

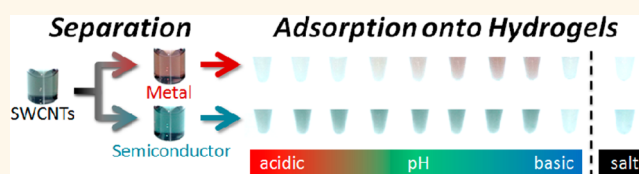
# pH- and Solute-Dependent Adsorption of Single-Wall Carbon Nanotubes onto Hydrogels: Mechanistic Insights into the Metal/Semiconductor Separation

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**ABSTRACT** The gel separation of single-wall carbon nanotubes (SWCNTs) suspended in sodium dodecyl sulfate (SDS) is expected to be one of the most successful methods of large-scale and high-purity separation. Understanding the mechanism of the gel separation helps improve the quality and quantity of separation and reveals the colloidal behaviors of SWCNTs, which reflects their band structures.

In this study, we characterize the pH- and solute-dependent adsorption of SWCNTs onto agarose and Sephacryl hydrogels and provide a mechanistic model of the metal/semiconductor separation. The adsorbability of SWCNTs is substantially reduced under acidic pH conditions. Importantly, the pH dependence differs between metallic and semiconducting species; therefore, the adsorbability is related to the band-structure-dependent oxidation of the SWCNTs. Oxidation confers positive charges on SWCNTs, and these charges enhance the electrostatic interactions of the SWCNTs with SDS, thereby leading to the condensation of SDS on the SWCNTs. This increase in SDS density reduces the interactions between the SWCNTs and hydrogels. Under highly basic conditions, such as pH  $\sim$ 12.5, or in the presence of salts, the adsorption is dissociative because of the condensation of SDS on the SWCNTs through electrostatic screening by counterions. Desorption of the SWCNTs from the hydrogels due to the addition of urea implies a hydrophobic interface between SDS-dispersed SWCNTs and the hydrogels. These results suggest that the metal/semiconductor separation can be explained by the alteration of the interaction between SDS-dispersed SWCNTs and the hydrogels through changes in the conformation of SDS on the SWCNTs depending on the SWCNTs' band structures.



**KEYWORDS:** adsorption · carbon nanotube · hydrogel · pH · salt · separation · urea

The high-purity and large-scale separation of single-wall carbon nanotubes (SWCNTs) into metallic and semiconducting species is a critical technique that enables their applications as electronic devices and medical materials. Various approaches have been used for this separation,<sup>1,2</sup> such as ultracentrifugation,<sup>3–6</sup> dielectrophoresis,<sup>7,8</sup> gel electrophoresis,<sup>9,10</sup> selective oxidation,<sup>11</sup> extraction with amines<sup>12</sup> and aromatics,<sup>13,14</sup> synthetic polymer wrapping,<sup>15,16</sup> biopolymer wrapping,<sup>17,18</sup> and a two-phase system with polymers.<sup>19</sup> We and others have discovered and developed hydrogel-based separation techniques,<sup>20</sup> including metal/semiconductor separations,<sup>5,21,22</sup> diameter-based separations,<sup>23–25</sup> length-based separations,<sup>26,27</sup> chirality separations,<sup>28–30</sup> and purification.<sup>24</sup> These hydrogel-based methods are expected to lead to

breakthroughs in the industrial applications of SWCNTs because of their simplicity, scalability, and amenability to high-throughput separations.

Our previous investigation showed that sodium dodecyl sulfate (SDS) and its analogues are almost the only materials that can achieve the hydrogel-based separations.<sup>31</sup> Therefore, these results suggest that the behavior of SDS on the SWCNT sidewalls is a critical factor that enables separation. However, less is known about which parameters lead to differences in the interactions of SDS with metallic *versus* semiconducting SWCNTs. Only a few studies have reported that the conformation of SDS on SWCNTs differs between metallic and semiconducting SWCNTs.<sup>32–34</sup> Niyogi *et al.* showed that the conformation and density of SDS molecules on SWCNTs are affected

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Received for review September 6, 2013 and accepted October 15, 2013.

Published online October 15, 2013  
10.1021/nn4046776

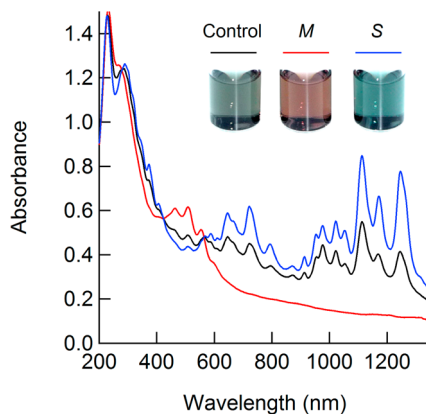
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by image charges that exert an electrostatic screening effect on SDS.<sup>33</sup> In addition, the hydrogels that have resulted in successful separations are limited to agarose gels and Sephacryl which is composed of allyl dextran and *N,N'*-methylene bisacrylamide. Therefore, the chemical structures of the hydrogels are also critical for the interaction between SDS-dispersed SWCNTs and hydrogels. We have further shown that the adsorption reaction of SWCNTs onto Sephacryl is more endothermic than that onto agarose gel and that this difference affects the separation quality.<sup>35</sup>

Changes in solution pH alter the optical properties of SWCNTs. An early study of the pH dependence of SWCNT optical properties was performed by Strano *et al.*<sup>36</sup> They showed that the absorption, fluorescence, and resonant Raman intensities of the semiconducting SWCNTs are suppressed by reversible protonation on the SWCNT sidewalls in the presence of dissolved O<sub>2</sub>. The suppression of the intensities of the spectral peaks was later attributed to oxidation of the SWCNTs mediated by both protons and O<sub>2</sub>.<sup>37–41</sup> Among surfactants, this type of spectral suppression has been observed almost exclusively in the cases of SDS and its analogues, although it has also been reported for polymers.<sup>40,42–44</sup> The characteristic property of SDS upon oxidation is currently ascribed to the loose organization of SDS around the SWCNTs.<sup>45</sup> The addition of salt also affects the optical properties of semiconducting SWCNTs. Doorn's group showed that the addition of NaCl alters the fluorescence intensities of the SWCNTs depending on NaCl concentration,<sup>46</sup> which is due to changes in the packing density and the reorientation of SDS.<sup>33,34</sup> The conformational changes of SDS are supported by the fact that the critical micelle concentration decreases and the surface aggregation number increases with increasing salt concentration.<sup>47,48</sup>

In contrast to salts, urea, which is known as a chaotrope, has the opposite effect on the SDS conformation: the critical micelle concentration increases and the aggregation number decreases with increasing urea concentration.<sup>49</sup> Chaotropes, in general, reduce hydrophobic interactions, and this reduction is considered to be the mechanism for the effects of urea on the SDS conformation.<sup>50</sup> To the best of our knowledge, no studies have examined the conformation of SDS on SWCNTs and the adsorbability of SDS-dispersed SWCNTs onto a hydrogel in a chaotropic solution.

The previous discussion suggests that the adsorbability of the SWCNTs onto the hydrogels is pH- and solute-dependent, which should be related to the mechanism of separation. In the present study, the amounts of metallic and semiconducting SWCNTs adsorbed onto the agarose gel and Sephacryl medium at equilibrium were measured *via* the SWCNT absorbance at 280 nm at various pH values or in the presence

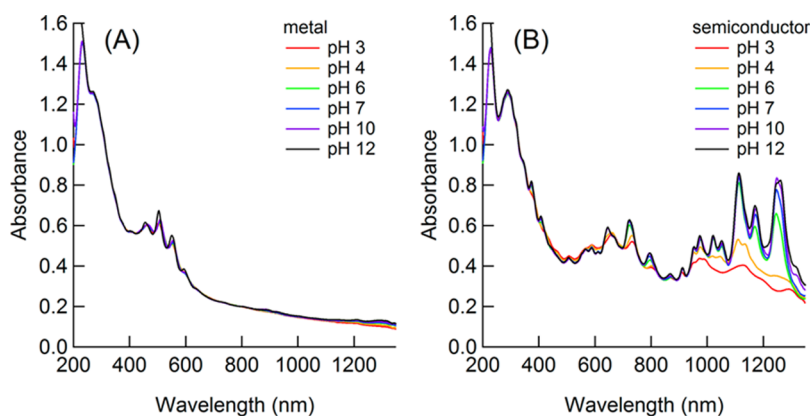


**Figure 1.** Absorption spectra and photographs of the unseparated (black line), metallic (red line), and semiconducting (blue line) SWCNTs prepared using Sephacryl. The inset shows a photograph of each SWCNT solution. Control, *M*, and *S* denote the unseparated, metallic, and semiconducting SWCNTs, respectively.

of salts such as NaCl or CsCl. Acidic pH conditions and the addition of salt reduced the adsorbability. These results were consistent with those related to metal/semiconductor separation using columns described in this study and in a previous study.<sup>51</sup> Urea was also used as an additive for the separation of SWCNTs and resulted in the elution of the SWCNTs from the columns. Thus, the results of this study suggest a mechanistic model in which metal/semiconductor separation is achieved using hydrogels because of differences in the adsorbability of the SWCNTs onto the hydrogels. These differences in adsorbability are due to the conformational differences of SDS on the sidewalls, which reflect the band structures and chemical structures of the SWCNTs and the solution conditions.

## RESULTS AND DISCUSSION

**Spectral Properties of Metallic and Semiconducting SWCNTs at Various pH Values.** We prepared metallic and semiconducting SWCNTs *via* the previously reported separation technique<sup>24</sup> to examine the pH and solute dependence of their adsorption onto the hydrogels. Figure 1 shows spectra of the prepared SWCNTs. The spectrum of the metallic SWCNT solution shows characteristic absorption peaks assigned to the  $M_{11}$  band at approximately 400–620 nm, and the spectrum of the semiconducting SWCNT solution shows peaks assigned to the  $S_{11}$  and  $S_{22}$  bands at approximately 940–1350 and 620–940 nm, respectively. The unseparated SWCNT solution shows absorption peaks in the  $M_{11}$ ,  $S_{11}$ , and  $S_{22}$  bands. Thus, the metallic and semiconducting SWCNTs were found to be well-separated (see also the photograph of each solution in Figure 1). The peak at approximately 280 nm was commonly observed and is attributed to the  $\pi$ -plasmon absorption of the SWCNTs because of the collective excitation of the  $\pi$ -electron system polarized along the SWCNT axis.<sup>52</sup> The peak at approximately 220 nm was also



**Figure 2.** Absorption spectra of the metallic (A) and semiconducting (B) SWCNTs at various pH values.

commonly observed and corresponds to the  $\pi$ -electron system polarized across the SWCNT axis. Because the peak at approximately 220 nm was affected to a significant degree by coexisting amorphous carbon<sup>53</sup> or NaOH,<sup>54</sup> the absorbance at 280 nm was used to quantify the SWCNT concentration. In addition, the SDS concentration in each SWCNT solution was measured with a density meter. Thus, the stock solutions of the metallic and semiconducting SWCNTs were adjusted to contain 1 wt % SDS and  $\sim 10 \mu\text{g/mL}$  SWCNTs, corresponding to an absorbance at 280 nm (A280) of 1.2 (see also Supporting Information, Figures S1 and S2).

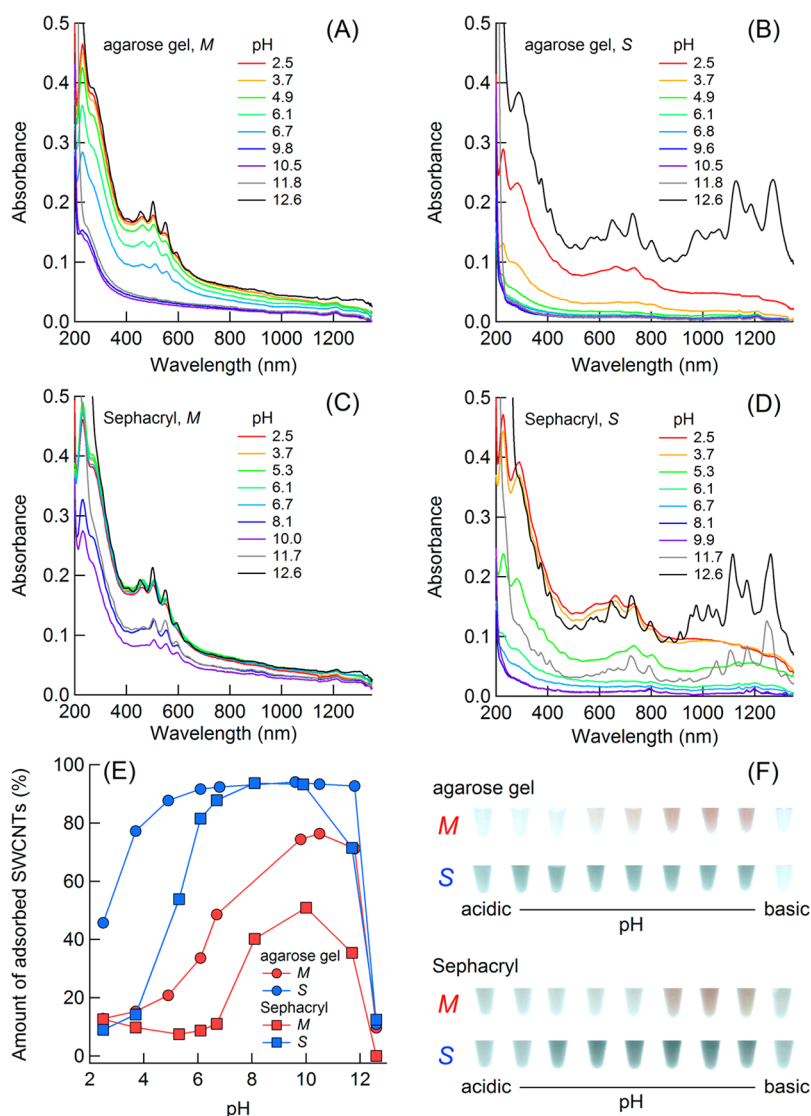
Figure 2 shows the pH dependence of the absorption spectra for the metallic and semiconducting SWCNTs. Whereas the metallic SWCNT solution did not exhibit any spectral changes with pH, the semiconducting SWCNT solution showed significant attenuations of absorbance in the infrared region as pH was decreased.<sup>36</sup> The spectral changes observed in the semiconducting SWCNT solution are ascribed to the oxidation of the SWCNTs mediated by oxygen and protons.<sup>37–39</sup> Larger-diameter tubes are more sensitive to oxidation,<sup>40</sup> which is consistent with larger attenuations of the intensity at longer wavelengths (Figure 2B). Importantly, A280 exhibits no pH dependence, which allowed the SWCNT concentration to be determined at any pH value when A280 was used.

**Adsorption of Metallic and Semiconducting SWCNTs onto Hydrogels at Various pH Values.** Figure 3 shows the absorption spectra and amounts of SWCNTs unadsorbed onto agarose gel and Sephacryl at various pH values after they were mixed for 24 h. The pH values were adjusted using HCl or NaOH. The absorbance intensities for each SWCNT diminished as the pH was increased from acidic values to neutral values for both hydrogels (Figure 3A–D), whereas the intensities remained almost constant or slightly increased as pH was increased from neutral values to basic values. Notably, the intensities dramatically increased at pH  $\sim 12.5$ , which indicates that the adsorption of SWCNTs onto the hydrogels is significantly reduced at this pH.

A decrease in peak sharpness of the  $S_{11}$  and  $S_{22}$  bands of the semiconducting SWCNTs with decreasing pH is mainly accounted for by oxidation, as previously described (Figure 2).

The amounts of SWCNTs adsorbed onto the hydrogels were quantified using the A280 and are shown in Figure 3E (see also the photograph of the SWCNTs on the hydrogels in Figure 3F). For both the metallic and semiconducting SWCNTs, higher adsorption onto agarose gel was observed compared to the adsorption onto Sephacryl at almost all pH values, which is consistent with our previous study that demonstrated that the agarose gel has a higher “net adsorbability” than Sephacryl.<sup>35</sup> The adsorption amounts exhibited maxima in the pH range of 9–11 for the metallic SWCNTs and in the pH range of 7–11 for the semiconducting SWCNTs. At pH 3, the metallic SWCNTs showed almost no adsorption to either hydrogel, whereas the semiconducting SWCNTs showed almost no adsorption for Sephacryl. The slight increase in the adsorption of the metallic SWCNTs for Sephacryl with decreasing pH may be due to the protonation of SDS because the acidic dissociation constant of SDS is approximately 2.3.<sup>55</sup> The semiconducting SWCNTs still exhibited substantial adsorption onto the agarose gel even at pH 3, which is attributed to the higher net adsorbability for the semiconducting SWCNTs onto agarose gel.<sup>35</sup> Importantly, the tendency of the adsorption to increase with increasing pH was observed to depend on the electrical properties of the SWCNTs. The amount of semiconducting SWCNTs adsorbed increased at lower pH values compared to the amount of the metallic SWCNTs adsorbed for both hydrogels. In addition, a significant decrease in the adsorption was observed at the extremely basic pH value of  $\sim 12.5$ , which is attributed to the concentration of sodium ions present in the solution, as will be discussed later.

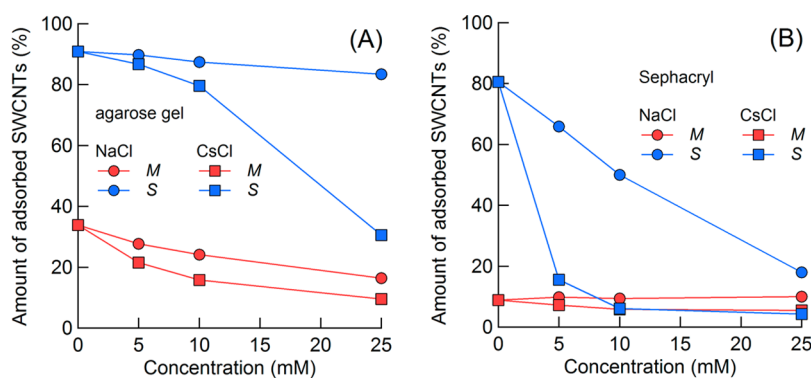
The SDS concentration used is higher than the critical micelle concentration of SDS even at acidic pH values.<sup>56</sup> In addition, given that the acidic dissociation constant of SDS is approximately 2.3,<sup>55</sup> the pH dependence of the adsorption is unlikely to be



**Figure 3.** pH-dependent adsorption of the SWCNTs onto the hydrogels in the batch separation. (A–D) Absorption spectra of the fractions unadsorbed onto agarose gel (A,B) and Sephacryl (C,D) for metallic (A,C) and semiconducting (B,D) SWCNTs. (E) Amount of SWCNTs adsorbed at each pH value. (F) Photograph of the SWCNTs adsorbed onto agarose gel and Sephacryl at various pH values. *M* and *S* denote the metallic and semiconducting SWCNTs, respectively.

explained by the protonation of SDS. Rather, the pH dependence is associated with oxidation of SWCNTs. SWCNTs are known to gain positive charges through reversible oxidation mediated by oxygen and protons in aqueous solutions;<sup>38–40</sup> therefore, SWCNTs have more positive charges delocalized at lower pH values.<sup>40</sup> The pH dependence of the  $\zeta$ -potential of SWCNTs has been previously reported.<sup>57,58</sup> The protonation of SWCNTs has been shown to depend on their band structures<sup>36</sup> due to the redox potential of the valence bands.<sup>37</sup> Thus, metallic SWCNTs are more readily oxidized than semiconducting SWCNTs due to their lack of band gaps. For both the metallic and semiconducting SWCNTs, the SWCNT sidewalls are more positively charged at lower pH values, and metallic SWCNTs tend to be more positively charged than semiconducting SWCNTs.

The previous results and discussion enable the following mechanistic insight into the interactions between SWCNTs dispersed in SDS and hydrogels. SDS interacts with metallic SWCNTs more favorably than with semiconducting SWCNTs, and it interacts with them more favorably at more acidic pH levels. These differences are due to the electrostatic interactions between the negative charges of SDS and the delocalized positive charges of the oxidized SWCNTs. This interaction increases the density of SDS on the SWCNT sidewalls, which reduces the interaction between the SWCNTs and hydrogels<sup>32</sup> and leads to the low adsorbability of the SWCNTs onto the hydrogels. The above mechanistic model based on the oxidation of SWCNTs is supported by previous studies that show that the adsorbability of SWCNTs onto Sephacryl increases as the SWCNT diameter decreases.<sup>28,59</sup>



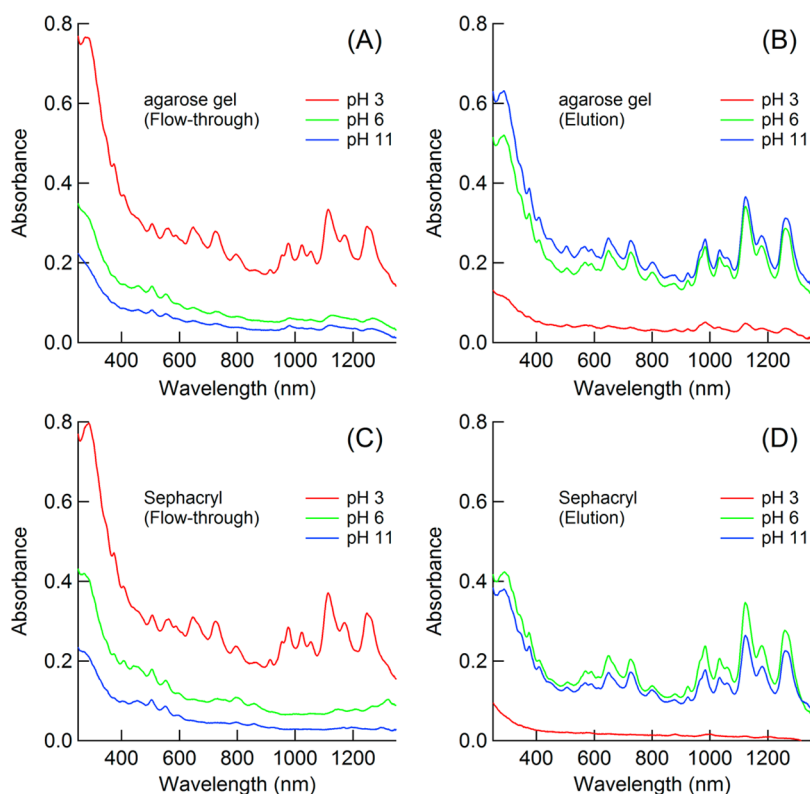
**Figure 4.** Amount of SWCNTs adsorbed onto agarose gel (A) and Sephacryl (B) in the presence of NaCl and CsCl. *M* and *S* denote metallic and semiconducting SWCNTs, respectively.

Notably, the diameter is related to the redox potentials of the valence bands, which explains the tendency toward oxidation.<sup>37,60</sup> In fact, the absorbance intensities at longer wavelengths for Sephacryl were retained even at higher pH values (Figure 3D), indicating that larger-diameter tubes tend to be desorbed from the hydrogel than smaller-diameter tubes. In addition, the enhanced adsorbability of SWCNTs onto the hydrogels with increasing temperature reported by our group also supports this mechanism<sup>61</sup> because the oxidation of SWCNTs decreases with increasing temperature due to the decrease in  $O_2$ ,  $H^+/H_2O$  reduction potential, or the removal of  $O_2$  from the solutions.<sup>60</sup> Importantly, the oxidation of SWCNTs is observed almost exclusively in SDS solution. Surprisingly, the hydrogel-based separation of SWCNTs is also successful exclusively with SDS or its analogues, as we have previously reported (see also Supporting Information, Figure S3).<sup>31</sup> The remarkable consistency strongly supports the previously described model. The distinctive property of SDS is its loose organization around SWCNTs, which allows the adsorption of  $O_2$  onto the SWCNTs and leads to the generation of a chemisorbed 1,4-endoperoxide, that is, SWCNT oxidation.<sup>45</sup> Notably, the maximum values for the amount of adsorption are higher for semiconducting species than for metallic species (Figure 3E). The previously discussed protonation appears to be insufficient to explain this difference in the maximum values, although it can explain the difference in the pH values at which the adsorbability increases. Image charges on metallic SWCNTs should be included in the explanation of this phenomenon.

**Adsorption of Metallic and Semiconducting SWCNTs onto Hydrogels in Salt Solutions.** The previously suggested mechanistic model is further reinforced by consideration of the electrostatic screening of SDS on the SWCNT sidewalls. Doorn's group suggested that the image charges of metallic SWCNTs condense SDS molecules on the sidewalls by reducing the interactions of SDS molecules by electrostatic screening.<sup>33</sup> This effect can account for the difference in the density of SDS on the

sidewalls between metallic and semiconducting SWCNTs; specifically, SDS molecules are more dense on the metallic SWCNTs than on the semiconducting SWCNTs. This difference most likely explains the difference between the metallic and semiconducting SWCNTs with respect to the maximum adsorption onto the hydrogels, as shown in Figure 3E. Doorn's group also reported that the condensation of SDS through electrostatic screening is enhanced by the addition of salts; CsCl exhibits a more pronounced effect than NaCl.<sup>34</sup> Thus, the amount of the SWCNTs adsorbed onto the hydrogels in salt solutions must be measured to demonstrate that the SDS density on the SWCNT sidewalls is critical for the adsorbability. Figure 4 shows the amount of adsorbed SWCNTs in the presence of various concentrations of NaCl and CsCl at neutral pH, that is, in the absence of HCl or NaOH. For the agarose gel, the amounts of metallic and semiconducting SWCNTs without salts were approximately 30 and 90%, respectively (Figure 4A), which are consistent with the data at neutral pH reported in Figure 3E. All amounts were reduced as the salt concentration was increased. As expected, CsCl led to a more pronounced reduction in adsorbability than did NaCl. In particular, the amount of semiconducting SWCNTs adsorbed remarkably decreased with increasing CsCl concentration. For Sephacryl, the amount of semiconducting SWCNTs adsorbed decreased with increasing salt concentration, similar to the results for the agarose gel, whereas the adsorption of the metallic SWCNTs did not change significantly due to the low original adsorbability (Figure 4B). The difference in the effect of the salts between the agarose gel and Sephacryl may be accounted for by the higher net adsorbability of the SWCNTs onto the agarose gel than Sephacryl.<sup>35</sup> Cations larger than sodium ions, such as cesium ions, can associate with a greater number of anionic sulfate headgroups through electrostatic interactions such that the density of SDS on the SWCNTs is greater in CsCl solution than in NaCl solution.<sup>34</sup> The results shown in Figure 4 thus demonstrate that the SDS density on the SWCNTs is a critical parameter affecting the adsorption of





**Figure 5.** pH-dependent adsorption of the SWCNTs onto the hydrogels using columns. Absorption spectra of the SWCNTs in the flow-through (A,C) and eluted (B,D) fractions from agarose gel (A,B) and Sephacryl (C,D) columns were measured after the addition of aliquots of NaOH to avoid decreases in absorbance due to oxidation.

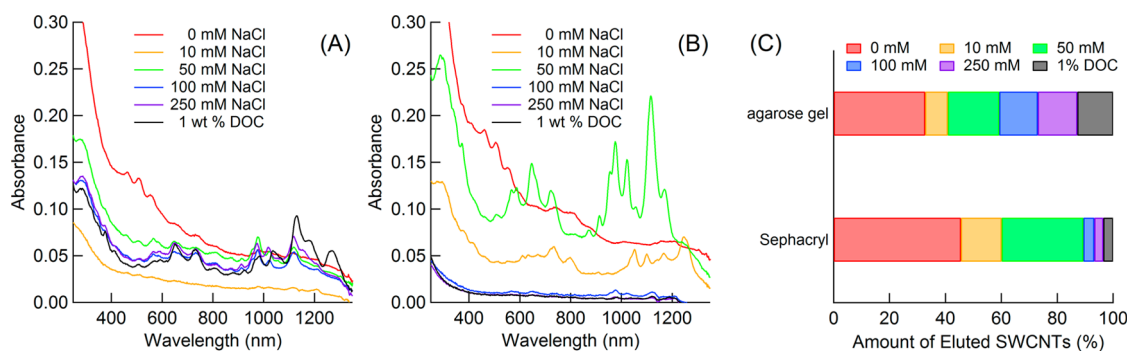
SDS-dispersed SWCNTs onto the hydrogels. The concentrated sodium ions also play the role of an adsorption inhibitor in extremely basic environments, such as pH  $\sim 12.5$ , as shown in Figure 3E, because pH 12.5 corresponds to approximately 100 mM NaOH. In addition, ionization of hydroxyl groups of the hydrogels may also be associated with the decrease in the adsorption at pH  $\sim 12.5$ .<sup>62</sup>

Taken together, the differences in the adsorbabilities of the SWCNTs onto the hydrogels are ascribed to the condensation of SDS on the SWCNTs through the oxidation of SWCNTs mediated by protons and oxygen and through the electrostatic screening of SDS because of image charges and counterions. Antaris *et al.* showed metal/semiconductor SWCNT separation using neutral polymers by density gradient ultracentrifugation, which was accounted for by the repulsion between the image charges of SWCNTs and the polymers.<sup>63</sup> Neutral polymers differ from negatively charged SDS in terms of the contribution of the image charges to the interaction.

**pH and Solute Dependence of SWCNT Separations Using Hydrogel Columns.** Because the previously discussed adsorption measurements were performed only at equilibrium, it is important to demonstrate that the pH and solute dependence of the adsorption are also reflected in the metal/semiconductor separation of SWCNTs using the hydrogel columns, where the adsorption is

basically at nonequilibrium, except for the existence of a local equilibrium.<sup>35,59,64</sup> Figure 5A shows the spectra of SWCNTs obtained as flow-through fractions from agarose gel columns in the presence of 1 wt % SDS and as subsequent fractions eluted by 1 wt % DOC at acidic, neutral, and basic pH values. As expected from the results of the adsorption measurements at equilibrium (Figure 3), the intensity at 280 nm in the flow-through fractions decreases in the pH order acidic > neutral > basic. A similar tendency was obtained for Sephacryl (Figure 5C). These results are consistent with the results of the previous study reported by Flavel *et al.* The spectra for the acidic conditions have apparent intensities in the  $S_{11}$  and  $S_{22}$  bands as well as the  $M_{11}$  band, which indicates that the flow-through fractions contain metallic and semiconducting SWCNTs. In contrast, the spectra for neutral and basic conditions have insignificant intensities in the  $S_{11}$  and  $S_{22}$  bands. In contrast, the spectral intensities of the eluted fraction at 280 nm are greater for the neutral or basic conditions than for the acidic conditions (Figure 5B,D). Thus, the pH-dependent adsorption affects the separation quality of SWCNTs, thereby resulting in the highest quality at neutral pH (see also the normalized spectra in Figure S4).

Figure 6 shows the spectra of SWCNTs obtained as flow-through fractions from the hydrogel columns and subsequent fractions obtained by stepwise elution with various concentrations of NaCl in the presence

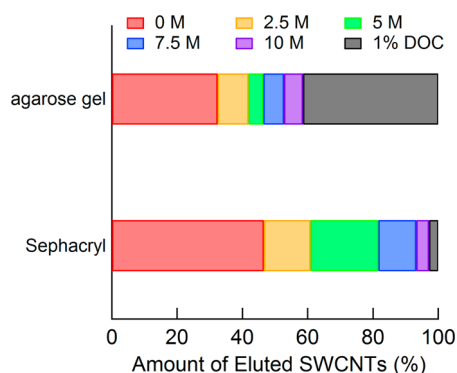


**Figure 6.** (A,B) Absorption spectra of the SWCNTs eluted from agarose gel (A) and Sephacryl (B) columns by the stepwise elution with NaCl. (C) Amounts of SWCNTs eluted from the hydrogel columns.

of 1 wt % SDS at neutral pH, that is, in the absence of HCl or NaOH. For each hydrogel, the flow-through fraction shows absorption peaks in the  $M_{11}$  band corresponding to metallic SWCNTs, which is consistent with the results of previous studies.<sup>21,65</sup> Elution in the presence of 10 mM NaCl resulted in a low absorbance value for each hydrogel. Subsequent elution in the presence of 50 mM NaCl resulted in the highest intensity absorption spectrum with absorption peaks in the  $S_{11}$  and  $S_{22}$  bands, indicating the presence of semiconducting SWCNTs. Interestingly, fractions eluted by the subsequent steps of 100 and 250 mM NaCl and 1 wt % DOC exhibited similar intensities in the  $S_{11}$  and  $S_{22}$  bands for the agarose gel (Figure 5A) but marginal intensities in these bands for Sephacryl (Figure 5B). These results indicate that the adsorbed semiconducting SWCNTs are gradually eluted from the agarose gel column by 50–250 mM NaCl, whereas they are nearly completely eluted from the Sephacryl column by 50 mM NaCl. The absorbance intensities at longer wavelengths for Sephacryl were observed at a lower concentration of NaCl (10 mM), as shown in Figure 6B, indicating that larger-diameter tubes tend to be desorbed from the hydrogel than smaller-diameter tubes. Figure 6C shows the amounts of SWCNTs in the flow-through and eluted fractions from the hydrogel columns estimated using the A280. The flow-through fractions from agarose gel and Sephacryl columns contain approximately 30 and 50% of the total SWCNTs loaded onto the column, respectively. The first fractions eluted by 10 mM NaCl contained less than 10 and 20% of the total SWCNTs for agarose gel and Sephacryl, respectively. The second fractions eluted from agarose gel and Sephacryl columns by 50 mM NaCl contained approximately 20 and 30% of the total SWCNTs, respectively. The third, fourth, and final fractions eluted by 100 and 250 mM NaCl and 1 wt % DOC, respectively, contained approximately 10% of the total SWCNTs for the agarose gel and less than 5% for Sephacryl. Thus, the agarose gel was found to be more robust for elution by NaCl than Sephacryl: 250 mM NaCl was needed to elute 90% of the total SWCNTs from the agarose gel column, whereas only 50 mM NaCl was

needed to elute the same proportion from the Sephacryl column. These results conclusively demonstrate that the electrostatic screening of SDS by salts affects the metal/semiconductor separation of SWCNTs using hydrogel columns, which depends on the chemical structure of the hydrogels.

We next addressed the issue of whether the effect of solutes on the separation is limited to electrostatic screening. In general, small solutes such as salts affect the stability of colloids, including biopolymers, by altering their electrostatic interactions and hydrophobic interactions. The reduction of electrostatic interactions by solutes due to electrostatic screening occurs primarily at concentrations less than 1 M. However, the alteration of hydrophobic interactions by solutes typically appears at a concentration greater than 1 M—a phenomenon known as the Hofmeister effect.<sup>66,67</sup> The solutes that reduce hydrophobic interactions are referred to as “chaotropes”, whereas those that enhance these interactions are known as “kosmotropes”. Thus, an examination of the elutions of SDS-dispersed SWCNTs from the hydrogel columns by the reduction of the hydrophobic interactions is worthwhile to elucidate the nature of the interactions between the SWCNTs and the hydrogels. Urea is used to investigate only the chaotropic solute effect without any electrostatic screening because it has no charged group, in contrast to the ionic chaotrope guanidine hydrochloride. Figure 7 shows the amounts of SWCNTs in the flow-through and eluted fractions from the hydrogel columns by stepwise elution with various concentrations of urea in the presence of 1 wt % SDS at neutral pH, as determined using the A280, similar to the experiments whose results are shown Figure 6C (see also the absorption spectra in Figure S5). Each flow-through fraction from the agarose gel and Sephacryl columns exhibited the same profile as the same conditions in Figure 6C. To our surprise, approximately 40% of the total SWCNTs remained on the agarose gel even in 10 M urea, whereas almost all SWCNTs were eluted from the Sephacryl column by 10 M urea. Notably, despite the preferential binding of urea to SWCNTs,<sup>68</sup> urea induced no aggregation of SWCNTs (data not



**Figure 7.** Amounts of SWCNTs eluted from agarose gel and Sephacryl columns by the stepwise elution with urea.

shown), which most likely indicates that no SDS dissociation occurred. Because urea reduces the aggregation number of SDS micelles by interacting with the micellar surface or the hydrocarbon tails of SDS,<sup>49,50</sup> condensation of SDS on SWCNTs, as induced by NaCl, is excluded from the mechanism of elution by urea. In addition, urea slightly increases the dielectric constant;<sup>69</sup> nevertheless, reduction of the electrostatic interactions of SDS by urea appears to be negligible because the critical micelle concentration increased in the presence of urea, unlike the effect of salts.<sup>48–50</sup> Khripin *et al.* showed that the chaotrope NaSCN transfers SWCNTs from the hydrophobic phase into the hydrophilic phase by reducing the solvation free energy more in the latter phase than in the former phase.<sup>19</sup> Thus, urea likely directly reduces the hydrophobic interactions of SDS-dispersed SWCNTs with the hydrophobic moieties of the hydrogels.

In addition to the fact that urea is more effective in the elution from Sephacryl than from agarose gel (Figure 7), condensation or conformational changes of SDS on the SWCNTs has been shown in response to an increase in NaCl concentration (Figure 6) as well as

to an increase in SDS concentration,<sup>35</sup> and this effect is also greater in the elution from Sephacryl than in the elution from agarose gel. These results suggest that SWCNTs have more hydrophobic interactions with Sephacryl than with the agarose gel. Flavel *et al.* have shown that 1-dodecanol elutes semiconducting SWCNTs from Sephacryl,<sup>51</sup> which could be explained by the reduction of the hydrophobic interactions by 1-dodecanol. In addition, the changes in hydrogen bonding by urea may also influence the effectiveness.<sup>70,71</sup>

## CONCLUSION

Since our discovery of hydrogel-based metal/semiconductor separation in 2008, the mechanism has been studied by our group and others. This study provides a well-developed mechanistic model of the separation. The pH-dependent adsorption of SWCNTs onto the hydrogels indicates the role of the oxidation of SWCNTs in the separation; the solute-dependent adsorption indicates the role of the electrostatic screening of SDS on the SWCNTs. These properties alter the density of SDS on the SWCNTs depending on their band structures. For example, metallic SWCNTs have denser SDS layers than semiconducting SWCNTs. Such alterations of SDS density affect the adsorbability onto the hydrogels, which is why SDS is able to accomplish metal/semiconductor separation. The chaotrope-dependent desorption implies that the interaction between SDS-dispersed SWCNTs and the hydrogels is related to the interfacial hydrophobicity between SDS-dispersed SWCNTs and the hydrogels, particularly for Sephacryl. The separation of SDS-dispersed SWCNTs using these hydrogels can thus be understood on the basis of the band structures, chemical structures, and colloidal stabilities of the SWCNTs.

## METHODS

**Preparation of Debundled SWCNTs.** Raw SWCNTs produced by high-pressure catalytic CO (HiPco) decomposition were purchased from Nano-Integris and were used as the starting materials. Aliquots of 30 mg of HiPco SWCNTs were pre-dispersed at 1 mg/mL 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. 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<sup>-2</sup>. 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 000g 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 with 1 wt % SDS.

**Preparation of Metallic and Semiconducting SWCNTs.** Metallic and semiconducting SWCNTs were prepared in 1 wt % SDS using an open column that contained hydrogel formed from the

cross-linked dextran Sephacryl (Sephacryl S-200 HR, GE Healthcare). The debundled SWCNT solution (10 mL) prepared as previously described, but with 0.5 wt % SDS, was applied to the top of the column containing approximately 30 mL of Sephacryl in 0.5 wt % SDS. The metallic species were obtained as the flow-through fraction upon the addition of 0.5 wt % SDS. Additionally, 1% SDS allowed the remaining metallic SWCNTs to be eluted. The subsequent addition of 5 wt % SDS allowed for the elution of the semiconducting SWCNTs. The SDS concentrations of the metallic and semiconducting SWCNT solutions were measured with a density meter (DMA 5000M, Anton Paar) and were adjusted to 1 wt % using 5 wt % SDS or water. Finally, the SWCNT solutions were diluted with 1 wt % SDS to adjust the absorbance of the solutions at 280 nm to 1.2 using the standard curve (see Figure S1).

**Adsorption of Metallic and Semiconducting SWCNTs onto Hydrogels.** Batch adsorption of the SWCNTs onto the hydrogels was conducted to assess their adsorbability. The hydrogel beads (0.25 mL) were mixed with each separated SWCNT solution (0.4 mL) and 1 wt % SDS solution (0.75 mL) in the presence of various solutes at various pH levels under gentle rotation



at 25 °C for 24 h; the mixtures were subsequently briefly centrifuged (500g for 1 min). The supernatants were then collected as the unadsorbed fractions. The absorbance of the fractions was used to assess the SWCNT concentration. The hydrogels used here were agarose gel (Sepharose 2B, GE Healthcare) and Sephacryl.

**Metal/Semiconductor Separation of SWCNTs Using Hydrogel Columns.** The hydrogel columns were used to separate SWCNTs into metallic and semiconducting species. Debundled SWCNTs (0.1 mL in 1 wt % SDS) prepared as previously described were loaded onto the top of a column that contained approximately 0.75 mL of agarose gel or Sephacryl in 1 wt % SDS at various pH values. A 1 wt % SDS solution at each pH value was added to obtain the flow-through fraction. Subsequently, each eluted fraction was collected by 1 wt % DOC or by stepwise elution with solutes (*i.e.*, NaCl, CsCl, or urea). For the stepwise elution, the remaining material was eluted using 1 wt % DOC, which resulted in complete elution.

**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) using a quartz cell with a path length of 10 mm. In the present study, the absorption peaks at approximately 940–1350 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. The absorption peak at approximately 400–620 nm was assigned to the first optical transition of metallic SWCNTs, designated as the  $M_{11}$  band.<sup>35,65,72</sup>

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

**Acknowledgment.** This work was supported in part by KAKENHI of MEXT, Japan.

**Supporting Information Available:** Determination of the concentration of separated SWCNTs. Determination of SDS concentration in SWCNT solution using a density meter. Effect of alkyl chain length of SDS on the metal/semiconductor separation. Normalized absorption spectra of the SWCNTs eluted from agarose gel and Sephacryl columns. Absorption spectra of the SWCNTs eluted from the hydrogel columns by the stepwise elution with urea. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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