Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Manganese hexacyanoferrate reinforced by PEDOT coating toward high-rate and long-life sodium-ion battery cathode

Xiao Wang,[a] Baoqi Wang,[a] Yuxin Tang,[b] Ben Bin Xu,[c] Chu Liang,[d] Mi Yan,[a] Yinzhu Jiang[a*]

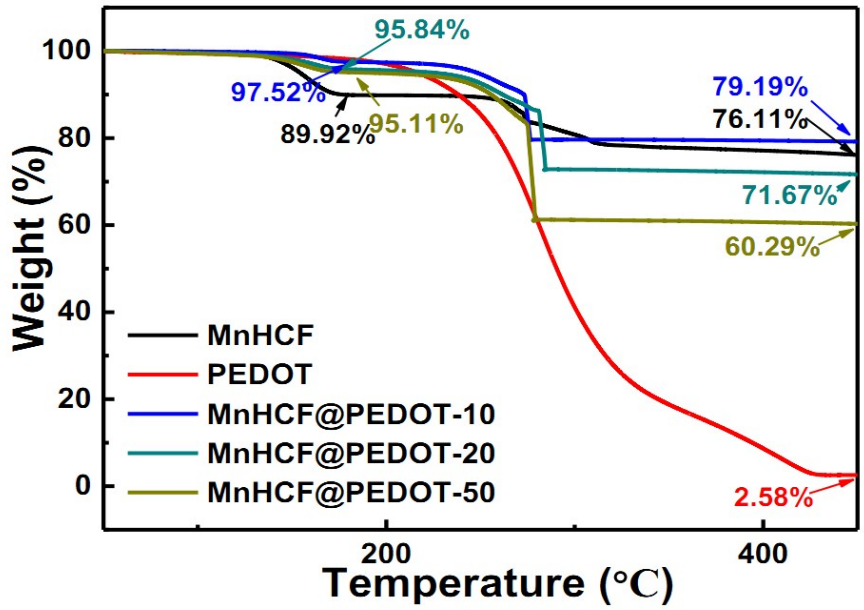

Fig. S1 TG profiles of MnHCF, PEDOT, MnHCF@PEDOT-10/20/50.

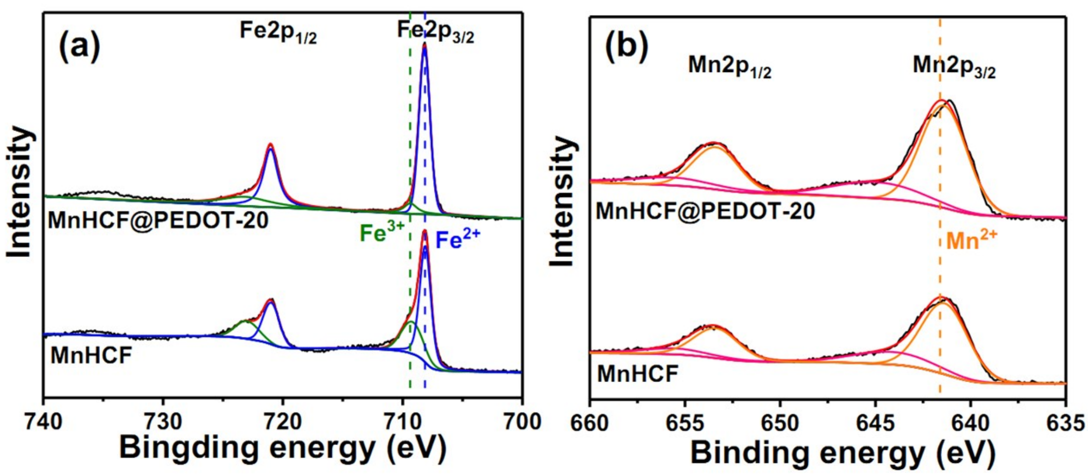

Fig. S2 Fe 2p and Mn 2p XPS spectra of MnHCF and MnHCF@PEDOT-20.

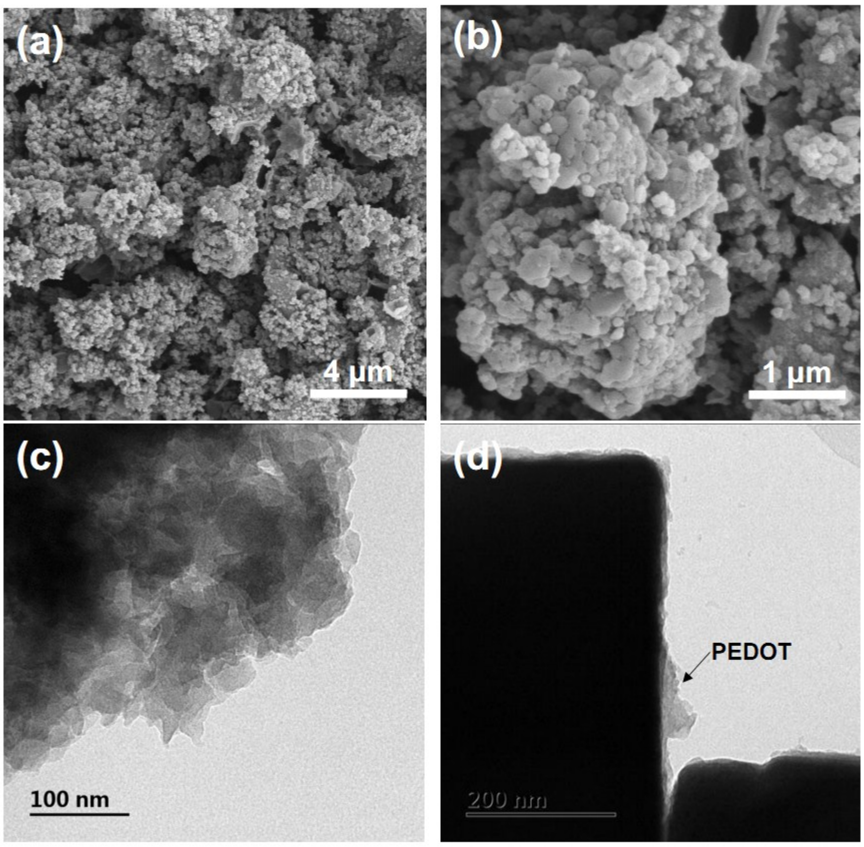

Fig. S3 (a, b) SEM images of PEDOT; TEM images of (c) PEDOT and (d) MnHCF@PEDOT-50.

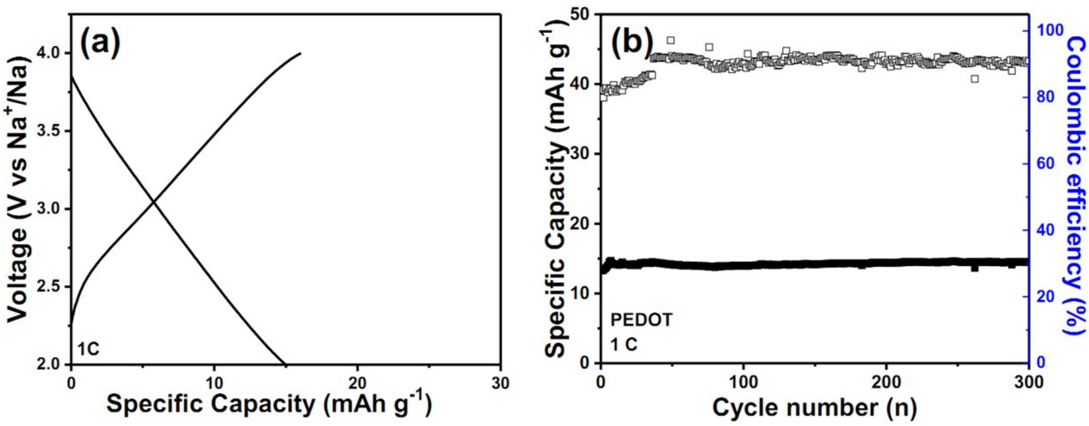

Fig. S4 (a) Galvanostatic charge–discharge profile and (b) cycling performance and coulombic efficiency of PEDOT at 1 C.

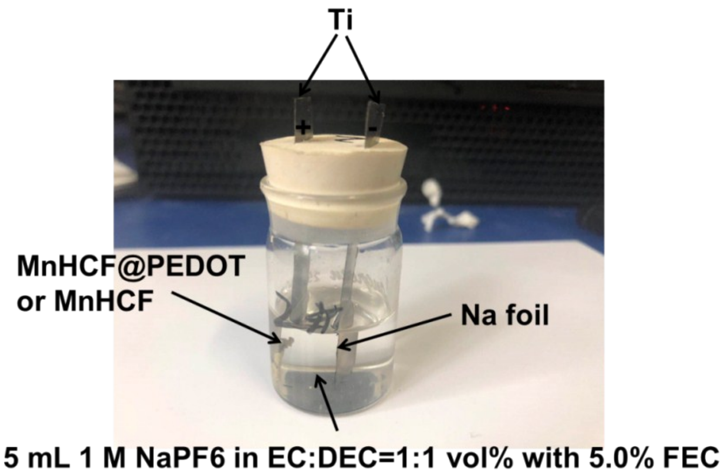

Fig. S5 Photo image of amplified half-cell.

The amplified half-cell is assembled in an Ar-filled glovebox by using the MnHCF or MnHCF@PEDOT electrode as cathode, Na foil as anode, titanium sheet as current collector, and 1 mol L^{-1} $NaPF_6$ in EC/DEC (1:1 by volume) as electrolyte. The active material loading of all cathode electrode is 2 mg and the active area is 1 cm^2. the amounts of electrolyte solution are kept at 5 mL and the working electrode is totally immersed in the electrolyte. After 100 galvanostatic charge-discharge cycles at a current density of 100 mA g^{-1}, the contents of element Mn and Fe in the electrolyte solution are analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES).

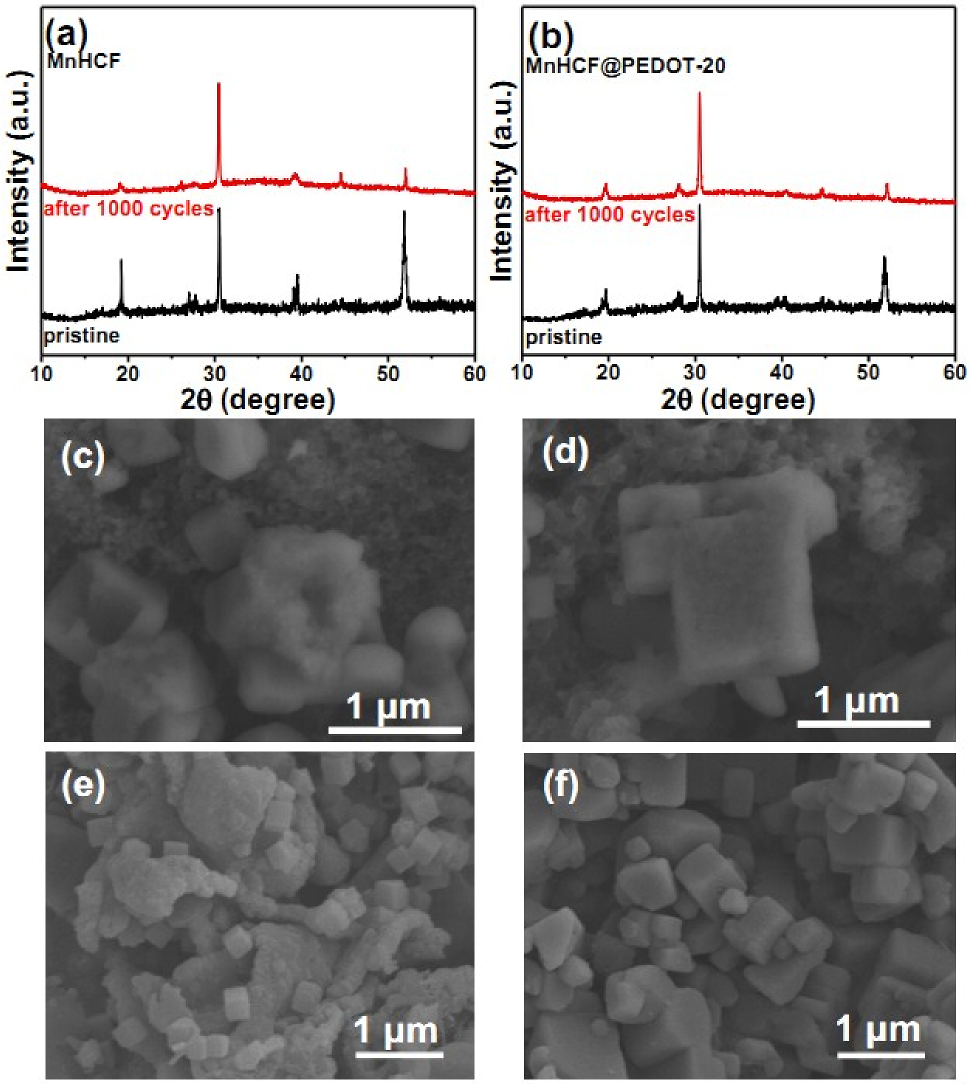

Fig. S6 XRD of (a) MnHCF and (b) MnHCF@PEDOT-20 after 1000 cycles; SEM of (c) MnHCF and (d) MnHCF@PEDOT-20 after 1000 cycles, and (e) MnHCF and (f) MnHCF@PEDOT-20 after etching in 0.1 M HF solution at 100 °C for 4 h.

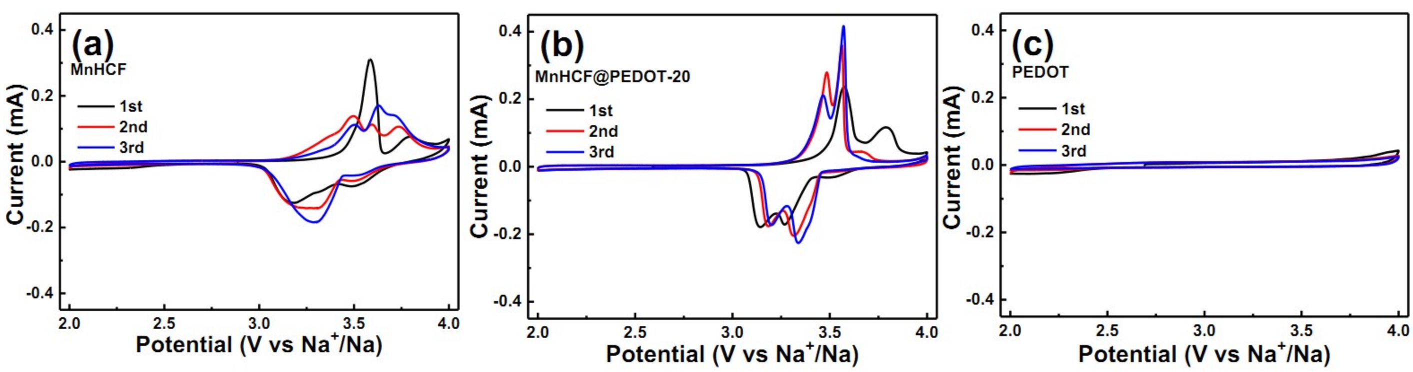

Fig. S7 CV curves of (a) MnHCF, (b) MnHCF@PEDOT-20 and (c) PEDOT at a sweep rate of 0.1 mV s^{-1}.

Table S1 Comparison between MnHCF@PEDOT-20 and reported MnHCF for SIBs.

Cathode Active material (loading mg cm^{-2}, percentage)	Specific capacity （capacity mAh g^{-1}, rate）	Cycle life （retention, cycles, rate）	Rate capability （capacity mAh g^{-1}, rate）
This work ~2, 70%	**147.9, 15 mA g^{-1}**	**78.2%, 1000, 1.5 A g^{-1}**	**95.2, 1.5 A g^{-1}**
$Na_{1.40}MnFe(CN)_6$[1] /	111, 6 mA g^{-1}	95.9 %, 30, 6 mA g^{-1}	/
$Na_{1.72}MnFe(CN)_6$[1] /	134, 6 mA g^{-1}	89.5 %, 30, 6 mA g^{-1}	45, 4.8 A g^{-1}
$Na_{1.72}MnFe(CN)_6$@PPy[2] ~7, 70 %	124, 12 mA g^{-1}	67 %, 200, 240 mA g^{-1}	55.6, 4.8 A g^{-1}
$Na_{2-\delta}$MnHCF[3] 6~10, 70%	150, 15 mA g^{-1}	75 %, 500, 100 mA g^{-1}	121, 3 A g^{-1}
$Na_{1.32}Mn[Fe(CN)_6]_{0.83}\cdot 3.5H_2O$[4] /, 70%	109, 0.5 C	90 %, 100, 0.9 C	19, 40 C
R-$Na_xMnFe(CN)_6\cdot zH_2O$[5] 4.5~5, 70%	150.1, 31 mA g^{-1}	88 %, 50, 155 mA g^{-1}	/
$Na_2MnFe(CN)_6$@PPy[6] ~1.5, 70%	118, 10 mA g^{-1}	90.7 %, 150, 10 mA g^{-1}	65, 0.2 A g^{-1}
$Na_{1.80}Mn[Fe(CN)_6]_{0.98}\square_{0.02}\cdot 1.76H_2O$[7] ~2, 70%	144, 15 mA g^{-1}	72.7 %, 2100, 150 mA g^{-1}	86.6, 1.5 A g^{-1}
$Na_{1.66}Mn[Fe(CN)_6]_{0.94}\square_{0.06}\cdot 1.66H_2O$@G[8] ~2, 70%	142.7, 15 mA g^{-1}	90.6 %, 500, 150 mA g^{-1}	89.7, 3 A g^{-1}
$Na_{1.73}K_{0.13}Mn[Fe(CN)_6]_{0.97}\square_{0.03}$@3DNC[9] /, 70%	211, 20 mA g^{-1}	68 %, 100 , 40 mA g^{-1}	105, 0.5 A g^{-1}
$Na_{1.76}Ni_{0.12}Mn_{0.88}[Fe(CN)_6]_{0.98}\square_{0.02}$[10] 3~4, 70%	123.3, 10 mA g^{-1}	83.8 %, 800 , 100 mA g^{-1}	50.2, 0.6 A g^{-1}
$Na_{1.87}Ni_{0.05}Mn_{0.95}[Fe(CN)_6]_{0.98}\square_{0.02}\cdot 4.06H_2O$[11] ~2, 70%	120, 50 mA g^{-1}	96.7 %, 100 , 50 mA g^{-1}	78, 1.6 A g^{-1}
$Na_{1.44}Mn_{0.72}Fe_{0.28}[Fe(CN)_6]_{0.86}\square_{0.14}\cdot 4.1H_2O$[12] ~0.15, 70%	119, 0.1 C	88 %, 50 , 0.3 C	30, 50 C
$Na_{1.64}Mn_{0.74}Ni_{0.26}[Fe(CN)_6]_{0.91}\square_{0.09}\cdot 3.9H_2O$[12] ~0.15, 70%	139 , 0.1 C	73 %, 50 , 0.3 C	50, 50 C
$Na_{1.58}Mn[Fe(CN)_6]_{0.8}\square_{0.2}\cdot 1.8H_2O$[13] /, 70%	126, 30 mA g^{-1}	60 %, 50 , 30 mA g^{-1}	7, 2 A g^{-1}
$Na_{1.38}Ni_{0.07}Mn_{0.93}[Fe(CN)_6]_{0.82}\square_{0.18}\bullet 1.4H_2O$[14] ~2, 70%	123, 50 mA g^{-1}	82.9 %, 600 , 50 mA g^{-1}	52, 3.2 A g^{-1}

$Na_{1.60}Mn[Fe(CN)_6]_{0.9}\square_{0.1}$@NVOPF[15] ~2, 70%	112.9, 10 mA g^{-1}	84.3 %, 500 , 100 mA g^{-1}	91.4,1 A g^{-1}

Reference

[1] L. Wang, Y. Lu, J. Liu, M. Xu, J. Cheng, D. Zhang, J. B. Goodenough, *Angewandte Chemie*, 2013, **52**, 1964.

[2] W. Li, S. Chou, J. Wang, J. Wang, Q. Gu, H. Liu, S. Dou, *Nano Energy*, 2015, **13**, 200.

[3] J. Song, L. Wang, Y. Lu, J. Liu, B. Guo, P. Xiao, J. J. Lee, X. Q. Yang, G. Henkelman, J. B. Goodenough, *Journal of the American Chemical Society*, 2015, **137**, 2658.

[4] T. Matsuda, M. Takachi, Y. Moritomo, *Chemical Communications*, 2013, **49**, 2750.

[5] I. Jo, S. Lee, H. Kim, B. Jin, *Journal of Alloys and Compounds*, 2017, **729**, 590.

[6] F. Hu, L. Li, X. Jiang, *Chinese Journal of Chemistry*, 2017, **35**, 415.

[7] Z. Shen, S. Guo, C. Liu, Y. Sun, Z. Chen, J. Tu, S. Liu, J. Cheng, J. Xie, G. Cao, X. Zhao, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 16121.

[8] Z. Shen, Y. Sun, J. Xie, S. Liu, D. Zhuang, G. Zhang, W. Zheng, G. Cao, X. Zhao, *Inorganic Chemistry Frontiers*, 2018, **5**, 2914.

[9] Y. Mao, Y. Chen, J. Qin, C. Shi, E. Liu, N. Zhao, *Nano Energy*, 2019, **58**, 192.

[10] D. Yang, J. Xu, X. Z. Liao, Y. S. He, H. Liu, Z. F. Ma, *Chemical Communications*, 2014, **50**, 13377.

[11] R. Chen, Y. Huang, M. Xie, Z. Wang, Y. Ye, L. Li, F. Wu, *ACS Applied Materials & Interfaces*, 2016, **8**, 31669.

[12] Y. Moritomo, S. Urase, T. Shibata, *Electrochimica Acta*, 2016, **210**, 963.

[13] X. Bie, K. Kubota, T. Hosaka, K. Chihara and S. Komaba, *Journal of Power Sources*, 2018, **378**, 322-330.

[14] Y. Huang, M. Xie, Z. Wang, Y. Jiang, Y. Yao, S. Li, Z. Li, L. Li, F. Wu, R. Chen, *Small*, 2018, **14**, e1801246.

[15] F. Peng, L. Yu, S. Yuan, X. Z. Liao, J. Wen, G. Tan, F. Feng, Z. F. Ma, *ACS Applied Materials & Interfaces*, 2019, **11**, 37685-37692.