Highlight Review

Fundamentals and Applications of Soluble Carbon Nanotubes

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Abstract

In this review article, we describe i) a strategy for individual solubilization of single-walled carbon nanotubes (SWNTs) in water or organic solvents and ii) some fundamental properties and applications of the solubilized SWNTs.

1. Introduction

Since the discover by Iijima in 1991,[1] carbon nanotubes (CNTs) have received considerable attention from many researchers because of their remarkable electrical, mechanical, and thermal properties.[2] The electrical properties of CNTs, ranging from semiconducting to metallic, have made them excellent candidate materials for novel electronic devices. High Young's modulus and high aspect ratios of CNTs make them useful for reinforcing fibers. The use of CNTs in biological applications is also being exploited.

These potential applications are, however, often limited because of their insolubility in many solvents due to strong intertube van der Waals interactions and difficulty in solvation. Therefore, strategic approaches toward the solubilization of CNTs are essential for the applications of CNTs (Figure 1). The studies may open doors in the areas of chemistry, materials science, electronics, biochemistry, biology, pharmaceutics, and medicine. Mainly two approaches have been proposed for the solubilization/dispersion of CNTs. One is a chemical modification of CNTs via covalent bonding, and the other one is a physical modification via noncovalent bonding. In this review article, we mainly describe the fundamentals and the applications of single-walled carbon nanotubes (SWNTs) solublilized in common solvents via physical modifications.

2. Physical Modification of Carbon Nanotubes

The mechanism for the solubilization of SWNTs by the "solubilizers" is believed to an "unzipping" mechanism proposed by Smalley and co-workers.[3] Surfactant micelles, aromatic compounds, and synthetic and biological polymers act as solubilizers to disperse SWNTs via physical adsorption. Solubilization procedures are simple; SWNTs are placed in a solution of a solubilizer and then sonicated with a low-power (or a high-power) ultrasonic sonicator. Solubility of SWNTs in a solvent via physical modification depends on the type and concentration of the solubilizer and the purity of the SWNTs as well. Through solubilization of SWNTs with noncovalent bonding or physical adsorption is maintained intrinsic SWNTs properties. The method is applicable for as-produced full-length SWNTs and even for the multiwalled carbon nanotubes (MWNTs). Physical properties of SWNTs might be controllable by tuning the interactions of the solubilizers and SWNTs.

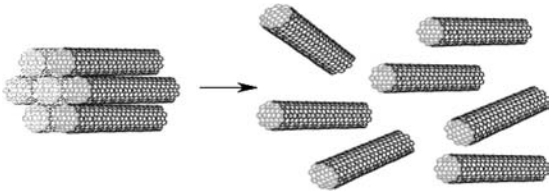

Figure 1. From bundled nanotubes to individually solubilized nanotubes.

2.1 Solubilization Using Surfactants

Smalley and co-workers have reported the preparation of individually dispersed SWNTs by sonication in a micelle of sodium dodecyl sulfate (SDS), followed by ultracentrifugation.[4] Weisman et al. have reported that the as-produced SWNTs individually dispersed in an aqueous micelle of SDS show photoluminescence in the near-IR region.[5] Since their reports, considerable attention has focused on these unique optical behaviors.

SWNTs are dispersed in aqueous micellar solutions of both ionic and nonionic surfactans,[6] such as SDS, sodium dodecylbenzene sulfonate (SDBS), cetyltrimethylammonium bromide (CTAB), Brij, Tween, and Triton X. Surfactants were initially utilized as dispersing agents for the purification of raw carbon materials.[6a] A suggested mechanism for the solubilization is encapsulation of SWNTs in the hydrophobic interiors of the micelles, which results in stable dispersion. Assembled structure of SDS on CNTs has been elucidated from transmission electron microscopic (TEM) observations.[6b] It is important to understand that surfactants are in dynamic equilibrium between the CNTs surfaces and the bulk solution.

Some biological surfactants are powerful for dispersing SWNTs in water.[6e] We have tested anionic, zwitter ionic, and nonionic biosurfactants carrying steroid moiety (bile salts) and sugar biosurfactants as well (Figure 2).[7] All these compounds have been known as membrane protein solubilizers.[8] The chemical structures, especially the substitute groups, of the surfactants play significant roles in the solubilization of SWNTs. Individual dispersion of the SWNTs is possible at concentrations below the cmc of the biosurfactants. Individually dispersed SWNTs in aqueous biosurfactants show photoluminescence in the near-IR

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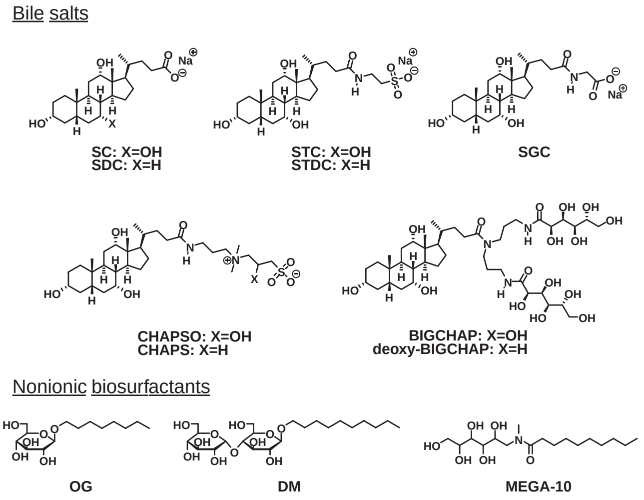


Figure 2. Chemical structures of bile salts and nonionic biosurfactants.

region. Of interest, the chirality indices of the SWNTs solubilized by the biosurfactants depend on the chemical structures of the biosurfactants. Individually dispersed SWNTs in aqueous biological surfactant solutions are attractive for biological applications.

2.2 Solubilization and Functionalization Using Polycyclic Aromatic Compounds

Dai et al. have developed a method for the immobilization of proteins and small biomolecules onto succinimidyl pyrenebutyrate-modified SWNTs.[9] Our strategy to obtain soluble SWNTs involves the use of polycyclic aromatic compounds (Figure 3), which are known to have an affinity for graphite surfaces through π–π interaction. We first synthesized pyrenecarbonylmethyltrimethylammonium bromide (**1**) (Chart 1) that can disperse SWNTs in water by sonication with a bath-type ultrasonic cleaner.[10] Individually dispersed SWNTs were observed in an AFM image although dispersed bundle SWNTs also existed. Near-IR photoluminescence spectrum of SWNTs in aqueous solution of **1** varied from those in aqueous solution of SDS, namely, SWNTs in the aqueous solution of **1** showed photoluminescence from SWNTs in the diameter range of 0.89–1.0 nm.[11] The pyrene ammonium **1** have been utilized by the other researchers for anchoring anionic molecules on the surface of SWNTs and MWNTs.[12] It is widely accepted that the pyrene is an efficient moiety for noncovalent functionalization of CNTs.[13]

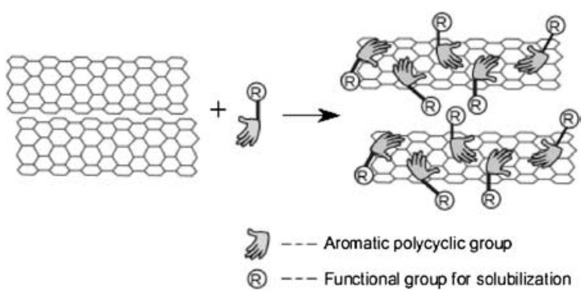
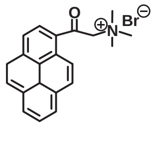


Figure 3. Schematic illustration of strategy for solubilizing SWNTs by a compound carrying anaromatic polycyclic group.



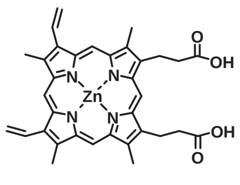
Compound 1

Chart 1.

Our group also found that porphyrin has ability to solubilize/disperse SWNTs for long periods in organic solvents.[14] We have reported that zinc protoporphyrin IX (**2**) solubilizes SWNTs in polar organic solvents such as methanol and DMF. The obtained **2**/SWNTs dispersion was stable even after six months upon storage at 5 °C. In the AFM image of the dispersion coated on mica, the top heights of the nanotubes were in the range of 0.9–1.5 nm, indicating the existence of individually dispersed SWNTs (Figure 4). Bundled SWNTs were also seen in the AFM image. Hemin and protoporphyrin IX diethyl ester can also act as solubilizers of SWNTs in DMF solution. Several groups have reported further investigations of the interactions of SWNTs with porphyrins[15] as well as phthalocyanines.[16]

2.3 Solubilization Using Biological Molecules

Combinations of carbon nanotubes and biological molecules are of interest in many chemical and biochemical areas in relation to both fundamentals and applications.[17] Biological molecules including peptides[18] and proteins[19] have been reported to interact with SWNT's sidewalls and make them more soluble in the solvents. Although there are several papers reporting the interactions between DNA and CNTs, no paper had been published describing CNT solubilization using DNA until our findings.[20] We[21] as well as Zheng et al.[22] have shown that DNA molecules disperse SWNTs in aqueous solutions. Our method was quite simple that is, SWNTs were placed in an aqueous solution of double-stranded DNA (dsDNA) and then sonicated with a bath-type sonicator at temperatures below 10 °C for 1 h. Centrifugation of the suspension for 1 h gave a black-colored transparent aqueous dispersion (Figure 5). The SWNTs/dsDNA dispersions were stable for more than six months upon storage at



Compound 2

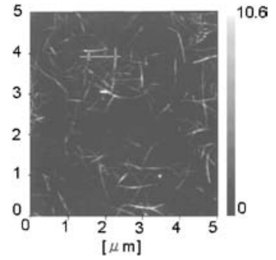


Figure 4. AFM image of SWNTs disperse in a DMF solution of **2**.

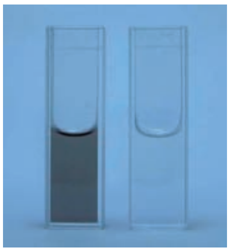


Figure 5. Photograph of aqueous dispersions of the DNA/SWNTs complex (left) and DNA only (right).

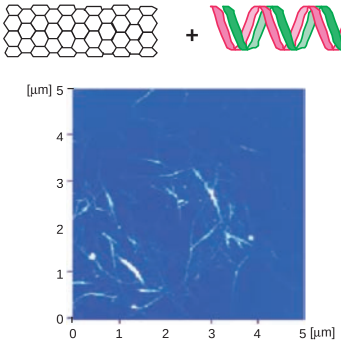


Figure 6. AFM image of SWNTs dispersed in an aqueous solution of DNA.

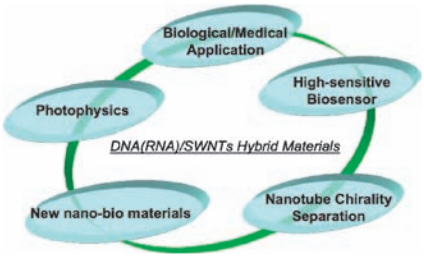
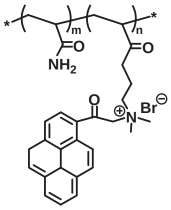


Figure 7. Fundamental and applications of DNA (RNA)/carbon nanotubes nano-biomaterials.

5 °C. AFM image for a SWNTs/dsDNA showed the individual nanotubes dispersed with the aid of dsDNA in water. Optical absorption and photoluminescence spectroscopy and AFM study showed the presence of individually solubilized SWNTs (Figure 6). Since the finding, increasing attention is being given to the fundamentals and applications of DNA (RNA)/CNTs nano-biohybrids (Figure 7).

2.4 Solubilization Using Synthetic Polymers

Wide varieties of synthetic polymers have been found to disperse SWNTs in a many kinds of solvents. Pioneering works solubilizing SWNTs into the solvents were carried out using *p*-phenylenevinylene derivatives (PPVs).[23] SWNTs formed a stable suspension in the presence of PPVs in organic solvents such as chloroform, suggesting that the polymer wraps around the tubes. SWNT complexes with rigid π-conjugated PPVs have remained considerable interest because of their promising opto-electronic properties.[24] It is also believed that the amphiphilicity of polymers may contribute to the dispersion. For example, amphiphilic copolymers, poly(ethylene oxide)-*b*-poly(propylene oxide)[25] and poly(styrene)-*b*-poly(acrylic acid),[26] disperse SWNTs in water and DMF–water mixed solvents, respectively, for which the mechanism is micelle-encapsulation rather than wrapping.



Compound 3

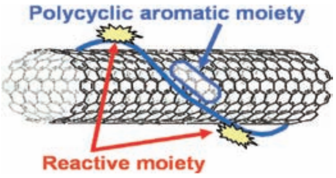


Figure 8. Design of reactive carbon nanotube solubilizers.

When the pendant groups of polymers have strong affinities for the sidewalls of SWNTs, the polymers can wrap the tubes effectively, resulting in the formation of stable dispersions. We synthesized a copolymer of pyrene-carrying acryl amide and acryl amide copolymer **3** and found that the copolymer disperses SWNTs in water, producing a dispersed phase that possesses high thermal stability that is, no precipitate was observed by heating up to 95 °C.[27] AFM images of the aqueous solution showed that SWNTs were dispersed individually. Petrov et al. have reported poly(methyl methacrylate-*co*-(1-pyrene)methyl-2-methyl-2-pronenoate) disperses MWNTs in some organic solvents.[28] The dispersions of SWNTs and MWNTs with the pyrene copolymers is the result of physical adsorption of the pyrene moieties onto the sidewall of the nanotubes.

We have proposed a novel concept (Figure 8) called "reactive carbon nanotube solubilizers," which were synthesized from *alt*-copolymers of styrene and maleic anhydride (P1).[29] Since P1 itself did not have the capability of dispersing SWNTs, several kinds of pendant moieties were introduced onto part of the maleic anhydride units. It was found that P1-bearing anthracene group (Anth-P1, Figure 9) showed high ability for individual solubilization of SWNTs. Figures 10 and 11 show a typical photograph and an AFM image of SWNTs dispersed in DMF using Anth-P1. From the height distribution histogram of the AFM image, the diameters of ca. 80% nanotubes were in the range of 0.8–1.8 nm. Figure 10 (right) shows the surface plot of the AFM image, which suggests individually dispersed SWNTs are wrapped with the solubilizer. We call the Anth-P1 a "reactive nanotube solubilizers" because the copolymers still carry reactive maleic anhydride groups. The concept was demonstrated by introducing 1-hexylamine to the SWNTs/Anth-P1 complex in a THF solution. Our concept should be applicable to the construction of individually dispersed SWNTs with a variety of chemical, physical, biochemical, and medical functions.

Further studies revealed that near-IR light irradiation to SWNTs/Anth-P1 in DMF caused flocculation of the SWNTs. As shown in Figure 12, near-IR laser irradiation to the SWNTs/Anth-P1 solution generates black flocculates, and the dark gray color of the solution was lost with an increase in the irradiation

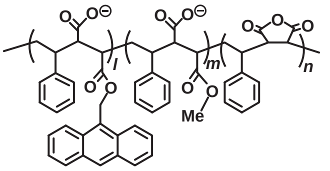


Figure 9. Chemical structure of Anth-P1.

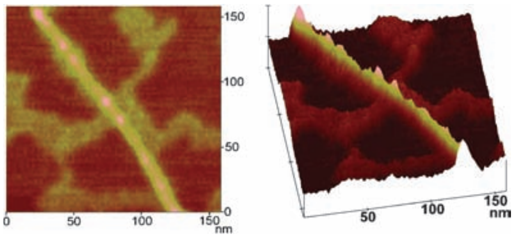


Figure 10. Typical AFM images (left: top view, right: its surface plot) of the SWNTs/Anth-P1 on mica. The heights of the tube are 1.93 and 0.92 at highest and lowest points, respectively.

Figure 11. Photograph of SWNTs dispersed by Anth-P1.

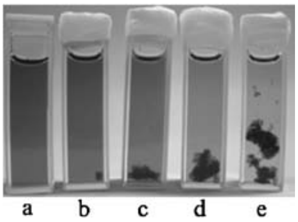


Figure 12. Photograph of the SWNTs/Anth-P1 solutions in DMF before and after laser irradiation for (a) 0 min, (b) 5 min, (c) 10 min, (d) 30 min, and (e) 60 min.

time. Photothermal conversion of SWNTs provided intense heat just around them over a very short period. As a result, Anth-P1 dissociates from the laser-irradiated SWNTs and SWNTs start to form bundles through strong π–π and van der Waals interactions. In fact, we observed an increase in the temperature of the composite solution upon photoirradiation. The finding reveals that carbon nanotubes act as a "molecular heater"-triggering structural changes in the carbon nanotube nanocomposites. The present finding should be useful for many carbon nanotube applications. Similar near-IR-induced release of the wrapping polymer has been reported for a SWNTs/DNA composite by Dai et al.[30] The strategies are promising for new gene and drug delivery materials.

3. Formation of Topological Structures

Construction of nanoscaled superstructures through self-organization of carbon nanotubes is a great challenge, and soluble carbon nanotubes are suitable materials for this goal. Ring-shape formation of SWNTs[31] as well as MWNTs[32] has been described in several reports. Cohen and Madadeva have described a theoretical approach to the formation of kinks, rings, and a "racket" structure of carbon nanotubes.[33] We have reported that helical superstructures of SWNTs with shapes of rings, lassos, figure-8 are formed in aqueous dispersions of empty SWNTs and of fullerene peapods dispersed by compound **1** (Figure 13).[34] To shed light on the mechanism of the helical structure formation from the dispersed carbon nanotubes in water, we adapted an off-lattice Monte Carlo simulation with Metropolis algorithm on a single stiff polymer chain in three-dimensional space, in which the polymer was described as a sequence of $N = 500$ spherical monomers with diameters connected by elastic bonds and determined a way to produce such unique morphologies (for detail, see reference No. 34).

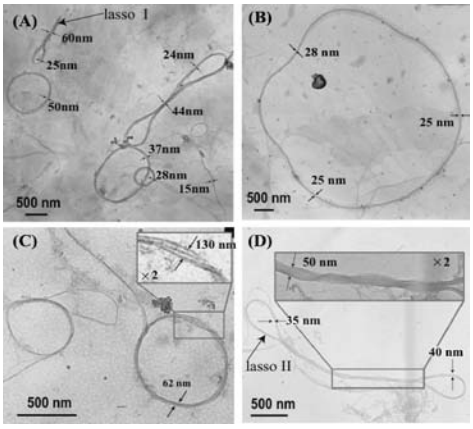
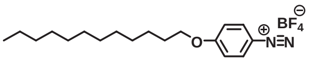


Figure 13. Typical TEM images of an aqueous dispersion of the C70@SWNTs dispersed with the aid of compound **1**.

4. Separation of Metallic and Semiconducting SWNTs

Recently, considerable attention has been focused on the separation of metallic SWNTs and semiconducting SWNTs.[35] Solubilization based on physical adsorption is sometimes done in conjunction with chemical modification utilized separating them. Several groups have achieved separation of metallic and semiconducting SWNTs by utilizing the difference in reactivity[36] and preferential interaction[37,15b] to the one type of SWNT's sidewall. We successfully developed a simple method for separating semiconducting SWNTs.[38] 4-Dodecyloxybenzenediazonium tetrafluoroborate (**4**) (Chart 2) preferentially reacted with metallic SWNTs via kinetic control, and alkylated metallic SWNTs were removed by washing with tetrahydrofuran.

Recently, Hersam and co-workers have described an efficient method for the separation of metal and semiconducting SWNTs using a convenient and scalable technique called density-gradient ultracentrifugation.[39] They have also demonstrated



Compound 4

Chart 2.

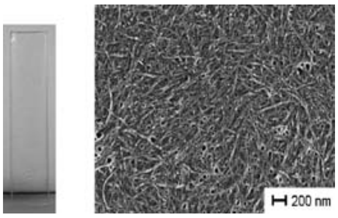


Figure 14. (Left): Photograph of an assembled layer-by-layer film of SWNTs/Poly(G) and SWNTs/Poly(C) on quartz. (Right): SEM image of an assembled layer-by-layer film of SWNTs/Poly(G) and SWNTs/Poly(C) on quartz.

the separation of SWNTs with a specific chirality index in high purity by optimizing the nature of surfactants and the ratio of co-surfactants.

5. Preparation of Nanotube Thin Films

Formation of thin and ultrathin films of CNTs is of interest from both fundamental and application viewpoints. A homogeneous dispersion of CNTs in solutions is essential for the preparation of ultrathin CNTs films with high homogeneity.

A Langmuir–Blodgett (LB) technique is used for the formation of ultrathin composite films of carbon nanotube and amphiphiles.[40] A layer-by-layer method is also applicable for assembling multilayer films as demonstrated by Mao et al.[41] We have constructed unique multilayer assemblies with alternating monolayers of poly(G)-wrapped SWNTs and of poly(C)-wrapped SWNTs on quartz.[42] The method was simple: SWNTs were dispersed in aqueous solutions of different RNAs, poly(C) and poly(G), then a layer-by-layer technique was applied to fabricate a thin film from RNA-dispersed SWNT solutions on a substrate (Figure 14, left). No such multilayer films were obtained when poly(A) was used instead of poly(C), indicating the importance of complementary base pairing between nucleic bases G and C for the formation of the films on the substrate (Figure 15). The deposition process was monitored by the change in the UV–visible–near IR spectra of the assembled film on the quartz. The absorbance of the films increased almost linearly with an increase in the number of cycle numbers. Figure 14 (right) shows a SEM image of the film on quartz.

We have demonstrated the unique approach in preparing the ultrathin films on electrode by means of electrodeposition. The formation of SWNT films was carried out by shortened SWNTs in aqueous micelle of an electroactive surfactant, 11-ferrocenylundecy poly(ethylene glycol), of which the process was monitored by using electrochemical quartz crystal microbalance (EQCM).[43]

6. Summary

Individual dispersions of SWNTs are necessary for a wide range of sciences and technologies. Especially, individual solubilization based on physical modification can keep SWNTs intact and is an attractive route for taking advantage of their intrinsic properties. The preparation of individually dispersed SWNTs is the first step to put SWNTs to practical use. Individual dispersions of SWNTs are imperative for fundamental studies, especially photoluminescence spectroscopy, where only debundled SWNTs give a meaningful spectrum. Combinations of various spectroscopy provide a wealth of information about how they interact and are perturbed by surrounding molecules. Also, individually dispersed SWNTs in solution are useful for fabricating nanodevices such as transistors, sensors, emission sources, and so forth. The areas, in which SWNTs are useful keep expanding, whereas the importance of stable individual solubilization has not chenged.

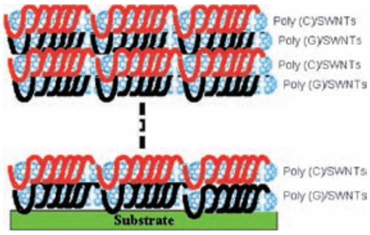


Figure 15. Schematic draw for a layer-by-layer assembly of poly (G)/SWNTs and poly (C)/SWNTs.

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