Supporting information

High rate hybrid MnO$_2$@CNT fabric anode for Li-ion batteries: properties and lithium storage mechanism study by in situ synchrotron X-ray scattering

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**Figure S1.** FESEM images of MnO$_2$@CNTF hybrid at different magnifications, showing uniform coating of hierarchical MnO$_2$ nanoflowers. The preoxidized CNTF allows the uniform growth of MnO$_2$ as can be seen in (c) and (f). Inset pictures in (a) show the flexible nature of the macroscopic samples.
Figure S2. FESEM images of (a,b) pristine CNT fibers veils and (c,d) MnO$_2$ nanoflowers on pristine CNTF showing non-uniform oxide coverage on CNT bundles.

Figure S3. (a) Electron dispersive X-ray spectrum of MnO$_2$@CNTF hybrid. (b) BET isotherm of MnO$_2$@CNT hybrid.
**Figure S4.** Comparison of (a) TGA and (b) DTA curves of MnO$_2$/CNTF hybrid with pristine CNTF in aerial atmosphere.

**Figure S5.** (a) First two cyclic voltammograms of pristine CNT at a scan rate of 0.1 mV/s. (b) First three voltage profiles of MnO$_2$@CNTF for charge-discharge process at a current density of 25 mA/g. (c) Fitting of Cunn-Donway (equation 1) at 2V during anodic scan (R-Square = 0.92). (d) Comparison of rating for this material and literature data (from table ST1).
Figure S6. Rate profiles of (a) MnO$_2$@CNT with 43% MnO$_2$ loading and (b) commercial MnO$_2$ at current densities of 25 mA/g to 5 A/g. (c) voltage profiles of commercial MnO$_2$ at different current densities.

Table ST1. Comparison of specific capacitance values of Li-ion battery anodes with MnO$_2$@CNTF hybrid.

| Sr. No. | Material (crystal structure)                           | Specific capacity (mAh/g) | Current density (mA/g) | reference |
|--------|-------------------------------------------------------|---------------------------|------------------------|-----------|
| 1.     | MnO$_x$@CNT                                           | 1153                      | 25 mA/g                | This work |
|        |                                                       | 955                       | 50 mA/g                |           |
|        |                                                       | 882                       | 100 mA/g               |           |
|        |                                                       | 838                       | 200 mA/g               |           |
|        |                                                       | 783                       | 500 mA/g               |           |
|        |                                                       | 722                       | 1 A/g                  |           |
|        |                                                       | 650                       | 2 A/g                  |           |
|        |                                                       | 519                       | 5 A/g                  |           |
|        |                                                       | 344                       | 10 A/g                 |           |
| 2.     | MnO/Carbon Nanopeapods                                | 463                       | 5 A/g                  | [1]       |
| 3.     | MnO$_2$/Carbon Nanotube Array                         | 500                       | 50 mA/g                | [2]       |
| 4.     | putty-like MnO$_2$/CNT                                 | 796                       | 500 mA/g               | [3]       |
|        |                                                       | 236                       | 10 A/g                 |           |
| 5.     | MnO$_2$/Conjugated Polymer/Graphene                   | 948                       | 50 mA/g                | [4]       |
|        |                                                       | 698                       | 400 mA/g               |           |
| 6.     | Nanoflaky MnO$_2$/carbon nanotube                     | 820                       | 200 mA/g               | [5]       |
|   |   |   |   |
|---|---|---|---|
|   | Mn$_2$O$_4$/C nanospheres | 1237 | 200 mA/g |
|   |   | 425 | 4 A/g |
| 7. |   |   |   [6] |
|   | MnO$_2$ nanorods | 1075 | 100 mA/g |
|   |   | 489 | 1 A/g |
| 8. |   |   |   [7] |
|   | Graphene-Wrapped MnO$_2$–Graphene Nanoribbons | 890 | 100 mA/g |
|   |   | 550 | 1 A/g |
| 9. |   |   |   [8] |
|   | monodisperse α-Mn2O3 octahedra | 791 | 100 mA/g |
|   |   | 435 | 3200 mA/g |
| 10. |   |   |   [9] |
|   | Thin Film of Graphene-MnO$_2$ Nanotube | 495 | 100 mA/g |
|   |   | 208 | 1.6 A/g |
| 11. |   |   |   [10] |
|   | Mn$_3$O$_4$–Graphene | 810 | 40 mA/g |
|   |   | 390 | 1.6 A/g |
| 12. |   |   |   [11] |
|   | Graphene/Ni$_2$P | 599 | 100 mA/g |
|   |   | 260 | 5 A/g |
| 13. |   |   |   [12] |
|   | Mesoporous Co$_3$O$_4$ | 1033 | 100 mA/g |
|   |   | 622 | 5 A/g |
| 14. |   |   |   [13] |
|   | MnO/C | 1165 | 0.3 A/g |
|   |   | 580 | 3 A/g |
| 15. |   |   |   [14] |
|   | Mesoporous Dual Carbon Armored MnO Nanoparticles | 865 | 100 mA/g |
|   |   | 425 | 2 A/g |
| 16. |   |   |   [15] |
|   | Mn3O4 Nanoparticles on Hollow Carbon Nanofiber | 835 | 200 mA/g |
|   |   | 528 | 2 A/g |
| 17. |   |   |   [16] |
|   | (TMO = CoO, Ni$_2$O$_3$, Mn$_3$O$_4$) NPs Encapsulated into B/N Co-Doped Graphitic Nanotubes | For CoO 1554 | 96 mA /g |
|   |   | 410 | 1.75 A /g |
| 18. |   |   |   [17] |
|   | Hollow C sphere with open pore encapsulated MnO$_2$ nanosheets | 780.4 | 500 mA/g |
|   |   | 398 | 5 A /g |
| 19. |   |   |   [18] |
|   | 3D δ-MnO$_2$ nanostructure | 905 | 0.1 A/g |
| 20. |   |   |   [19] |
|   | Sample Description                                                                 | Capacity (mAh/g) | Current (mA/g) | Ref. |
|---|------------------------------------------------------------------------------------|------------------|----------------|------|
| 21. | coaxial MnO$_2$/CNTs nanocomposite                                                  | 271              | 1 A/g          |      |
|    |                                                                                    | 1064             | 0.1 A/g        |      |
|    |                                                                                    | 474              | 1.6 A/g        | [20] |
| 22. | Nanoflake δ-MnO$_2$ deposited on carbon nanotubes-graphene-Ni foam scaffolds        | 500              | 4 A/g          | [21] |
| 23. | nanostructured MnO$_2$                                                              | 1095             | 100 mA/g       | [22] |
|    |                                                                                    | 464              | 2 A/g          |      |
| 24. | MoS$_2$-on-MXene Heterostructures                                                   | 646              | 100 mA/g       | [23] |
|    |                                                                                    | 182              | 2 A/g          |      |
|    |                                                                                    | 90               | 5 A/g          |      |
| 25. | Urchin-like α-Fe$_2$O$_3$/MnO$_2$ hierarchical hollow composite microspheres        | 716              | 0.2 A/g        | [24] |
|    |                                                                                    | 413              | 1 A/g          |      |
Figure S7. (a) Digital image of the set-up for the operando synchrotron SAXS/ WAXS measurements and the customized cell with free-standing working electrode. (b, c) Consumption of lithium during in situ synchrotron charge-discharge process corresponding to galvanostatic profiles shown in Figure 4.
**Table ST2:** Details of the crystallographic analysis of in situ WAXS measurement.

| Material | Crystal phase (ICSD- reference number) | Peak position in q (Å⁻¹) | Lattice Plane | Ref. |
|----------|----------------------------------------|--------------------------|---------------|------|
| MnO₂     | Crystal system: Hexagonal Space group: P6₃/mmc a (Å): 2.829 b (Å): 2.829 c (Å): 4.410 Alpha (°): 90.0000 Beta (°): 90.0000 Gamma (°): 120 ICSD-76430, PDF 00-030-820 | 2.55 | (100) | 25 |
|          |                                        | 2.92 | (101) |      |
|          |                                        | 3.8 | (102) |      |
|          |                                        | 4.42 | (210) |      |
|          |                                        | 5.12 | (103) |      |
| Mn₂O₃    | Crystal system: Orthorhombic Space group: P b c a a (Å): 9.4120 b (Å): 9.4180 c (Å): 9.4230 Alpha (°): 90.0000 Beta (°): 90.0000 Gamma (°): 90.0000 Reference code: 98-002-4342 ICSD:24342, ICDD:00-024-0508 PDF code: 00-024-0508 | 2.42 | (230) | 26 |
|          |                                        | 2.79 | (114) |      |
|          |                                        | 3.96 | (244) |      |
|          |                                        | 4.73 | (435) |      |
|          |                                        | 4.87 | (336) |      |
| MnO      | Crystal system: Cubic Space group: F m -3 m a (Å): 4.4880 b (Å): 4.4880 c (Å): 4.4880 Alpha (°): 90.0000 Beta (°): 90.0000 Gamma (°): 90.0000 PANICSD:98-065-7312 ICSD:657312 | 2.45 | (111) | 27 |
|          |                                        | 2.82 | (002) |      |
|          |                                        | 3.99 | (113) |      |
|          |                                        | 4.66 | (222) |      |
|          |                                        | 4.85 | (004) |      |
| LiMnO₂   | Crystal system: Orthorhombic Space group: P m m n a (Å): 2.8050 b (Å): 4.5810 c (Å): 5.7490 Alpha (°): 90.0000 Beta (°): 90.0000 Gamma (°): 90.0000 Reference code: 98-008-1050 ICSD: 81050 | 2.54 | (012) | 28 |
|          |                                        | 2.95 | (021) |      |
|          |                                        | 4.17 | (113) |      |
|          |                                        | 4.91 | (104) |      |
|          |                                        | 5.12 | (114) |      |
| Crystal system: Cubic | Crystal system: Tetragonal | Crystal system: Cubic |
|----------------------|-----------------------------|----------------------|
| Space group: I -4 3 m | Space group: I 41/a m d | Space group: F m -3 m |
| a (Å): 8.9050 | a (Å): 5.6720 | a (Å): 4.6890 |
| b (Å): 8.9050 | b (Å): 5.6720 | b (Å): 4.6890 |
| c (Å): 8.9050 | c (Å): 9.1820 | c (Å): 4.6890 |
| Alpha (°): 90.0000 | Alpha (°): 90.0000 | Alpha (°): 90.0000 |
| Beta (°): 90.0000 | Beta (°): 90.0000 | Beta (°): 90.0000 |
| Gamma (°): 90.0000 | Gamma (°): 90.0000 | Gamma (°): 90.0000 |
| ICSD:164349, PANICSD:98-016-4349 | ICSD:62047, PANICSD:98-006-2047 | ICSD:642216, PANICSD:98-064-2216 |
| 2.62 (123) | 2.33 (013) | 2.32 (111) |
| 2.83 (004) | 2.73 (004) | 2.67 (002) |
| 2.99 (114) | 3.77 (132) | 3.79 (022) |
| 3.31 (233) | 4.23 (244) | 4.44 (113) |
| 4.98 (055) | 4.88 (444) | 4.64 (222) |
Figure S8. (a, b) WAXS pattern of electrochemically cycled MnO$_2$/CNTF hybrid after 60 cycles. The vertical blue and red bars indicate the simulated XRD pattern of ε-MnO$_2$ and LiMnO$_2$ respectively. (c) Raman spectrum of electrochemically cycled sample after 60 cycles.
Figure S9. Convoluted XPS spectra of Mn3s recorded for (a) pristine MnO$_2$@CNTF, (b) sample at 0V after first lithiation and (c) sample at 3V after first delithiation.
Figure S10. (a, b) FESEM images of the MnO$_2$@CNTF hybrid after lithiation and delithiation process. (c) HAADF and (d-h) corresponding EDS elemental mapping images for (d) carbon, (e) manganese, (f) oxygen, (g) phosphorus and (h) fluorine.

Figure S11. Comparison of the electrochemical impedance spectra (EIS) of MnO$_2$@CNTF before and after electrochemical cycling. Inset shows the equivalent circuit model. The fitting parameter are listed in table ST1.
**Table ST3:** Fitting parameters for the EIS spectra of MnO$_2$@CNTF before and after potential cycling.

| Parameters                          | Before electrochemical cycling | After electrochemical cycling |
|-------------------------------------|--------------------------------|-------------------------------|
| R1 (equivalent series resistance)   | 11.16 Ohm                      | 11.71 Ohm                     |
| Q2 (double layer capacitance)       | 13.69e-6 F.s$^a$(a - 1)        | 11.76e-6 F.s$^a$(a - 1)      |
| R2 (charge transfer resistance)     | 217.7 Ohm                      | 118.1 Ohm                     |

**Figure S12.** TEM images of the sample after CD process.
Figure S13. (a) Rate profile and (b) corresponding voltage profiles of commercial MnO2-C@Cu at different current densities. The specific capacity values are normalized with respect to the total electrode weight. (c) A plot of weight saving factor at different current densities.
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