

Supporting Information

“Simple and Scalable Gel-Based Separation of Metallic and Semiconducting Carbon Nanotubes”

Takeshi Tanaka¹, Hehua Jin¹, Yasumitsu Miyata¹, Shunjiro Fujii¹, Hiroshi Suga¹, Yasuhisa Naitoh¹, Takeo Minari¹, Tetsuhiko Miyadera¹, Kazuhito Tsukagoshi¹, and Hiromichi Kataura^{1,2}

¹Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ibaraki 305-8562, Japan.

²JST, CREST, Kawaguchi 330-0012, Japan.

Supplemental Methods

Preparation of SWCNT dispersion and SWCNT-containing Gel

SWCNTs synthesized by laser vaporization (LV1, 1.2 ± 0.1 nm in diameter; LV2, 1.4 ± 0.1 nm) and by a high-pressure carbon monoxide process (HiPco, R ϕ 500, Carbon Nanotechnology, 1.0 ± 0.3 nm) were employed. LV1 nanotubes were synthesized by the laser vaporization of carbon rods doped with nickel (0.6 wt%) and cobalt (0.3 wt%) under a nitrogen atmosphere at 1050°C . The thicker laser-vaporized SWCNTs (LV2) were prepared in a similar manner at 1250°C . The raw soot containing the SWCNTs was refluxed in an aqueous solution of 15% H_2O_2 for 1.5 h at 100°C in order to burn out amorphous carbon. After refluxing, the sample was soaked in HCl to remove the remaining metal catalyst. The sample was then heated in air from 20 to 430°C at a heating rate of $10^{\circ}\text{C}/\text{min}$ in order to eliminate remaining impurities and chemicals used in the above treatments. The HiPco nanotubes were used as received without further purification.

Dispersions of the SWCNTs were prepared by dropping 0.3 mg/mL of the as-prepared SWCNTs in 2% sodium dodecyl sulfate (SDS, 99%, Sigma-Aldrich) solution and then ultrasonicationating the mixture using a tip-type ultrasonic homogenizer (VP-30S, Taitec) for 5.7 h at a duty cycle of 70% (total on-time, 4 h). The solution was then centrifuged to remove bundles and impurities ($16100\times g$ for 15 h at 25°C). The resulting supernatant was collected as a dispersion of surfactant-coated SWCNTs.

A gel was prepared from the SWCNT dispersion by mixing and gelling the dispersion with liquid agarose gel. In a typical preparation, 0.8% of agarose (Nacalai Tesque, Kyoto, Japan) melted in $\times 2$ TB buffer (100 mM tris(hydroxymethyl) aminomethane, 97 mM boric acid, pH 8.2) by heating in a microwave oven was mixed well with an equal amount of the SWCNT dispersion. The mixture was then let stand at room temperature to induce gelation. The resulting gel (SWCNT-containing gel) was used for MS separation experiments. Other surfactants, sodium cholate hydrate (SC, 99%, Sigma-Aldrich), sodium deoxycholate monohydrate (DOC, 99%, Sigma-Aldrich), and sodium dodecylbenzene sulfonate (SDBS, 80% mixture of homologous alkyl benzene sulfonates, Sigma-Aldrich) were also examined for use in place of SDS. Gelrite and gellan gum (Wako Pure Chemical Industries, Osaka, Japan) as the gel matrix were used at a final concentration of 0.05% supplemented with 5 mM of MgCl_2 for gelation.

MS separation

Freeze and squeeze method: 2 mL of the SWCNT-containing gel (0.15 mg/mL SWCNT, 1% SDS, 0.4% agarose in TB buffer) was frozen in a plastic tube (inner diameter, 15 mm) at -20 °C. The gel was then thawed at room temperature and squeezed.

Centrifugation method: 0.4 mL of the SWCNT-containing gel was centrifuged in a microtube for 3 h at 16100×g.

Diffusion method: 0.4 mL of the HiPco SWCNT-containing gel was prepared in glass tube (inner diameter, ca. 2.5 mm) then removed and cut to ca. 3 mm in length. The gel particles were added to elution buffer (1% SDS in TB buffer) and shaken gently overnight. The solution was recovered by pipette, and the gel particles were washed twice with 1 mL of elution buffer.

Permeation method: virgin gel particles (0.4% agarose, 2% SDS in TB buffer) were dropped into the SWCNT dispersion (0.15 mg/mL HiPco SWCNTs, 2% SDS) and the mixture was shaken gently overnight.

For measurement of optical absorbance spectra, the gel was melted in TB buffer by heating, and then cooled to ca. 60 °C. Spectra were measured using an ultraviolet–near-infrared spectrophotometer (SolidSpec-3700DUV, Shimadzu).

FET preparation

Semiconducting nanotubes were obtained by centrifugation from 40 mL of the SWCNT-containing gel (0.15 mg/mL HiPco SWCNTs, 0.05% agarose gel in TB buffer). The separated gel was purified by degradation in 1% citric acid at 95 °C for 3 h followed by washing with distilled water and methanol. This purification step (degradation and washing) was repeated twice. The purified semiconducting SWCNTs were dispersed in N-methylpyrrolidone solution by ultrasonication for 2 h (Sonifier 450D, Branson). The dispersion (20 µg SWCNT per mL) was then centrifuged for 15 min at 12000 rpm. The centrifuged solution (50 µL) was dropped on an SiO₂(200 nm)/Si substrate covered with self-assembled monolayer of 3-aminopropyltriethoxysilane (APTS, Aldrich). APTS was used to obtain homogeneous SWCNT network.²⁵ The dropped solution was kept on the substrate for 3 minutes. Then, the substrate was rinsed with isopropanol and dried by N₂ blow. Then, Au(50 nm)/Cr(3 nm) electrodes were deposited on the substrate. The topography of SWCNT network

was characterized using non-contact atomic force microscope (JSPM-5200, JEOL). The resulting FET structure was characterised by electrical measurements in air at room temperature using a semiconductor parameter analyzer (4200-SCS, Keithley). Mobility was estimated using the standard formula $\mu = (dI_{ds}/dV_g)/(\epsilon V_{ds}W/L_{ox}L_{ds})$, where I_{ds} is drain-source current, V_g is gate voltage, L_{ox} is SiO₂ thickness, L_{ds} is channel length, ϵ is the dielectric constant of SiO₂ (4.0), V_{ds} is drain-source voltage, and W is channel width.

- (25) Liu, J.; Casavant, M. J.; Cox, M.; Walters, D. A.; Boul, P.; Lu, W.; Rimberg, A. J.; Smith, K. A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, 303, 125.

Supplemental Figures

Combinations of detergent and gel

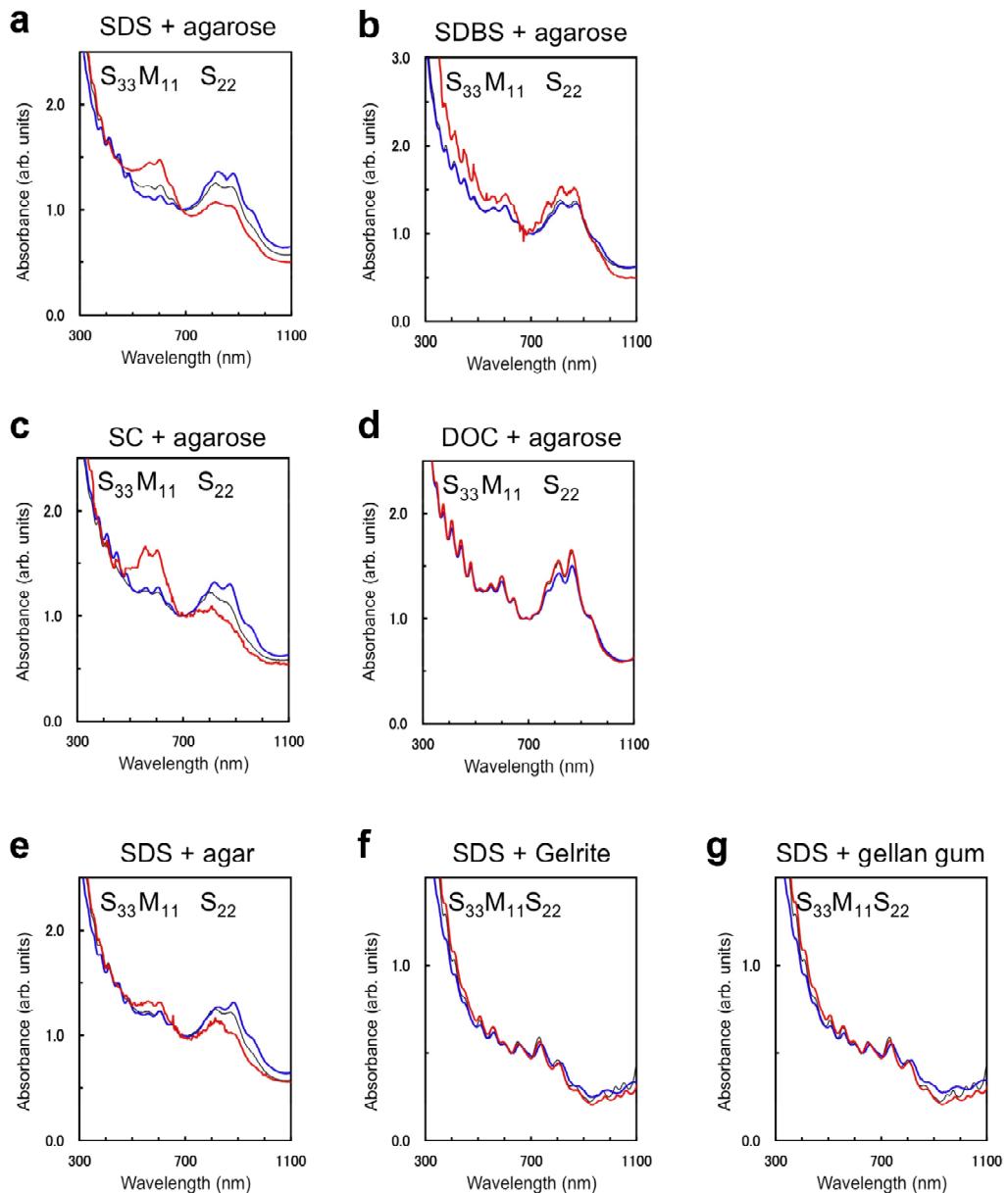
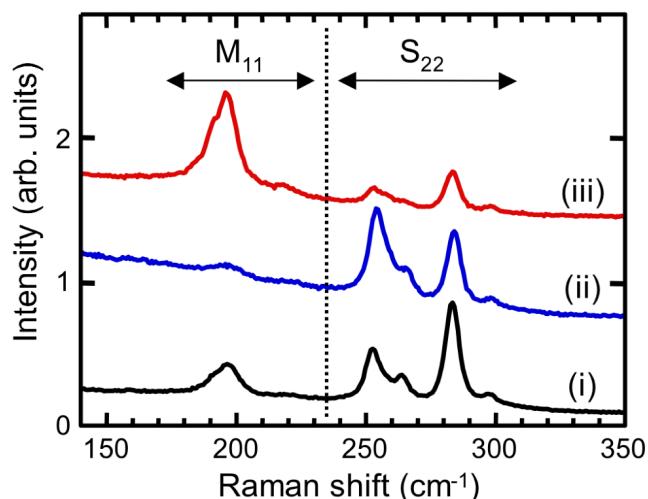


Figure S1. MS separation using various combinations of detergent and gel by centrifugation method. (a–d) Separation using various surfactants and agarose gel. (a) SDS, (b) sodium dodecylbenzene sulfonate (SDBS), (c) sodium cholate (SC), (d) sodium deoxycholate (DOC). (e–g) Separation using SDS and various gels. (e) Agar gel, (f) Gelrite gel, (g) gellan gum gel. LV1 SWCNTs (a–e) and HiPco SWCNTs (f, g) were used. Absorption spectra of gel fractions and solution fractions are shown as blue and red lines, respectively. Black spectra are the results for the SWCNT dispersion before separation.

Raman spectroscopic analysis

Raman spectroscopy is a powerful tool for the ratio evaluation of metallic and semiconducting SWCNTs because radial breathing mode (RBM) Raman spectra show the well-separated peaks of different types of SWCNTs. For the ratio evaluation, the SWCNT sample with wide diameter distribution is necessary to excite both electronic types at the same time. For this reason, the ratio of separated HiPco sample was evaluated in this study. The metal-enriched and semiconductor-enriched samples for Raman measurement were prepared using the centrifugation method at the concentration of 0.5% and 0.05% agarose, respectively. Figure S2 shows the Raman spectra of the pristine and the separated samples in 1% SDS in TB buffer at 633 nm laser excitation. Because of the diameter distribution of 0.7–1.3 nm for the HiPco sample, both the M_{11} and S_{22} bands are on resonance for 633 nm excitation.²³ The RBM peaks are separated into two resonance groups: the resonances of the S_{22} band of semiconducting SWCNTs (254, 265, 284, and 298 cm^{-1}) and that of the M_{11} band of metallic SWCNTs (197 and 218 cm^{-1}). It can be seen that the relative intensity of metallic (semiconducting) SWCNTs increases for the metal-enriched (semiconductor-enriched) sample compared with the pristine sample. For the ratio evaluation, the metal-to-semiconductor ratio of the pristine sample was assumed to be 1:2. From the change of the peak area, the purity for the metal-enriched and the semiconductor-enriched samples were estimated to be above 70% and 90%, respectively.

Figure S2. Raman spectra of (i) pristine, (ii) semiconductor-enriched, and (iii) metal-enriched HiPco samples at 633 nm laser excitation. The spectra were shifted vertically for clarity.



MS separation by diffusion method

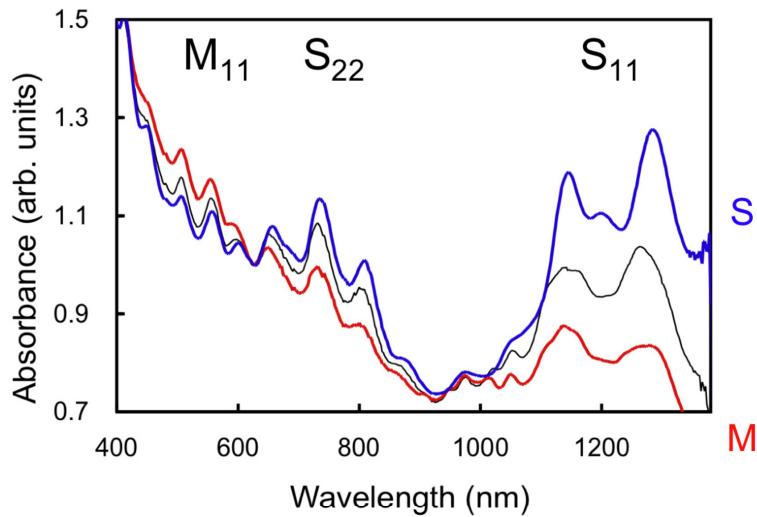


Figure S3. Absorption spectra of HiPco SWCNTs separated by diffusion method. Spectra of gel and solution fractions after separation by diffusion method are indicated S and M, respectively. Spectrum of SWCNTs dispersion before separation is shown as a black thin line.

MS separation by permeation method

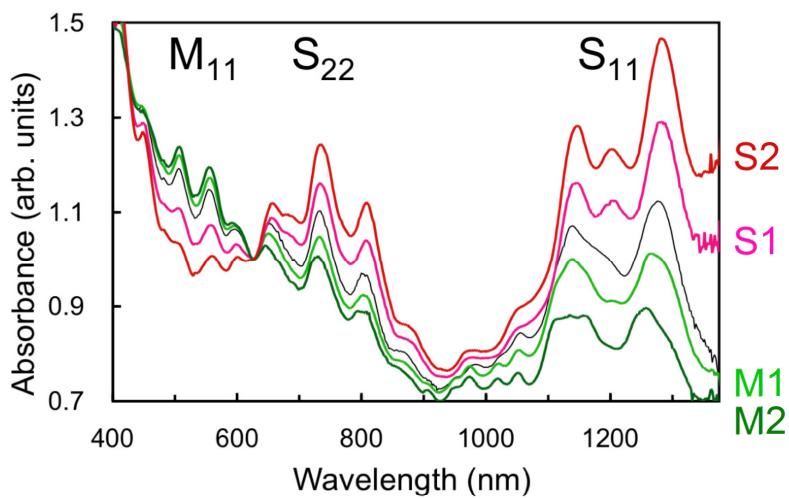


Figure S4. Absorption spectra of HiPco SWCNTs separated by permeation method followed by centrifugation. The semiconducting nanotube-containing gel fraction is denoted S₁, and the metallic nanotube-containing solution fraction is denoted M₁. Further separation of the gel fraction (S₁) by centrifugation affords a second gel fraction (S₂) and solution (M₂) fraction. Black spectrum denotes result for the SWCNT dispersion before separation.

Comparison of SWCNTs density on FET devices

AFM images of FET devices using the separated semiconducting SWCNTs (Figure 4c) and un-separated SWCNTs (Figure S5) exhibited sub-monolayer networks, i.e. surface of the SiO_2/Si substrate was exposed. The average density and lengths of SWCNTs were estimated from the 5 AFM images at separate $2 \mu\text{m} \times 2 \mu\text{m}$ regions. The densities and length were almost same (densities, 39 and $31 \mu\text{m}^{-2}$; lengths, 0.3 and 0.4 μm for the separated and un-separated SWCNTs, respectively). In the both cases, the densities are above the percolation threshold $\rho_{\text{th}} \sim 1/\langle L \rangle^2$, where $\langle L \rangle$ is an average length of nanotubes.²⁶

- (26) Snow, E. S.; Novak, J. P.; Campbell, P. M.; Park, D. *Appl. Phys. Lett.* **2003**, 82, 2145.

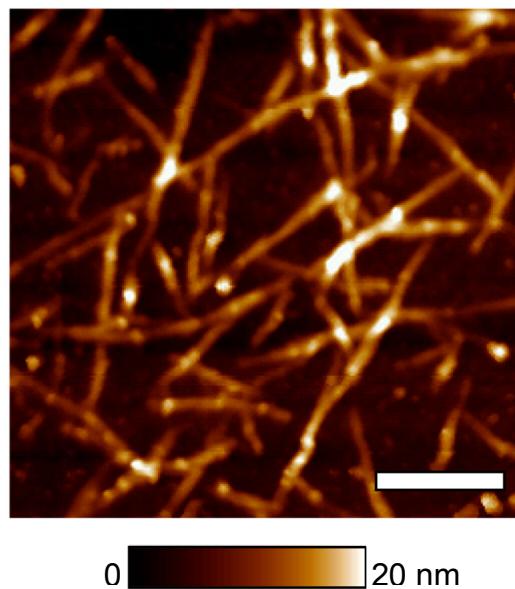


Figure S5. AFM image of un-separated SWCNTs networks on SiO_2/Si substrate (scale bar, 250 nm).

Scalability

We have already been successful in MS separation of 30 mg of SWCNTs by centrifugation method (5×40 mL of 0.15 mg/mL SWCNT-containing gel in five centrifugal bottles were centrifuged at $15000\times g$ for 2 hour at 25°C using F-34-6-38 rotor (Eppendorf)). For industrial production, kilograms of SWCNTs could be separated by simple scale-up. For example, when continuous freeze and squeeze method is applied to 20 m³ of SWCNT-containing gel (Fig. 5S), we can separate 3 kg of SWCNTs in a day.

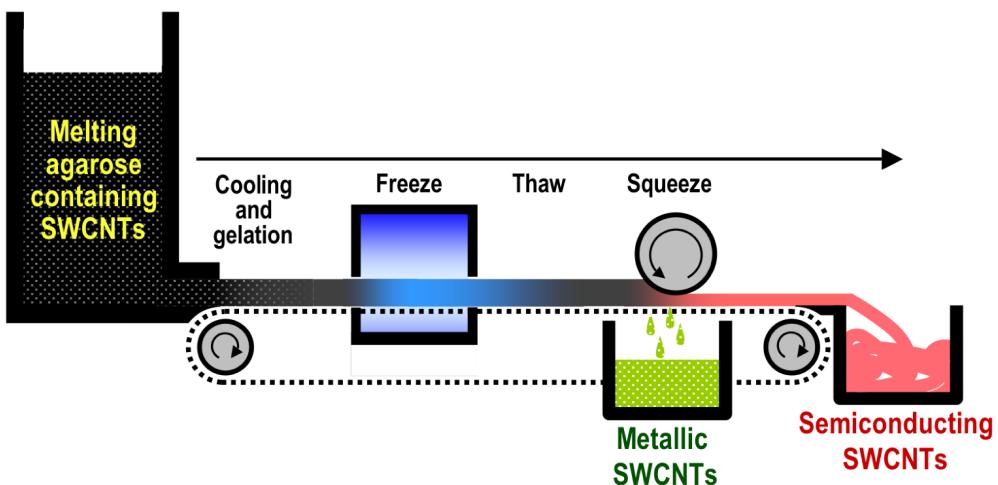


Figure S6. Illustration of continuous MS separation by freeze and squeeze method.