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[Supplementary Information]

DC-field-driven combustion wave for one-step fabrication of reduced manganese oxide/multi-walled carbon nanotube hybrid nanostructures as high-performance supercapacitor electrodes

*Taehan Yeo, Dongjoon Shin, Jungho Shin, Hayoung Hwang, Byungseok Seo, Jaeho Lee and Wonjoon Choi**

School of Mechanical Engineering, Korea University, Seoul, Korea, 136-701

*Author to whom correspondence should be addressed.

E-mail: *wojchoi@korea.ac.kr*, Phone: +82 2 3290 5951, Fax: +82 2 926 9290

Keywords: supercapacitor; combustion; manganese oxide; multi-walled carbon nanotubes; pseudocapacitor; chemical synthesis

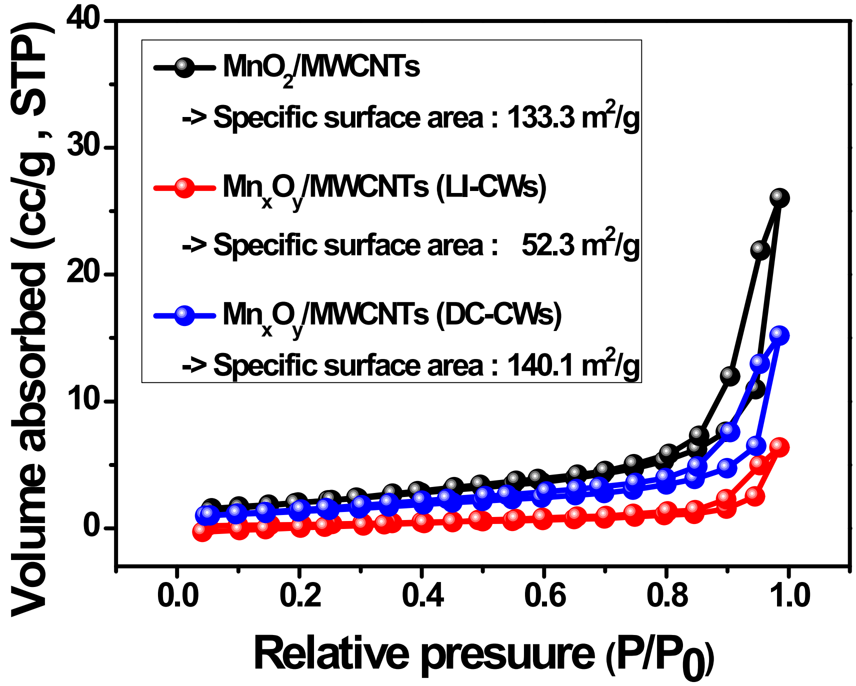

Fig. S1 BET (Brunauer–Emmett–Teller) specific surface areas of MnO_2/MWCNTs, Mn_xO_y/MWCNTs fabricated by applying LI-CWs, and Mn_xO_y/MWCNTs fabricated by applying DC-CWs.

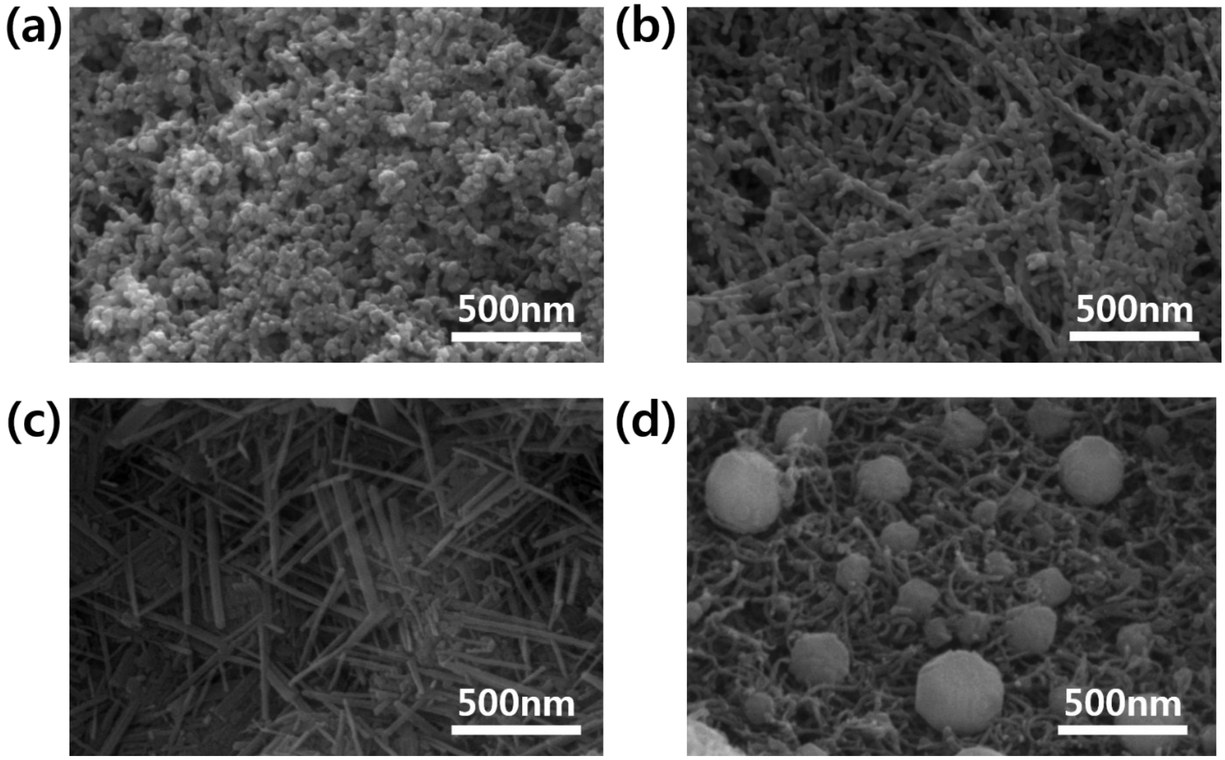

Fig. S2 Optimization of DC-field for fabrication of Mn_xO_y/MWCNT hybrid nanostructures. SEM images of Mn_xO_y/MWCNT hybrid nanostructures fabricated by applying DC-field driven CW at different voltages and currents; (a) no DC field, (b) 20 V and 0.75 A, (c) 30 V and 1 A, (d) 150 V and 1A.

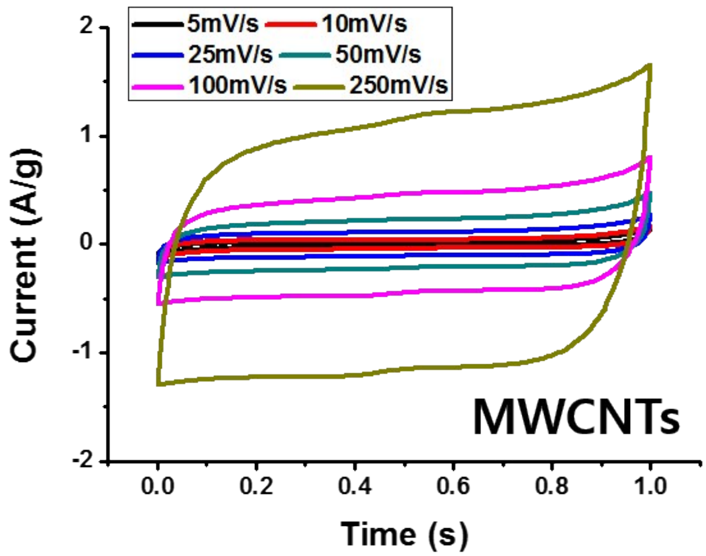

Fig. S3 Cyclic voltammograms (CV) of electrode made from MWCNTs at scan rate of 5, 10, 25, 50, 100, 250 mV/s.

Optimization of DC-field for fabrication of Mn_xO_y/MWCNT hybrid nanostructures

The SEM image of the crystalline structure of manganese oxide fabricated by thermal synthesis using a DC-field is presented in Fig. S2. In the case of the pristine MnO_2 layer, Fig. S2a shows that the particles with dimensions of 20−30 nm make only physical contact with each other. SEM images of MnO_2 prepared under thermal conditions of 20 V and 0.75 A are shown in Fig. S2b. Because these conditions are not severe enough to transform the MnO_2 particles into the vapor state through the plasma arc discharge, the manganese oxide particles grow in a rod shape along the arc discharge, but the shape of the individual particles remains intact. In the case where the thermal synthesis was performed at 30 V and 1 A (Fig. S2c), the voltage and current were sufficiently high to completely convert MnO_2 to the vapor state through the plasma arc discharge, and no individual particles were observed. The crystal structure of the sample prepared by thermal synthesis at 150 V and 1 A (Fig. S2d) shows that during combustion of the chemical fuel, the MnO_2 particles were converted to the vapor state due to the high temperature and low oxygen content, in contrast with the previous synthesis. A spherical crystal structure was thus obtained. In addition, the structure of the spherical crystal is hexoctahedral, which is exactly the same as the crystal structure of MnO, where Mn adopts the lowest oxidation number among that of the manganese oxides. These results show that it is possible to control the crystal structure of manganese oxide by changing the electrical source applied to the same MnO_2/MWCNT/nitrocellulose composite.

Calculation of the specific and areal capacitance

The specific capacitance and areal capacitance of the as-prepared MnO_2/MWCNTs, LI-CWs Mn_xO_y/MWCNTs, DC-CWs Mn_xO_y/MWCNTs electrodes were obtained by CV curves and the equation is as follows:

$$C_{specific\ capacitance} = \frac{\int_{V_1}^{V_2} \{I_v(Mn_xO_y/MWCNTs) - I_v(MWCNTs)\}dV}{\Delta V \times v \times m_{Mn_xO_y}}$$

Where C is the specific capacitance (F/g), I_v is the current at the scan rates in CV curve (A), ΔV is the applying voltage (V), v is the scan rate (V/s), m is the mass of each manganese oxides (g).

$$C_{Areal\ capacitance} = \frac{\int_{V_1}^{V_2} \{I_v(Mn_xO_y/MWCNTs) - I_v(MWCNTs)\}dV}{\Delta V \times v \times A}$$

Where C is the areal capacitance (mF/cm^2), I_v is the current at the scan rates in CV curve (A), ΔV is the applying voltage (V), v is the scan rate (V/s), A is the area of the electrode (cm^2).

Charge storage mechanism in the manganese oxides

$$Mn_xO_y + Na^+ + e^- \underset{discharge}{\overset{charge}{\rightleftarrows}} Mn_xO_{y-1}ONa$$