

Supporting Information

Three-dimensional network of coaxial carbon nanotube/manganese oxides electrode for supercapacitors

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Experimental Section

Preparing of 3DNC/MnO_x Composites:

As described previously,^{25, 27} the fabrication procedure of MnO_x coated 3DNC nanostructure is briefly shown as follows. Si pillar structures were fabricated on Si (100) wafers (N-type, Siltron) via deep reactive ion etching process. The bared Si wafer (without etching process) was used for comparison. Those two kinds of Si substrates were soaked in a piranha solution (H₂SO₄:H₂O₂=7:3) for 3 hours in order to clean and modify the Si surface with hydroxyl groups. After rinsing with de-ionized (DI) water several times, the Si pillar substrates were dipped into the Fe–Mo catalyst solution, which was made of Fe(NO₃)₃·9H₂O (Junsei) and Mo solution (ICP/DCP standard solution, Aldrich), for 60 min, and then fully rinsed with ethanol several times. The CNTs were synthesized on Si substrates in C₂H₂ ambient (750°C, 10 sccm, 20 min) after NH₃ treatment (750°C, 300 sccm, 10 min) by means of low pressure thermal CVD.

A thin layer of Pt was firstly coated on synthesized CNTs using ion sputter (E-1045, Hitachi). Pt deposition was processed for 200 sec with an applied current of 15 mA. The deposition of MnO_x was processed by potentiostat/galvanostat work station (WPG 100, WonATech) in a three-electrode system. Pt coated 3DNC (1×0.5cm) was used as working electrode. Pt wire (>99%, Aldrich) and standard calomel electrode (SCE, BASi, USA) were used as counter electrode and reference electrode, respectively. 0.02 M of potassium permanganate (≤99.3%, Samchun Chemical) was used as precursor. The applied current for deposition was 1mA for 1 sec with 60 sec intervals of zero current. The total coating time was 3 min. After deposition, all of the samples were dipped into DI-water several times to wash off residual precursor and annealed at 200 °C for 2 hours. The loading mass of manganese was about 0.108 mg cm⁻².

Materials Characterization and Electrochemical Evaluation:

Sample morphologies were characterized by field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi), transmission electron spectroscopy (TEM, JEOL-2100F, JEOL), and X-ray photoelectron spectroscopy (XPS, Al Kα excitation

laser, ESCA 2000). The electrochemical properties of samples were determined by cyclic voltammetry (CV) in the potential range of 0 to 0.8V at a scan rate of 10, 20, 50 and 100 mV s^{-1} by the same three-electrode configuration in 1M Na_2SO_4 aqueous solution (>99.9%, Aldrich). Life cycle tests were characterized by CV curves at a rate of 100 mV s^{-1} for 2000 cycles. The ohmic cell information was characterized by electrochemical impedance spectroscopy (AUT 302N, Autolab). The electrolyte and electrodes were the same as with the CV curve test. Solution resistance and charge transfer resistance were characterized over a frequency range from 100 kHz to 10 Hz at sinusoidal voltage amplitude of 5 mV and room temperature.

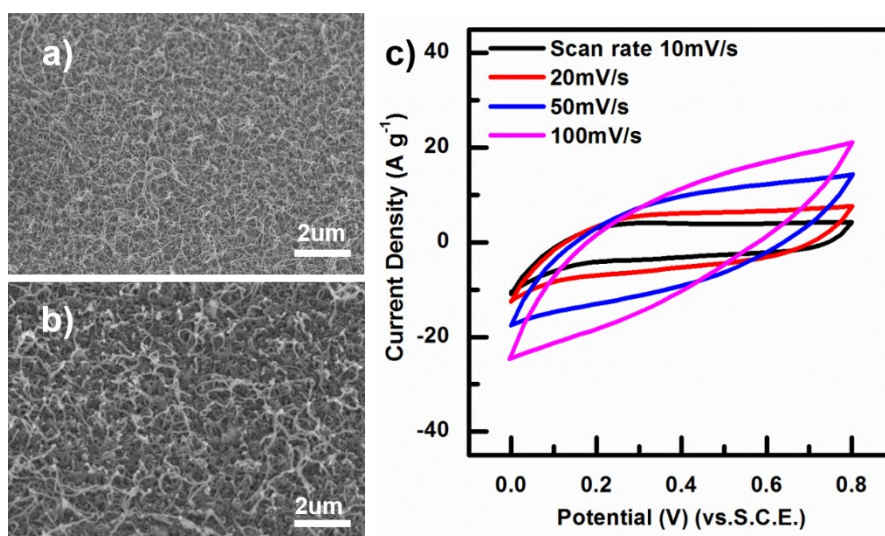


Fig. S1 SEM images of (a) amorphous CNTs grown on flat Si template; (b) manganese oxide deposited 2DNC; (c) CV curves of 2DNC/ MnO_x at scan rate of 10, 20, 50 and 100 mV s^{-1} in 1M Na_2SO_4 solution and the specific capacitance are 271, 201, 117 and 60 F g^{-1} , respectively.

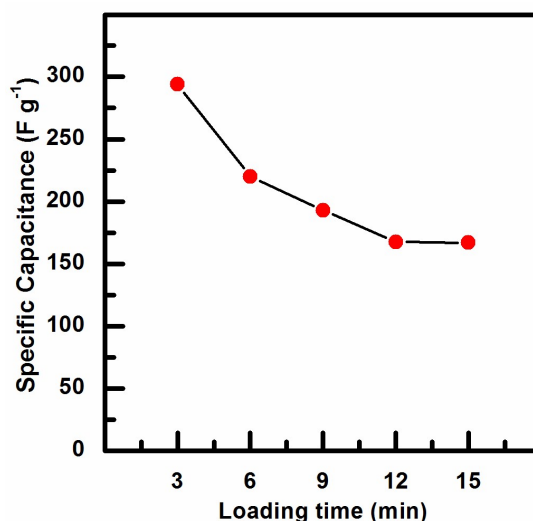


Fig. S2 Specific capacitance of 3DNC/ MnO_x for different loading time. The calculated C_{sp} values of 3DNC/ MnO_x at 10 mV s^{-1} are 294, 220, 193, 168 and 167 F g^{-1} at loading time of 3, 6, 9, 12 and 15 min, respectively.

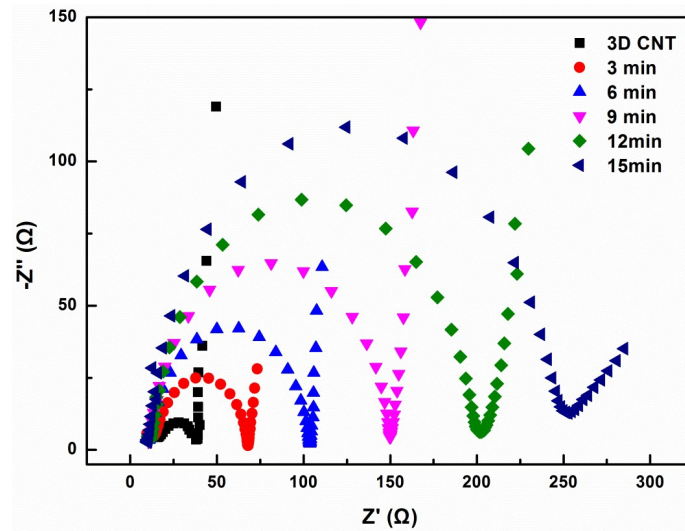


Fig. S3 Nyquist plots of 3DNC/MnO_x for different loading time. According to the Randle circuit, the calculated average R_s is about 11.66 Ω . The calculated R_{CT} for 0, 3, 6, 9, 12 and 15 min of deposition time are 23.6, 54.88, 93.31, 139.36, 190.94 and 242.96 Ω , respectively. The calculated Z_w values are 11.70, 11.86, 16.57, 39.93, and 139.5 Ω , respectively. The Z_w values are 45° slope portions of curves, and these values are results of the frequency dependence of ion diffusion and transport. Thicker layer of MnO_x hinders the charge transfer reaction because part of the MnO_x layer can not react with electrolytes. As the deposition time increased, the specific capacitance per unit mass decreases due to decreased ion diffusion.

Table S1. Peak intensities and peak height ratio of Mn 2p 3/2 and O 1s for 3DNC/MnO_x. Specific capacitance is also measured by CV. The peak height ratio data of Mn₂O₃ and MnO₂ were taken from reference.³¹

Sample	Peak intensitiy		Peak Heght Ratio	C_{sp} (F g ⁻¹)
	Mn 2p 3/2 (CPS)	O 1s (CPS)		
Mn ₂ O ₃	-	-	1.15	
1	36947.4	35753.9	1.03	190
2	36240.4	35664.2	1.01	250
3	37576.5	37612.8	0.99	294
MnO ₂	-	-	0.95	

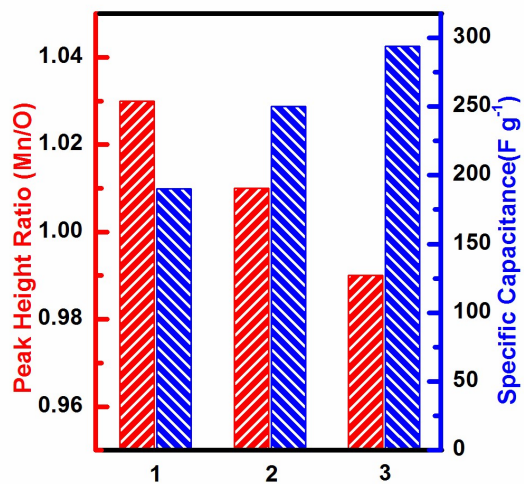


Fig. S4 Graph of peak height ratio (left) and specific capacitance (right) for 3DNC/MnO_x with different intervals.

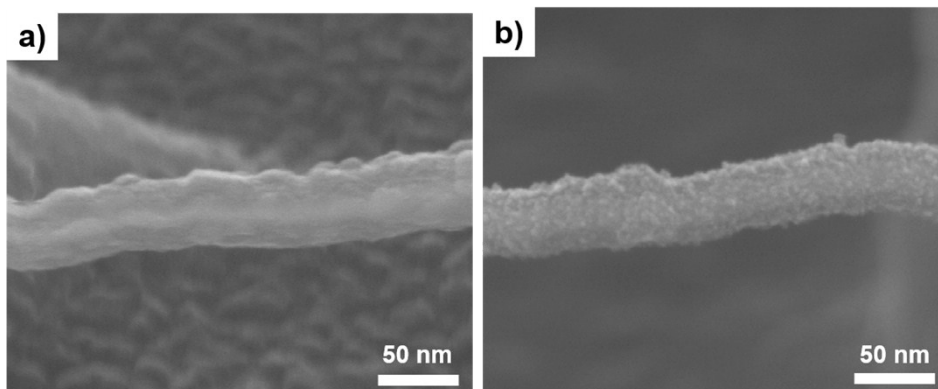


Fig. S5 SEM images of 3DNC/MnO_x coaxial bundles before (a) and after (b) 2000 cycling test.