Strong Chemical Structure Dependence for Individual Dissolution of Single-Walled Carbon Nanotubes in Aqueous Micelles of Biosurfactants

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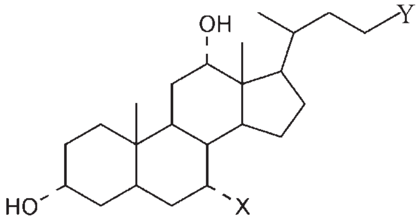
We report a strong chemical structure dependence for the individual dissolution of single-walled carbon nanotubes (SWNTs) in aqueous micelles of six steroid biosurfactants including sodium cholate (SC), sodium deoxycholate (SDC), sodium taurodeoxycholate (STDC), sodium glycocholate (SGC), 3-[(3-cholamidopropyl)dimethylammonio]propane-1-sulfonic acid (CHAPS), and sucrose monocholate (SMC) and two sugar surfactants, *n*-octyl β-D-glucoside (OG) and *n*-decyl β-D-maltoside (DM).

Due to the insolubility of nanotubes in solvents, chemical, biochemical, and biological (medical) approaches using these materials have been very limited.[1] We are interested in the design of carbon nanotube (CNT) solubilizers as well as the fundamentals and applications of soluble CNTs. We have reported that compounds carrying a polycyclic aromatic moiety, such as pyrene and porphyrin, act as CNT solubilizers.[2,3] Recently, we[4] and others[5] reported the finding that DNA molecules dissolved SWNTs in aqueous solutions. Several types of surfactants, such as sodium dodecyl sulfate, hexadecyltrimethylammonium bromide, and Triton X-100, are known to dissolve SWNTs in water.[1] It is important to find biosurfactants that dissolve SWNTs for applications of carbon nanotubes in many biochemical areas. Here, six different steroid moiety-carrying biosurfactants including SC, SDC, STDC, SGC, CHAPS, and SMC, and two different sugar biosurfactants including OG and DM (Figs. 1 and 2) that have been known as membrane protein solubilizers[6] were used, in which SC, SDC, STDC, and SGC are anionic and CHAPS is zwitter ionic. SMC, OG, and DM are nonionic. In this study, we found a strong chemical structure dependence for the solubilization of SWNTs. Very recently, we[7] and Hertel's group[8] described that aqueous micelles of SC could dissolve SWNTs.

SWNTs (HiPcoTM, the length and diameter of pristine SWNTs are ca. 1–10 µm and 0.8–1.2 nm, respectively) were purchased from Carbon Nanotechnologies Inc. and were used as received. All biosurfactants (Dojindo Laboratories, Japan) were used as received. A typical procedure for the solubilization of SWNTs is as follows.[2,7] About 0.5 mg of SWNTs were added to an aqueous micellar solution (1.0 wt %, 5 mL) and then sonicated (Branson 5510) for 1 h. After centrifugation at 60000 g for 1 h to remove undissolved SWNTs, the supernatant was collected and then characterized.



X = OH, Y = COONa : Sodium cholate
X = H, Y = COONa : Sodium deoxycholate
X = OH, Y = CO-NH-$(CH_2)_3$-$N^+(CH_3)_2$-$(CH_2)_3$-SO_3^- : CHAPS
X = OH, Y = CO-NH-CH_2-COONa : Sodium glycocholate
X = H, Y = CO-NH-$(CH_2)_2$-SO_3Na : Sodium taurodeoxycholate
X = OH, Y = sucrose : Sucrose monocholate

Fig. 1. The chemical structures of biosurfactants.

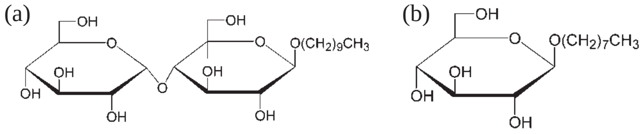


Fig. 2. Chemical structures of sugar surfactants, *n*-decyl β-D-maltoside (a) and *n*-octyl β-D-glucoside (b).

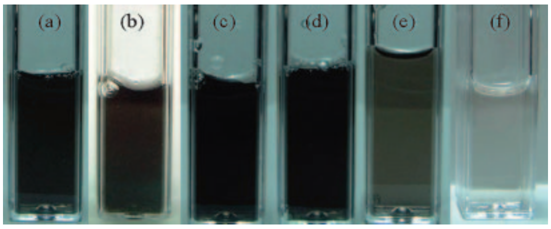


Fig. 3. A photo of SWNTs in water in the presence of 1.0 wt % of SC (a), SDC (b), STDC (c), SGC (d), SMC (e), and CHAPS (f).

Figure 3 shows a photo of SWNTs in aqueous micelles of the given biosurfactants. It is clear that SDC, STDC, and SGC produced transparent deep black-colored solutions like SC micelles, indicating that these biosurfactants could dissolve/disperse SWNTs. No precipitate was generated in the solutions for more than two months at room temperature. In contrast, almost no color change was observed in the micellar solution of CHAPS and a light black color was observed when SMC was used.

The visible–near IR spectra (JASCO, V-570) of biosurfactant-assisted solutions of SWNTs are shown in Fig. 4, where in the near-IR region, spectral features attributable to individually dissolved SWNTs[9] were observed for micellar solutions of SC, SDC, STDC, and SGC; that is, the bandgap transitions in the first pair of singularities in the density of states of the semiconducting SWNTs (S1) near 1100–1400 nm are very sharp. These results indicate that individually dissolved semi-

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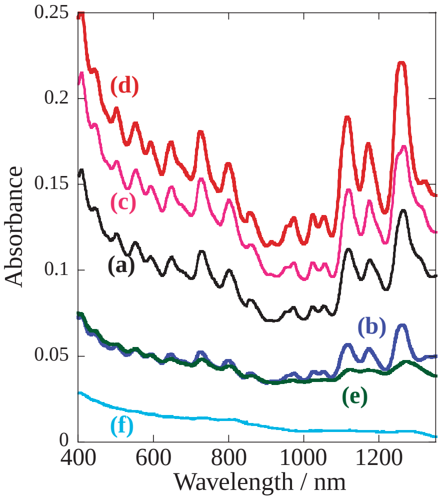

Fig. 4. The visible–near IR spectra for SWNTs in aqueous solutions containing 1.0 wt % of SC (a), SDC (b), SGC (c), STDC (d), SMC (e), and CHAPS (f). Optical cell length is 1 mm for (a)–(e) and 1 cm for (f).

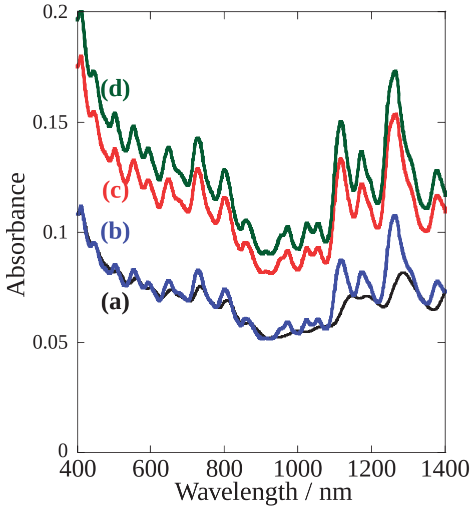

Fig. 5. The visible–near IR spectra of solutions of SWNTs in aqueous solutions containing SC = 1 mM (a), 14 mM (b), 20 mM (c), and 50 mM (d). Optical cell length, 1 mm.

conducting SWNTs existed in these micellar solutions. SWNTs concentrations in these micellar solutions after centrifugation at 60000 g were approximately 0.1–0.2 mg mL^{-1}, which were higher than those of SWNTs dissolved in sodium dodecyl sulfate.[8] Among these, the concentration of SWNTs in the micelle of STDC was the highest. Compound SMC gave a broad S1 band (Fig. 4, spectrum e), suggesting a formation of bundled SWNTs in water. As can be seen in Fig. 4 (spectrum f), the solubilization ability of CHAPS micelles was found to be extremely low.

The effects of the critical micelle concentration (cmc) of SC (cmc = 14 mM, 1 M = 1 mol dm^{-3})[10] on the solubilization of SWNTs were examined and the results are shown in Fig. 5. It was evident that even at concentrations below the cmc, SWNTs could be dispersed in water. This might be due to the adsorption of the hydrophobic steroid structure onto the sidewalls of SWNTs. However, for the 1.0 mM SC solution, S1 peaks near 1100–1400 nm were very broad, suggesting that colloidal dispersion of SWNTs existed in the solutions. The absorbance of the near-IR spectra of SWNTs in water containing SC increased with increasing concentration above the cmc, while the shapes of the spectra resembled each other. Almost no absorbance was detected for 1.0 mM aqueous solutions of CHAPS (data not shown). It is clear that the affinity of CHAPS toward SWNTs is very low.

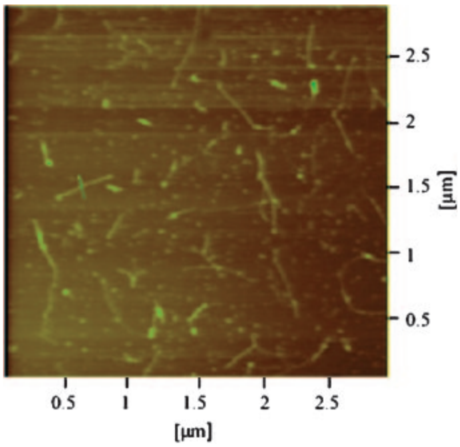

Fig. 6. AFM image of SWNTs dissolved in an aqueous micelle of SC.

Together with the obtained data and the fact that the fundamental physical properties of the six biosurfactants are not much different and the side chains of CHAPS and SMC are bulky compared to those of the other four biosurfactants, it is suggested that the unexpected strong chemical structure dependence of the dissolution behaviors might be due to steric effects; that is, adsorption of the steroid moiety of CHAPS and SMC to the sidewalls of SWNTs might be hindered by steric effects. Even at concentrations higher than the cmc, the adsorption of the steroid moiety to SWNTs might play an important role in the solubilization of SWNTs.

An atomic force microscope (AFM) was used to visualize SWNTs in aqueous solutions of different biosurfactants. A typical AFM image on mica is shown in Fig. 6. From the top heights of the nanotubes in the AFM image, the diameters more than 80% (for 40 nanotubes) of the nanotubes were found to range between 0.8–1.8 nm, indicating the existence of individually dissolved SWNTs in the solution since the diameter of the SWNTs used was ca. 0.8–1.2 nm. The results are in accordance with those of near-IR spectroscopy.

A search was made to find a nonionic biosurfactant that dissolves SWNTs individually in water since the nonionic steroid surfactant SMC gave the broad S1 band of SWNTs. We examined two different sugar surfactants, OG and DM, and found that an aqueous micelle of DM could dissolve SWNTs (Fig. 7). As shown in Fig. 8, the spectral feature of the near-IR spectra of SWNTs dissolved in a DM micelle resembled that of SWNTs in a micelle of SC, suggesting that SWNTs were dissolved individually, while the concentration of SWNTs in the solution of DM was much lower than that of SC. Here again, we see a strong chemical structure dependence for the dissolution of SWNTs, namely, the sugar surfactant OG

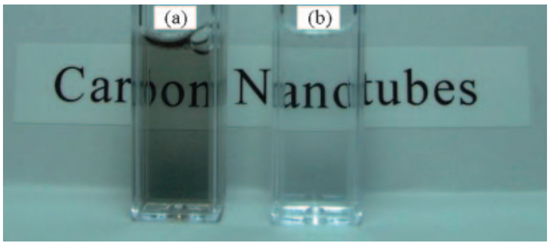

Fig. 7. A photo of SWNTs in water in the presence of 1.0 wt % of *n*-decyl β-D-maltoside (a) and *n*-octyl β-D-glucoside (b).

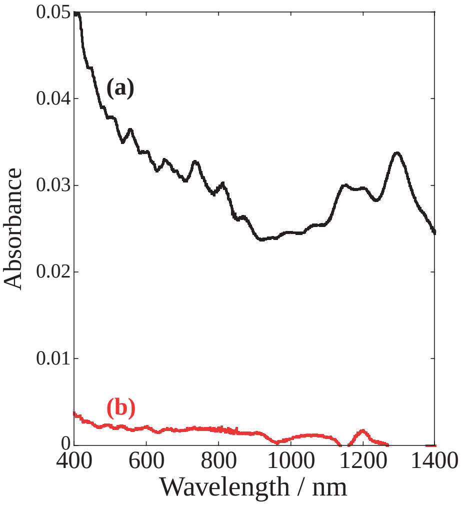

Fig. 8. The visible–near IR spectra of SWNTs in aqueous solutions containing 1.0 wt % of *n*-decyl β-D-maltoside (a) and *n*-octyl β-D-glucoside (b). Optical cell length, 1 mm.

did not dissolve SWNTs at all as exhibited in Figs. 7 and 8. The strong chemical structure dependence might be due to the difference of micellar structures.

In conclusion, we found a strong chemical structure dependence for the solubilization of SWNTs in aqueous micelles of biosurfactants, that is, micelles of SDC, STDC, SGC, and DM dissolve SWNTs individually like SC micelles. At concentrations below the cmc, SWNTs could be dispersed as bundled structures (colloidal dispersions). In sharp contrast, SMC, CHAPS, and OG did not act as good SWNT solubilizers. The obtained strong chemical structure dependence for the solubilization of SWNTs is important for designing novel SWNT solubilizers and their applications in the fields of chemistry and biochemistry.

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