Fig.S1** EDS elemental maps for MnO<sub>2</sub>.

**Fig.S2** EDS elemental maps for P-MnO<sub>x</sub>

**Fig.S3** High-resolution Mn 2p (a) and O 1s (b) X-ray photoelectron spectroscopy of MnO<sub>2</sub>.

**Fig.S4** High-resolution Mn 3s X-ray photoelectron spectroscopy of MnO<sub>2</sub> and P-MnO<sub>x</sub>.

**Fig.S5** High-resolution P 2p X-ray photoelectron spectroscopy of P-MnO<sub>x</sub>.

**Fig.S6** Pore distributions of MnO<sub>2</sub> and P-MnO<sub>x</sub>.

**Fig.S7** (a) CV profiles of MnO<sub>2</sub> at various scan rates and (b) lgI vs lgv patterns for MnO<sub>2</sub>.

**Fig.S8** Cycle lifetime of MnO<sub>2</sub> and P-MnO<sub>x</sub>.

**Fig.S9** The CV curve of MnO<sub>2</sub> at 0.1 mV/s.

**Fig.S10** The CV curve of MnO<sub>2</sub> at different scan rates.

**Fig.S11** The GCD curves of MnO<sub>2</sub> at different cycle number.

**Fig.S12** The constructed structure of MnO<sub>2</sub> (left: lateral view, right: top view).

**Fig.S13** The constructed structure of P-MnO<sub>x</sub> (left: lateral view, right: top view).

**Table S1** The capacity performance of some reported cathode materials.

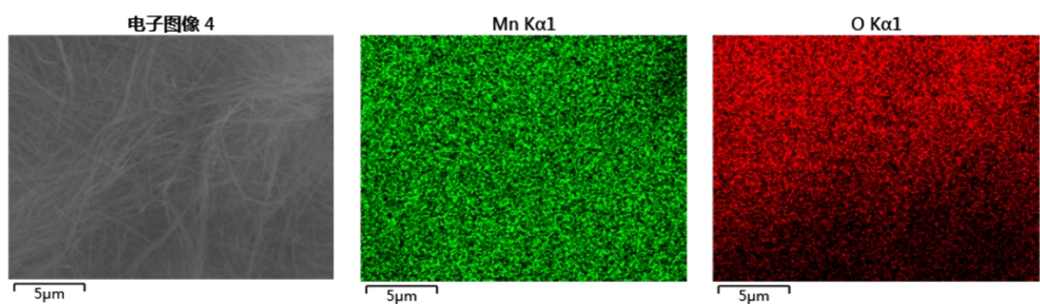


Fig. S1 EDS elemental maps for  $\text{MnO}_2$

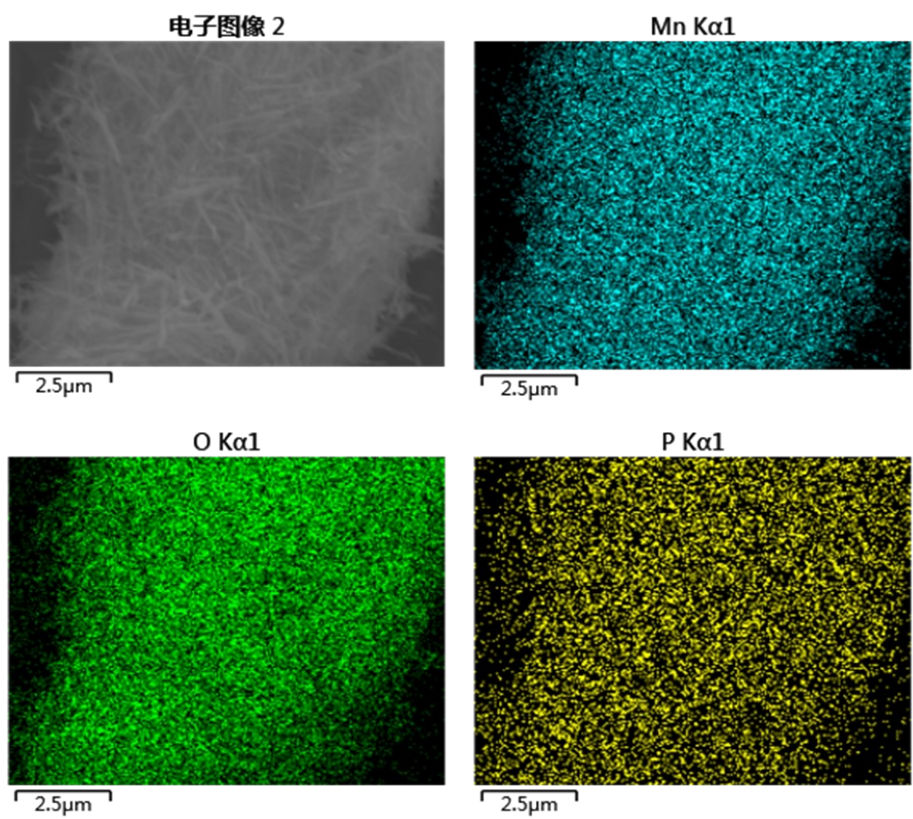


Fig. S2 EDS elemental maps for  $\text{P-MnO}_x$

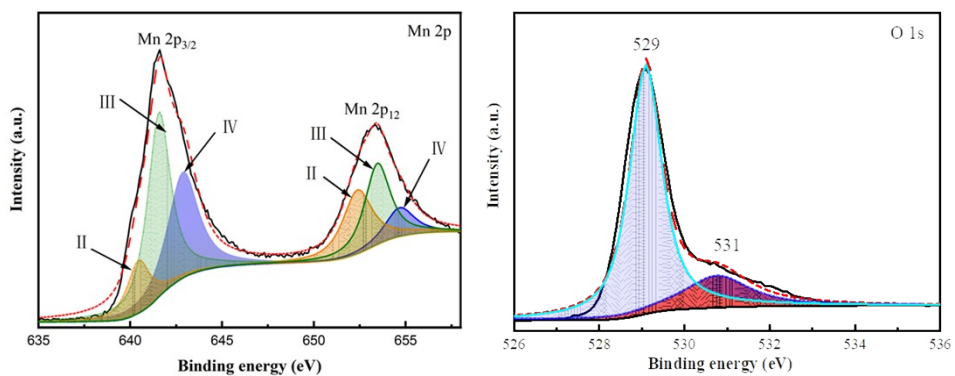


Fig. S3 high-resolution Mn 2p (a) and O 1s (b) X-ray photoelectron spectroscopy of MnO<sub>2</sub>

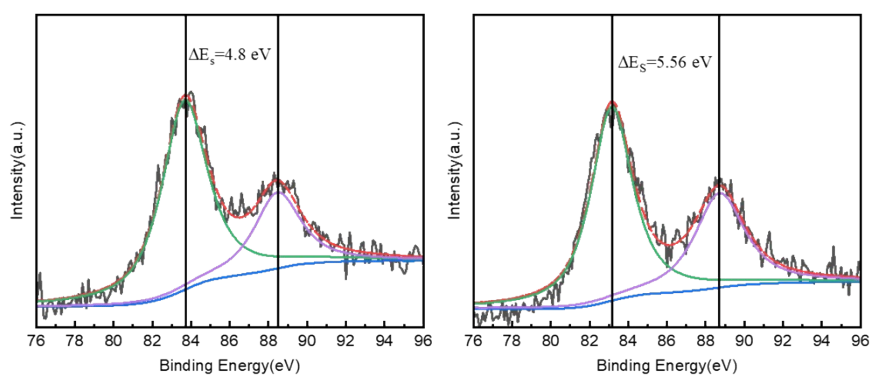


Fig. S4 high-resolution Mn 3s X-ray photoelectron spectroscopy of MnO<sub>2</sub> and P-MnO<sub>x</sub>

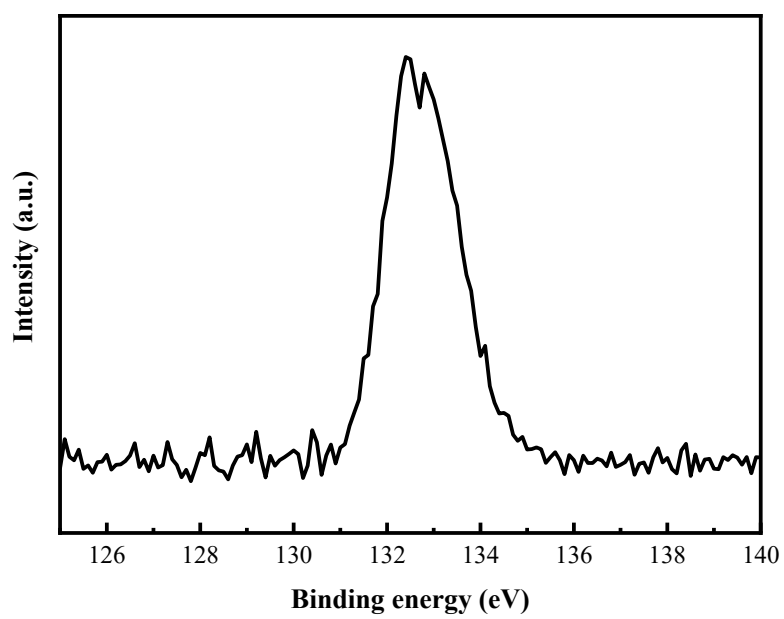


Fig. S5 high-resolution P 2p X-ray photoelectron spectroscopy of P-MnO<sub>x</sub>

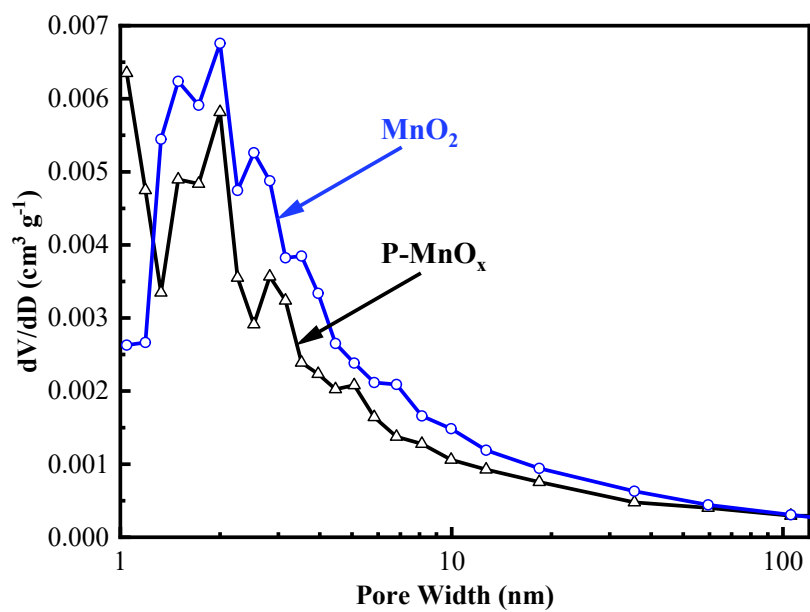


Fig. S6 pore distributions of MnO<sub>2</sub> and P-MnO<sub>x</sub>

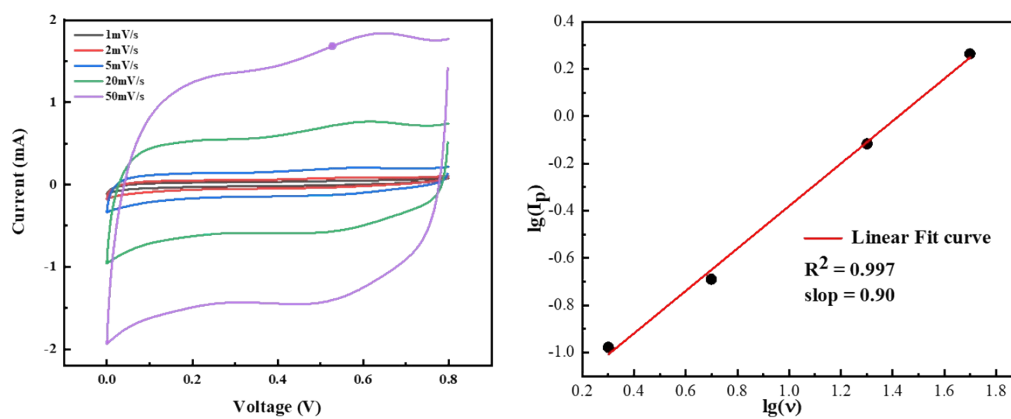


Fig. S7 (a) CV profiles of MnO<sub>2</sub> at various scan rates and (b) lgI vs lgv patterns for MnO<sub>2</sub>

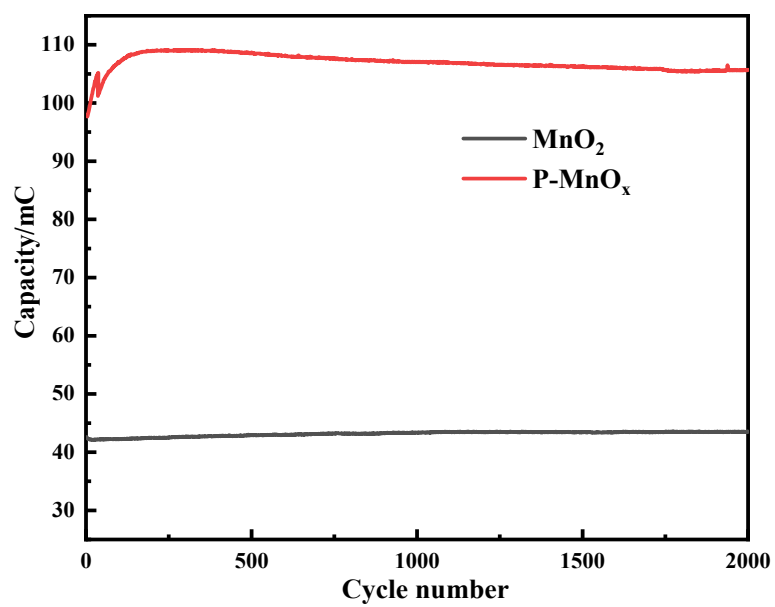


Fig. S8 Cycle lifetime of MnO<sub>2</sub> and P-MnO<sub>x</sub>



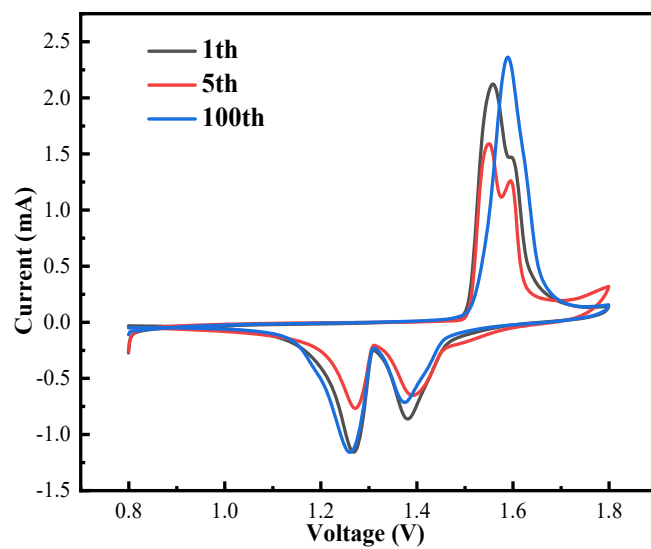


Fig. S9 the CV curve of MnO<sub>2</sub> at 0.1 mV/s

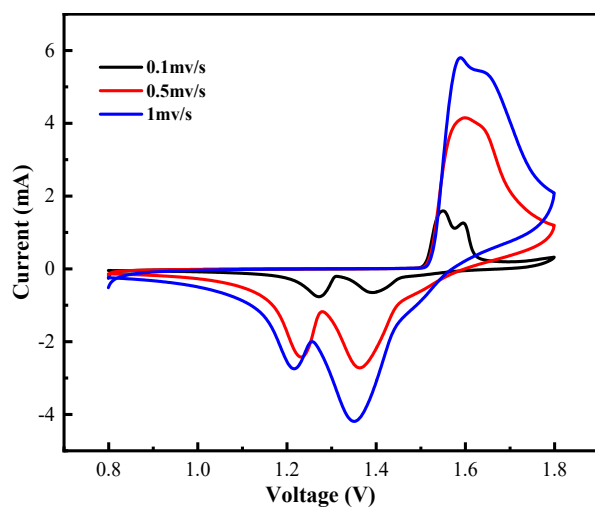


Fig. S10 the CV curve of MnO<sub>2</sub> at different scan rates

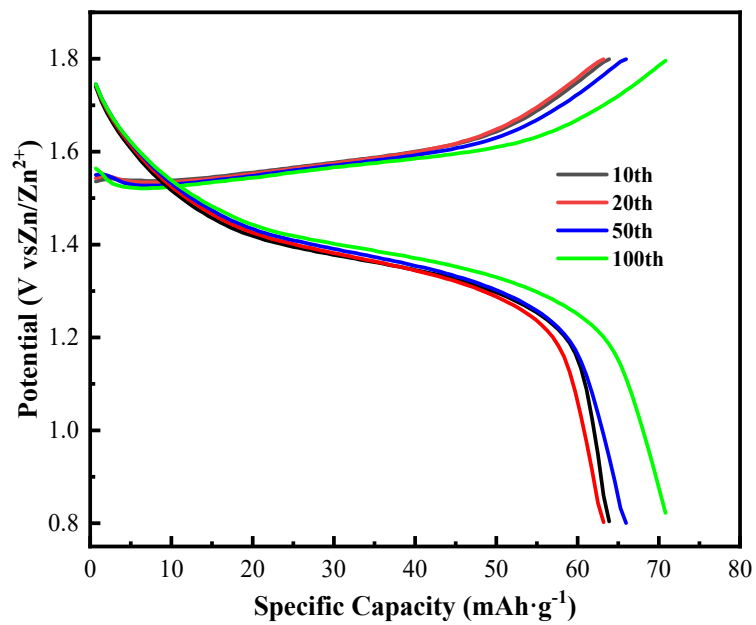


Fig. S11 the GCD curves of MnO<sub>2</sub> at different cycle number

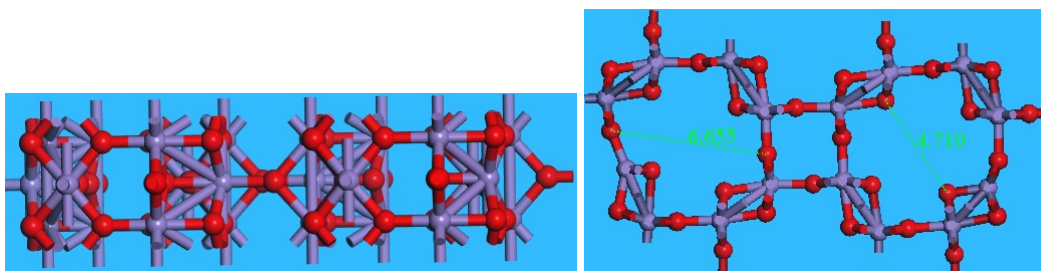


Fig. S12 the constructed structure of MnO<sub>2</sub> (left: lateral view, right: top view)

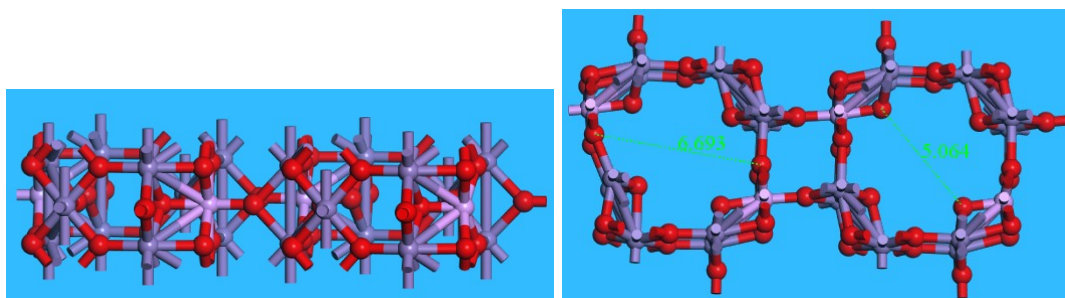


Fig. S13 the constructed structure of P-MnO<sub>x</sub> (left: lateral view, right: top view)

Table S1 The capacity performance of some reported cathode materials

Cathode	Capacity ( mAh g <sup>-1</sup> )	Reference
VO <sub>2</sub>	276 mAh g <sup>-1</sup> (0.2 A g <sup>-1</sup> )	[1]
α-Mn <sub>2</sub> O <sub>3</sub> cathode	148 mAh g <sup>-1</sup> (0.1 A g <sup>-1</sup> )	[2]
Na <sub>1.1</sub> V <sub>3</sub> O <sub>7.9</sub> nanoribbons/graphene	84.8 mAh g <sup>-1</sup> (1 A g <sup>-1</sup> )	[3]
Ni-PTA-Mn	139 mAh g <sup>-1</sup> (0.1 A g <sup>-1</sup> )	[4]
β-MnO <sub>2</sub>	110 mAh g <sup>-1</sup> (0.2 A g <sup>-1</sup> )	[5]
★ This work	155 mAh/g (0.1 A g <sup>-1</sup> )	

[1] S. Zuo, J. Liu, W. He, S. Osman, Z. Liu, X. Xu, J. Shen, W. Jiang, J. Liu, Z. Zeng, M. Zhu, *The Journal of Physical Chemical Letter*, 2021, 12, 7076-7084.

[2] B. Jiang, C. Xu, C. Wu, L. Dong, J. Li, F. Kang, *Electrochimica Acta*, 2017, 229, 422-428.

[3] Y. Cai, F. Liu, Z. Luo, G. Fang, J. Zhou, A. Pan, S. Liang, *Energy Storage Materials*, 2018, 13, 168-174.

[4] C. Li, C. Zheng, H. Jiang, S. Bai, J. Jia, *Journal of Alloys and Compounds*, 2021, 882, 160587.

[5] W. Liu, X. Zhang, Y. Huang, B. Jiang, Z. Chang, C. Xu, F. Kang, *Journal of Energy Chemistry*, 2021, 56, 365-373.