Supporting Information

Three dimensional hierarchically porous crystalline MnO_2 structure design for high rate performance lithium-ion battery anode

Shikun Liu,[a] Xusong Liu,[a] Jiupeng Zhao,*[a] Zhongqiu Tong,[b] Jing Wang,[a] Xiaoxuan Ma,[a] Caixia Chi,[a] Dapeng Su,[a] Xiaoxu Liu,*[ac] Yao Li,*[b]

a MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, PR China

b Center for Composite Materials Harbin Institute of Technology, Harbin 150001, PR China

c Heilongjiang University of Science and Technology, Harbin 150022, PR China

**Corresponding authors. E-mail: jpzhao@hit.edu.cn; liu88062321@163.com; yaoli@hit.edu.cn*

Electrodeposited Processes of Manganese Dioxide:

Anode: $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$ (1)

Cathode: $2H^+ + 2e^- \rightarrow H_2$ (2)

Overall: $Mn^{2+} + 2H_2O \rightarrow MnO_2 + H_2 + 2H^+$ (3)

Water electrolysis: $2H_2O \rightarrow 2H_2 + O_2$ (4)

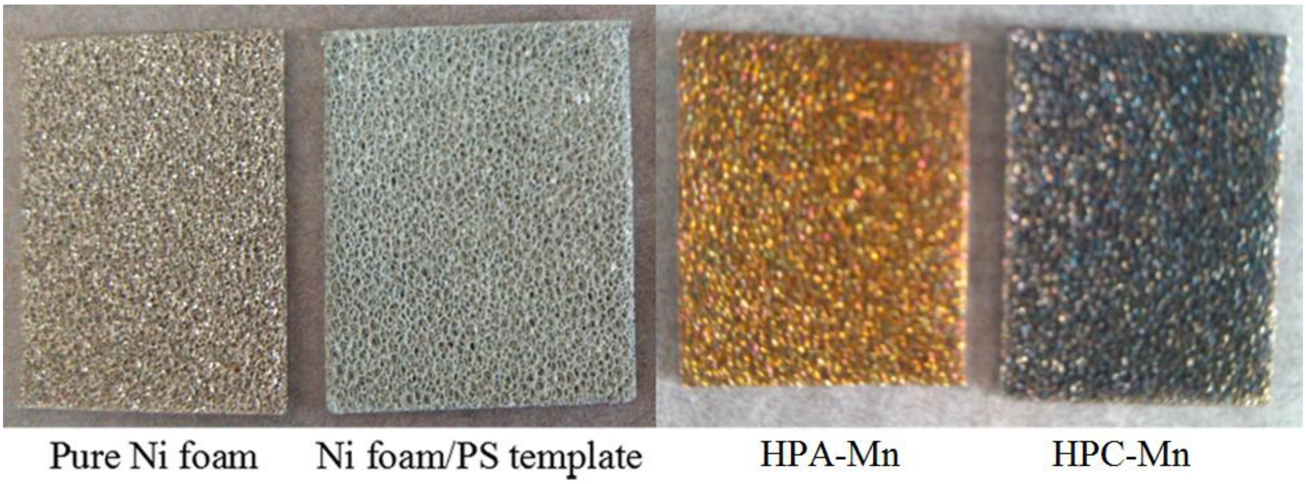

Fig. S1 Optical image of Ni foam substrate, Ni foam/PS template, HPA-Mn and HPC-Mn samples directly grown on Ni foam.

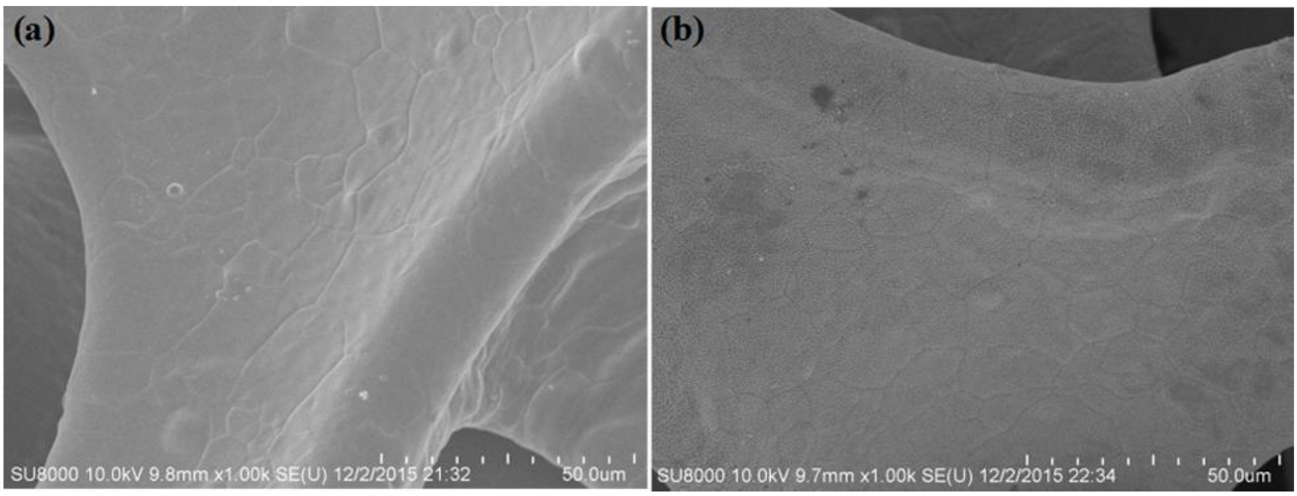

Fig. S2 Low resolution SEM images of (a) pure Ni foam and (b) HPC-Mn sample.

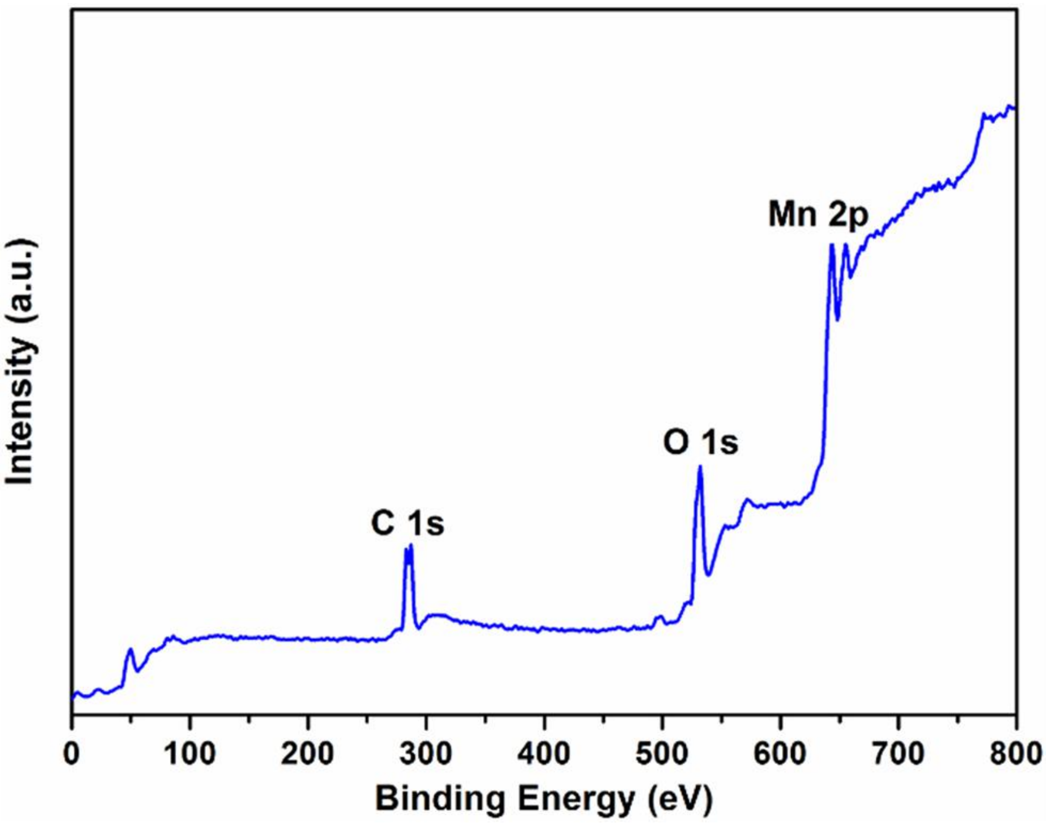

Fig. S3 The wide scan XPS spectrum of HPC-Mn sample.

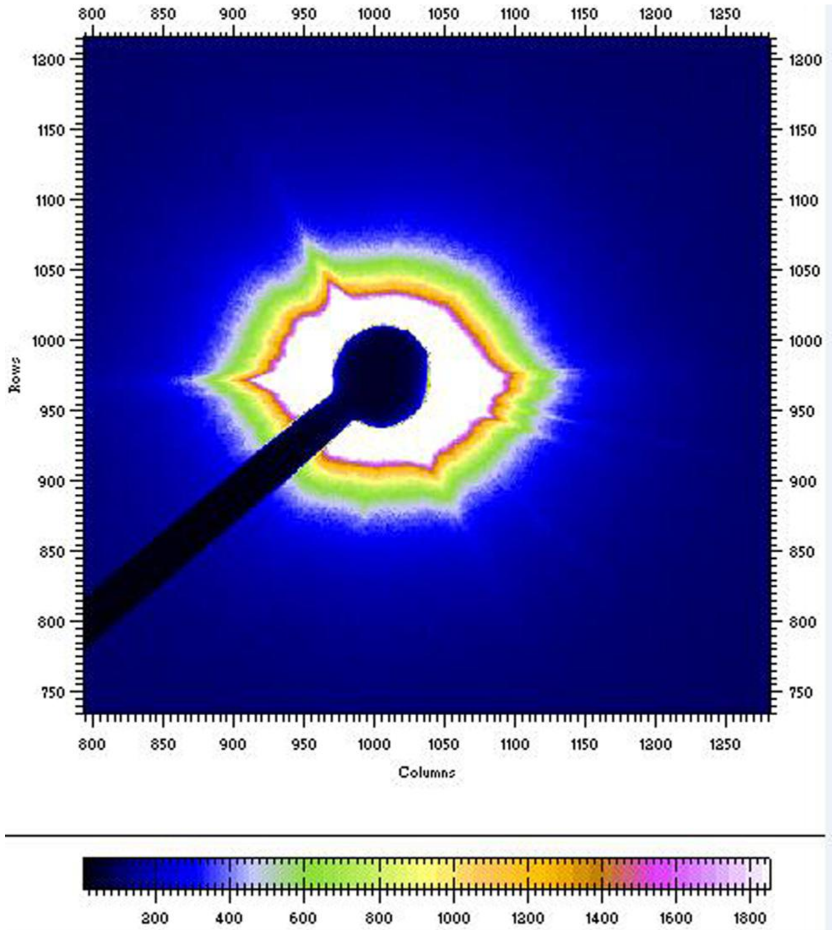

Fig. S4 Two-dimensional SAXS patterns of HPA-Mn anode.

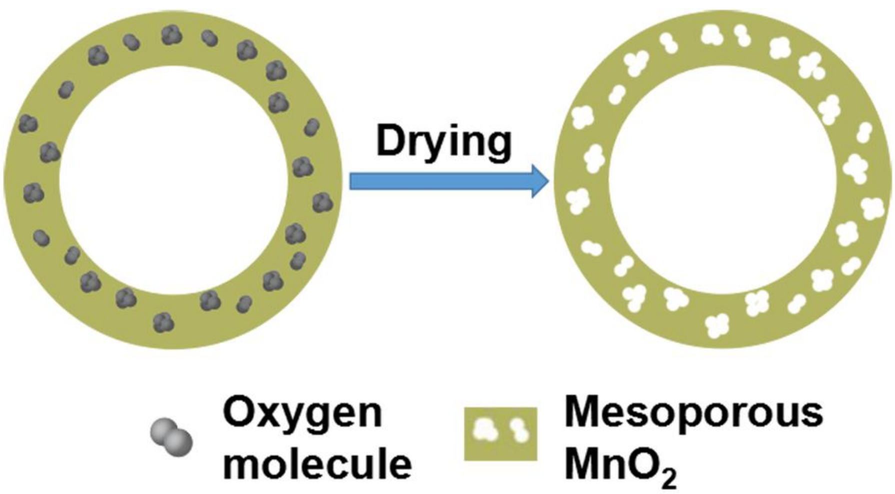

Fig. S5 Schematic representation of the mesoporous formation assisted by oxygen.

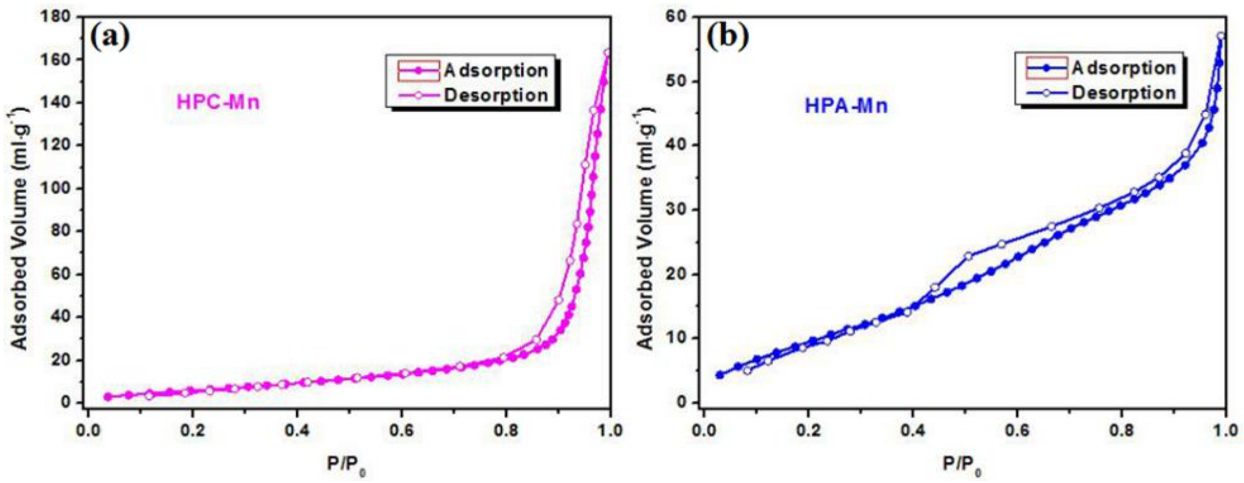

Fig. S6 N_2 adsorption-desorption isotherms of (a) HPC-Mn anode and (b) HPA-Mn anode.

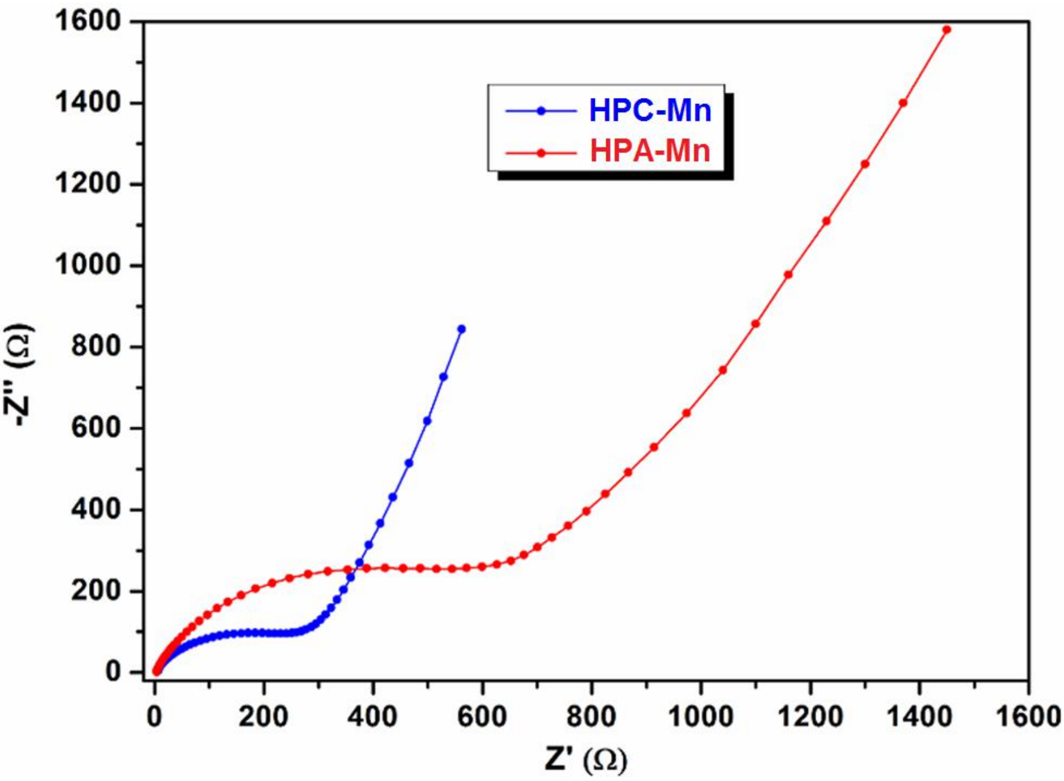

Fig. S7 Nyquist plots of HPC-Mn and HPA-Mn anodes.

Table S1 Rate performance comparison of the HPC-Mn and other reported MnO_2-based anodes for LIBs.

MnO_2 Based Anodes	**Low Current Density ($A\ g^{-1}$) Capacity ($mAh\ g^{-1}$)**	**High Current Density ($A\ g^{-1}$) Capacity ($mAh\ g^{-1}$)**	**Current Density Ratio**	**Capacity Retention (%)**	**Ref.**
HPC-Mn	0.1 (973.8)	2.0 (798.8)	20	~82.0	Our Work
MnO_2/3D porous graphene	0.1 (926.0)	1.6 (433.0)	16	~46.8	1
MnO_2 network-Ni/PVDF double shell/core fiber	0.05 (1079.0)	0.6 (544.7)	12	~50.5	2
MnO_2@N-doped carbon nanotubes	0.05 (1146.0)	1.0 (620.7)	20	~54.2	3
Freestanding MnO_2/Ni /PVDF coaxial fiber	0.05 (1178.4)	1.0 (415.0)	20	~35.2	4
MnO_2 on 3D N-doped graphene hybrid aerogels	0.1 (1003.0)	1.5 (636.0)	15	~63.4	5
MnO_2 nanoflakes on reduced graphene oxide nanosheets	0.1 (1430.0)	2.0 (1000.0)	20	~69.9	6
Nanoflaky MnO_2 on carbon microbeads	0.1 (700.0)	1.5 (230.0)	15	~32.9	7
Mesoporous MnO_2 nanosheet arrays	0.1 (-)	1.0 (-)	10	~50.0	8
Nanoflaky MnO_2/carbon nanotube	0.2 (820.0)	2.0 (420.0)	10	~51.2	9

Table S2 Cycling performance comparison of the HPC-Mn and other reported MnO_2-based anodes for LIBs.

MnO_2 Based Anodes	Current Density (A g^{-1})	Cycling Number	Specific Capacity (mA h g^{-1}) After Cycling	Capacity Retention (%)	Ref.
HPC-Mn	0.4	200	778.0	~97.6	Our Work
MnO_2/3D porous graphene	0.1	100	836.0	~84.6	1
MnO_2 network-Ni/PVDF double shell/core fiber	0.2	70	500.2	-	2
MnO_2@N-doped carbon nanotubes	0.1	100	1415.0	>100	3
Freestanding MnO_2/Ni /PVDF coaxial fiber	0.05	70	1031.2	-	4
MnO_2 on 3D N-doped graphene hybrid aerogels	0.4	200	909.0	>100	5
MnO_2 nanoflakes on reduced graphene oxide nanosheets	1.0	200	1000.0	~100	6
Nanoflaky MnO_2 on carbon microbeads	0.1	100	525.0	-	7
Mesoporous MnO_2 nanosheet arrays	1.0	200	900.0	>100	8
Nanoflaky MnO_2/carbon nanotube	0.2	50	620.0	~77.0	9

Note: The specific capacities of some MnO_2 based anodes would increase with the increase of cycling number, so the capacity retention is >100%.

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