

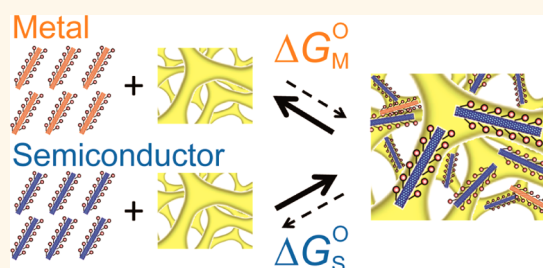
Thermodynamic Determination of the Metal/Semiconductor Separation of Carbon Nanotubes Using Hydrogels

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ABSTRACT The metal/semiconductor separation of single-wall carbon nanotubes (SWCNTs) using hydrogels, such as agarose gel and Sephacryl, together with sodium dodecyl sulfate is one of the most successful techniques necessary for industrial applications. Despite recent improvements in the technique, little is known about the separation mechanism. Here, we show that SWCNTs are reversibly adsorbed onto hydrogels in the presence of sodium dodecyl sulfate. The results enabled us to examine the thermodynamics of the adsorption reaction and thereby elucidate the separation mechanism. The

adsorbability of SWCNTs onto the hydrogels was described by the standard Gibbs free energy for the adsorption, as well as the area of the hydrogels allowing the adsorption. We demonstrated, for the first time, that the free energy of adsorption for semiconducting SWCNTs was 0–12 kJ/mol lower than that for metallic SWCNTs in the temperature range of 290–320 K (*e.g.*, *ca.* –4 kJ/mol for the agarose gel and *ca.* –9 kJ/mol for Sephacryl at 300 K), which permits metal/semiconductor separation. Importantly, the difference in the free energy was attributed to the difference in the enthalpy of adsorption: the enthalpy of adsorption of metallic SWCNTs was *ca.* 70 kJ/mol higher than that of semiconducting SWCNTs. Thus, the enthalpy of adsorption was found to be an important parameter in the metal/semiconductor separation of SWCNTs using hydrogels. In addition, the thermodynamic parameters depended on the hydrogel type and the surfactant concentration, which is most likely why under certain conditions hydrogels and surfactants produce different separations, *e.g.*, chirality-selective or diameter-selective separation.



KEYWORDS: adsorption · carbon nanotube · hydrogel · Langmuir isotherm · separation · thermodynamics

The separation of as-synthesized single-wall carbon nanotubes (SWCNTs) into metallic and semiconducting species is necessary for the application of these materials in various devices or composites. Previous research has led to the development of separation methods such as ultracentrifugation,^{1–4} dielectrophoresis,^{5,6} gel electrophoresis,^{7,8} selective oxidation,⁹ extraction with amines^{10,11} and aromatics,^{12,13} polymer wrapping,¹⁴ DNA wrapping,^{15,16} and protein wrapping.¹⁷ We and other groups have recently discovered and developed metal/semiconductor separation using hydrogel columns in the presence of surfactants; the associated method is simple and high-throughput, which makes it useful for the commercial-scale production of separated SWCNTs.¹⁸ Recently, this method has been applied to other separations such as the chirality- and diameter-selective separation

of SWCNTs. The single-chirality separation of SWCNTs was performed using a Sephacryl column by overloading SWCNTs onto the column¹⁹ or by using binary gradient elution with two surfactants.²⁰ Diameter separation was accomplished using an agarose gel column by controlling the surfactant concentration.^{21,22} Additionally, zigzag SWCNTs were separated using a Sephacryl column with SDS and sodium cholate hydrate.²³

In our exhaustive search for new surfactants that permit separation, sodium dodecyl sulfate (SDS) was found to be the most effective.²⁴ Although some research groups, including our own, have investigated metal/semiconductor separation using hydrogels with SDS,^{3,25,26} little is known about the mechanisms responsible for this phenomenon. Many factors may play a role in the separation mediated by SDS, such as interactions between SWCNTs and SDS and

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interactions between SWCNTs and hydrogels in SDS solution. The interaction between SWCNTs and SDS has been previously investigated in experiments and simulations that show that the conformation of SDS on SWCNTs depends on the concentration of SDS and the diameters of the SWCNTs.^{27–30} It was found that surfactant concentration affects the dispersibility of SWCNTs; for example, some surfactants interact with SWCNTs and disperse SWCNTs into individual tubes below the critical micelle concentration, but they tend to lower the dispersibility of SWCNTs at higher concentrations,²⁷ most likely because of their depletion effect.^{31–34} The difference between metallic and semiconducting SWCNTs under such surfactant conformations was suggested to affect the tubes' interaction with the hydrogels and thus result in separation.²⁵ Furthermore, the interaction of surfactants with hydrogels should be possible. It was reported that SDS interacts with some neutral polymers but most likely not with agarose or dextran;^{35–37} therefore, the conformation of SDS on the hydrogels should be considered to affect the separation of SWCNTs using certain hydrogels. In addition, the concentration of the hydrogels also affects the separation quality, which has been attributed to the dependence of the effective adsorption area of the hydrogels on the hydrogel concentration, as reported in our previous study.²⁶ The eluent flow speed and column length should also be considered as factors involved in the separation in columns.^{26,38}

When metallic and semiconducting SWCNTs are reversibly adsorbed onto hydrogels, the adsorption reaction at equilibrium is determined by thermodynamic parameters, that is, free energy, enthalpy, and entropy, which should provide new insights into the separation mechanism. To our knowledge, no attempt has been made to investigate the thermodynamics of the adsorption reaction. This study focused on the adsorption reaction of metallic and semiconducting SWCNTs onto two hydrogels, an agarose gel and Sephacryl composed of allyl dextran and *N,N'*-methylene bisacrylamide; these hydrogels are well-known to induce metal/semiconductor separation. The adsorption reaction was performed by mixing the SWCNTs with hydrogel beads. In this study, it was assumed that the adsorption occurs between SWCNTs with SDS and the hydrogels. The reversibility of the reaction and its conformation to Langmuir isotherms, as was assumed in our previous studies,^{22,26} enabled us to conduct a thermodynamic analysis of the adsorption reaction at equilibrium. The observed difference between metallic and semiconducting SWCNTs with respect to the adsorption free energy explained the separation of the SWCNTs using the hydrogels. The adsorption was found to be an endothermic reaction, that is, the enthalpy for the reaction was positive, which suggests that the adsorption is an entropy-driven reaction. Thus, our present study offers a powerful approach to

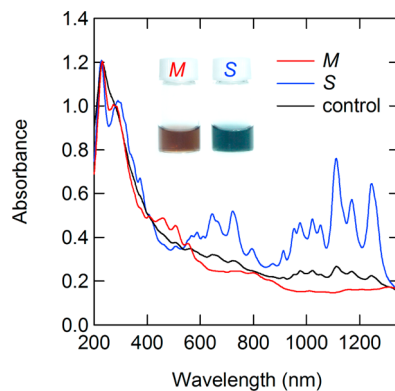


Figure 1. (A) Spectra and photographs of metallic (red line) and semiconducting (blue line) SWCNTs separated using a hydrogel column, and a spectrum of unseparated SWCNTs (black line). *M* and *S* denote metallic and semiconducting SWCNTs, respectively.

evaluating the separation of SWCNTs, even in columns, and should be useful to the further development of the separation technique.

RESULTS

Preparation and Characterization of Metallic and Semiconducting SWCNTs. Metallic and semiconducting SWCNTs were obtained from the raw SWCNT material for thermodynamic analysis of the interaction between the SWCNTs and the hydrogels. Average length of the SWCNTs was determined to be *ca.* 300 nm using atomic force microscopy (see Supporting Information for details, Figure S1). Figure 1 shows the normalized spectra of the unseparated SWCNTs and the metallic and semiconducting SWCNTs separated using the column, where the concentration of the coexisting SDS was measured by a density meter and adjusted to 1 wt % with water (see Supporting Information for details, Figure S2). The unseparated SWCNTs showed characteristic peaks assigned to the M_{11} band at approximately 400–620 nm and to the S_{11} and S_{22} bands at approximately 940–1350 nm and 620–940 nm, respectively. The separated metallic and semiconducting species showed peaks corresponding to the M_{11} band and the S_{11} and S_{22} bands, respectively, indicating that the SWCNTs were well separated (see also a photograph of each solution in Figure 1). The metallic and semiconducting SWCNTs were therefore concluded to be appropriate for a thermodynamic analysis of their interaction with the hydrogels. As observed in Figure 1, peaks at approximately 220 and 280 nm were also observed for each SWCNT solution. The peaks at approximately 280 nm can be accounted for by the π plasmon absorption of the SWCNTs, which was characterized by the collective excitation of the π -electron system polarized along the SWCNT axis, whereas the other peaks at approximately 220 nm can be attributed to the π -electron system polarized across the SWCNT axis.⁴⁰ However,

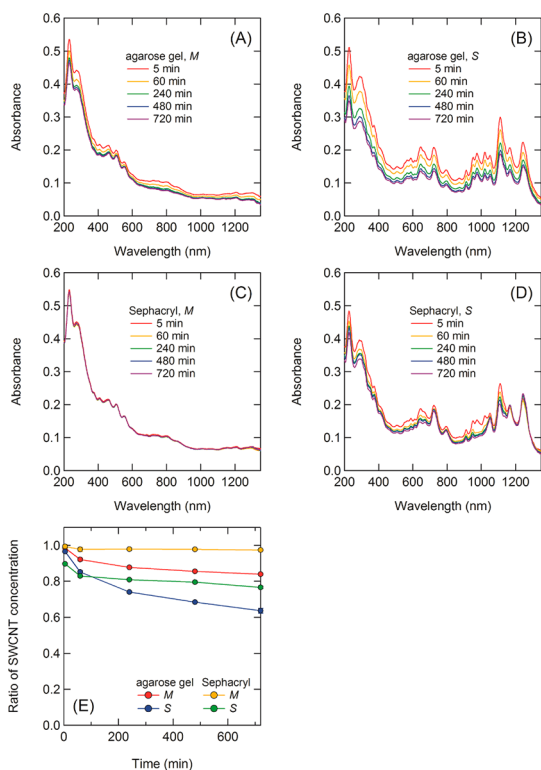


Figure 2. (A–D) Spectral changes in the metallic (A,C) or semiconducting (B,D) SWCNTs upon their adsorption onto the agarose gel (A,B) or Sephacryl (C,D), respectively. (E) Time course of the normalized concentration of unadsorbed SWCNTs onto the hydrogels. *M* and *S* denote metallic and semiconducting SWCNTs, respectively.

the peaks at approximately 220 nm were significantly affected by coexisting amorphous carbon⁴¹ or SDS. Thus, in this study, the absorbance at 280 nm was used to quantify the concentration of SWCNTs.

Time Course of SWCNT Adsorption onto Agarose Gel and Sephacryl. The metallic or semiconducting SWCNTs prepared above were mixed with and adsorbed onto the hydrogels, that is, agarose gel and Sephacryl, at 22 °C for various periods of time. Figure 2A–D shows the time course of the spectra of the unadsorbed metallic and semiconducting SWCNTs after they were mixed with the hydrogels, where the initial concentration of SWCNTs was 5 $\mu\text{g/mL}$ and the volumes of the agarose gel and the Sephacryl were 0.6% (v/v) and 1.7% (v/v), respectively. The spectral intensities decreased with increasing incubation time, which indicates the adsorption of the SWCNTs onto the hydrogels. The metallic and semiconducting SWCNTs showed insignificant changes in their spectral shape, except for the semiconducting SWCNTs mixed with Sephacryl, which demonstrated an apparent spectral change (see also Supporting Information for the normalized spectra, Figure S3). This finding suggests that the chirality-selective adsorption for the semiconducting SWCNTs occurred on Sephacryl, as reported in our previous study.¹⁹ Figure 2E shows the time course of the unadsorbed SWCNT concentration normalized by the

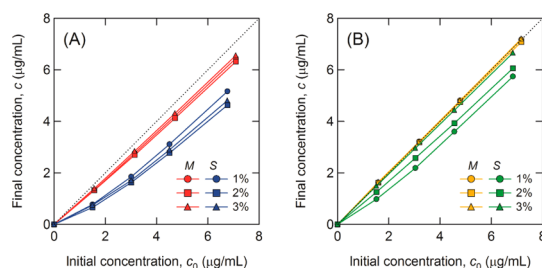


Figure 3. Relationship between final and initial concentration of SWCNTs upon incubation with agarose gel (A) and Sephacryl (B) at 21 °C for over 12 h. Circles, 1 wt % SDS; squares, 2 wt % SDS; triangles, 3 wt % SDS. *M* and *S* denote metallic and semiconducting SWCNTs, respectively.

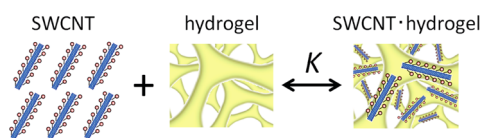
initial concentration, which was determined by using the absorbance of the SWCNTs at 280 nm as mentioned above. For both hydrogels, the concentration of the semiconducting SWCNTs was more significantly reduced compared with that of the metallic SWCNTs throughout the incubation time, which indicates that the hydrogels have a higher adsorbability for semiconducting SWCNTs than for metallic SWCNTs under these conditions.

Adsorption of SWCNTs onto Agarose Gel and Sephacryl at Equilibrium.

The concentration of unadsorbed SWCNTs on the hydrogels at equilibrium, that is, the final concentration, was determined after incubation in various concentrations of SDS over 12 h, during which the adsorption reaction was considered to reach equilibrium. Figure 3 shows the final concentration plotted against the initial concentration at 21 °C. Note that if no SWCNT is adsorbed onto the hydrogels, then the final concentration should be proportional to the initial concentration, as indicated by the dotted lines in Figure 3. The final concentration of the SWCNTs increased monotonically with the initial concentration. Under each condition, the slope of the curves for the semiconducting species was lower than that for the metallic species, which indicates that both of the hydrogels adsorbed the semiconducting SWCNTs more strongly than the metallic SWCNTs. In addition, the slope of the curves tended to increase with the concentration of SDS, which indicates that the amount of SWCNTs adsorbed decreased with the SDS concentration. For Sephacryl, the data for the metallic SWCNTs in 1–3 wt % SDS as well as those for the semiconducting SWCNTs in 3 wt % SDS approached the dotted line (Figure 3B), such that no metallic and no semiconducting SWCNTs were found to be essentially adsorbed onto Sephacryl under the stated conditions.

Application of Langmuir Isotherms to the Adsorption Reaction of SWCNTs onto Agarose Gel and Sephacryl.

The adsorption reaction performed in this study could be described by Langmuir isotherms. SWCNTs are adsorbed onto the hydrogel surfaces, but they should hardly be adsorbed onto a surface prefilled with SWCNTs; thus, the adsorption reaction can be described by Scheme 1, which assigns one equilibrium constant (*K*) between the unadsorbed and adsorbed forms. Throughout



Scheme 1. Model of interaction between SWCNTs with SDS and the hydrogels based on Langmuir isotherm.

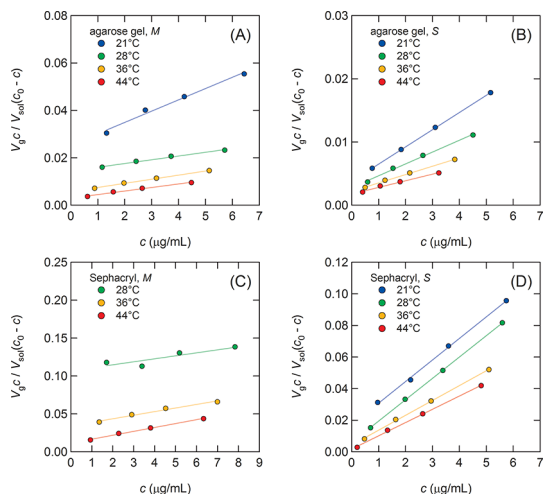


Figure 4. Linear plot of Langmuir isotherms for the adsorption of metallic (A,C) SWCNTs or semiconducting (B,D) SWCNTs onto the agarose gel (A,B) or Sephacryl (C,D) in 1 wt % SDS at various temperatures. The data were fitted by a linear regression. *M* and *S* denote metallic and semiconducting SWCNTs, respectively.

this study, it was assumed that the adsorption occurs between SWCNTs with SDS and the hydrogels but not between pristine SWCNTs and the hydrogels. The reaction satisfies the following equation by assuming a Langmuir isotherm.

$$\theta = \frac{Kc}{1 + Kc} \quad (1)$$

where, in the present case, θ corresponds to the fractional coverage of the hydrogel surface by SWCNTs and c corresponds to the final concentration of unadsorbed SWCNTs at equilibrium.²² As shown in our previous study,^{22,26} the initial SWCNT concentration (c_0) is related to the final concentration (c) as follows:

$$c = c_0 - \theta \alpha \frac{V_{\text{gel}}}{V_{\text{sol}}} \quad (2)$$

where α is the saturation weight of the adsorbed SWCNTs per unit gel volume and V_{gel} and V_{sol} are the volumes of the gel fraction and the aqueous solution fraction, respectively. The two equations can be combined to yield the following equation:

$$\frac{V_{\text{gel}}c}{V_{\text{sol}}(c_0 - c)} = \frac{1}{\alpha K} + \frac{c}{\alpha} \quad (3)$$

Figure 4 shows the data corresponding to the left side of eq 3 against the final concentration (c) in 1 wt % SDS,

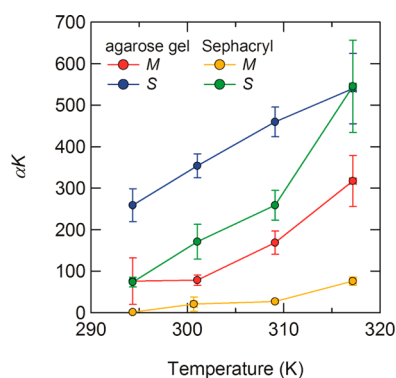


Figure 5. Net adsorbability (αK) of SWCNTs onto the agarose gel and Sephacryl at various temperatures. *M* and *S* denote metallic and semiconducting SWCNTs, respectively.

which is a linear plot of a Langmuir isotherm. If the reaction follows the Langmuir isotherms, then it is necessary that the data satisfy eq 3; indeed, the plots shown in Figure 4 should show linear behavior because α and K are constant. Actually, the plots were found to be almost linear; therefore, the adsorption reaction was concluded to follow the Langmuir isotherms. Similarly, linearity was also observed under the other conditions, that is, 2 wt % and 3 wt % SDS (data not shown). As observed in eq 3, the inverse slopes and inverse intercepts in the plots yield α and αK , respectively, such that α and K can be analytically determined. However, when few SWCNTs are adsorbed onto the hydrogels, $c \approx c_0$, it is difficult to determine α and K precisely, as shown in eq 3. Nonetheless, only the dimensionless adsorption parameter (αK), which indicates the net adsorbability of the SWCNTs onto the hydrogels, can be determined using the following equation, as shown in our previous study.²²

$$\alpha K = \frac{V_{\text{sol}}}{V_{\text{gel}}} \left(\frac{1}{\left(\frac{dc}{dc_0} \right)_{c_0=0}} - 1 \right) \quad (4)$$

Thus, values of αK at each temperature were calculated using eq 3 or eq 4, as shown in Figure 5. The values were found to increase with increasing temperature, which indicates that the net adsorbability of the SWCNTs onto the hydrogels was enhanced with increasing temperature. α and K are more informative parameters for understanding the interaction of SWCNTs with the hydrogels. Table 1 presents the values of α and K at each temperature. Note that the values for metallic SWCNTs adsorbed onto Sephacryl at 21 °C were undetermined because few SWCNTs were adsorbed onto the hydrogels, that is, $c \approx c_0$, under this condition. The values of α for the agarose gel were higher than those for Sephacryl, which indicates that the agarose gel used in this study has a larger area for the adsorption of SWCNTs than Sephacryl. Interestingly,

TABLE 1. Saturation Weight of the Adsorbed SWCNTs per Unit Hydrogel Volume (α) and Equilibrium Constant (K) for the Adsorption of SWCNTs onto Agarose Gel and Sephacryl^a

| temperature (°C) | α (mg/mL) | | | | K (mL/mg) | | | |
|------------------|------------------|---------------|---------------|---------------|-------------|----------|-----------|------------|
| | agarose gel | | Sephacryl | | agarose gel | | Sephacryl | |
| | <i>M</i> | <i>S</i> | <i>M</i> | <i>S</i> | <i>M</i> | <i>S</i> | <i>M</i> | <i>S</i> |
| 21 | 0.887 ± 0.376 | 0.443 ± 0.039 | | 0.085 ± 0.007 | 86 ± 52 | 585 ± 73 | | 863 ± 122 |
| 28 | 0.724 ± 0.068 | 0.583 ± 0.025 | 0.368 ± 0.209 | 0.092 ± 0.011 | 108 ± 14 | 607 ± 42 | 57 ± 35 | 1869 ± 400 |
| 36 | 0.696 ± 0.067 | 0.789 ± 0.035 | 0.181 ± 0.027 | 0.117 ± 0.007 | 243 ± 32 | 583 ± 37 | 148 ± 10 | 2205 ± 278 |
| 44 | 0.826 ± 0.079 | 1.060 ± 0.102 | 0.183 ± 0.018 | 0.129 ± 0.008 | 384 ± 64 | 509 ± 63 | 419 ± 35 | 4220 ± 822 |

^a *M* and *S* denote metallic and semiconducting SWCNTs, respectively.

the values of α for the metallic SWCNTs were essentially constant and independent of temperature, whereas those for the semiconducting SWCNTs showed a tendency to increase with increasing temperature; these results may indicate that the form of the semiconducting SWCNTs with SDS changes with temperature, in contrast to the metallic SWCNTs. Here, it should be noted that the equilibrium constant (K) is related to some thermodynamic parameters, as will be discussed later. Most importantly, the values of K for the adsorption of SWCNTs onto both of the hydrogels were found to increase with increasing temperature, except for the adsorption of semiconducting SWCNTs onto the agarose gels. The values of K for the metallic SWCNTs were found to be lower than those for the semiconducting SWCNTs. Interestingly, the values of K for the semiconducting SWCNTs adsorbed onto the agarose gels were lower than those for the adsorption onto Sephacryl, although the values of net adsorbability (αK) for the semiconducting SWCNTs onto the agarose gels were higher than those for the adsorption onto Sephacryl, as shown in Figure 5. The higher net adsorbability of the semiconducting SWCNTs onto the agarose gels is therefore clearly dominated by the contribution of α ; recall that the values of α for the agarose gels were significantly higher than those for Sephacryl (Table 1). Thus, despite the lower equilibrium constant, the agarose gel has a higher net adsorbability for semiconducting SWCNTs than does Sephacryl.

The equilibrium constant was used to determine the fractional coverage of the hydrogel surface by SWCNTs *via* eq 1. Figure 6 shows the fractional coverage against various concentrations of SWCNTs at 21, 28, 36, and 44 °C. At 21 and 28 °C, the coverage of metallic SWCNTs for both hydrogels was found to be less than 0.5, even in 8 μ g/mL SWCNTs, whereas that of the semiconducting SWCNTs for both hydrogels was greater than 0.8. At 44 °C, the coverage of metallic SWCNTs also reached approximately 0.8 for 8 μ g/mL SWCNTs, whereas the coverage of semiconducting SWCNTs for Sephacryl was approximately 1.0. Thus, Sephacryl showed higher coverage for semiconducting

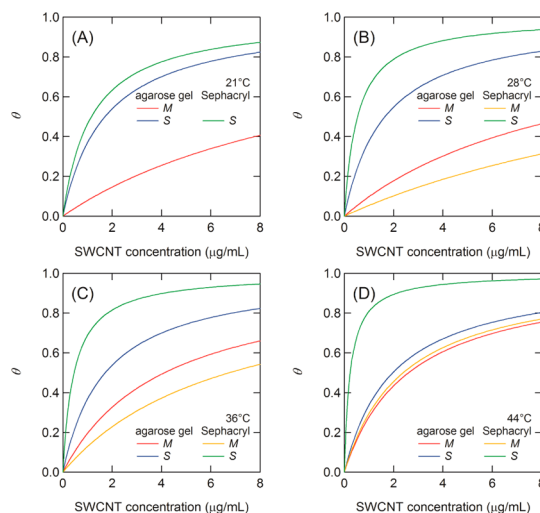


Figure 6. Fractional coverage of the hydrogel surface by the SWCNTs at 21 °C (A), 28 °C (B), 36 °C (C) and 44 °C (D). *M* and *S* denote metallic and semiconducting SWCNTs, respectively.

SWCNTs throughout the wide SWCNT concentration and temperature range.

Thermodynamic Analysis of SWCNT Adsorption onto Agarose Gel and Sephacryl. The equilibrium constant (K) provides insight into the thermodynamics of the adsorption reaction because it is related to certain thermodynamic parameters. The enthalpy for the reaction is generally expressed using the equilibrium constant as shown in the following equation, which is called the van't Hoff equation:

$$\Delta H^\circ = -R \frac{\partial \ln K}{\partial (1/T)} \quad (5)$$

where ΔH° is the standard molar enthalpy for the reaction with K , and R and T are the universal gas constant and absolute temperature, respectively. In the present study, the units of ΔH° derived from the van't Hoff equation should be noted: ΔH° is the enthalpy per mole cooperative unit for the adsorption of SWCNTs onto the hydrogels. The concept of a cooperative unit often appears in research fields concerning protein folding; in protein folding, a cooperative unit is used to define the protein domain that folds cooperatively into

its characteristic structure.⁴² Similarly, for the adsorption of SWCNTs onto hydrogels, a cooperative unit helps to understand the adsorption reaction of SWCNTs onto the hydrogels. If each entire SWCNT is adsorbed cooperatively onto the hydrogels, the mole cooperative unit is defined as one SWCNT; specifically, the thermodynamic parameters are expressed per mole of SWCNT. In contrast, if the hydrogels have adsorption sites where SWCNTs are adsorbed cooperatively, the mole cooperative unit is defined as the SWCNT domain that is adsorbed onto the adsorption sites; specifically, the thermodynamic parameters are expressed per mole of SWCNT domain. However, the cooperative unit used for the adsorption of SWCNTs was difficult to determine experimentally at the time of this study.

Figure 7A shows a logarithm of K against the reciprocal of T , which is called a van't Hoff plot. Each plot shows nearly linear behavior and negative slopes, except that for the semiconducting SWCNTs with the agarose gel. Although the standard molar enthalpy calculated from a van't Hoff plot is generally less accurate than that obtained using a calorimeter, the enthalpy for the adsorption reaction was estimated using eq 5 (Table 2), where the differential coefficients were obtained by the linear fits to the data shown in Figure 7A. The enthalpy for each condition was positive, except that for the semiconducting SWCNTs with the agarose gel, which means that the adsorption is basically an endothermic reaction. It is important to note that the enthalpy values for the metallic SWCNTs were approximately 70 kJ/mol higher than those for the semiconducting SWCNTs; this result is the first

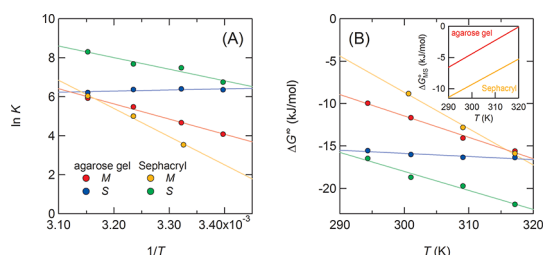


Figure 7. (A) van't Hoff plots for the adsorption reaction described by the Langmuir isotherm; (B) ΔG° for the adsorption of SWCNTs onto the hydrogels. M and S denote metallic and semiconducting SWCNTs, respectively. The data were fitted by a linear regression. Inset, ΔG°_{MS} for agarose gel and Sephacryl obtained using the fitted data of ΔG° .

to show the thermodynamic difference between metallic and semiconducting SWCNTs with respect to their adsorption onto hydrogels. In addition, the enthalpy values for Sephacryl were found to be higher than those for the agarose gel, which indicates that the adsorption reaction for Sephacryl is more endothermic.

Here, the standard Gibbs free energy and standard molar entropy for the adsorption were obtained using the equilibrium constant or the standard molar enthalpy as shown below. The chemical potentials of the SWCNTs in the solutions (μ_i) and on the hydrogels (μ_{gel}) are defined as follows:

$$\mu_i = \mu_i^\circ + RT \ln a_i \approx \mu_i^\circ + RT \ln \frac{m_{\text{SWNT}}}{m_{\text{H}_2\text{O}}} \quad (6)$$

$$\mu_{\text{gel}} = \mu_{\text{gel}}^\circ + RT \ln \frac{\theta}{1 - \theta} = \mu_{\text{gel}}^\circ + RT \ln Kc \quad (7)$$

where μ_i° and μ_{gel}° are the standard chemical potentials of the SWCNTs in the solutions and on the hydrogels, respectively; a_i is the mole fraction of SWCNTs in the solutions; m_{SWNT} and $m_{\text{H}_2\text{O}}$ are the molar concentration of the cooperative unit of SWCNTs and the molar concentration of water, *ca.* 55.5 M, in the solutions, respectively. Note that when the coverage (θ) is 0.5, the chemical potential on the hydrogels (μ_{gel}) is equal to the standard chemical potential (μ_{gel}°).⁴³ At equilibrium, the chemical potential in the solutions (μ_i) should be equal to that on the hydrogels (μ_{gel}); therefore, the standard Gibbs free energy for the adsorption (ΔG°) is given by the following equation:

$$\begin{aligned} \Delta G^\circ &= \mu_{\text{gel}}^\circ - \mu_i^\circ \\ &\approx -RT \ln \frac{Kc m_{\text{H}_2\text{O}}}{m_{\text{SWNT}}} \quad (8) \\ &= -RT (\ln m_{\text{H}_2\text{O}} M_{\text{SWNT}} + \ln K) \end{aligned}$$

where M_{SWNT} is the apparent molecular weight of the cooperative unit of SWCNTs in the solutions. As mentioned above, the cooperative unit of SWCNTs was difficult to determine; thus, the parameter ($\Delta G'^\circ$), which is obtained by subtraction of the unknown constant term ($-RT \ln m_{\text{H}_2\text{O}} M_{\text{SWNT}}$) from the standard Gibbs free energy (ΔG°), was introduced in addition to ΔG° as follows.

$$\begin{aligned} \Delta G'^\circ &= \Delta G^\circ + RT \ln m_{\text{H}_2\text{O}} M_{\text{SWNT}} \\ &= -RT \ln K \quad (9) \end{aligned}$$

TABLE 2. Thermodynamic Parameters for the Adsorption of SWCNTs onto Agarose Gel and Sephacryl at 27°C (300 K)^a

| gel | SWCNT | ΔH° (kJ/mol) | ΔS° (J/K/mol) | ΔG° (kJ/mol) | ΔG°_{MS} (kJ/mol) |
|-------------|-------|---------------------------|----------------------------|---------------------------|--------------------------------|
| agarose gel | M | 64.0 ± 12.0 | 251.5 ± 37.4 | -11.5 ± 0.8 | -4.4 ± 0.8 |
| | S | -4.9 ± 3.5 | 36.6 ± 11.6 | -15.9 ± 0.2 | |
| Sephacryl | M | 119.4 ± 33.4 | 427.0 ± 105.4 | -8.7 ± 1.8 | -9.3 ± 1.8 |
| | S | 49.3 ± 3.5 | 224.3 ± 12.0 | -18.0 ± 0.4 | |

^a M and S denote metallic and semiconducting SWCNTs, respectively.

Note that $\Delta G'^{\circ}$ is greater than ΔG° , that is, $\Delta G'^{\circ} > \Delta G^{\circ}$. In addition, the standard molar entropy for the adsorption reaction is simply described as follows:

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} = \frac{\Delta H^{\circ} - \Delta G'^{\circ}}{T} + R \ln m_{\text{H}_2\text{O}} M_{\text{SWNT}} \quad (10)$$

Similarly to $\Delta G'^{\circ}$, the parameter ($\Delta S'^{\circ}$), which is related to the entropy, was defined as follows:

$$\Delta S'^{\circ} = \Delta S^{\circ} - R \ln m_{\text{H}_2\text{O}} M_{\text{SWNT}} = \frac{\Delta H^{\circ} - \Delta G'^{\circ}}{T} \quad (11)$$

It should also be noted that $\Delta S'^{\circ}$ is less than ΔS° ; that is, $\Delta S'^{\circ} < \Delta S^{\circ}$. Here, $\Delta G'^{\circ}$ and $\Delta S'^{\circ}$ at 27 °C (300 K) could be estimated using these equations as shown in Table 2. It is important to note that $\Delta S'^{\circ}$ was positive under each condition. Thus, it was concluded that the adsorption of SWCNTs onto the hydrogels is an entropy-driven reaction; that is, $\Delta H^{\circ} > 0$ and $\Delta S^{\circ} > 0$, at 27 °C (300 K). The quality of the metal/semiconductor separation will be described as the difference in ΔG° between metallic SWCNTs and semiconducting SWCNTs because it is related to the ratio between K for semiconducting SWCNTs and that for metallic SWCNTs, that is, K_S/K_M , and is also expressed by the difference in $\Delta G'^{\circ}$ as shown in the following equation:

$$\begin{aligned} \Delta G_{\text{MS}}^{\circ} &= \Delta G_S^{\circ} - \Delta G_M^{\circ} = -RT \ln(K_S/K_M) \\ &= \Delta G_S'^{\circ} - \Delta G_M'^{\circ} \end{aligned} \quad (12)$$

where $\Delta G_{\text{MS}}^{\circ}$ is defined as the difference in the standard Gibbs free energy between metallic SWCNTs and semiconducting SWCNTs and the subscripts M and S denote the metallic and semiconducting SWCNTs, respectively. Figure 7B shows $\Delta G'^{\circ}$ calculated using eq 9, which tends to decrease with temperature. Interestingly, the free energies for the metallic and semiconducting SWCNTs with the agarose gel were found to overlap each other at approximately 320 K, which indicates that the metal/semiconductor separation using the agarose gel occurred to an insignificant degree under these conditions, which was confirmed by batch separation (see Supporting Information for details, Figure S4C). Using the fitted data, the relationship between $\Delta G_{\text{MS}}^{\circ}$ and temperature was obtained (Figure 7B, inset). Note that the value of $\Delta G_{\text{MS}}^{\circ}$ for Sephacryl was more negative than that for the agarose gel, for example, *ca.* -4 kJ/mol for agarose gel and *ca.* -9 kJ/mol for Sephacryl at 300 K (Table 2). In addition, $\Delta G_{\text{MS}}^{\circ}$ for both the hydrogels was found to increase with temperature to a similar extent. These results indicate that Sephacryl mediates a higher quality of separation than agarose throughout the measured temperature range, which was actually observed in the batch separation (see Supporting Information, Figure S4).

It is important to study the effect of SDS on the free energy to evaluate the interaction of SWCNTs with the hydrogels in SDS solution. Figure 8 plots $\Delta G'^{\circ}$ for the

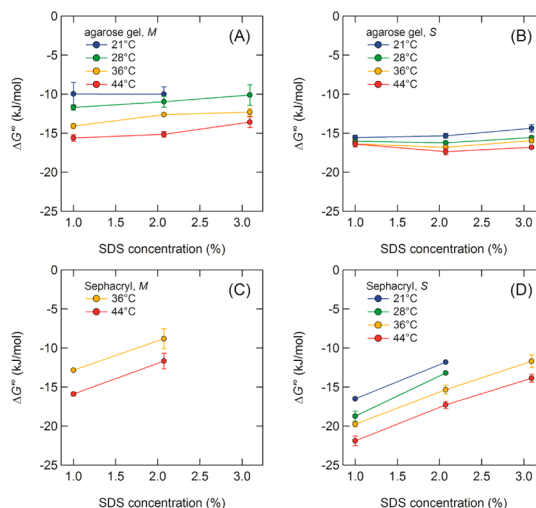


Figure 8. SDS concentration dependence of $\Delta G'^{\circ}$ for the adsorption of metallic SWCNTs or semiconducting SWCNTs onto the agarose gel (A,B) or Sephacryl (C,D) at various temperatures. M and S denote metallic and semiconducting SWCNTs, respectively.

adsorption of SWCNTs onto the hydrogels at various concentrations of SDS. Overall, $\Delta G'^{\circ}$ had a tendency to increase with increasing SDS concentration, and this tendency was almost independent of temperature. The effect of SDS on the free energy can be described by another parameter, that is, the transfer free energy, which generally indicates the degree of stabilization of an object by a solute.⁴⁴ Although the dispersibility of SWCNTs generally depends on the surfactant concentration,³¹ the dispersibility was retained in 1–3 wt % SDS solution under these conditions (see Supporting Information, Figure S5); therefore, the debundled state of SWCNTs seems to be insignificantly affected by the SDS concentration. Thus, it was assumed that the standard chemical potential of the SWCNTs in SDS solution but not on the hydrogels is independent of the SDS concentration. The transfer free energy per molar concentration of SDS for the SWCNTs on the hydrogels (ΔG_{tr}) is expressed by $\partial \Delta G'^{\circ} / \partial m_{\text{SDS}}$, which is equal to $\partial \Delta G'^{\circ} / \partial m_{\text{SDS}}$, as follows:

$$\Delta G_{\text{tr}} = \frac{\partial \Delta G'^{\circ}}{\partial m_{\text{SDS}}} = -RT \frac{\partial \ln K}{\partial m_{\text{SDS}}} = \frac{\partial \Delta G'^{\circ}}{\partial m_{\text{SDS}}} \quad (13)$$

where m_{SDS} is the molar concentration of SDS. The transfer free energy was obtained from the slope of $\Delta G'^{\circ}$ against m_{SDS} as the average of the data for each temperature. It was found that the transfer free energy of the SWCNTs on Sephacryl was significantly higher than that of the SWCNTs on agarose (Table 3), which indicates that SDS destabilizes the SWCNTs more substantially on Sephacryl than on the agarose gels.

DISCUSSION

Since our discovery of the metal/semiconductor separation of SWCNTs using hydrogels with SDS in 2008,⁷ this technique has been further developed by us

TABLE 3. Transfer Free Energy of SWCNTs Adsorbed on Agarose Gel or Sephacryl in SDS Solution^a

| gel | SWCNT | ΔG_{tr} (kJ/mol/M) |
|-------------|-------|----------------------------|
| agarose gel | M | 18 ± 6 |
| | S | 5 ± 3 |
| Sephacryl | M | 109 ± 15 |
| | S | 123 ± 7 |

^a M and S denote metallic and semiconducting SWCNTs, respectively.

and others.^{3,18,45} Furthermore, both single-chirality separation of SWCNTs and diameter separation of SWCNTs have recently been achieved.^{19,21,38} The mechanism underlying these separations was, however, unclear. In this study, it was found that the adsorption of SWCNTs onto hydrogels is reversible, as shown in Scheme 1, because the adsorption reaction followed a Langmuir isotherm (Figure 4); therefore, the adsorption reaction can be described by thermodynamics, which should be a powerful approach for understanding the mechanism. The equilibrium constant (K) for metallic SWCNTs was lower than that for semiconducting SWCNTs (Table 1), which mainly accounts for the metal/semiconducting separation. The difference in K is likely the result of the difference in the conformation of SDS on each type of SWCNT.^{25,46,47} In addition to the equilibrium constant, the saturation weight of the adsorbed SWCNTs per unit hydrogel volume, which is denoted by α , should also be taken into account when evaluating the separation because the net adsorbability (αK) is given by both K and α ; actually, the value of α depended more on temperature for the semiconducting SWCNTs than for the metallic SWCNTs (Table 1), which affects the net adsorption at each temperature (Figure 5). The higher net adsorbability of the semiconducting SWCNTs onto the agarose gel throughout the studied temperature range was caused by higher values of α and K ; in contrast, the lower net adsorbability of the metallic SWCNTs onto Sephacryl was caused by lower values of α and K (Table 1). Thus, the metal/semiconducting separation of SWCNTs can be attributed to the difference in the values of α and K for each SWCNT type and for each hydrogel.

However, K and α are likely insufficient to describe the separation, particularly in columns, because the separation is typically performed within several tens of minutes;^{18,38} hence, the adsorption in the hydrogel column is considered to be a nonequilibrium process, as shown in Figure 2. Such adsorption is described by the integrated kinetic Langmuir equation.⁴⁸ If it is simply expressed by a single exponential function, then the distribution of SWCNTs in the column is that reported in our previous studies;²⁶ indeed, the quality of the separation is affected by the flow speed and adsorption rate (k) as well as α and K . Because K should be basically connected with k , kinetic analyses should be performed in the future to evaluate the

metal/semiconductor separation thermodynamically and kinetically in greater detail, which will clarify how the thermodynamics of the adsorption reaction are related with the kinetics. Moreover, size-exclusion chromatography of SWCNTs can also be performed, which affects the separation in the column to some extent.^{3,23} It should be noted that the thermodynamic analysis in this study did not account for the chirality or diameter of the SWCNTs. In fact, chirality selectivity or diameter selectivity in SWCNT separation using the hydrogels in the presence of SDS has been reported, as shown in Supporting Information, Figure S3.^{19,21,38} Such separations of SWCNTs can be attributed to the difference in the equilibrium constant of each SWCNT type, which is also described as the difference in the ratio of the probability of trapping events to that of detrapping events upon the interaction of SWCNTs with the hydrogels.³⁸ The equilibrium constants for each chiral SWCNT should be determined by preparing high-quality single-chirality SWCNTs.¹⁹ Future studies are necessary to determine these constants.

Thermodynamic analysis provided new insights for evaluating the interaction of SWCNTs and hydrogels. The difference in the standard Gibbs free energy (ΔG_{MS}°), which affects the quality of the metal/semiconducting separation, was mainly derived from the enthalpy; the higher enthalpy of metallic SWCNTs relative to that of semiconducting SWCNTs resulted in increases in $|\Delta G_{MS}^{\circ}|$ with decreasing temperature, as shown in Figure 7B. Actually, the separation quality is improved by decreasing the temperature, unless semiconducting SWCNTs remain unadsorbed or SDS is aggregated because of an excessively low temperature (see also Supporting Information, Figure S4).⁴⁹ Thus, enthalpy is an important parameter affecting the separation quality, which in turn depends on temperature. The enthalpy for the adsorption of substances onto surfaces is generally negative because the adsorption results in a decrease in entropy. However, the enthalpy for the adsorption of SWCNTs onto the hydrogels was found to be positive in this study (Table 2); that is, the adsorption was an endothermic reaction. The enthalpy for the metallic SWCNTs was approximately 70 kJ/mol higher than that for the semiconducting SWCNTs for both hydrogels, which makes this study the first thermodynamic report to imply a difference between the two SWCNT species with respect to their interaction with hydrogels. The standard Gibbs free energy (ΔG°) was lower than the standard molar enthalpy (ΔH°); that is, $\Delta G^{\circ} < \Delta H^{\circ}$; thus, the standard molar entropy (ΔS°) should be positive; hence, the adsorption reaction was concluded to be entropy-driven. It is presently unclear how the negative entropy needed for the adsorption reaction is compensated for, but a possible mechanism is the rearrangement of SDS on the SWCNTs. Because SDS can be adsorbed around SWCNTs,⁵⁰ the entropy of the

system is likely to be decreased upon the adsorption of SDS onto SWCNTs. If the rearrangement of SDS on the SWCNTs occurs when SWCNTs with SDS are adsorbed onto the hydrogels, the entropy can be compensated for by the adsorption reaction. In addition, the desorption of SDS from the SWCNTs may also be involved in the entropy. The different entropies between the metallic and semiconducting SWCNTs are likely accounted for by the difference in the conformation of SDS on SWCNTs,²⁵ although the mechanism responsible for the conformational changes is unclear. In any case, SDS should play an important and specific role in the thermodynamics of the adsorption reaction. In fact, our group reported that only a few surfactants, including SDS, permit the separation of SWCNTs using agarose gels, which indicates the specificity of SDS in the interaction with SWCNTs.²⁴

The transfer free energy (ΔG_{tr}) presented in Table 3 implies that SDS interacts with Sephacryl to a greater extent than with agarose gel because the transfer free energy of the SWCNTs on Sephacryl was substantially higher than that of SWCNTs on the agarose gel (Table 3). Some reports revealed a lack of an interaction or an insignificant interaction of SDS with agarose gel and dextran;^{35–37} therefore, they hardly explain the difference in the transfer free energy. Here, recall that Sephacryl is composed of allyl dextran and *N,N'*-methylene bisacrylamide. SDS more likely interacts with the hydrophobic moiety of Sephacryl but not with their dextran moiety, which may permit the destabilization of SWCNTs on Sephacryl. Additionally, the conformation of SDS on the SWCNTs may also be associated with the change in the chemical potential of the SWCNTs on the hydrogels because the conformation likely depends on the SDS concentration, as indicated by molecular dynamics simulations.^{27–30} As mentioned above, the chemical potential of the SWCNTs in the solution was assumed to be independent of the SDS concentration because the adsorbability was retained in 1–3% SDS. The conformational changes of SDS on the SWCNTs depending on the SDS concentration may more dramatically affect the chemical potential of the SWCNTs on the hydrogels than that in the solution. Figure 9 schematically summarizes each chemical potential of the SWCNTs in the presence of SDS at 300 K; note that the chemical potential in solution (μ_i°) for metallic and semiconducting SWCNTs is adjusted to the same level for convenience. The figure also shows that the agarose gel differed from Sephacryl with respect to the chemical potential of SWCNTs and with respect to the effect of SDS on the chemical potential.

It is important to consider the units of the thermodynamic parameters obtained in this study. The standard Gibbs free energy and the standard molar entropy were calculated using the values of standard molar enthalpy. Recall that the standard molar enthalpy (ΔH°) is obtained from a van't Hoff plot such that

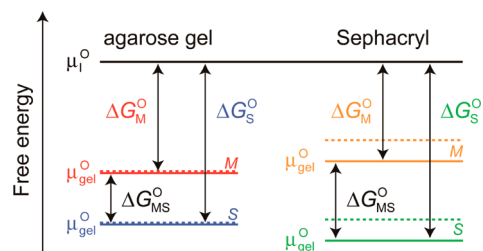


Figure 9. Schematic free energy diagram for the adsorption of metallic and semiconducting SWCNTs onto agarose gel and Sephacryl in the presence of SDS at 300 K. *M* and *S* denote metallic and semiconducting SWCNTs, respectively. Dotted lines indicate each chemical potential at a higher concentration of SDS. Note that the chemical potential in the solution (μ_i°) for metallic and semiconducting SWCNTs is adjusted to the same level for convenience.

ΔH° is the enthalpy per mole cooperative unit for the adsorption; therefore, the values of all thermodynamic parameters, that is, ΔG° , ΔS° , and ΔH° are based on the cooperative unit. As mentioned above, the cooperative unit of SWCNTs for adsorption was difficult to determine experimentally at the time of this study. If the mole cooperative unit is defined as one SWCNT, the length of SWCNTs should affect the thermodynamic parameters. In contrast, if the mole cooperative unit is defined as the SWCNT domain that is adsorbed onto the adsorption sites, the length of SWCNTs likely has no effect on the thermodynamic parameters. This point of view is important to consider when trying to determine how SWCNTs behave upon interacting with the hydrogels, that is, whether SWCNTs behave just as one tube on the hydrogels or as fragmented tubes interacting with every adsorption site of the hydrogels. This issue may possibly be resolved by conducting calorimetric analyses such as those performed in studies determining the cooperative unit for protein folding.⁴²

SDS was used in this study to investigate the adsorption reaction of SWCNTs onto hydrogels because SDS is the most effective surfactant for separating SWCNTs.²⁴ Other surfactants or mixtures of surfactants are also available for various separations such as chirality- or diameter-selective separation.^{20,22} Although it is not easy to elucidate the mechanism underlying this complex separation, for mixed surfactant systems in particular, the thermodynamic analysis proposed in this paper will provide a powerful approach.

CONCLUSION

The thermodynamics of the interaction between SWCNTs and hydrogels were analyzed for the first time based on Langmuir isotherms. It was inferred that the adsorption of SWCNTs onto the hydrogels used in this study is an entropy-driven process because it was found to be an endothermic reaction. The higher enthalpy of metallic SWCNTs than that of semiconducting SWCNTs resulted in a difference in the free energy for adsorption of the respective SWCNT types, which

accounted for the metal/semiconductor separation. Sephacryl showed a significant difference in the free energy between the metallic and semiconducting SWCNTs over a wide temperature range; hence, it permits high-quality separation. The agarose gel showed a weaker dependence of the free energy on the surfactant concentration; hence, it permits stable separation against fluctuations in the concentration. The thermodynamic analysis conducted in this study

using van't Hoff plots yielded the thermodynamic parameters for the adsorption reaction, which are expressed in cooperative units of SWCNTs adsorbed onto the hydrogels. Thus, this study provides new insight, that is, from a thermodynamic perspective, into the adsorption reaction and separation of SWCNTs using hydrogels and indicates further problems to be solved, such as the identification of mole cooperative units of SWCNTs for the adsorption.

EXPERIMENTAL SECTION

Dispersion of SWCNTs. Raw SWCNTs produced by high-pressure catalytic CO (HiPco) decomposition were purchased from Nano-Integris and were used as the starting materials for the following methods. Aliquots of 30 mg of HiPco SWCNTs were pre-dispersed in 30 mL of purified water with 1 wt % SDS (Sigma-Aldrich) using an ultrasonic processor (Nanoruptor NR-350, Cosmo Bio) for 1 min at a power of 350 W. Subsequently, the solutions were dispersed using an ultrasonic homogenizer (Sonifire 250D, Branson) equipped with a 0.5-in. flat tip for 1 h at a power density of 20 W cm^{-2} . To prevent heating during sonication, the bottle containing the sample solution was immersed in a water bath at 18°C . The dispersed sample solution was centrifuged at $210,000 \times g$ for 1 h using an ultracentrifuge (S80AT3 rotor, Hitachi Koki) to remove the residue of the catalytic metal particles, the nanotube bundles and other impurities. The upper 70% of the supernatant was collected as a debundled SWCNT solution.

Preparation of Metallic and Semiconducting SWCNTs. Metallic and semiconducting SWCNTs in 1 wt % SDS were prepared using an open column containing hydrogels formed from cross-linked dextran, Sephacryl (Sephacryl S-200 HR, GE Healthcare), which is composed of allyl dextran and *N,N'*-methylene bisacrylamide. Ten milliliters of the debundled SWCNT solution prepared as mentioned above were applied to the top of the column containing ca. 30 mL of Sephacryl in 1 wt % SDS. The metallic species were obtained as the flow-through fraction by the addition of 1 wt % SDS. The subsequent addition of 5 wt % SDS allowed the semiconducting SWCNTs to be eluted. The SDS concentration of the semiconducting SWCNT solutions was measured by a density meter (DMA 5000M, Anton Paar) and adjusted to 1 wt % with water.

Measurement of Absorption Spectra. The absorption spectra of the SWCNTs were recorded over a wavelength range of 200–1350 nm using a UV–vis–NIR spectrophotometer (UV-3600, Shimadzu) with a quartz cell that had a path length of 10 mm. In the present study, the absorption peaks at approximately 940–1350 nm and 620–940 nm were assigned to the first and second optical transitions of the semiconducting species, which were designated as the S_{11} and S_{22} bands, respectively, whereas the absorption peak at approximately 400–620 nm was assigned to the first optical transition of metallic SWCNTs, designated as the M_{11} band.^{26,39}

Adsorption of SWCNTs onto Gels. To assess the adsorbability of the SWCNTs onto the gels, batch adsorption of the materials was conducted as follows: the gel beads were mixed with the dispersed SWCNT solutions in the presence of various concentrations of SDS at various temperatures by gentle rotation for different periods of time, and subsequently the mixtures were briefly centrifuged ($500 \times g$ for 1 min). Finally, the resultant supernatants were collected as the unadsorbed fractions. The absorbance of the fractions was used to assess the concentration of the SWCNTs. The gels used here were agarose gel (Sephacryl 2B, GE Healthcare) and Sephacryl.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Determination of SWCNT length using atomic force microscope. Determination of SDS concentration in SWCNT solution using a density meter; absorption spectra of the metallic and semiconducting SWCNTs normalized at 280 nm upon their adsorption onto the hydrogels; batch separations of the SWCNTs using the hydrogels; dispersibility of SWCNTs in SDS solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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