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

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Carbon nanotube (CNT)-related materials have great potential for their applications in energy and environmental fields. In particular, single-wall carbon nanohorns (SWNHs)[1] have been proposed as promising materials for supercritical gas storage, catalyst support, and drug delivery.[2] As-grown SWNHs do not have high surface area and pore volume because of their closed single-wall structures; therefore, various attempts to develop the porosity of SWNHs have been reported.[2a,3] Oxidation treatment of SWNHs in O_2 gas could create nanoscale holes, so-called "nanowindows", on the closed SWNHs, and thereby the porosity of SWNHs was dramatically developed.[3] Therefore, after the hole-opening of SWNHs, various guest molecules are accessible to the internal spaces through the nanowindows, and they can be accommodated within the spaces.[4] Our previous study revealed that the molecular sieving effect of oxidized SWNHs is dependent on the nanowindow size controlled by oxidation temperature.[5] It was shown that a SWNH exhibits n-type semiconductivity, being different from a single-wall carbon nanotube.[6] The extended X-ray absorption fine structure (EXAFS) study revealed the presence of an intensive dehydration of ions confined in interstitial spaces of SWNHs.[7]

Supercapacitors have attracted much attention as energy storage devices. Since 1997, several attempts have been reported on application possibilities of CNTs to electrode materials for supercapacitors, which have shown the specific capacitances of 15−130 F/g, depending on a respective electrolyte system.[8] However, these studies did not provide any evidence for a relationship between the solvated ion size of an electrolyte and the nanowindow size of CNTs in specific capacitance of supercapacitors. This is because it is difficult to separately evaluate the internal and interstitial spaces of CNTs owing to the variable bundle structure of the CNT assembly.[9] On the other hand, the internal space of the SWNHs accessible to guest molecules can be quantitatively determined because of their stable spherical bundle structure (Figure 1a).[1] The SWNHs can be considered as a promising candidate for electrode material of supercapacitors, owing to their porous structure and novel physical properties.

Here, we report for the first time fabrication of electrodes for supercapacitors using the SWNHs. We also investigated the hole-opening effect of the SWNHs on their capacitive properties. In addition, capacitance behaviors of the SWNH electrodes were compared for the electrolytes with different solvated ion sizes to elucidate the nanowindow size dependence on the specific capacitance.

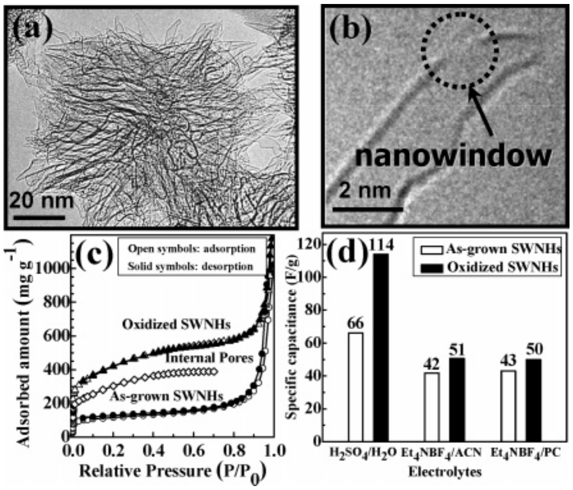

Figure 1. TEM images of (a) as-grown SWNHs and (b) oxidized SWNHs, (c) N_2 adsorption isotherms at 77 K, and (d) specific capacitances of the SWNH electrodes at discharge current density of 1 mA/cm^2.

We measured N_2 adsorption isotherms to determine the pore structure of the SWNHs (Figure 1c). The N_2 adsorption isotherm of as-grown SWNHs is defined as type II. The N_2 adsorption amount of as-grown SWNHs at low relative pressure (P/P_0) should be related to interstitial spaces between nanohorns because of their closed single-wall structures. Oxidation treatment in O_2 atmosphere (at 693 K) does not affect the type of N_2 adsorption isotherm. However, the amount of N_2 adsorbed in oxidized SWNHs at low P/P_0 remarkably increases compared with that of as-grown SWNHs, indicating nanowindow formation on SWNH particles by oxidation treatment, which was supported by direct transmission electron microscopy (TEM) observation (Figure 1b) and increase of the integrated intensity ratio of the D-band to G-band in Raman spectra (Supporting Information (SI) Figure S1). Since as-grown SWNHs are completely closed, N_2 molecules are adsorbed only in interstitial spaces and on external surfaces. Accordingly, the subtraction of the N_2 adsorption isotherm of as-grown SWNHs from that of oxidized SWNHs gives the isotherm of the internal pores created by hole-opening in SWNHs (Figure 1c). The N_2 adsorption isotherm of only internal pores is close to type I, indicating the dominant microporosity. The oxidation treatment remarkably increases the micropore surface area and micropore volume due to the hole-opening of SWNHs (Table 1). Average internal pore size is 2.4 nm, which is in good agreement with the diameters of individual nanohorns (about 2∼3 nm) obtained by TEM observation.[1] After oxidation treatment of the SWNHs, the enhanced CO_2 adsorption capacity should be attributed to the developed ultramicroporosity (<0.7 nm) (SI Figure S2). However, an increment of the micropore volume determined from CO_2 adsorption isotherm is not notable,

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Table 1. Pore Structure Parameters of SWNH Samples[a]

	N$_2$ (77 K): subtracting pore effect (SPE) method							CO$_2$ (273 K)
			microporosity			mesoporosity		
sample	a_t (m^2/g)	V_t (mL/g)	a_{micro} (m^2/g)	V_{micro} (mL/g)	w (nm)	a_{ext} (m^2/g)	V_{meso} (mL/g)	V_{DR} (mL/g)
as-grown SWNHs (interstitial pores)	291	1.02	190	0.10	1.1[b]	101	0.92	0.08
oxidized SWNHs	1045	1.23	800	0.48		245	0.75	0.21
internal pores	753	0.48	623	0.38	2.4[c]	130	0.10	

[a] a_t, total surface area; V_t, total pore volume; a_{micro}, micropore surface area; V_{micro}, micropore volume; w, average pore size; a_{ext}, external surface area; V_{meso}, mesopore volume; V_{DR}, micropore volume determined by Dubinin−Radushkevich (DR) method. [b] Calculated by assuming slit pores. [c] Calculated by assuming cylindrical pores.

which suggests that larger micropores are mainly created after oxidation of the SWNHs.

Figure 1d shows specific capacitances of the SWNH electrodes as a function of electrolytes. For aqueous electrolyte (H_2SO_4/H_2O), as-grown SWNHs show the specific capacitance of 66 F/g. After oxidation of the SWNHs, the specific capacitance dramatically increases to 114 F/g, which is attributed to the developed internal porosity. Cyclic voltammograms for the oxidized SWNH electrode did not exhibit any pseudocapacitive behavior that is related to Faradaic reaction in the interface between the electrode and electrolyte (SI Figure S3). Therefore, this enhanced capacitance may be imparted by a high accessibility of the solvated ions ($SO_4^{2-}(H_2O)_n$) to internal pores through the nanowindows. The diameter of $SO_4^{2-}(H_2O)_{12}$ determined by computer simulation study is 0.53 nm.[10] To confirm the dependence of the solvated ion size of electrolytes on specific capacitance, we also used two organic electrolytes (($(C_2H_5)_4NBF_4$ (Et_4NBF_4) with propylene carbonate (PC) and acetonitrile (ACN)). The solvated ion size of electrolytes increases in the following order: H_2SO_4/H_2O < Et_4NBF_4/ACN < Et_4NBF_4/PC (Et_4N^+•7ACN, 1.30 nm; BF_4^-•9ACN, 1.16 nm; Et_4N^+•4PC, 1.35 nm; BF_4^-•8PC, 1.40 nm).[11] SWNH electrodes using organic electrolytes show lower capacitances compared to those using aqueous electrolyte. Moreover, when using the organic electrolytes, the oxidized SWNHs do not show notable enhancement in specific capacitances. Specific capacitances per surface area of the internal pores for Et_4NBF_4/ACN and Et_4NBF_4/PC show extremely low values of 0.9 and 1.2 μF/cm^2, respectively, compared to that of H_2SO_4/H_2O electrolyte (6.4 μF/cm^2) (SI Figure S4). Although oxidized SWNHs donate large internal pore-size (2.4 nm), enough to accommodate the organic electrolyte ions as well as high surface area and pore volume (Table 1), the entrance (nanowindow) size of internal pores might be too small for the organic electrolyte ions to pass through the nanowindow; according to a previous study, the nanowindow size of oxidized SWNHs at 693 K was estimated to be more than 1 nm.[5] Size difference between the nanowindows and the solvated ions should be an important factor in the accessibility of the ions to the internal spaces. Recently, Chmiola et al. reported that, for carbide-derived carbons, the solvated electrolyte ions (Et_4NBF_4/ACN) could penetrate into pores smaller than the solvated ion size, and they could be accommodated inside the narrow spaces.[12] They insisted that the solvated ions are squeezed and distorted through the narrow pore. For the Et_4NBF_4/ACN electrolyte, as-grown SWNHs (interstitial pores, average pore size of 1.1 nm) have specific capacitance per surface area of 14.4 μF/cm^2 (SI Figure S4), which is slightly higher than the highest value obtained from carbide-derived carbon with small pore size (about 0.7 nm).[12] Therefore, we assume that solvated ions are distorted and accommodated inside the narrow interstitial pores of SWNHs, and the distorted solvated ions might block the nanowindows. Moreover, unlike the restricted space of a slit-shaped pore whose potential field can distort the solvated ions, it is difficult for the solvated ions to pass through the narrow nanowindow. The molecular distortion can be induced owing to a strong interactive potential field such as narrow nanopores. Unfortunately, nanowindows cannot offer the attractive potential field but the repulsive barrier. Therefore, the specific capacitance strongly depends on correlation between the solvated ion size of the electrolyte and the nanowindow size of the SWNHs.

In conclusion, we presented for the first time nanowindow size dependence of single-wall nanocarbons on specific capacitance and application possibility of the SWNHs to electrodes for supercapacitors. Our study clearly revealed that the nanowindow size of the SWNHs is an important parameter for improving the performance of supercapacitors. If we use the SWNHs with larger nanowindow size, high-capacitance supercapacitors using organic electrolytes could be fabricated. We also expect that single-wall nanocarbons with high ion selectivity can be designed by controlling the nanowindow size.

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Supporting Information Available: Detailed experimental procedures, Raman spectra, CO_2 adsorption isotherms, cyclic voltammograms, specific capacitances per surface area, discharge profiles, and energy density. This material is available free of charge via the Internet at http://pubs.acs.org.

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