

Supplementary Information

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

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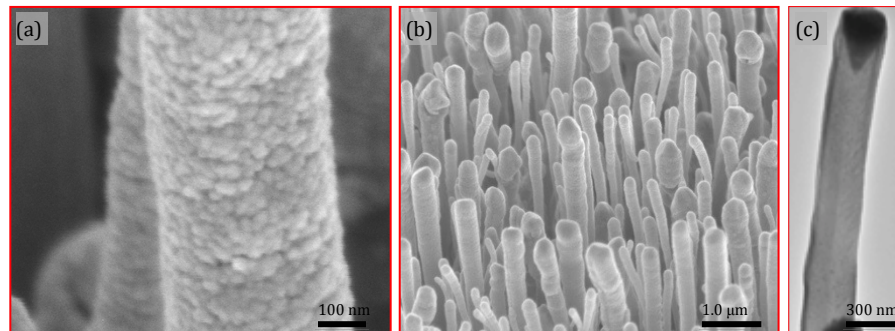
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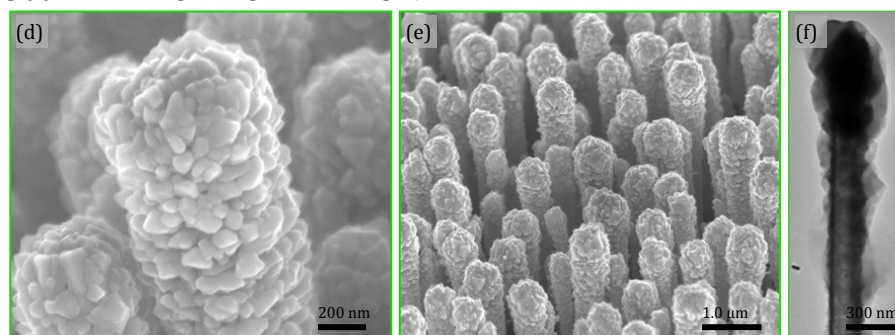
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100 nm BEFORE OXIDATION



300 nm BEFORE OXIDATION



600 nm BEFORE OXIDATION

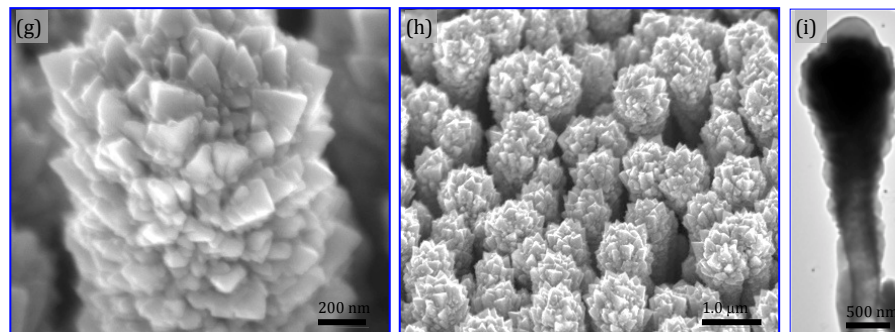
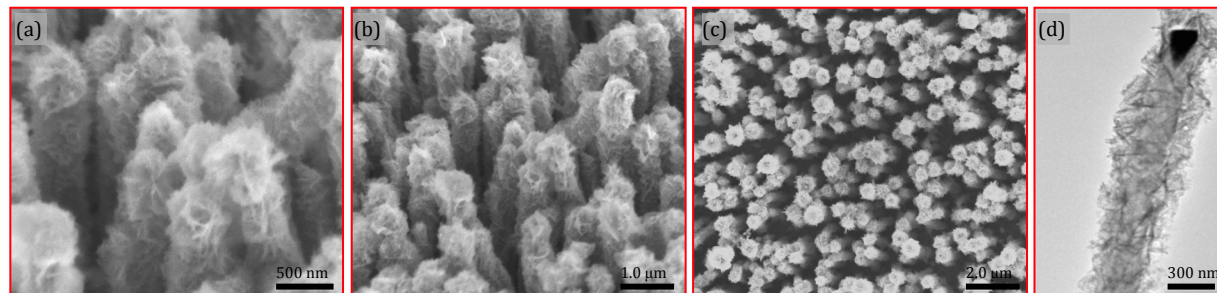
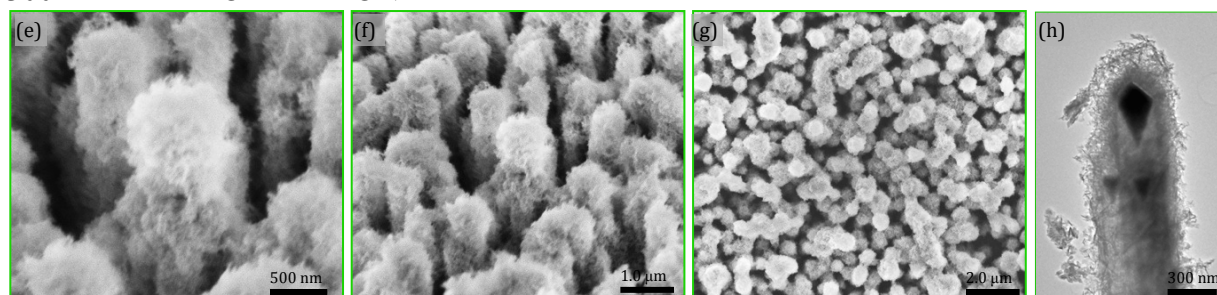


Figure S1. Scanning electron microscopy (SEM) and tunneling electron microscopy (TEM) of the Mn-coated VACNFs just after Mn sputtering to various nominal thicknesses of 100, 300, and 600 nm. Scale bars are 100 nm, 1.0 μm , 300nm; 200 nm, 1.0 μm , 300nm; 200 nm, 1.0 μm , 500nm, respectively.

100 nm AFTER OXIDATION



300 nm AFTER OXIDATION



600 nm AFTER OXIDATION

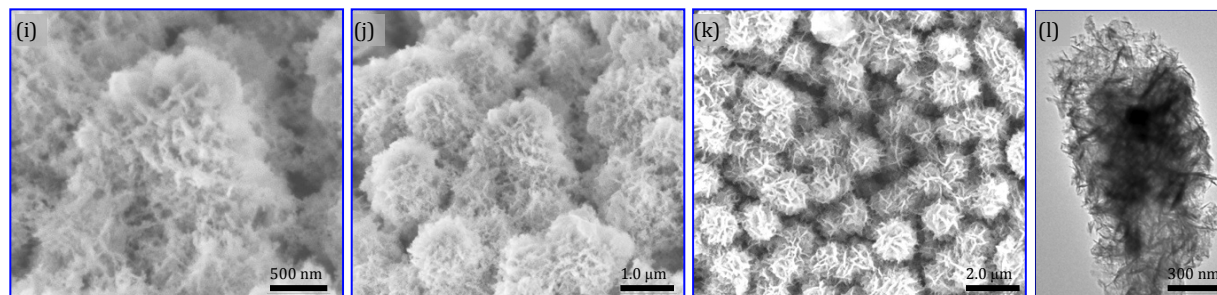


Figure S2. SEM and TEM of the MnO_x-coated VACNFs after oxidation and cycling characterizations of MnO_x material. Images are shown in respect to their various nominal thickness of 100, 200, 300, or 600 nm. Scale bars are 500 nm in panels (a), (e) and (i); 1.0 μm in panels (b), (f) and (j); 2.0 μm in panels (c), (g) and (k); and 300nm in panels (d), (h) and (l).

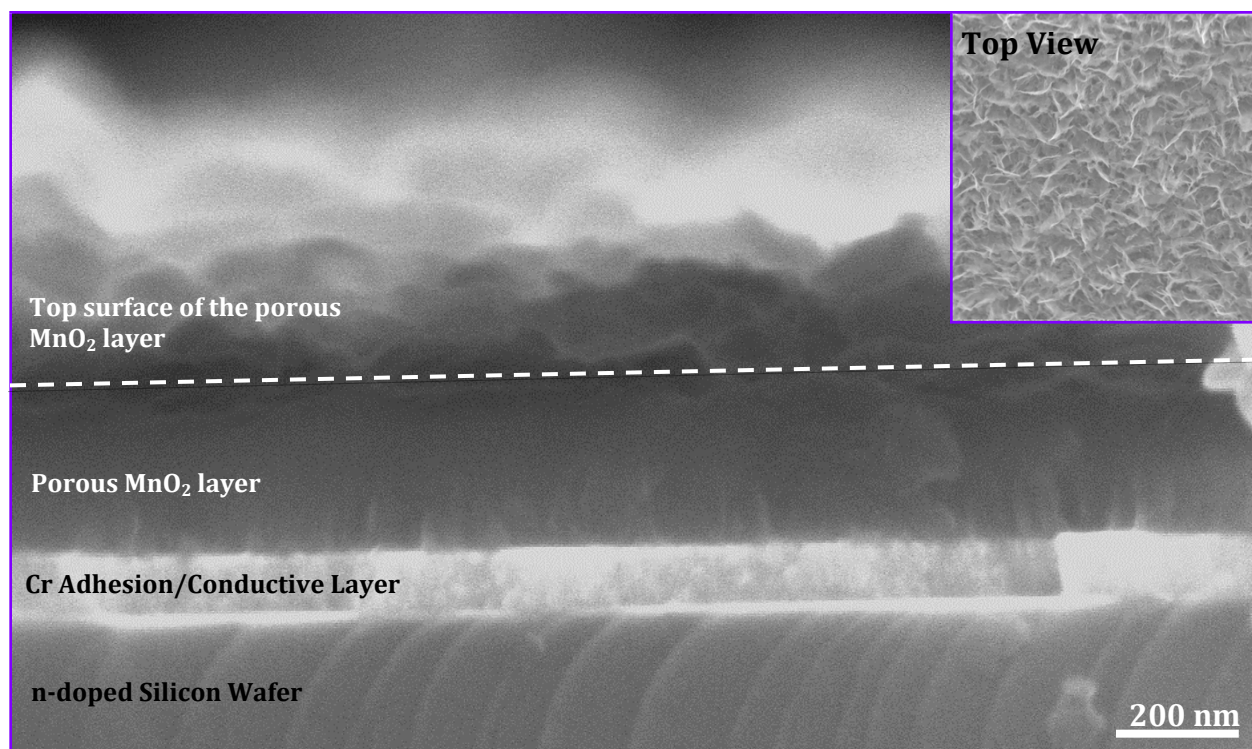


Figure S3 – A cross-sectional SEM image of a 100 nm thick Mn film on Cr-coated Si wafer after electrochemical oxidation in 1.0 M Na₂SO₄. The oxidation of Mn into MnO₂ caused the expansion of the film thickness and the formation of the rough, billowy texture. A 100 nm Cr layer was deposited on the n-doped silicon wafer to promote adhesion and provide good conductivity to the Mn or MnO_x film. The inset is the top-view image (5 μm x 5 μm) of the outer surface of the MnO_x 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:

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

$$[\text{Mn}^{2+}] = 1.9 \times 10^{-13} / [\text{OH}^-]^2 = 1.9 \times 10^{-13} / (2.51 \times 10^{-5})^2 = 0.30 \text{ mM}$$

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% |

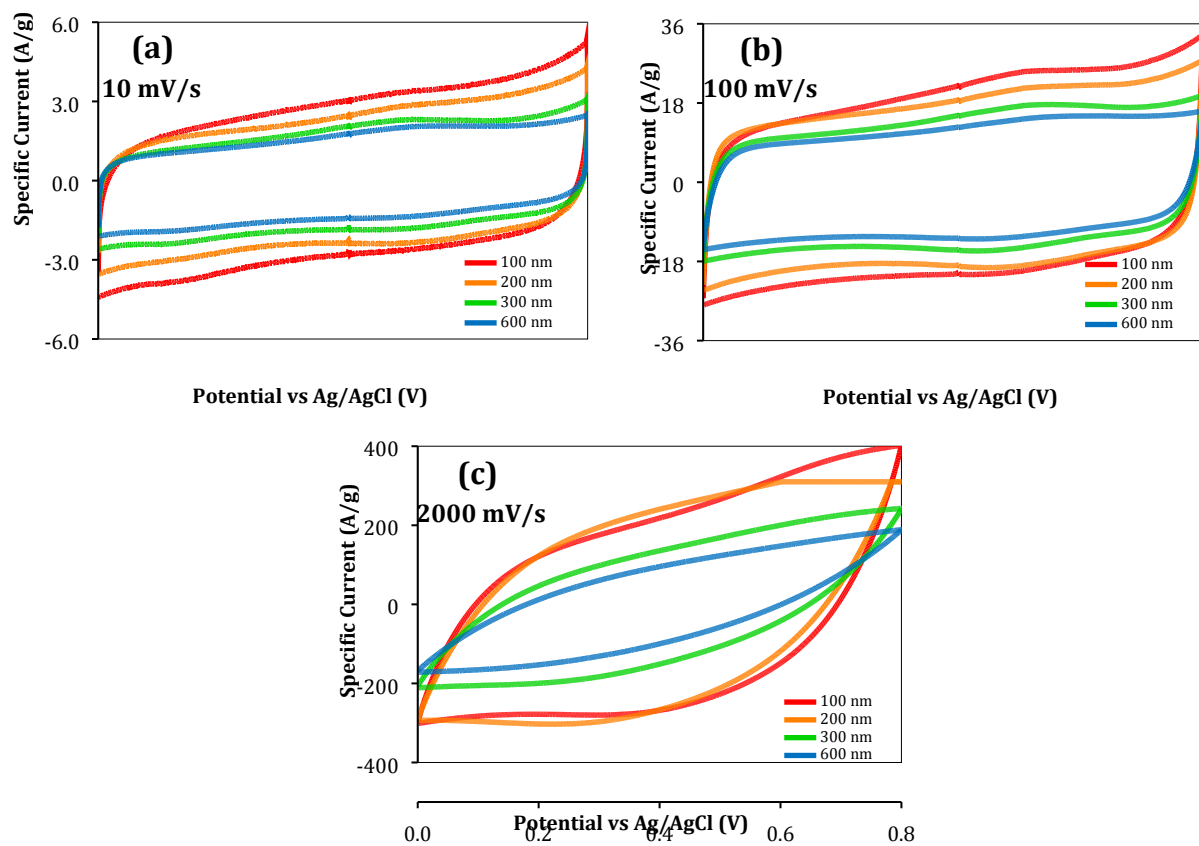


Figure S4. Cyclic voltammetric I-V curves of Mn-coated VACNF electrodes with nominal thickness of 100, 200, 300, and 600 nm, performed at the scan rates of (a) 10 mV s⁻¹, (b) 100 mV s⁻¹, and (c) 2000 mV s⁻¹.

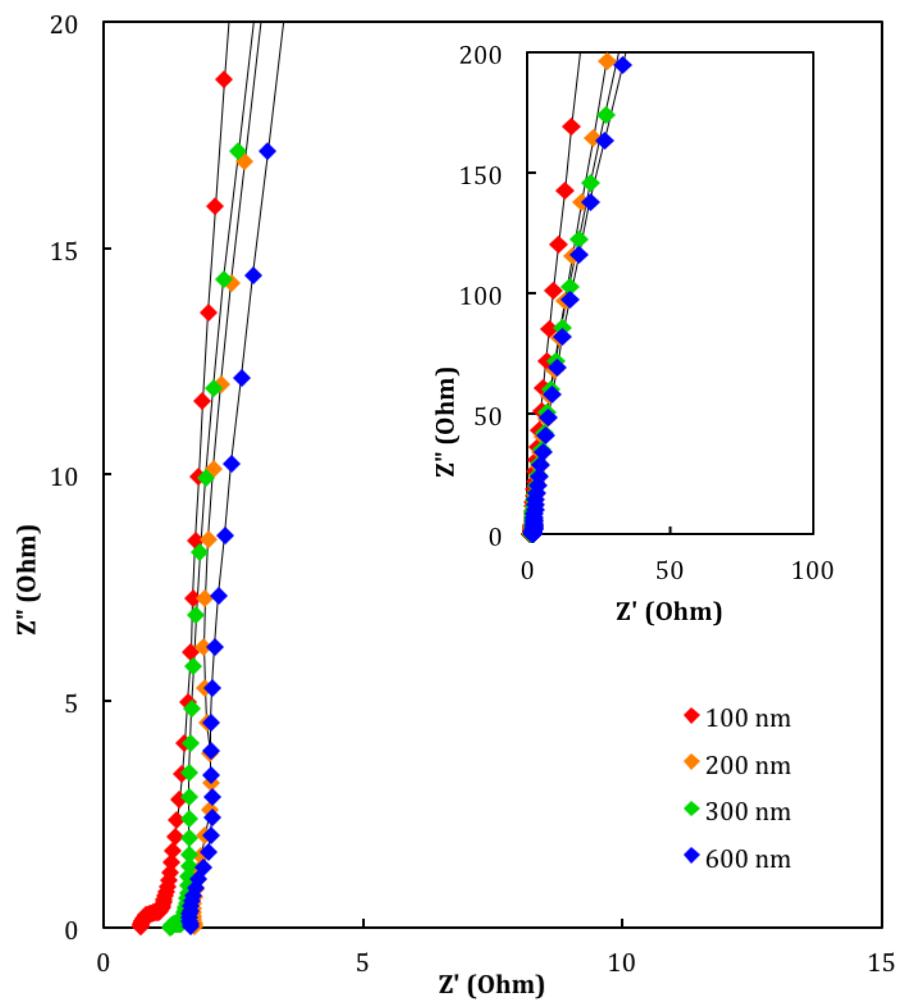


Figure S5. Nyquist plot of electrochemical impedance spectra of the MnO₂-coated VACNFs. The inset shows the full spectra.

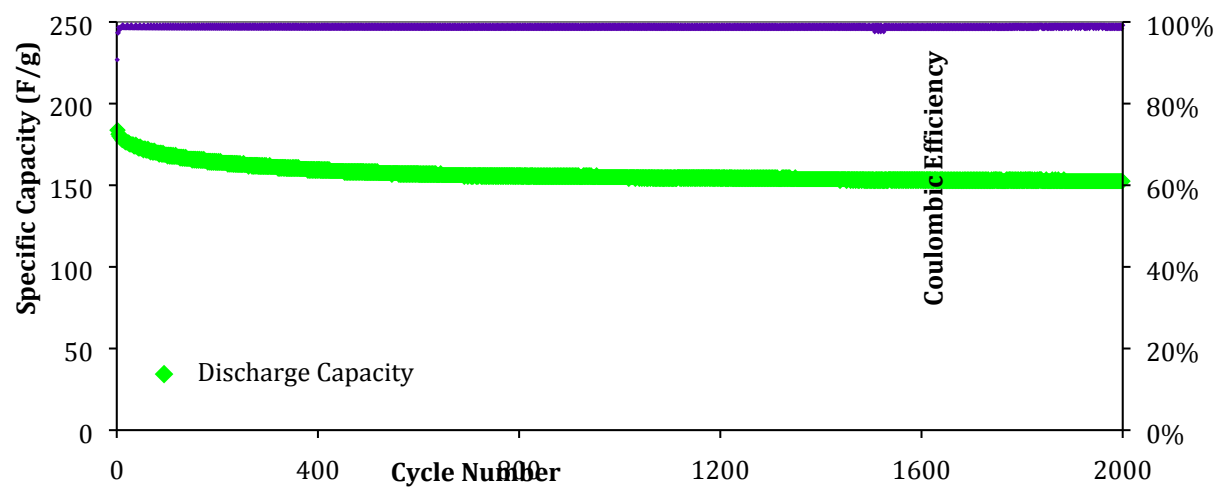


Figure S6 – The cycling performance of an $\text{MnO}_2/\text{VACNF}$ electrode started with 300 nm nominal Mn thickness during charge-discharge at 10 A g^{-1} for 2,000 cycles, showing discharge capacity (green line) and coulombic efficiency (purple line) versus the cycle number.