

Understanding the Electrophoretic Separation of Single-Walled Carbon Nanotubes Assisted by Thionine as a Probe

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Received: July 23, 2010; Revised Manuscript Received: September 29, 2010

Single-walled carbon nanotubes (SWNTs) dispersed by sodium dodecyl sulfate (SDS) can be simply and effectively separated into semiconducting (s) and metallic (m) fractions by the method of agarose gel electrophoresis, in which s-SWNTs cannot migrate like m-SWNTs and remain unmoved under electric field. The role of SDS is suggested to be crucial for such separation effect. Its mechanism, however, is still unclear and hard to probe. In the present study, by employing thionine (TN), a positively charged dye molecule which may show unique interaction with SDS molecules, we can roughly evaluate the changes of SDS aggregates during the agarose gel electrophoresis. On the basis of the results of the electrophoretic and spectroscopic characterizations, we propose that the unique interaction of s-SWNTs with agarose and the exfoliation of some SDS molecules from SDS-s-SWNT entities lead to the separation of s- and m-SWNTs.

Introduction

Single-walled carbon nanotubes (SWNTs) are a kind of one-dimensional electronic nanomaterial with great promise for a variety of applications,¹ such as building blocks for optoelectronic nanodevices,² field effect transistors,³ electrodes and transparent conducting films,⁴ etc. However, a big hurdle that limits wide application of SWNTs comes from the fact that as-grown SWNTs often exist in a mixture, typically with 1/3 metallic (m) tubes and 2/3 semiconducting (s) tubes. Many methods have therefore been developed recently in an attempt to separate SWNTs. On the basis of their different reactivities with some small molecules or macromolecules, m- or s-SWNTs can be sorted out by destruction of one fraction through oxidative etching,^{5,6} chemical transformation from m-SWNTs to s-SWNTs,⁷ selective functionalization,^{8–10} density gradient ultracentrifugation,^{11,12} electrophoresis,^{13,14} and chromatography,^{15–17} etc.

Recently, Tanaka et al. reported that SWNTs could be fractionized into s- and m-tubes by agarose gel on the basis of electrophoresis¹⁴ and centrifugation.¹⁸ They proposed that the SDS surfactant played an important role in the separation. s-SWNTs were probably adsorbed by fewer SDS molecules compared to m-SWNTs, which led to the selective entrapment of s-SWNTs in the gel and migration of m-SWNTs toward anode after agarose gel electrophoresis. Such explanation seems kind of intuitive and lacks sufficient and direct evidence.^{14,18,19} The mechanism of such a separation process is still unclear, since there are no characterization methods available so far to confirm the aggregation changes of SDS molecules on SWNTs before and after gel electrophoresis.

Thionine (TN), also called Lauth's violet, is a strong staining metachromatic dye that is widely used for biological staining. TN molecules are readily bonded with anionic surfactant micelles such as SDS through the electrostatic and hydrophobic interaction.²⁰ Interestingly, the absorption bands of TNs are very sensitive to their aggregated structures of SDS in aqueous solution.²¹ Therefore, TN molecules may serve as a probe to

investigate the aggregation properties of SDS related systems.²¹ In this study, through monitoring color changes and absorption bands of TN molecules, we can roughly estimate the migration and adsorption properties of SDS micelles in the gel as well as on SWNT surfaces to some extent during the electrophoresis and consequently acquire more understanding on the separation. Combining electrophoretic results with spectroscopic characterizations, we proposed a possible separation mechanism.

Experimental Methods

Chemicals. HiPCO SWNT powders were used as purchased in our experiments.(Lot No. P0276, Carbon Nanotechnologies, Inc.). Sodium dodecyl sulfate (SDS) was purchased from Sigma-Aldrich (99%). Thionine was purchased from Sinapharm Chemical Reagent Co., Ltd. Agarose (fine powder, Nacalai Tesque) was used for the matrix of the gel electrophoresis.

Preparation of SWNT Dispersion. SWNT dispersions were prepared as follows. A certain amount of SWNT powder was dispersed in aqueous solution of 1% SDS at 0.3 mg/mL and sonicated by using a tip-type ultrasonic homogenizer (Misonix XL2000) for 2 h at 8 W. The temperature of the mixture was kept below 35 °C by immersing it in a water bath. After sonication, the solution was centrifuged to remove the bundles and impurities (20 000g for 6 h at 25 °C). The resulting supernatant was collected as SWNT dispersion, where SWNTs were coated by SDS molecules. The concentrations of TN and SDS in SDS-TN, SDS-SWNT and SDS-SWNT-TN dispersions were fixed at 3.2×10^{-4} and 3.3×10^{-2} M (2%), respectively.

Agarose Gel Electrophoresis of SDS-TN Gel, SDS-SWNT Gel, and SDS-SWNT-TN Gel. The three kinds of gels were prepared by mixing their solution or dispersions well with an equal amount of 0.8% agarose melted by heating in $\times 2$ TB buffer (50 mM tris(hydroxyl-methyl) aminomethane, 48.5 mM boric acid (pH 8.2)) and then jelling in the glass tube at room temperature. The 0.4% agarose and 0.2% SDS in TB buffer were melted by heating, then poured into a glass tube, and jelled, which was used for the electrophoresis channel. The SDS-TN gel, SDS-SWNT gel, and SDS-SWNT-TN gel as initial gels were connected with blank agarose gel, respectively. The 0.2%

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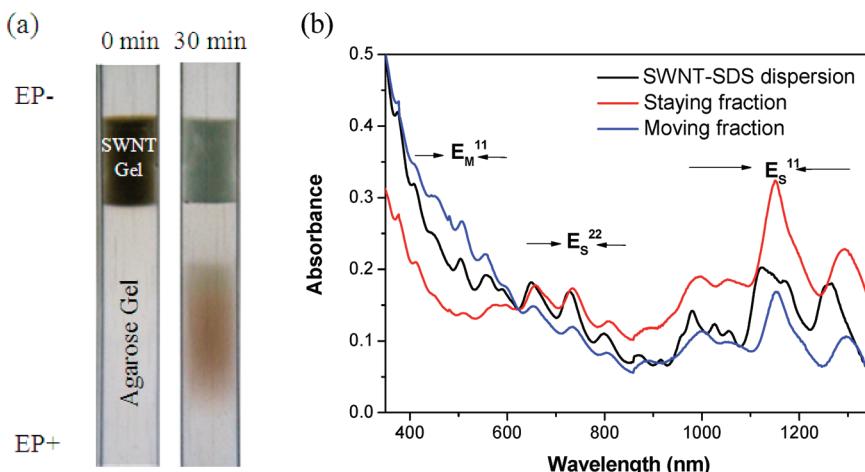


Figure 1. Typical separation result of the SDS-SWNT gel by agarose gel electrophoresis: (a) photographs showing the migration and color changes of the SWNT gel before and after agarose gel electrophoresis; (b) UV-vis-near-IR absorption spectra of initial SDS-SWNT dispersion and the separated moving and staying fractions.

SDS in TB buffer was used for the electrophoresis buffer. A constant voltage of 50 V was applied.

Spectroscopic Characterization. For absorption spectroscopy, initial SWNT dispersions diluted 10 times with 1% SDS aqueous solution were measured. For gel samples, they were used directly for spectroscopic measurements. The absorption spectra were recorded in a Perkin-Elmer Lambda 950 instrument. Fluorescence spectra (laser excitation at 658 nm) were obtained on the NS1 NanoSpectralyzer.

Results and Discussion

SWNTs can be separated into s and m two fractions by the electrophoresis of SDS-SWNT agarose gel, where SDS plays a critical role in the separation. A typical result of agarose gel electrophoresis was shown in Figure 1a. Under the electric field, the initial SDS-SWNT gel was separated into two fractions: one fraction with a brownish red color moving toward the anode and the other fraction with a Spanish green color staying in the initial gel. In general, when SWNTs are monodispersed in a SDS solution, a typical absorption curve can be obtained due to the van-Hove singularity features of m- and s-tubes. For HiPco SWNTs, the absorption peaks around 800–1600 and 550–900 nm were derived from first and second optical transitions of s-SWNTs and were designated as E_S^{11} and E_S^{22} , respectively. The absorbance peak around 400–600 nm represented the first optical transition of m-SWNTs (E_M^{11}).²² As shown in Figure 1b, the UV-vis-near-IR absorption spectroscopic characterization of the two fractions revealed that m-SWNTs were enriched in the moving fraction and s-SWNTs were entrapped in the staying fraction. The result was similar to what was reported by Tanaka et al.¹⁴

The reason why s-SWNTs cannot migrate like m-SWNTs but prefer to be captured in the initial gel is still under discussion. Moshammer et al. once proposed that s-SWNTs tended to exist in the form of small bundles whereas m-SWNTs were predominantly suspended as individual tubes.¹⁹ They thought that the selective dispersionability of SDS led to the different mobilities of m- and s-SWNTs during the gel electrophoresis and finally sorted SWNTs into two fractions. However, Tanaka et al. insisted that the separation effect was due to less SDS molecules adsorbed on the surface of s-SWNTs than those on m-SWNTs. s-SWNTs were easily captured by agarose gel and got separated from m-SWNTs.¹⁸

In our studies, we have proved that the trapping of s-SWNTs in the gel did not result from the size effect by the following two facts. First, agarose gel is a porous matrix, whose pore sizes are generally distributed in the range from 200 to 800 nm depending on its concentrations.²³ Since most of sizes of individual SDS-SWNTs, even for bundles of SDS-SWNTs, are smaller than 1 μm , the gel networks are obviously spacious enough for them to travel back and forth. Second, when we repeated the agarose gel electrophoresis of SDS-SWNT-PVP (poly(vinylpyrrolidone)) dispersion prepared by adding PVP to SDS-SWNT dispersion, surprisingly, separation phenomenon could not be observed any more and all SWNTs migrated toward the anode (see the data in Figure S1 of the Supporting Information). In SDS-PVP dispersed SWNT suspension, the solubility of SWNTs may be enhanced by PVP wrapping, which may make SDS-SWNT entities thicker. If the size effect works here, s-SWNTs should be more difficult to migrate through the agarose gel network. We thus believe that there should be another reason to account for the immobilization of s-SWNTs in the gel. It is well-known that the thermodynamic stability of SDS-SWNT dispersion depends greatly on the aggregated structures of SDS on SWNTs. SDS aggregates adsorbed on SWNTs are often in the dynamic balance with free SDS molecules in dispersion. As a result, some environment changes, such as variations in pH and temperature, and salt additions may cause the aggregation and distribution changes of SDS in the dispersion, leading to the precipitation of SWNTs.²⁴ Considering the important role of SDS in the dispersion and separation, we ought to pay more attention to the aggregated structure changes of SDS molecules on s- and m-SWNTs before and after the electrophoresis.

Figure 2 shows the influence of SDS concentrations on the adsorption behaviors of TN molecules. When TN molecules are dissolved in aqueous solutions with SDS concentrations above (1%) and below (0.02%) its critical micelle concentration (cmc, 0.24%), as shown in Figure 2a, SDS-TN solutions show light blue and violet colors, respectively. Their absorption curves were shown in Figure 2b. At the SDS concentration above the cmc, TN molecules exhibited two absorption bands, one absorption peak at 601 nm and one shoulder peak at 560 nm, respectively. It has been well-accepted that, at the SDS concentrations above the cmc, TN molecules prefer to intercalate with SDS micelles in the form of monomers by strong electrostatic and hydrophobic interactions, showing a strong peak

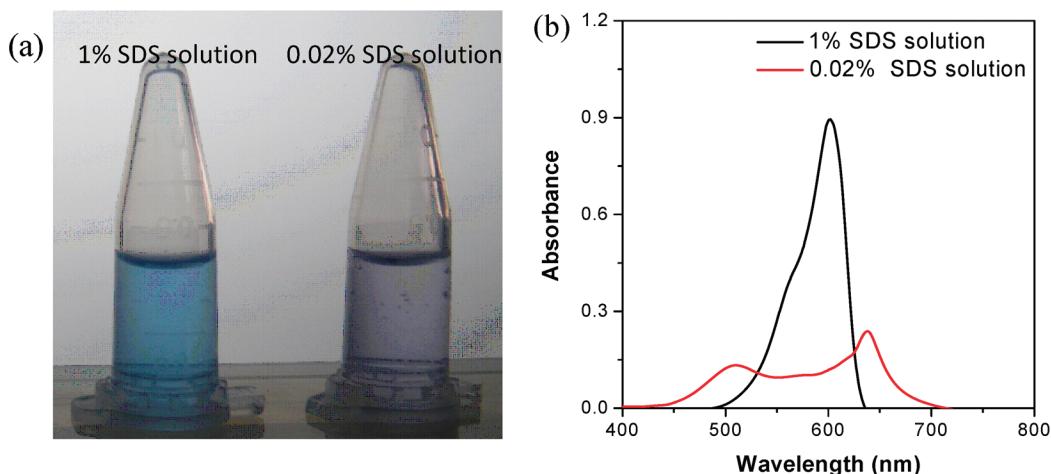


Figure 2. (a) Photographs of TN molecules in aqueous SDS solutions with the concentrations at 1 and 0.02%, respectively; (b) their corresponding UV-vis absorption spectra.

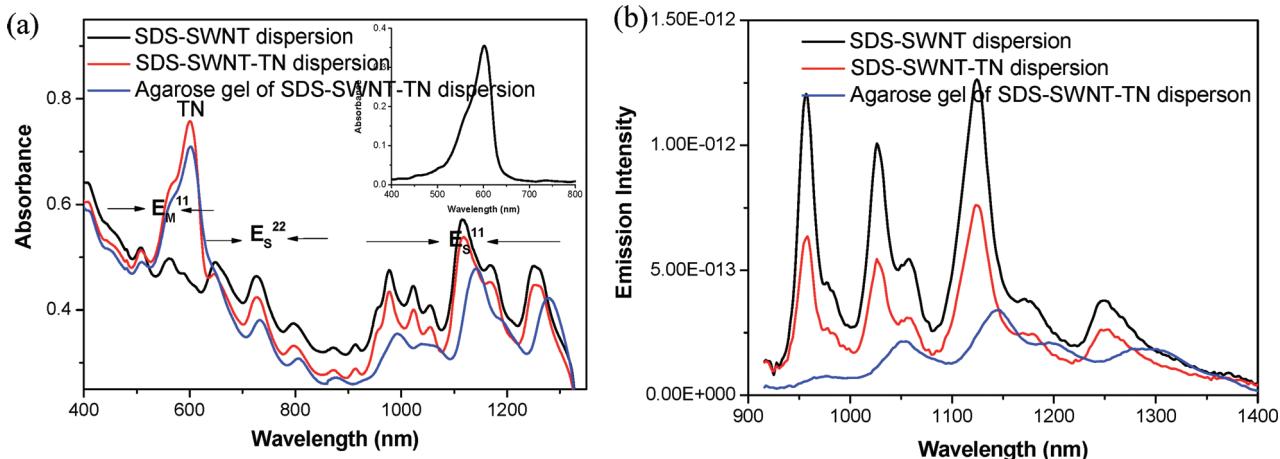


Figure 3. (a) UV-vis-near-IR absorption spectra of SDS-SWNT dispersion before and after the addition of TN and agarose as well as the inset showing the curve subtracted from SDS-SWNT spectra before and after the addition of TN; (b) their corresponding fluorescence spectra excited at 658 nm.

around 601 nm.²¹ When the SDS concentrations dropped below the cmc, the absorbance of TN monomer at 601 nm decreased obviously and two new absorption bands appeared at 509 and 637 nm, indicating that TN molecules favorably exist in the form of dimers due to the weak interaction between TN and SDS.

In the case of SDS-SWNT dispersions, the SDS concentration used is usually above the cmc. In our experiments, the SDS concentration in all SWNT dispersions was fixed at 1% (around $4 \times$ cmc). Under this condition, SDS molecules tend to self-assemble into cylindrical or semicylindrical aggregates on SWNT surfaces (called as SDS-SWNT entities) with hydrophobic alkyl chains interacting with tube surface and hydrophilic sulfate headgroups pointing toward the water.²⁵ As a matter of this fact, SDS-SWNT entities were negatively charged, excluding each other and steadily existing in the solution. Therefore there are two kinds of SDS aggregation states in the SDS-SWNT dispersion, free SDS micelles and SDS aggregates adsorbed on SWNT surfaces, i.e., SDS-SWNTs entities.

When TN molecules are added into the above SDS-SWNT dispersion, undoubtedly, they may intercalate with SDS micelles by the hydrophobic and electrostatic interactions. As such, TN molecules prefer to interact with SDS-SWNT entities without selectivity in the electronic structure of tubes, implying that such nonspecific interaction more likely arises from the binding of TN molecules with outer SDS aggregates of SDS-SWNTs entities (see the data in Figure S2 of the Supporting Information).

Figure 3 shows the spectroscopic characterization results of SDS-SWNTs dispersions before and after the addition of TNs. When TN molecules are added into the 1% SDS-SWNT dispersion and kept at 3.2×10^{-4} M, the pristine absorption bands of SWNTs and their absorbance hardly change, except that the absorption bands of m-SWNTs are partly overlapped by the absorption band of TN molecules, as shown in Figure 3a. The subtraction spectrum of the two spectra obtained from the SDS-SWNT and SDS-SWNT-TN solutions helps take out the influence of SWNTs, as shown in the inset of Figure 3a. The appearance of the absorption peak at 601 nm and the shoulder peak at 560 nm indicates that TN molecules dominantly exist as monomers to interact with the SDS aggregates in SDS-SWNT entities.

Figure 3b shows the fluorescence spectra of the SDS-SWNT dispersions excited at 658 nm. As only s-SWNTs can fluoresce, the fluorescence peaks appeared are correlated with individual SDS-s-SWNTs with different chiralities.²² The addition of TNs merely resulted in slight fluorescence quenching but no peak shifts, which suggested a weak interaction of TNs with SDS-s-SWNT entities. Such a weak interaction arose probably from the intercalation of TNs into outerlayer SDS aggregates adsorbed on SWNTs rather than the direct interaction with SWNTs. Otherwise, obvious changes might have been observed in fluorescence intensities and peak positions. Moreover, when electroneutral agarose molecules were further added into TN-

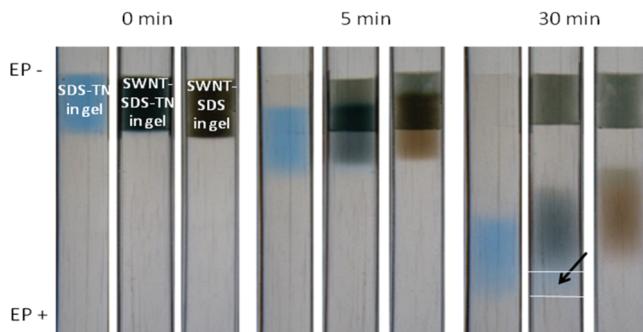


Figure 4. Sequential photographs of SDS-TN gel, SWNT-SDS gel, and SWNT-SDS-TN gel performed by agarose gel electrophoresis at 0, 5, and 30 min, respectively.

SDS-SWNT dispersions, remarkable red shifts were seen with the absorption bands and fluorescence peaks of SDS-s-SWNTs, indicating that agarose experienced a strong interaction with s-SWNTs.

The selective interaction of s-SWNTs with agarose can be further confirmed by the following facts: (1) as shown in Figure S3 (Supporting Information), we prepare an agarose gel film and immerse it into the SDS-SWNT dispersion. After a thorough rinsing, both absorption and Raman bands reveal that s-SWNTs are selectively and favorably adsorbed onto the agarose film. (2) Such interaction is unique. If SWNTs are dispersed by sodium dodecylbenzenesulfonate (SDBS) and SDS-PVP, the s-SWNTs will migrate with m-SWNTs when performing agarose gel electrophoresis. Meanwhile, with the addition of agarose, the characteristic absorption and emission peaks of s-SWNTs hardly shift and quench, suggesting that the entrapment of s-SWNTs in the gel shown in Figure 1 is related to the surface properties of tubes.

Figure 4 illustrates the electrophoresis results of SDS gel and SDS-SWNT gels with and without the TN probe, respectively. It could be observed that although TN is a positively charged dye, when dissolved in 1% SDS solution, TNs would interact with SDS micelles to form negatively charged SDS-TN micelles and migrate toward the anode under the electric field, if, without the presence of SDS, positively charged TN molecules in the gel would migrate toward the opposite direction, the cathode (not shown here). The electrophoresis of SDS-SWNT gel with TNs also resulted in the separation of SWNTs into two fractions, such as the case of SDS-SWNT gel without TNs. The staying

fraction in the initial gel showed a Spanish green color, pretty similar to that observed in the staying fraction of SDS-SWNT gel without TNs. The moving fraction, however, showed two color regions, a light blue region (arrow direction), which migrated faster and displayed color similar to the case of SDS-TN, and a gray-blue region (the region above arrow), different from the color obtained with SDS-SWNTs without TN probe. Electrophoresis of a shorter SDS-SWNT gel with TNs leads to the appearance of two separately dyed regions, the one in blue corresponding to SDS-TN micelles and the other in palumbine arising from SDS-m-SWNT-TN entities, well-confirmed that the TN molecules migrate with SDS-m-SWNT entities under the electric field (see Figure S4a in the Supporting Information). Their corresponding absorption spectra further prove our suggestion (see Figure S4b in the Supporting Information).

Figure 5a shows the absorption spectra of the moving fractions in the above-mentioned gels. Compared with the absorption features of initial SDS-SWNT dispersion, the moving fractions in SDS-SWNT and SDS-SWNT-TN gels exhibited obvious decreases of the band absorbance featured by s-SWNTs and relative increase in the band absorbance featured by m-SWNTs, indicating the enrichment of m-SWNTs. Moreover, TN molecules in the moving fraction of SDS-SWNT-TN gel showed the strong absorption bands of TN monomers, which agreed well with the results of electrophoresis; i.e., TN molecules tended to bind with free SDS micelles as well as SDS-m-SWNT entities, and they would migrate at slightly different rates due to different charged status of the two components.

Figure 5b shows the absorption spectra of the staying fractions of the two cases. It can be seen clearly that m-SWNTs have been largely sorted out and s-SWNTs were enriched in the initial gel. More importantly, we cannot detect the presence of TN molecules either in monomer or dimer forms. Absorption spectroscopy is a sensitive method to detect the presence of TN molecules, whose detection limit to TN is around the order of magnitude of 10^{-7} M. The absorption absence of TN molecules in the staying gel indicated that free SDS micelles as well as outlayer SDS aggregates of s-SWNTs bound with TN molecules more likely preferred to migrate to the anode under the electric field.

Regarding the separation mechanism, our spectroscopic studies have provided the direct evidence that agarose had a selective interaction with SDS-s-SWNTs rather than SDS-m-SWNTs, probably through a hydrophobic interaction.²⁶ Com-

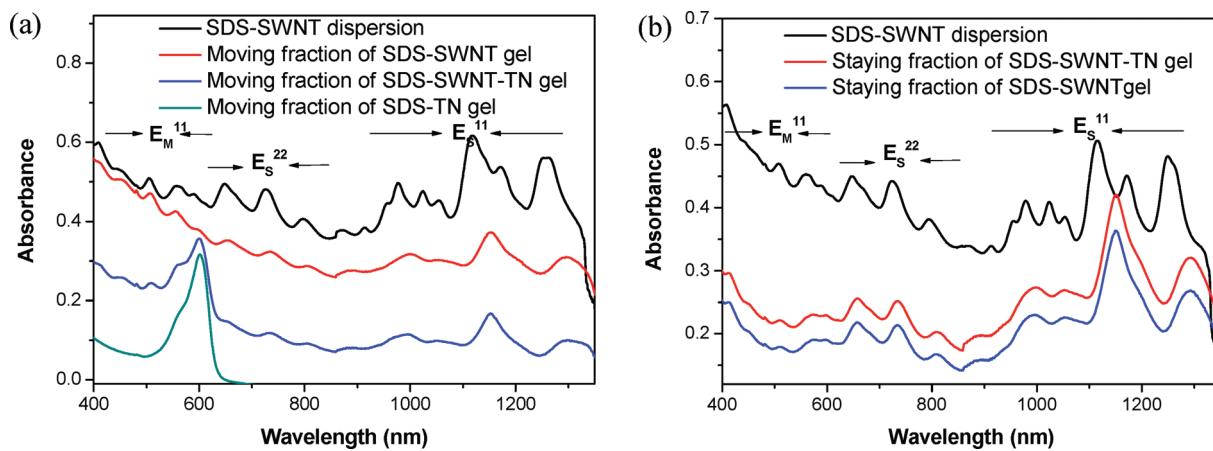


Figure 5. (a) UV-vis-near-IR absorption spectra of initial SDS-SWNT dispersion and the moving fractions collected from the three kinds of gels after agarose gel electrophoresis shown in Figure 4; (b) UV-vis-near-IR absorption spectra of initial SDS-SWNT dispersion as well as the staying fractions collected from SDS-SWNT gels with and without TNs after agarose gel electrophoresis.

parison of the absorption bands of s-SWNTs interacted with agarose before and after electrophoresis (see the data in Figure S5 of the Supporting Information) revealed a slight difference as well, in which absorption peaks featured by E_{S}^{11} transitions of s-SWNTs shifted red obviously after electrophoresis. Such a difference could be only attributed to the SDS changes on s-SWNTs, in good agreement with what we observed in Figure 4 and Figure 5b. The absence of TN molecules in the staying fraction enriched by s-SWNTs revealed by absorption spectroscopy suggested that the SDS aggregates sitting on the outer layer of SDS-s-SWNTs entities were probably desorbed during electrophoresis.

As a result the selective interaction of s-SWNTs with agarose and easy exfoliation of SDS aggregates from s-SWNTs could be ascribed to less SDS numbers on s-SWNT surfaces, as suggested by Tanaka et al. Less SDS molecules assembled on the s-SWNT surface were attributed to the low density of charges on s-SWNTs, in return, causing the weak interaction between SDS and s-SWNT and less charged surfaces of s-SWNTs, which may allow a hydrophobic interaction between SDS-s-SWNTs and electroneutral agarose molecules. When an electric field was applied, outer SDS molecules preferred to exfoliate from SDS-s-SWNTs entities and migrate downward, destroying the thermodynamic stability of SDS-SWNT entities. s-SWNTs were thus entrapped in the gel and could not migrate like m-SWNTs. On the other hand, the selective interaction between s-SWNTs and agarose also limited the mobilities of s-SWNTs in the gel. In contrast, more SDS molecules adsorbed on m-SWNT surfaces caused the SWNT surfaces to be more negatively charged, therefore showing a weak or no interaction with agarose gel, making SDS-m-SWNTs free and movable in the gel, as observed in the brownish red region and palumbine region enriched by m-SWNTs after the agarose gel electrophoresis of SDS-SWNT and SDS-SWNT-TN gels, respectively.

In addition, we also examine if TN probe is available for the case of agarose gel centrifugation suggested by Tanaka et al.¹⁸ Upon the SWNT separation by centrifugation, the absorption spectra of both the supernatant and redispersed precipitation show the existence of TN molecules, very different from the case of electrophoretic separation (see Figure S6 in the Supporting Information). We consider that there more likely underlies a different mechanism between electrophoresis and centrifugation separation. By electrophoresis, the free SDS and the m-SWNTs which hardly interact with agarose will migrate toward the anode. However, by centrifugation, only the SWNTs which are free in the porous agarose gel tend to be drained out into the supernatant. Since the centrifugal force cannot be strong enough to drain all free SDS micelles out of the gel network, as well as exfoliate the outlayer SDS molecules from SDS-s-SWNT entities, TN molecules are reasonably left in both supernatant and precipitate. It means that the TN probe seems more effective for the electrophoretic separation of SWNTs.

Conclusions

In summary, employing TN dye molecules, whose absorption bands are sensitive to the aggregated structures of SDS, we can roughly evaluate the changes of SDS aggregates during the agarose gel electrophoresis. It has been proved that the separation effect originated from two main factors, the unique interaction of s-SWNTs with agarose gel and exfoliation of SDS molecules from SDS-s-SWNT entities which may cause the precipitation of s-SWNTs in the gel. By understanding the role of SDS in the separation, we are able to further optimize the purification of each fraction and develop a more effective and low-cost separation strategy.

Acknowledgment. We acknowledge the financial support from the 100 Talents Program of the Chinese Academy of Sciences (Grant O9AJ011001), the National Natural Science Foundation of China (Grant O8BF041002), the 973 project (Grant 2011CB932600-G), and the International Cooperation Projects supported by the Ministry of Science and Technology of China (Grant 2009DFB50150).

Supporting Information Available: Electrophoresis experimental details and results of the SDS-SWNT-PVP and short SDS-SWNT-TN gels, well-demonstrating interactions of TN molecules with SDS-SWNT entities as well as selective interactions between s-SWNT and agarose, details of an agarose gel centrifugation experiment of SDS-SWNT-TN gel, and comparison of the absorption spectra of the initial SDS-SWNT gel and staying fraction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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