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Discovery of Surfactants for Metal/Semiconductor Separation of Single-Wall Carbon Nanotubes via High-Throughput Screening

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Supporting Information

ABSTRACT: We report novel surfactants that can be used for the separation of metallic (M) and semiconducting (S) single-wall carbon nanotubes (SWCNTs). Among the M/S separation methods using surfactants in an aqueous solution, sodium dodecyl sulfate plays a key role in density gradient ultracentrifugation (DGU) and agarose gel separations. In this study, we screened 100 surfactants for M/S separation using a high-throughput screening system. We identified five surfactants, which could be used for both DGU and agarose gel separations, suggesting that the basic principle of these separations is common. These surfactants have relatively low dispersibilities, which is likely due to their common structural features, i.e., straight alkyl tails and charged head groups, and appeared to enable M- and S-SWCNTs to be distinguished and separated. These surfactants should stimulate research in this field and extend the application of electrically homogeneous SWCNTs not only for electronics but also for biology and medicine.

On the basis of different configurations of the carbon atoms of single-wall carbon nanotubes (SWCNTs), there are two types of SWCNTs: metallic (M) and semiconducting (S).[1] The current SWCNT synthetic methods generally produce mixtures of SWCNTs. However, these two SWCNT types should be separated for electrical applications. M- or S-SWCNTs are also used in biological applications, because the photoluminescence properties and near-infrared absorption of S-SWCNTs are useful in imaging, thermotherapy, etc.[2] The methods used to obtain electrically homogeneous SWCNTs can be classified into three categories: selective disruption, selective extraction, and separation.[3−5] Although selective disruption[6,7] and selective extraction[8−10] methods produce only M- or S-SWCNTs, both M- and S-SWCNTs can be obtained by the M/S separation method.[11−13] Sodium dodecyl sulfate (SDS, **1**) (Chart 1) plays a key role in density gradient ultracentrifugation (DGU)[12] and agarose or dextran gel separation.[13−16] At first, a mixture of SDS and sodium cholate (SC, **7**) was used when M/S was separated by DGU.[12] However, the separation was also shown to be successful with SDS and NaCl (without SC)[17] or only SDS.[16] In all cases of M/S separations using gels, electrophoresis,[14] mechanical squeezing,[13] diffusion,[13] and chromatography,[15] the combination of SDS and agarose is important because S-SWCNTs but not M-SWCNTs selectively adsorb to the gel.[18] In this communication, we screened various types of surfactants for M/S separation using agarose gels. In a two-step screening, we found five surfactants that can be used for both DGU and agarose gel separations. The discovery of these surfactants should support scientific research and increase the number of applications for separated M- and S-SWCNTs.

To effectively screen over 100 surfactants, we first constructed an experimental system for high-throughput screening. We used a surfactant screening kit for protein crystallization containing 96 types of amphiphiles (anionic, cationic, nonionic, and zwitterionic surfactants (details provided in the Supporting Information, Table S1)) (Detergent Screen HT, Hampton Research Co.); however, the kit contains only a small amount of the reagents (250 μL solution of 10 times the critical micelle concentration (CMC) of each amphiphile). Then, the centrifugation method using agarose gels[13] was applied for screening, because it is suitable for multiple and micro separations. However, we encountered a problem with the preparation of SWCNT dispersions. Usually, SWCNTs are sonicated in a solution containing a surfactant to disperse and isolate them before separation. However, it is quite difficult and laborious to sonicate each surfactant separately, especially on a small scale of <1 mL. Therefore, the SWCNT/SC dispersion was first prepared, and then the surfactants were added to the dispersion.

An SWCNT-dispersed solution was prepared as follows. SWCNTs synthesized by the arc discharge method (Meijo Nano Carbon Co., APJ, 1.4 ± 0.1 nm in diameter) were dispersed in 2% SC (99%, Sigma-Aldrich) at 1 mg/mL and then sonicated using a tip-type ultrasonic homogenizer (Sonifier 250D, Branson) for 33 h. The solution was ultracentrifuged to remove bundles and impurities (210 000*g* for 15 min at 25 °C). The resulting supernatant (upper 80%) was recovered.

M/S separation using the agarose gel centrifugation method[13] was performed as follows. Five microliters of the SWCNT/SC dispersion was mixed with 50 μL of each surfactant solution and incubated for 16 h to complete the surfactant exchange, although there is a possibility that some surfactants cannot displace SC. Next, 45 μL of 0.89% melting agarose in 111 mM TB buffer (pH 8.2) (tris(hydroxymethyl)aminomethane (Tris) aqueous solution pH adjusted to 8.2 with borate) was added, mixed well, and cooled in a microtube for solidification. The resulting gel (100 μL) contained the SWCNTs, 0.4% agarose, 0.1% SC (equal to 2.3 mM, which is one-sixth of the CMC of SC (14 mM)), five times the CMC of each screened surfactant, and 50 mM TB buffer.

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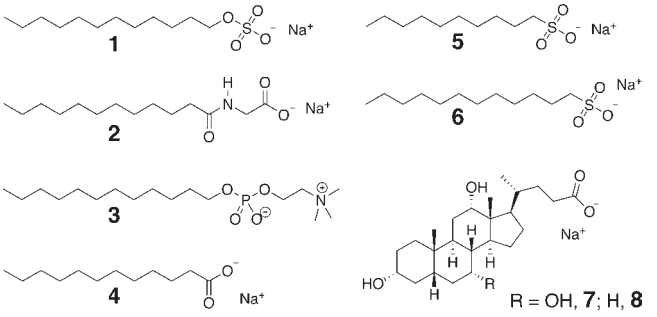
Chart 1. Chemical Structures of the Main Surfactants[a]



[a]Legend: **1**, SDS; **2**, sodium dodecanoyl sarcosine; **3**, dodecylphosphocholine; **4**, sodium dodecanoate; **5**, sodium decanesulfonate; **6**, sodium dodecanesulfonate; **7**, SC; **8**, sodium deoxycholate (DOC).

The microtubes containing the SWCNT gels were centrifuged for 2 h at 16 100*g*. After centrifugation, the squeezed solution (~70 μL) and the gel debris (~30 μL) were separated and collected as the nonadsorbed and adsorbed fractions, respectively. The 40 μL solution containing 0.1% SC and 50 mM TB buffer was added to the gel (adsorbed) fraction, and the mixture was heated to melt the gel before measurements.

For measuring the optical absorption spectra during the screening, we used a microplate reader (400−1000 nm, SH-1000 Lab, Corona Electric Co.), which could measure small amounts (~100 μL) and a few hundred samples at once using a 384-well plate. To evaluate the M/S separation, the intensities of the optical absorptions from metallic SWCNTs (M_{11}) and semiconducting SWCNTs (S_{22} or S_{33}), which vary in their diameters,[19] were compared. For M/S purity evaluation, optical absorption spectra were measured using an ultraviolet−visible−near-infrared spectrophotometer (200−1400 nm, Shimadzu, UV-3600). The purities were estimated from the areas of M_{11} and S_{22} absorptions in reference to those for the sample before separation containing 33% M-SWCNTs and 67% S-SWCNTs.

After the first screening, although clear M/S separation was detected only in SDS as a positive control (Figure 1a), two surfactants (sodium dodecanoyl sarcosine (**2**) and dodecylphosphocholine (**3**)) demonstrated a slight M/S separation (Figure 1b,c). With 65 surfactants, the SWCNTs were dispersed after centrifugation but not separated (Supporting Information, Table S1). The remaining 28 surfactants caused aggregation of the SWCNTs during the course of the separation, resulting in no SWCNTs in the solution fractions. The cationic surfactants, which are oppositely charged to anionic SC, showed no SWCNTs in the solution fractions (2 of 3 cases, Supporting Information, Table S1, nos. 6−8). A comparison of the nonionic or zwitterionic surfactants with surfactants having the same hydrophilic group revealed that the surfactants possessing short alkyl chains tended to result in no SWCNTs in the solution fractions (Supporting Information, Table S1, nos. 28−30, 35−37, 71−73, 74−77, 83, 84, and 86−88).

The positively screened surfactants and SDS shared common features of a straight alkyl tail and a charged head group. Five surfactants (sodium dodecanoate (**4**), sodium myristate, disodium dodecyl phosphate, sodium decanesulfonate (**5**), and sodium dodecanesulfonate (**6**)) were used for the second screening. Three of these surfactants were found to demonstrate M/S separation (Figure 1d−f). The metallic and semiconducting purities after the separation using sodium dodecanesulfonate (55% and 80%)

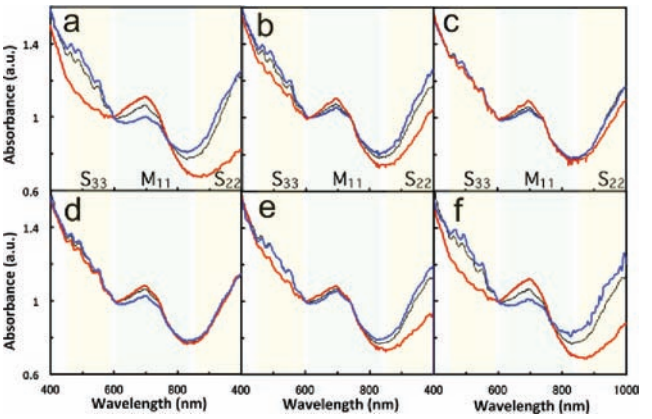


Figure 1. Absorption spectra of separated SWCNTs after the first (a−c) and second (d−f) screenings by a gel centrifugation method: (a) SDS; (b) sodium dodecanoyl sarcosine; (c) dodecylphosphocholine; (d) sodium dodecanoate; (e) sodium decanesulfonate; (f) sodium dodecanesulfonate. The blue and red spectra are the gel (adsorbed) and solution (nonadsorbed) fractions, respectively. Black spectra are the results of the SWCNT dispersion before separation. All spectra were normalized at 600 nm.

were nearly equivalent to those of SDS (60% and 81%) under these conditions, respectively. No loss of SWCNTs occurred in the course of the separation: i.e., the yield was 100%. The amounts of SWCNTs separated into solution and gel fractions were 31% and 69% for sodium dodecanesulfonate while they were 42% and 58% for SDS, respectively.

For the first and second screenings, SC derived from the original SWCNT dispersion was included in addition to the surfactants to be screened. We checked the ability of the screened surfactants to separate M- and S-SWCNTs. SWCNT dispersions using the screened surfactants were separately prepared and used for the agarose gel centrifugation method. The M/S separation was confirmed for sodium decanesulfonate and sodium dodecanesulfonate. For sodium dodecanoyl sarcosine, the separation was confirmed after removing the TB buffer salt from the separation conditions. For sodium dodecanoate, the separation was confirmed without borate (50 mM Tris (pH 11) used instead of the TB buffer). Conditions for the separation of M/S SWCNTs could not be found for dodecylphosphocholine. As a control, no M/S separation was detected using SC or DOC (**8**) (data not shown).

DGU separation was conducted using the screened surfactants. The surfactants were mixed with a separately prepared SWCNT/SC dispersion at a final concentration of 0.5% surfactant and 2.0% SC, and the mixtures were applied to DGU (see experimental details in the Supporting Information). These separation conditions yielded highly pure S-SWCNTs and low-purity M-SWCNTs when SDS/SC was used as the cosurfactant (Figure 2a). Clear M/S separations were obtained with sodium dodecanoyl sarcosine/SC and sodium dodecanesulfonate/SC (Figure 2b,f). For dodecylphosphocholine/SC and sodium dodecanoate/SC, slight M/S separations were observed (Figure 2c, d). For sodium decanesulfonate/SC, results similar to those for only SC without another surfactant were obtained (Figure 2e,g), indicating that a diameter separation of SWCNTs occurred because DGU using only SC as a surfactant led to a diameter separation.[12] The higher absorption ratio S_{22}/M_{11} in the case of sodium dodecanesulfonate/SC as compared to the absorption

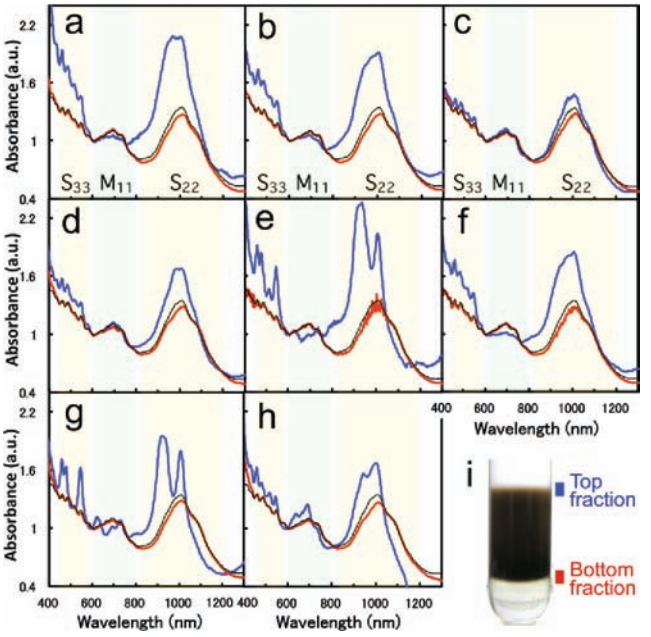


Figure 2. Absorption spectra after DGU separation: (a) SDS/SC; (b) sodium dodecanoyl sarcosine/SC; (c) dodecylphosphocholine/SC; (d) sodium dodecanoate/SC; (e) sodium decanesulfonate/SC; (f) sodium dodecanesulfonate/SC; (g) 2% SC without another surfactant; (h) 0.5% DOC and 2% SC. (i) Photograph of the centrifuge tube after DGU separation using a cosurfactant mixture of 0.5% sodium dodecanesulfonate and 2% SC. A mixture of 2% SC and 0.5% screened surfactant was used for the DGU (a−f). The blue and red spectra are the top and bottom fractions as indicated in (i), respectively. Black spectra are the results of the SWCNT dispersion before separation. All spectra were normalized at 600 nm.

ratio of only SC indicated that M/S separation also occurred in addition to diameter separation. The diameter separation observed in sodium decanesulfonate/SC was likely caused by insufficient exchange between SC and sodium decanesulfonate, which have shorter alkyl tails (i.e., weaker hydrophobicity) than the other screened surfactants. When DOC/SC was used for DGU as a control experiment, no M/S separation was detected (Figure 2h). These results indicate that all of the surfactants screened by agarose gel separation can also be used for M/S separation by DGU.

We found five surfactants for M/S separation using a micro, high-throughput screening system. However, some surfactants that can be used for separations were possibly missed because only one condition was conducted for each surfactant in the screening. The M/S separation was successful when only one parameter was changed not to use the TB buffer in the cases of sodium dodecanoyl sarcosine and sodium dodecanoate, as described above. In some cases, the concentration of SC retained from the original SWCNT dispersion was much higher than that of the screened surfactants (Supporting Information, Table S1). In other cases, the separation ability of the screened cationic surfactants might have been canceled out by the oppositely charged anionic SC. If the separation conditions are changed, e.g., pH, concentration of the surfactants, and use of nonionic or cationic surfactants for the original SWCNT dispersion, it may be possible to find other surfactants that can be used for M/S separations.

Although some types of surfactants that can be used to separate M- and S-SWCNTs may have been missed, all of the screened surfactants could be used for both agarose gel and DGU separations. These results suggest that the basic principle of the separations using agarose gel and DGU is common for both. In the M/S separation using agarose gel, M- and S-SWCNTs show different interactions with the gel and SDS (or the surfactants screened here). Although it was reported that M/S separation by DGU is possible using only SDS as a surfactant,[16] efficient M/S separation was achieved when cosurfactants of SDS and SC were used.[12] Similar to agarose gel separation, M- and S-SWCNTs seem to interact with SC and SDS (or the screened surfactants) with different affinities in DGU separation.

Differences in surfactants enable the separation of M- and S-SWCNTs. SC and DOC are known to disperse SWCNTs very well[20] but cannot separate M- and S-SWCNTs. These surfactant molecules have flat structures and are thought to interact with SWCNTs at the hydrophobic face of the surfactants.[21] As a result, their superior dispersibility that is derived from the stickiness of the hydrophobic face is not able to discriminate between M- and S-SWCNTs. In contrast, all of the surfactants found by this screening study have straight alkyl tails and charged head groups as their hydrophobic and hydrophilic groups, respectively. These surfactants seem to interact with SWCNTs via the tip or side of the straight alkyl tail,[22,23] resulting in weak interactions between these surfactants and SWCNTs. Indeed, the stability of the SWCNT/SDS dispersion is not high. Using old dispersions prepared more than a few weeks in advance resulted in poor M/S separation, which is presumably due to the aggregation of the SWCNTs (data not shown). The lower dispersibility of these surfactants, i.e., weak interactions between these surfactants and SWCNTs, allowed the discrimination of the differences between M- and S-SWCNTs, e.g., ζ potential. It is important to note that all the surfactants structurally similar to SDS which have linear alkyl tails and charged head groups cannot be used for the M/S separation (Supporting Information, Table S1, nos. 5, 71−73, 75−79, and 82−89). The surfactants with dispersibilities lower than that of SDS, such as some nonionic surfactants or surfactants with an imbalance between hydrophobicity and hydrophilicity, may be insufficient to maintain individual SWCNTs in isolated states, resulting in the failure of M/S separation.

In this study, we found five novel surfactants for use in the M/S separations. Although the purity of the separated SWCNTs was not as high as with some surfactants, such as SDS, it can be improved by changing various parameters. These surfactants should increase the number of applications that can use separated M- and S-SWCNTs. For example, dodecylphosphocholine is suitable for biological applications because of its similarity to biological lipids and its biocompatibility, as well as for electric applications due to its lack of sodium ions, which can be detrimental to electrical devices.[24] Most recently, we reported the separation of monostructured S-SWCNTs in addition to M/S separation.[25] Newly found surfactants could also be used to improve this type of separation.

In conclusion, a high-throughput surfactant screening system for the M/S separation of SWCNTs was constructed, and five surfactants were identified from 100 screened surfactants. The common features of the surfactants—a straight alkyl tail and a charged head group—suggest that the appropriate dispersibility of SWCNTs by these surfactants allows M- and S-SWCNTs to be discriminated and separated. Because these surfactants could be used for not only gel separation but also DGU, the fundamental principle of these separations was suggested to be common to both: i.e., gel separation (or DGU) utilizes different

affinities of the surfactants and gel (or SC) with M- and S-SWCNTs. The variety of the surfactants that were found in this study should accelerate and expand research efforts involving M/S separations and increase the number of applications using separated SWCNTs.

■ ASSOCIATED CONTENT

Supporting Information. Text and a table giving the first screening results, experimental details of DGU, and the complete ref 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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