Supplementary Information

Higher-Power Supercapacitor Electrodes Based on Mesoporous Manganese Oxide Coating on Vertically Aligned Carbon Nanofibers

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Figure S1. Scanning electron microscopy (SEM) and tunneling electron microscopy (TEM) of the Mn-coated VACNFs just after Mn sputtering to various nominal thicknesses of 100, 300, and 600 nm. Scale bars are 100 nm, 1.0 μm, 300 nm; 200 nm, 1.0 μm, 300 nm; 200 nm, 1.0 μm, 500 nm, respectively.
Figure S2. SEM and TEM of the MnOx-coated VACNFs after oxidation and cycling characterizations of MnOx material. Images are shown in respect to their various nominal thickness of 100, 200, 300, or 600 nm. Scale bars are 500 nm in panels (a), (e) and (i); 1.0 μm in panels (b), (f) and (j); 2.0 μm in panels (c), (g) and (k); and 300 nm in panels (d), (h) and (l).
Figure S3 – A cross-sectional SEM image of a 100 nm thick Mn film on Cr-coated Si wafer after electrochemical oxidation in 1.0 M Na₂SO₄. The oxidation of Mn into MnO₂ caused the expansion of the film thickness and the formation of the rough, billowy texture. A 100 nm Cr layer was deposited on the n-doped silicon wafer to promote adhesion and provide good conductivity to the Mn or MnOₓ film. The inset is the top-view image (5 µm x 5 µm) of the outer surface of the MnOₓ film showing a rose-petal-like film structure.

**Estimation of the maximum Mn²⁺ dissolution:**

During electrochemical oxidation, some manganese may dissolve into solution (1 M NaSO₄, pH = 9.4) in form of Mn²⁺. The amount varies, but the maximum [Mn²⁺] can be estimated below:

\[
\text{Mn(OH)}_2 \rightleftharpoons \text{Mn}^{2+} + 2\text{OH}^- \quad K_{sp} = 1.9 \times 10^{-13} \quad \text{pH} = 9.4 \quad [\text{OH}^-] = 2.51 \times 10^{-5} \\
[Mn^{2+}] = 1.9 \times 10^{-13} / [\text{OH}^-]^2 = 1.9 \times 10^{-13} / (2.51 \times 10^{-5})^2 = 0.30 \text{ mM}
\]

With 6 mL of electrolyte used, only 98.9 µg of Mn²⁺ can possibly dissolve. As a result, the maximum percentage of Mn mass loss for various nominal thickness is:

- 100 nm Sample = 63%  
- 200 nm Sample = 31%  
- 300 nm Sample = 21%  
- 100 nm Sample = 10%
Figure S4. Cyclic voltammetric I-V curves of Mn-coated VACNF electrodes with nominal thickness of 100, 200, 300, and 600 nm, performed at the scan rates of (a) 10 mV s$^{-1}$, (b) 100 mV s$^{-1}$, and (c) 2000 mV s$^{-1}$.
Figure S5. Nyquist plot of electrochemical impedance spectra of the MnO₂-coated VACNFs. The inset shows the full spectra.
Figure S6 – The cycling performance of an MnO$_2$/VACNF electrode started with 300 nm nominal Mn thickness during charge-discharge at 10 A g$^{-1}$ for 2,000 cycles, showing discharge capacity (green line) and coulombic efficiency (purple line) versus the cycle number.