Single-wall carbon nanotubes (SWCNTs) can be classified into two types on the basis of their electric properties, metallic and semiconducting ones. These two types of SWCNTs are defined by the helical configurations of carbon atoms.\(^1\) For the electronic application of SWCNTs, specific electric types of SWCNTs are required, but present SWCNT production methods produce a mixture of metallic and semiconducting SWCNTs. There are several methods of separating metallic and semiconducting SWCNTs (MS separation).\(^2\) For example, dielectrophoresis,\(^3\) amine extraction,\(^4\) polymer wrapping,\(^5\) selective oxidation,\(^6\) and density-gradient ultracentrifugation\(^7,8\) can be used. Recently, we reported a simple, novel separation method using agarose gel.\(^9\) When an electric field or a mechanical force was applied to an agarose gel containing SWCNTs dispersed by sodium dodecyl sulfate (SDS), only metallic SWCNTs were eluted from the gel, while semiconducting SWCNTs remained trapped in the gel. We also found that a simple mixing of an SWCNT/SDS dispersion and agarose gel caused MS separation, in which semiconducting SWCNTs were selectively adsorbed by the gel. These methods provide quick, high yield, low cost, and scalable MS separation, but present SWCNT production methods produce a mixture of metallic and semiconducting SWCNTs (MS separation).\(^2\) For example, dielectrophoresis,\(^3\) amine extraction,\(^4\) polymer wrapping,\(^5\) selective oxidation,\(^6\) and density-gradient ultracentrifugation\(^7,8\) can be used. Recently, we reported a simple, novel separation method using agarose gel.\(^9\) When an electric field or a mechanical force was applied to an agarose gel containing SWCNTs dispersed by sodium dodecyl sulfate (SDS), only metallic SWCNTs were eluted from the gel, while semiconducting SWCNTs remained trapped in the gel. We also found that a simple mixing of an SWCNT/SDS dispersion and agarose gel caused MS separation, in which semiconducting SWCNTs were selectively adsorbed by the gel. These methods provide quick, high yield, low cost, and scalable MS separation, but a viable process of separating the semiconducting SWCNTs from the gel was needed. Here, we report an improved MS separation method using agarose gel, in which semiconducting SWCNTs were selectively attached to agarose gel beads in a column, and then eluted as a solution phase (Fig. 1). This method has many advantages, such as rapidity, scalability, reusability of the gel, and compatibility with automation, in addition to providing gel-free semiconducting SWCNTs. SWCNTs synthesized by high-pressure carbon monoxide processing (Carbon Nanotechnology HiPco, R500, 1.0 ± 0.3 nm in diameter) were used in this study. An SWCNT-dispersed solution was prepared as follows. SWCNTs were dispersed in 2% SDS (99%, Sigma-Aldrich) at 0.3 mg/ml, and sonicated using a tip-type ultrasonic homogenizer (Tai tec VP-30S) for 4 h. The solution was ultracentrifuged to remove bundles and impurities (210,000 × g for 15 min at 25 °C),\(^12,13\) and the resulting supernatant was collected as an SWCNT dispersion, in which the SWCNTs were coated with the surfactant.\(^14,15\)

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In the previous study, batch separation by mixing this dispersion with self-made agarose gel beads (diameter ~2 mm) in a micro test tube was investigated.\(^11\) In this study, we applied a continuous separation method based on column chromatography. To prepare the column, the outlet of a 2.5 ml plastic disposable syringe was plugged with cotton, and the syringe was filled with agarose beads (GE Healthcare Sepharose 2B, bead size range, 60–200 μm). The column was washed with water, and then equilibrated with a 1% SDS solution. As shown in Fig. 2, when the SWCNT dispersion and successive 1% SDS solution were applied to the column, color separation was observed (Fig. 2, from 0°00′ to 2°40′). Greenish SWCNTs were trapped in the upper region of the column, while reddish SWCNTs were not adsorbed to the column. These colors correspond to those of semiconducting and metallic HiPco-SWCNTs, respectively. The greenish SWCNTs were tightly bound to the gel, and were not eluted when the column was washed with 1% SDS solution (until 7°20′). By the addition of other kinds of surfactant solution, 1% sodium deoxycholate (DOC; Wako Pure Chemical Industries), the bound SWCNTs were successfully eluted as a gel-free solution fraction (Fig. 2, from 7°20′ to 10°40′).

To check the components of the unbound and bound (eluted by DOC) fractions, their optical absorption spectra were measured using an ultraviolet–visible–near-infrared (UV–vis–NIR) spectrophotometer (Shimadzu UV-3600). Figure 3(a) shows the optical absorption spectra of the
samples. For HiPco SWCNTs, the absorption peaks around 950–1350, 650–950, and 300–450 nm were derived from first, second, and third optical transitions of semiconducting SWCNTs, and were designated as $S_{11}$, $S_{22}$, and $S_{33}$, respectively. The absorbance peak around 450–650 nm represented the first optical transition of metallic SWCNTs ($M_{11}$). In comparison to the original sample (before separation), the metallic SWCNTs were clearly concentrated in the unbound fraction (red spectrum), whereas an enrichment of semiconducting SWCNTs was observed in the eluted (bound) fraction (blue spectrum). This MS separation was confirmed by Raman spectroscopic analysis [Fig. 3(b)]. To evaluate the separation ratio, the metal-to-semiconductor ratio of the original sample was assumed to be 1:2. From a calculation of the areas of the metallic and semiconducting peaks, the purities of semiconducting and metallic SWCNTs in the respective fractions were estimated to be about 95 and 90%, respectively.

After the first separation, the column was re-equilibrated with SDS solution, and used for a second separation. The second set of optical absorption spectra was nearly identical to the first [Fig. 3(a), light blue and pink spectra], indicating that this MS separation method can be carried out repeatedly.

We investigated other surfactants for the elution of the adsorbed semiconducting SWCNTs. Sodium cholate (SC; Sigma-Aldrich), sodium dodecylbenzene sulfonate (SDBS; Sigma-Aldrich), Tween 20 (Wako Pure Chemical Industries), TritonX-100 (Wako Pure Chemical Industries), and cetyl trimethyl ammonium bromide (CTAB; Sigma-Aldrich) were used in addition to DOC (Fig. 4). Of these surfactants, DOC provided the highest recovery ratio of adsorbed SWCNTs. Anionic surfactants (DOC, SC, SDBS) were superior to nonionic surfactants (Tween 20 and TritonX-100), and no recovery was observed with cationic CTAB, which was oppositely charged to anionic SDS.

In the previous batch separation using millimeter-size agarose gel beads, although the separation took a very long time (more than 10 h), the present continuous column separation only took about 10 min (Fig. 2). This quick separation was thought to be achieved because of the smaller agarose beads (around 100 μm) used in this study. The greatly reduced bead size considerably increased the effective surface area of the agarose, resulting in faster separation and a higher adsorption capacity.

We reported previously that the purities of metallic and semiconducting SWCNTs were tunable by the agarose concentration of the SWCNT-containing gel. That is, a high
(or low) concentration of agarose brought high-purity metallic (or semiconducting) SWCNTs. However, metallic and semiconducting SWCNTs were not simultaneously obtained at a high purity. This previous result presumed that the length distribution of SWCNTs affected the purity of the separated sample, because the agarose concentration which defined the pore size of the gel strongly correlated with the purity of the separated SWCNTs.11) The present column method could obtain both metallic and semiconducting SWCNTs at once with higher purities than the previous ones. In the column separation, the separation (adsorption and desorption) was thought to occur mainly on the surface of the gel beads, where the separation was relatively unaffected by the pore size or the length of SWCNTs. In the previous method using SWCNTs-containing gel, the separation occurred mainly within the network of the gel. This difference may explain the difference in product purities.

In conclusion, we have developed a continuous method of separating metallic and semiconducting SWCNTs using a column with agarose gel beads. This method achieved quick, high-purity separation. Reusability of the agarose gel and compatibility for automation should enable low-cost separation. In addition, column chromatography is a well-established technique, which allows for straightforward scaling-up of the separation process. This very simple, rapid, high-purity, low-cost, and scalable method should enable industrial production of metallic and semiconducting SWCNTs, facilitating basic and applied research of SWCNT electronics.

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