

# Supporting Information

## Nanowindow-Regulated Specific Capacitance of Supercapacitor Electrodes of Single-Wall Carbon Nanohorns

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## EXPERIMENTAL PROCEDURES

The dahlia-like structured SWNHs were synthesized with CO<sub>2</sub> laser ablation of a graphite target in Ar atmosphere (101 kPa) (as-grown SWNHs). The as-grown SWNHs were heat-treated in O<sub>2</sub> atmosphere at 693 K for 10 min (oxidized SWNHs).

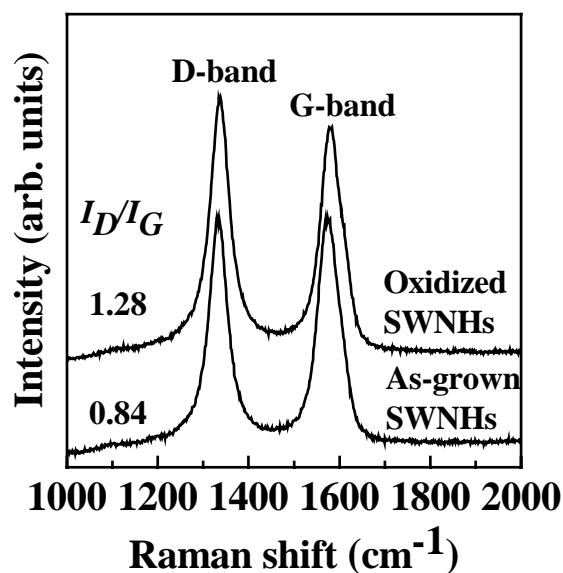
High-resolution transmission electron microscope (HRTEM) images were obtained with a Topcon EM-002B instrument at 200 kV accelerating voltage. Raman spectroscopy measurements were performed at room temperature under ambient conditions, using a RM1000 microprobe Raman spectrometer (Renishaw). The Raman spectra were excited by wavelength of 514 nm Ar ion laser.  $I_D/I_G$  values were determined by integrated intensity ratio of the *D*-band to *G*-band of SWNH samples. The pore structures were determined by adsorption of N<sub>2</sub> at 77 K and CO<sub>2</sub> at 273 K using a volumetric equipment (Micromeritics ASAP2020), after preevacuation for 12 h at 473 K, while maintaining the base pressure at 10<sup>-4</sup> Pa. Pore structure parameters were obtained by the subtracting pore effect (SPE) and Dubinin-Radushkevich (DR) methods. The SPE method was performed by using high-resolution  $\alpha_s$  plots constructed for standard adsorption data.

The electrode weight was adjusted to 40 mg. SWNH powders were well mixed with 5 wt.% of poly(tetrafluoroethylene) (PTFE) binders without a conducting material. Samples were subsequently pressed into the shape of a disk, 13 mm in diameter and *ca.*0.4 mm in thickness. The capacitor consists of a couple of electrodes which are arranged face to face, with a separator (glass paper) inserted between these electrodes. The

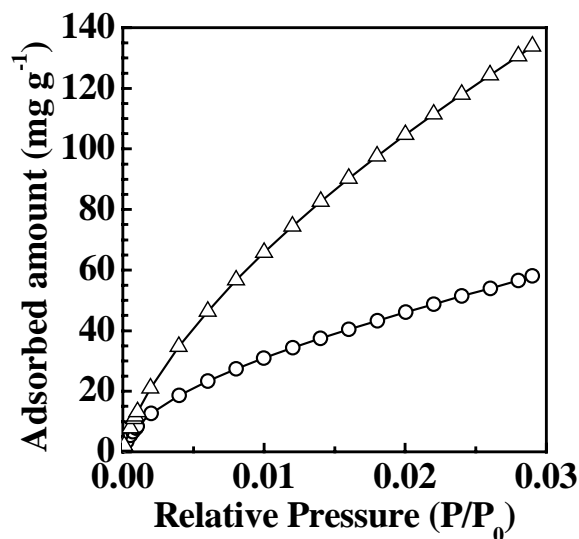
current collector used in each solvent was different to prevent side reaction between the solvent and materials for current collector by voltage applying. That is, Pt plate (endurable in strong acid) and glassy carbon were used in aqueous and organic systems, respectively. Electrolytes used in this study were two organic electrolytes (1M of tetraethylammonium tetrafluoroborate,  $((C_2H_5)_4NBF_4$  ( $Et_4NBF_4$ ), with propylene carbonate (PC) and acetonitrile (ACN)) and an aqueous electrolyte (30 wt. % of aqueous  $H_2SO_4$ ). The charging voltages have been limited at 0.9 V and 2.5 V in aqueous and organic electrolytes to ensure the stability of the solvents. The capacitance (C) of the electrodes was calculated on the basis of the following equation,  $C = (I \times \Delta t)/(W \times \Delta V)$ , where  $I$  is the current at discharge,  $\Delta t$  is the time variation between the 40 % and 60 % of the initial voltage,  $\Delta V$  is the voltage variation from the 40 % to 60 % of initial voltage, and  $W$  is the weight summed the both of electrodes in the cell composition. All specific capacitances were calculated from following relationship; Capacitance<sub>3E</sub> (in 3-electrode) = 4 x Capacitance<sub>2E</sub> (in 2-electrode); for comparing the Capacitance<sub>2E</sub> with the Capacitance<sub>3E</sub>.

A conventional three-compartment cell was also used to confirm the decomposition voltage window of each electrolyte system. The resultant voltammograms were obtained using a Pt wire as a counter electrode and working electrode that consists of SWNH paste (mixture with binder) pressed on Al mesh.  $Ag/Ag^+$  was used as a reference electrode with a potential sweep rate of  $10\text{ mVs}^{-1}$  using a HZ-3000 instrument. Solvents used in the reference electrode were changed by accompanying with that of each system. The composition of SWNH electrode was the same with that of galvano/potentiostat experiments as described above. Two organic electrolytes were limited in the range of -1.5~1.0 V (vs.  $Ag/Ag^+$ ) and an aqueous electrolyte was limited in the range of -0.2~0.8 V (vs.  $Ag/Ag^+$ ), due to difference in the decomposition voltage. Because the scan ranges include the both side of cathodic and anodic regime, ionic behavior of cation and anion simultaneously can be confirmed.

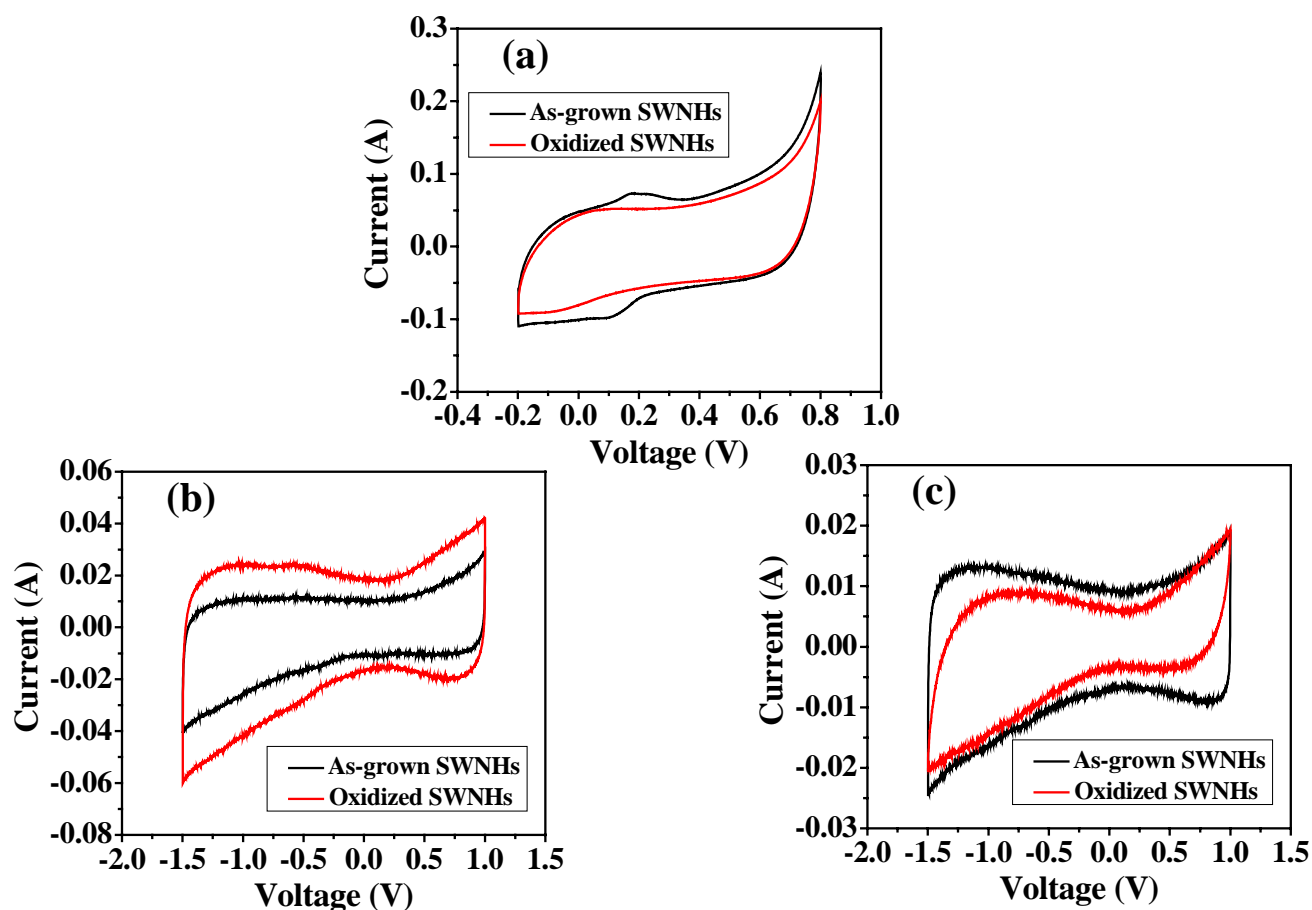
## RESULTS



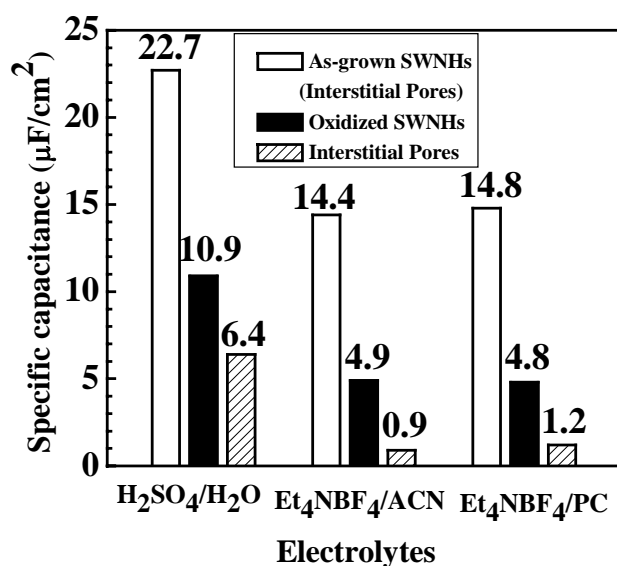
**Supporting Information FIGURE S1:** Raman spectra of as-grown and oxidized SWNHs.



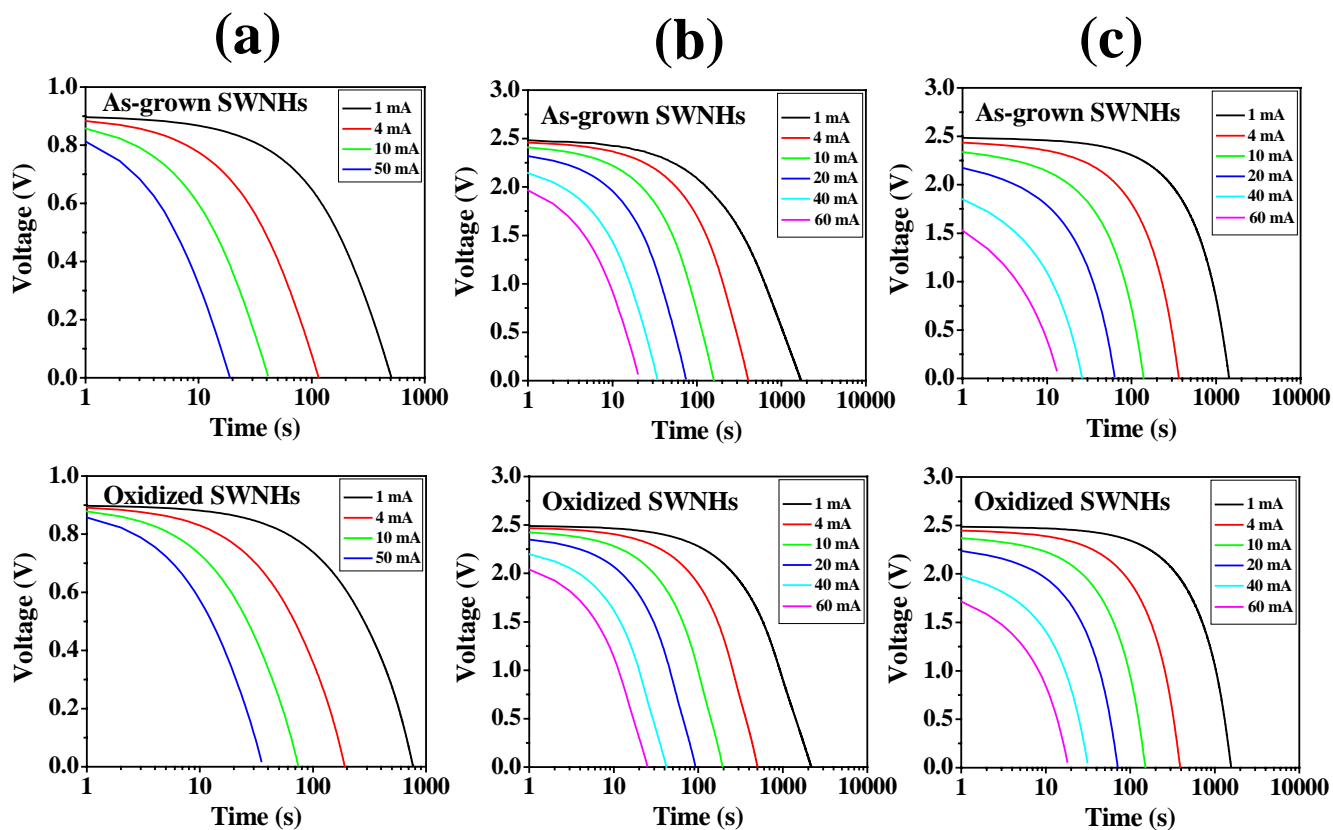
**Supporting Information FIGURE S2:** CO<sub>2</sub> adsorption isotherms at 273 K: (○) as-grown SWNHs; (Δ) oxidized SWNHs; since the saturation pressure of CO<sub>2</sub> at 273 K is extremely high (about 3.5 MPa), CO<sub>2</sub> adsorption was performed at relative pressure up to 0.029. CO<sub>2</sub> adsorption at 273 K is very effective method for the characterization of narrow micropores (< 0.7 nm), because CO<sub>2</sub> at 273 K easily diffuses into narrow micropores due to its larger kinetic energy, whereas N<sub>2</sub> at 77 K shows a restricted diffusion. Therefore, CO<sub>2</sub> adsorption at 273 K gives a much greater accuracy than N<sub>2</sub> adsorption at 77 K in microporosity determination of nanoporous materials.



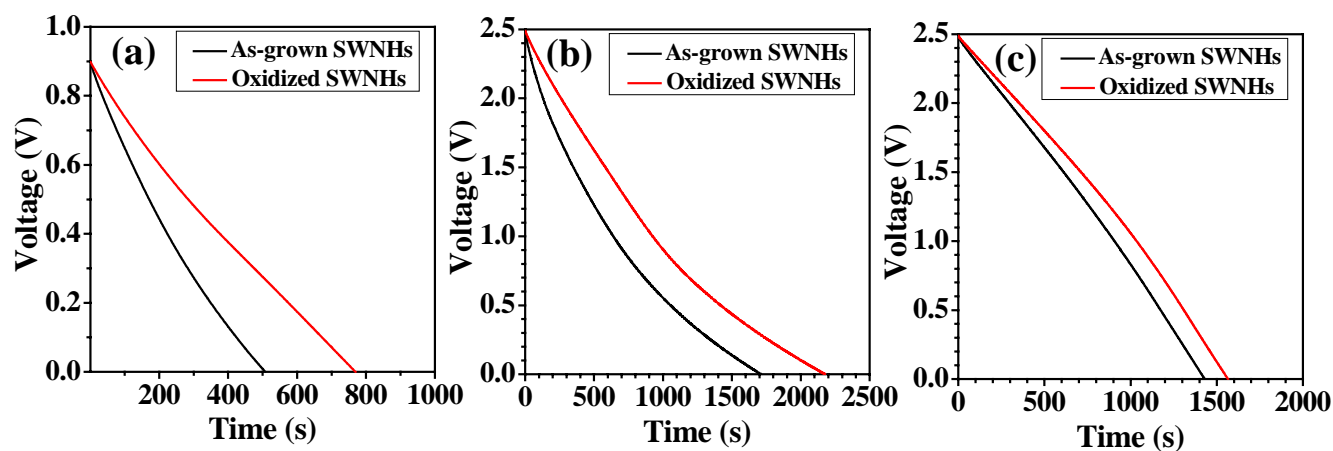
**Supporting Information FIGURE S3:** Cyclic-voltammograms of as-grown and oxidized SWNHs in a various electrolytes by using a 3-electrode compartment (vs.  $\text{Ag}/\text{Ag}^+$ ). All results were obtained at  $10 \text{ mVs}^{-1}$  of sweep rate: (a) 30 wt. % of aqueous  $\text{H}_2\text{SO}_4$ , (b) 1 M  $\text{Et}_4\text{NBF}_4/\text{ACN}$ , and (c) 1 M  $\text{Et}_4\text{NBF}_4/\text{PC}$ .



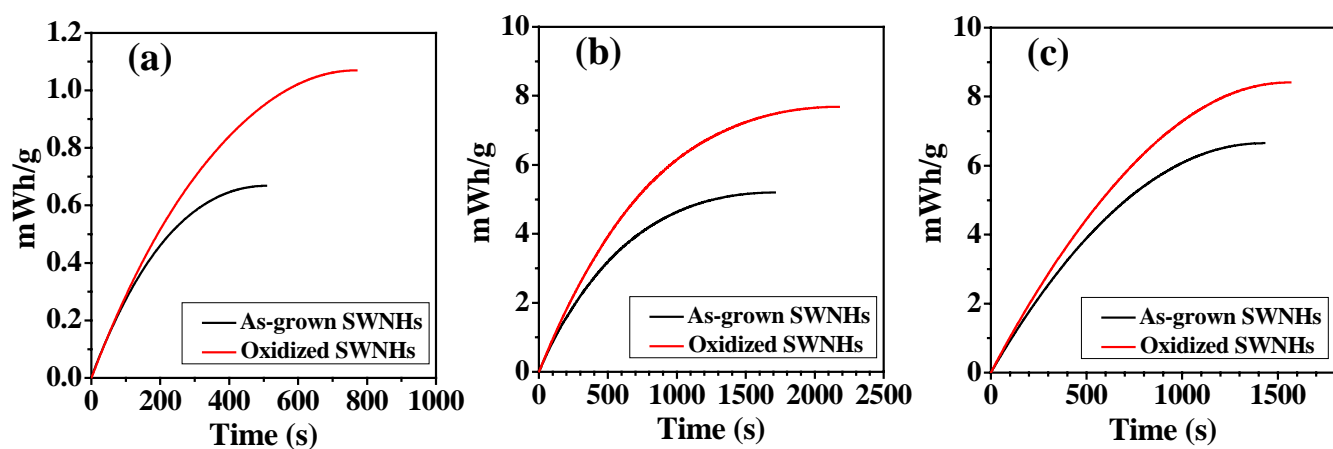
**Supporting Information FIGURE S4:** Specific capacitances per unit specific surface area of the SWNH electrodes at discharge current density of  $1 \text{ mA}/\text{cm}^2$  as a function of electrolytes.



**Supporting Information FIGURE S5:** Discharge profiles of as-grown and oxidized SWNHs with a log scale by using various electrolytes in the range of  $1\text{mA}/\text{cm}^2$  to  $60\text{mA}/\text{cm}^2$ : (a) 30 wt. % of aqueous  $\text{H}_2\text{SO}_4$ , (b) 1 M  $\text{Et}_4\text{NBF}_4/\text{ACN}$ , and (c) 1 M  $\text{Et}_4\text{NBF}_4/\text{PC}$ .



**Supporting Information FIGURE S6:** Comparison of the discharge profiles of as-grown and oxidized SWNHs with a linear scale at  $1\text{mA}/\text{cm}^2$ : (a) 30 wt. % of aqueous  $\text{H}_2\text{SO}_4$ , (b) 1 M  $\text{Et}_4\text{NBF}_4/\text{ACN}$ , and (c) 1 M  $\text{Et}_4\text{NBF}_4/\text{PC}$ .



**Supporting Information FIGURE S7:** Comparison of the energy density of as-grown and oxidized SWNHs with a linear scale at  $1\text{mA}/\text{cm}^2$  in various electrolytes: (a) 30 wt. % of aqueous  $\text{H}_2\text{SO}_4$ , (b) 1 M  $\text{Et}_4\text{NBF}_4/\text{ACN}$ , and (c) 1 M  $\text{Et}_4\text{NBF}_4/\text{PC}$ .