ELECTROCHEMICAL BEHAVIOR OF METALLIC AND SEMICONDUCTING SINGLE-WALL CARBON NANOTUBES

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Introduction

Electrochemical properties of single-wall carbon nanotube (SWCNTs) have attracted attention, especially in electronics such as electric double layer capacitor [1,2]. Although the effect of electrochemical doping on CNTs has been reported on the electrochemical method, the electrochemical behavior of the separated SWCNTs has not been reported except for the theoretical calculation [3] due to the difficulty of sorting large amount of semiconducting and metallic SWCNTs. This problem was overcome by the use of agarose gel [4]. In this work, separated metallic and semiconducting SWCNTs by gel centrifugation method were investigated for understanding the electrochemical behavior of SWCNT electrode.

Experimental

The super-purified SWCNTs (Grade #SP0344) prepared by HiPco method were obtained from Unidym. The outer diameter is 0.8- 1.2 nm, the tube length is 100-1000 nm and the metal content is <5 wt.% [5]. These CNTs were used for preparing metallic and semiconducting SWCNTs. 1 mg mL^{-1} of SWCNTs in 2 wt.% sodium dodecyl sulfate was sonicated using a tip-type ultrasonic homogenizer (VP-30S, Taitec) for 5 h. The solution was then centrifuged (415,000×*g* for 15 min at 298K), and the 80% of upper supernatant was collected. The collected CNTs were used as a reference sample and also used for separating CNTs. The supernatant was mixed with liquid agarose gel to prepare gel containing SWCNTs.

The agarose gel was prepared by dissolving 0.6 wt.% of agarose in ×2 TB buffer (100 mM tris(hydroxymethyl) aminomethane, 97 mM boric acid, pH 8.2) upon heating. The mixture was mixed well with an equal amount of the diluted (1:6) SWCNT supernatant. The mixture was then let stand to induce gelation.

The gel was centrifuged for 6 h at 15,000×*g* for separating metallic and semiconducting SWCNTs. The resulting solution and gel debris include metallic SWCNTs and semiconducting SWCNTs enriched fractions, respectively. The gel containing semiconducting SWCNTs were dissolved in water by heating and centrifuged to remove the melting agarose gel. The SWCNT precipitate was further purified by degradation of the remaining agarose in boiling 1 wt.% citric acid aqueous solution for 3 h, followed by washing with distilled water and methanol. The purification steps including degradation and washing were repeated twice. In the cases of the reference sample and metallic SWCNTs, these citric acid treatment and washing were also performed.

Properties of CNTs were analyzed by an UV-vis spectrophotometer (Shimadzu SolidSpec-3700DUV) and Raman spectroscopy (T-64000, Jobin Yvon) with 514.5 nm line of an argon ion laser at 400 mW output.

The CNT electrode was prepared by following method. Carboxy methyl cellulose sodium salt was dissolved in filtered water by sonication, and SWCNTs were added in the solution and poured on Pt electrode and dried. This electrode consists of 11wt.% of carboxy methyl cellulose sodium salt as a binder. The cyclic voltammogram (CV) and galvanostatic cycling with potential limitation were performed by VMP2 potentiostat/galvanostat (Bio-Logic). CVs were measured in 1 mol dm^{-3} (M) tetraethylammonium tetrafluoroborate ($TEABF_4$) dissolved in propylene carbonate (PC) vs. the Ag/Ag^+/PC reference by three electrode cells. The galvanostatic charge/discharge was monitored at a current density of 0.5 A g^{-1} and in the same potential range. The specific capacitance was calculated from the slope of the potential-time curve.

Results and discussion

Fig. 1 shows that the characteristic peak of semiconducting SWCNTs (S_{22}) and metallic SWCNTs (M_{11}) were clearly observed after separating SWCNTs by agarose gel. This difference was also observed by Raman spectroscopy as shown in Table 1 and Fig. 2. The intensity of characteristic peak of metallic SWCNTs (BWF) at 1550 cm^{-1} is higher than that of semiconducting CNTs. Band around 2650 cm^{-1} is the peak of G', and also shows the difference of separated SWCNTs. The results of Fig. 1 and Table 1 imply that most of SWCNTs were separated, but small amount of unseparated SWCNTs is still remaining in separated metallic and semiconducting SWCNTs.

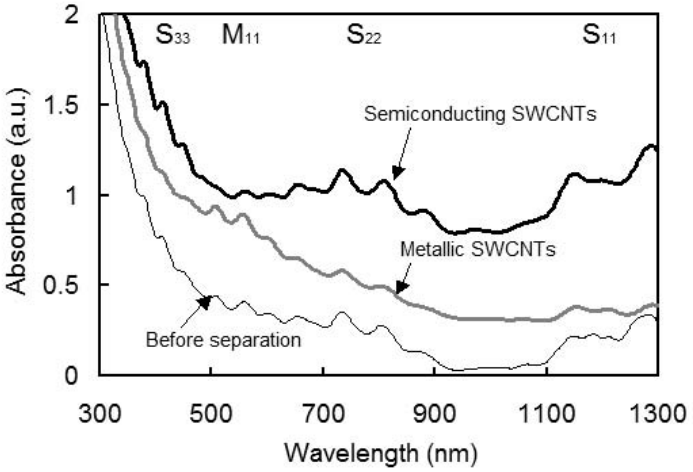

Fig. 1 SWCNTs before and after separation analyzed by UV-vis spectrometry.

Table 1. Ratio of intensity at Raman mode frequencies

	I_D/I_G	I_{BWF}/I_G
Metallic	0.14 ± 0.03	0.75 ± 0.04
Semiconducting	0.066 ± 0.010	0.38 ± 0.03
Before separation	0.093 ± 0.033	0.51 ± 0.05

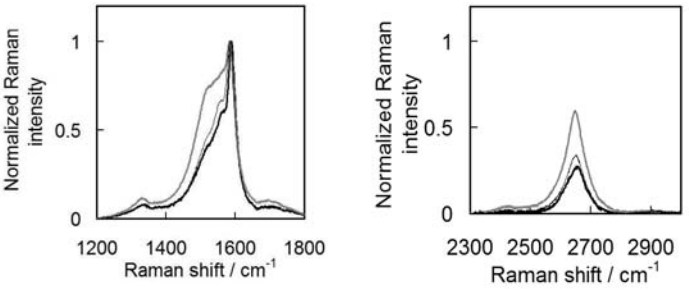

Fig. 2 Raman spectra of SWCNTs before and after separation Bold gray line: metallic SWCNTs, Bold black line: semiconducting SWCNTs, Thin line: SWCNTs before separation

Fig. 3 shows CVs of SWCNTs before and after separation. The CV curve of metallic SWCNTs shows rectangular shape which resembles that of general activated carbon or double walled carbon nanotube [6]. On the other hand, semiconducting SWCNTs with small diameter in this work has a butterfly shape which resembles that of SWCNTs with large diameter synthesized by super-growth method [1]. This effect by doping and undoping is considered to be relevant to density of state. There is no band gap for metallic SWCNTs, but semiconducting SWCNTs with 0.8-1.2 nm in diameter have band gap of 0.3-0.5 eV [7], which corresponds to the flat region of the curve near the flat band potential. The current density of semiconducting SWCNTs near the flat band potential is lower than that of metallic SWCNTs, but the current density is far from 0 mA g^{-1} because of the small amount of remaining unseparated metallic SWCNTs in semiconducting SWCNTs. Due to the doping and undoping effect on the semiconducting SWCNTs, the capacitance at 1 V (vs. Ag/Ag^+) reached 60 F g^{-1} for semiconducting-SWCNTs electrode. On the other hand, metallic-SWCNTs electrode showed 47 F g^{-1} which is smaller than semiconducting SWCNTs.

Conclusions

The separated metallic and semiconducting SWCNTs showed a clear difference in absorbance of light, Raman intensity, and shape of cyclic voltammograms. Semiconducting SWCNTs showed flat region of current density which corresponds to the band gap of semiconducting SWCNTs. The capacitance at 1V (vs. Ag/Ag^+) reached 60 F g^{-1} for semiconducting-SWCNTs electrode and 47 F g^{-1} for metallic-SWCNTs electrode at 0.5 A g^{-1} of current density.

Acknowledgments. Acknowledgments are made to New Energy and Industrial Technology Development Organization (NEDO).

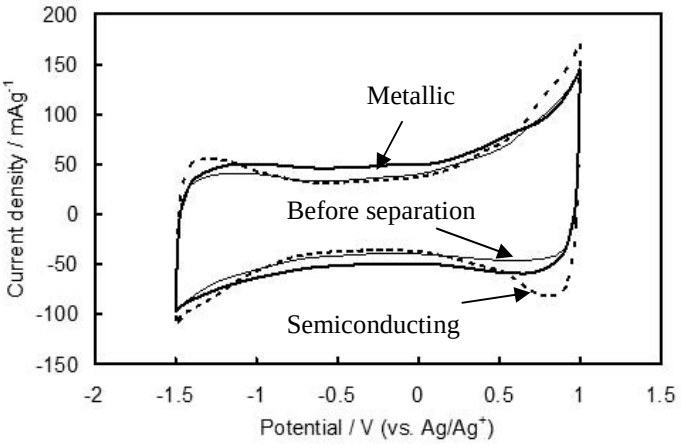

Fig. 3 CVs of SWCNTs before and after separation. The curves were recorded at scan rate of 1 mV s^{-1} in 1M $TEABF_4$/PC.

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