Dispersion of Single-Walled Carbon Nanotubes by Using Surfactants: Are the Type and Concentration Important?

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Single-walled carbon nanotubes (SWNTs) are of a great interest due to their unique mechanical, electronic, and optical properties as well as their interesting applications.[1,2] Unfortunately, their existence in the form of aggregated and parallel bundles[3] (as a result of substantial van der Waals tube–tube attractions) make this material inadequately soluble or dispersible in most of the common solvents, which is crucial to their processing.[4] In order to explore these unique properties and to understand the chemistry of SWNTs, so far, some developments have been made toward the dispersion or solubilization of SWNTs in both organic[5] and aqueous media.[6–8] The dispersion of SWNTs in organic media has been studied with both pristine and chemically modified SWNTs.[5,9,10] It can be improved by chemical substitution,[11] but this creates defects in SWNTs, which hamper the electronic properties.[12] Hence, SWNTs are generally dispersed using surfactants, which can successfully suspend them through supramolecular interactions. Further, stable dispersions of SWNTs in aqueous media are essential owing to potential biomedical applications, which have been facilitated by surfactants and polymers. However, in most of the studies the well-known common surfactant, namely sodium dodecylsulfate (SDS), has been used with particular concentrations, and, astonishingly, very few works have been reported on the optimization of the surfactants or experimental parameters. A few polymers such as poly(vinylpyrrolidone) (PVP),[13] poly(phenylene vinylene),[14] and in the biomedical field, poly(ethylene oxide) (PEO)[15] and DNA[16] are the favored solubilizing polymers to effectively solubilize SWNTs for various applications. Recently, Wenseleers et al. demonstrated that bile salt detergents are extremely efficient in solubilizing pristine SWNTs.[17] Despite the progress in the suspension of SWNTs with surfactants, there are only very few systematic studies on the dispersion of SWNTs by using different types of surfactants such as anionic, cationic, and neutral in view of the optimization of the surfactant concentration and mass percent conversion of SWNTs. Our research group has long been involved in the study of CNTs[18,19] and we have lately reported a novel and simple route to obtain supramolecular adducts[20] of DNA–CNT conjugates from both multi-walled carbon nanotubes (MWNTs) and SWNTs based on a novel solid-state mechanochemical reaction.[21] In a previous report we have also shown rapid purification[22] and individualization[23]/dispersion[24] techniques for SWNTs. Very recently, we introduced novel approaches to disperse SWNTs in aqueous solution by using polymers and to synthesize SWNTs-polymer nanocomposites.[25,26] Motivated by these approaches developed in our laboratory in connection with novel polymeric materials and surfactants[18,19,27–30] we thought of expanding this idea to the dispersion of SWNTs with different surfactants in water following a systematic scheme.

In this study, we used three different surfactants namely Igepal CO-990 [polyoxyethylene(100) nonylphenyl ether] (neutral), cetyltrimethylammonium bromide (CTAB) (cationic), and sodium dodecylsulfate (SDS) (anionic), for dispersing a high concentration of individual SWNTs in an aqueous solution by a supramolecular approach. To the best of our knowledge, this study is the first example of a systematic study on the dispersion of SWNTs in aqueous solution by comparing three different types (neutral, cationic, and anionic) of surfactants, and also considering the effect of significant parameters such as the surfactant and SWNT concentrations. More importantly, we calculated the maximum concentrations of SWNT that can be suspended under different experimental conditions for practical applications. This systematic approach presented here is anticipated to be commonly useful for the dispersion of SWNTs with a high mass percent conversion.

The primary move on the way to the dispersion of SWNTs was to define the appropriate concentration proportion of SWNTs to surfactant. To this point, 12 mg of SWNT

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was mixed with various surfactant concentrations in 30 mL of water and the suspension was subjected to the experimental procedure. The optimum surfactant concentration to disperse the SWNTs varied depending on the surfactant types. The optimum concentration observed for Igepal (IGP), CTAB, and SDS was 0.87, 1.51, and 9.00 m$_M$, respectively. The concentrations of SWNTs suspended with IGP, CTAB, and SDS at optimum concentration were found to be 0.12, 0.08, and 0.16 mg mL^{-1}, respectively. It is pertinent to note that the observed optimum concentration of the surfactants was slightly higher than the critical micelle concentrations (CMC) of the surfactants, and, therefore, it is assumed that most surfactants in the suspensions adsorbed onto the surfaces of the nanotubes.

It is clearly perceived that the SWNT dispersion is homogeneous at the optimum concentration (Table 1) for all three surfactants, whereas the SWNTs are not well dispersed and inhomogeneous at a concentration just below and above the optimum one. Interestingly, an aggregation of SWNTs was observed, when the concentration of the surfactants was much higher than the optimum concentration (Figure 1). Similar trends have been noticed for the other surfactants used, which have been confirmed directly by transmission electron microscope (TEM) images. The molecular structures and models of the surfactants employed in this study are shown in Figure 2.

For the TEM images, we placed a few drops of sample solution onto a copper mesh covered with a carbon film grid. Fig-
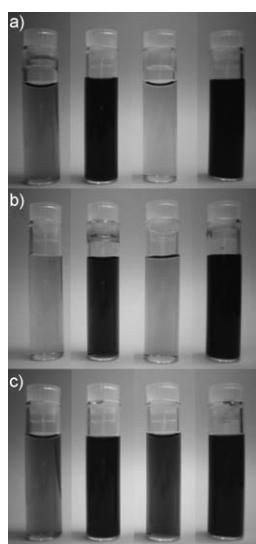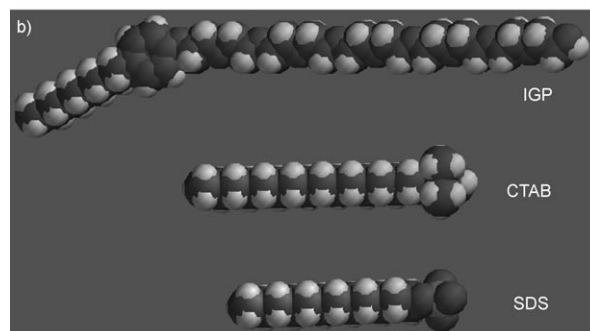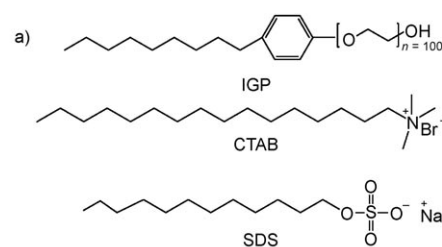

Figure 2. Molecular structures (a) and energy-minimized space-filling molecular models (b) of the surfactants used in this study. IGP: Igepal CO-990, CTAB: cetyltrimethylammonium bromide, and SDS: sodium dodecylsulfate. In the case of IGP a polymer chain containing 10 repeat units is shown in the model for the clarity.

Table 1. Different types of surfactants and their dispersion ability for SWNTs.

Surfactant	Optimum c [m$_M$]	SWNTs c at optimum c [mg L^{-1}]	SWNTs c at optimum c [mg mL^{-1}]	SWNTs c at 0.87 m$_M$ [mg L^{-1}]	SWNTs c at 0.87 m$_M$ [mg mL^{-1}]	Mass conversion at optimum c [%]	Mass conversion at 0.87 m$_M$ [%]
IGP	0.87	119.14	0.119	119.14	0.119	29.76	29.76
CTAB	1.51	78.47	0.078	45.21	0.045	19.60	11.29
SDS	9.00	160.69	0.161	15.53	0.016	40.17	3.88

Figure 1. Photographs of vials containing the aqueous dispersions of SWNTs using a) Igepal CO-990 at 0.21, 0.87, 0.97, and 1.08 m$_M$, (left to right) b) cetyltrimethylammonium bromide (CTAB) at 0.21, 1.51, 1.73, and 1.94 m$_M$, and c) sodium dodecylsulfate (SDS) 2.80, 9.00, 11.00, and 12.00 m$_M$.

ure 3a–d shows the representative TEM images of the IGP-stabilized nanotubes at various concentrations. The resulting final solutions contained mostly individual nanotubes at the optimum concentration that can be visibly seen in the TEM image (Figure 3b). It is worth to mention that at the optimum concentration, the population distributions of SWNTs are much greater than the individual nanotubes observed at just below and above the optimum concentration of IGP (Figure 3a and c). Therefore, we deem that the nanotubes are largely homogeneously covered by the IGP at optimum concentration. The optimum concentration observed slightly exceeded the CMC of IGP (0.83 m$_M$), however, the evidence of surfactant micelles or other phase could not been observed in the TEM images. The fact is that at higher concentrations the nanotubes were aggregated significantly and formed larger SWNT bundles (Figure 3d). This may be due to the higher populations of circular micelle formation at high concentrations. A similar tendency was observed for the other two surfactants and the TEM images (the images of other concentrations are shown in the Supporting Information) of well-dispersed SWNTs at optimum concentrations are shown in Figure 3e and f.
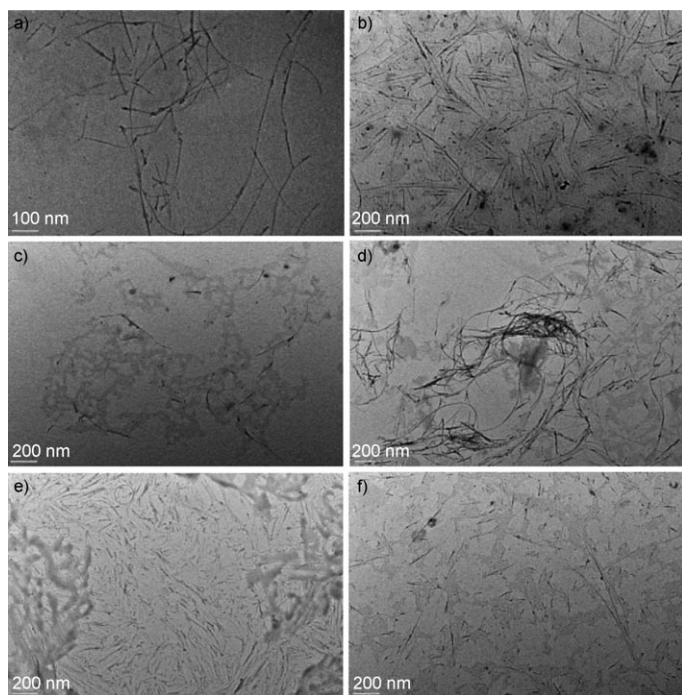
Figure 3. TEM images of a)–d) IGP-stabilized SWNTs, a) at 0.21 mM, b) 0.87 mM (optimum concentration), c) 0.97 mM, and d) 1.08 mM, e) CTAB-suspended SWNTs at 1.51 mM (optimum concentration), and f) SDS-suspended SWNTs at 9.00 mM (optimum concentration).

Figure 4. a) UV-visible, b) NIR absorption spectra of nanotubes suspended in surfactants. -----: SDS (9.00 mM), •••••: CTAB (1.51 mM), ——: Igepal (0.87 mM).

It is well established that the presence of individual SWNTs permits narrow absorbance features in the visible and infrared regions of their optical absorbance spectra due to the van Hove transitions of metallic and semiconducting SWNTs. Figure 4a is a comparison of the absorbance spectra of nanotubes suspended by the three different surfactants. Evidently, the spectra show well-resolved peaks, centered at a range from 440 to 600 nm, that are assigned to the first van Hove transition of metallic SWNTs (M_{11}), and the peaks centered at 600 to 800 nm are attributed to the second van Hove singularity of semiconducting SWNTs (S_{22}). These absorption peaks also corroborate that the electronic properties of nanotubes were sustained in the product, because broad and weak absorbance is a mark of aggregated SWNTs, since intertube van der Waals interactions perturb the electronic structure of the SWNTs.[31] Notably, in the case of individually suspended nanotubes, the semiconducting nanotubes also exhibit near-infrared peaks,[31] which were observed from 900–1300 nm, (Figure 4b), corresponding to the S_{11} transition.

Table 1 contains the results of the SWNT suspensions with the different surfactants studied. It was observed that the optimum concentration needed to disperse the SWNTs among the surfactants used are in the following order; SDS (9 mM) > CTAB (1.57 mM) > IGP (0.87 mM). However, the mass percent conversion trend for these surfactants was observed at an optimum concentration as: SDS (40.17) > IGP (29.76) > CTAB (19.60) and at 0.87 mM in the order IGP (29.76) > CTAB (11.29) > SDS (3.88). From the re-
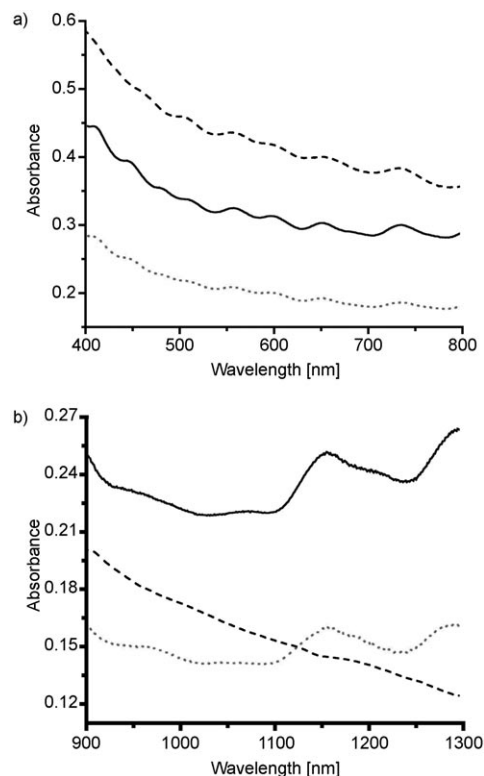
sults obtained, it is interesting to note that IGP could disperse well the SWNTs at a very minimum concentration (for the optimum concentration 0.87 mM) when compared to CTAB and SDS. This can be explained from the structures and models of the surfactants (Figure 2). We believe that the interaction of ionic surfactants with the nanotube surface may be weaker than that of a neutral surfactant (IGP), since they do not contain aromatic rings. Therefore, IGP exhibits much stronger π-orbital interactions with the surface of the nanotubes, which may enhance the binding and surface coverage of the IGP molecules to graphite considerably.[7] As reported in the literature, the agglomeration amount of adsorbed surfactant is dependent on graphite-surfactant interactions, the surface structure, and also on the length of the alkyl chains in the surfactant as well as the head group size and charge.[6,8,32] Among the ionic surfactants, CTAB can suspend better the nanotubes at minimum concentration (for the optimum concentration 1.51 mM) than the SDS, because it has a longer alkyl chain length (~2 nm, which has been derived from the professional program Spartan 04) than the SDS (~1.5 nm) and so the adsorption on graphite was induced exclusively by hydrophobic interactions.[7,32] Although a number of reports have been published on the important dispersion of SWNT by surfactants, until now, only few studies have been dedicated to explain the role of surfactants in the dispersion of SWNTs. Even though a number of neutral surfactants, in ad-

dition to ionic and zwitterionic surfactants,[17] have been used for the dispersion of SWNTs, the dispersion of SWNT by using the IGP has not been reported. Thus, for the first time we are introducing IGP to the catalogue of surfactants used for the SWNT dispersion. In addition, surprisingly, we found that IGP could disperse SWNTs at very low concentrations with a high yield of mass percent conversion. Indeed, a few studies on the surfactant adsorption on graphite indicate that surfactants adsorb forming hemimicelles[7,32,33] that sheath the surface. We also anticipate that the nanotubes are suspended or stabilized by hemimicelles formed by the surfactants (Figure 5), as the surfactants can cover the surface as well. It is important to mention here that the surfactant-suspended nanotubes were found to be stable for more than four months, except for the case of the CTAB-suspended SWNTs, which showed a slight aggregation after three months. Other groups studied the suspension of SWNT with different surfactants by using one particular concentration.[8,33] Here, we studied systematically (Supporting Information) the optimum concentration, in which most of the SWNTs are suspended by surfactants and observed well-dispersed, surfactant-stabilized SWNTs.

Bundle of SWNTs
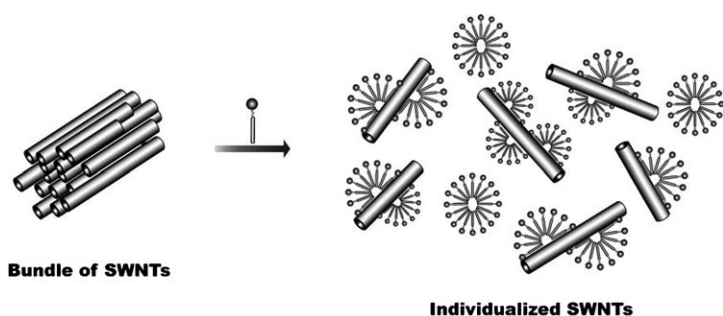
Individualized SWNTs

Figure 5. Illustration how surfactants may adsorb onto the SWNT surface.

We have demonstrated a facile method to disperse a high concentration of SWNTs in aqueous solution by determining the minimum concentration needed to suspend a particular fraction of nanotubes under specific experimental conditions. Three types of surfactants namely, IGP (neutral), CTAB (cationic), and SDS (anionic) have been examined for their capability to disperse SWNTs. All three surfactants could disperse SWNTs well at the optimum concentration, which was found to be slightly higher than that of their CMC value. At very high concentration, SWNTs were aggregated and formed bundles of SWNTs in all the cases. Therefore, by adding more surfactant than the optimum concentration means wasting material and may increase the cost of the process. It is worth to mention here that at a very minimum concentration, the ability of the surfactant IGP to suspend SWNTs was much better than that of CTAB, which in turn was better than the SDS. For the first time we investigated the ability of IGP to disperse SWNTs and the results obtained are encouraging. Therefore, this study may open up the door for the materials and biomedi-cal scientists to produce concentrated and stable aqueous dispersions of individual nanotubes for a variety of applications.

Experimental Section

Our starting materials were aqueous solutions of SWNTs (HiPCO) and three different surfactants (Table 1). After mixing the SWNT solution (400 mg L^{-1}, 0.04 wt%) with surfactant concentrations ranging from 0.21 to 12 mM at room temperature, well-dispersed individual nanotubes were observed after ultrasonication (for 30 min), centrifugation (at 16 000 g for 200 min) followed by ultracentrifugation (at 150 000 g for 3 h). Figure 1 shows the photographic images of the aqueous dispersions of the SWNTs. The transmission electron microscope (TEM) study was conducted using a Hitachi H-9000NA with an accelerating voltage of 120 kV. The TEM samples were prepared by placing a few drops of solution on a copper mesh covered with a carbon film. The absorption spectra of the dispersed SWNTs individuals were observed using a Varian Cary 500 spectrophotometer and a JASCO model V-570 dual beam UV-visible-NIR scanning spectrophotometer.

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