# Disassembling Single-walled Carbon Nanotube Bundles by Dipole/Dipole Electrostatic Interactions

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Dipole/dipole electrostatic attraction was used for the first time for disassembling the single-walled carbon nanotube (SWCNT) bundles. A self-assembled zwitterionic monolayer (SAZM) was created by modification of the SWCNT bundles with a sulfonate/quaternary-ammonium type of zwitterionic surfactants. The headgroups of the SAZM align at the terminal-end and form anti-parallel doublets. Dipole/dipole electrostatic attractions occurred readily as the SAZM approached to another. SWCNT bundles have been disassembled into individual tubes because of the strong dipole/dipole attractions. Large quantities of unbundled single-walled carbon nanotubes (SWCNTs) were obtained within a single step by this method. Concentric circular membranes containing the unbundled SWCNTs were prepared. The unbundled SWCNTs were found to have tendencies to curve around the circular direction.

Many potential applications implied by their remarkable electrical and mechanical properties and the unique morphologies have been proposed for the single-walled carbon nanotubes (SWCNTs).[1] Their self-assembling characteristics, i.e., they self-assemble to form crystalline bundles (ropes), on the other hand, have been the important barriers for their chemical and/or physical manipulation, and thus their use in practical applications.[2,3] Surfactant-based isolation, i.e., the use of surfactants, such as sodium dodecyl sulfate (SDS) to isolate the individual (unbundled) SWCNTs from the bundled ones, is the cornerstone for preparation of the unbundled SWCNTs. Although other methods, such as the so-called non-covalent[4] and/or the covalent[5] side-wall functionalization and the polymer-molecular wrapping[6–8] find also applications. The surfactant-based method, in fact, is rather time-consuming, for a number of reasons. First, a mechanical disassembling procedure (such as the high-shear mixing and/or sufficient ultra-sonication) must be used throughout to produce the primarily individual SWCNTs. In other words, the entire surfactant power is not high enough to disassemble the SWCNT bundles. Second, fine (smaller) bundles and the individual tubes are both contained in the homogeneous dispersion. A centrifugation machine of ultra-high performance was required for isolating the individual tubes from the fine bundles. Third, the procedures for mechanical disassembly, for surfactant dispersion, and for the centrifugation isolation must be done repetitively, till all the bundles were being converted into the individual tubules.

In this study, we have established a simple yet powerful method with which large quantities of unbundled SWCNTs can be obtained within a single step. Dipole/dipole electrostatic interactions were used as the driving forces to disassemble the SWCNT bundles. To our best knowledge, this is the first report dealing with the use of dipole/dipole electrostatic interactions for preparation of unbundled SWCNTs.

When mixed with 3-(*N*,*N*-dimethylstearylammonio)propanesulfonate, glycerol, and $\kappa$-carrageenan, the pristine SWCNTs formed highly viscous gels after being ground. The gels were highly dispersible in aqueous sodium iodide solution. Typical atomic force microscopy (AFM) and the scanning electron microscope (SEM) images of aqueous SWCNTs samples are shown in Figure 1. The aqueous SWCNTs samples were prepared by dispersing the SWCNT gels into a 1.0 mM aqueous sodium iodide solution. The SWCNT gels were prepared as following: 0.12 g of the as-received SWCNTs (CVD products of NANO-LAB), 0.42 g of 3-(*N*,*N*-dimethylstearylammonio)-propanesulfonate and approximately 4 mL of glycerol were roughly mixed; this mixture was then ground for about 20 min. A small amount of $\kappa$-carrageenan and approximately 4 mL of deionized water were then added and this mixture was further ground for about 40 min. As can be seen from Figure 1, well-dispersed SWCNTs were obtained; but each shows a diameter (17–20 nm) larger than that of the average value of the single SWCNTs.

The aqueous SWCNT solution was diluted using a warmer (45 °C) aqueous $\kappa$-carrageenan solution. This solution was then used to establish membranes of concentric circular shapes by casting the solution onto circular mesh mica. Direct observation of these thin membranes by high-resolution transmission electron microscopy (HR-TEM) revealed individual SWCNTs with a diameter of $2.5 \pm 0.2$ nm (Figure 2, lower photo). Note that the unbundled SWCNTs being embedded in the membranes were found to have tendencies to curve around the concentric circular direction (Figure 2, upper photo).

3-(*N*,*N*-dimethylstearylammonio)propanesulfonate (denoted as Z-3-18) is a typical linear zwitterionic surfactant, possessing a hydrophilic, sulfonate/quaternary-ammonium headgroup;

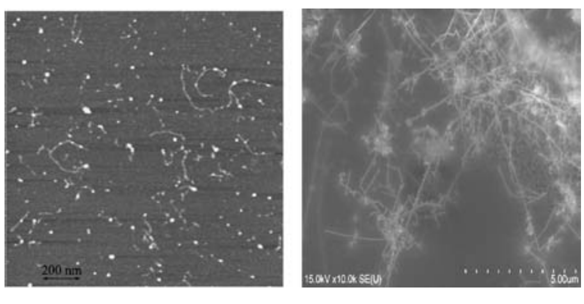


**Figure 1.** Typical AFM (left-photo; PicoPlus AFM, Molecular Imaging, Tempe, Arizona) and SEM (right-photo; Hitachi S4800) images of aqueous solutions containing the unbundled SWCNTs.

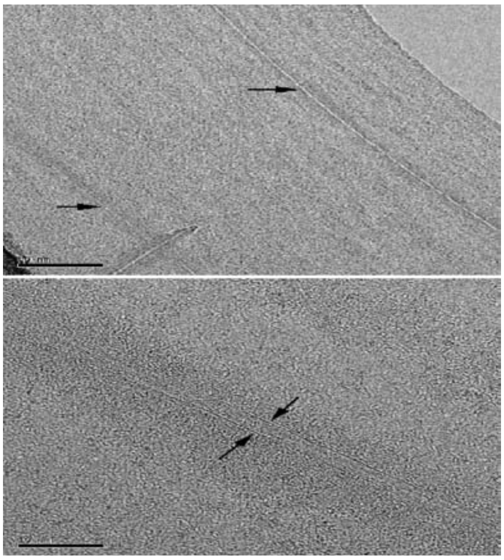

**Figure 2.** Typical HR-TEM (JEM-2100, JEOL, Tokyo, Japan) measurements of diameters of the unbundled SWCNTs (lower photo). The unbundled SWCNTs were found to have tendencies to curve around the circular direction (upper photo). Scale bars: 50 nm (upper) and 10 nm (lower), respectively. Arrows point the unbundled SWCNTs.

and a hydrophobic, C18-alkyl tail. According to the existing knowledge of the zwitterionic surfactant self-assembly,[9] the linear zwitterionic surfactants with a truly positive charge and a negative charge on their headgroups of each molecule forming diads and/or quartets because of the electrostatic interactions. In aqueous solutions, even cylindrical amphiphiles can be built up by using these diads and/or quartets as the building blocks.[10] When mixed with glycerol and the SWCNT bundles, Z-3-18 also form the self-assembled diads and/or quartets because of the electrostatic attraction and the hydrogen bonding interaction (glycerol molecules were adsorbed on to C18-alkyl tail and forming hydrogen bonding between them). These constituent blocks then attach on to the SWCNT bundles and aggregate with one another to form large amphiphiles, which may be called "self-assembled zwitterionic monolayer (SAZM)". FT-IR studies (data not shown) suggest that the Z-3-18 molecules were immobilized by attaching the C18-alkyl tail on to the surfaces of the SWCNT bundles. The sulfonate/quaternary-ammonium headgroups orientated toward the terminal-end, and most of them form anti-parallel doublets. The formation of the anti-parallel doublets is a general phenomenon, driven largely by the electrostatic forces to diminish the repulsions between the same charges of the headgroups of the zwitterionic surfactants. The self-assembled zwitterionic surfactant monolayer should have high propensities to interact with the others because of the strong dipole/dipole electrostatic interactions. The dipole/dipole electrostatic interactions occurred readily, typically as the SAZM/SWCNT-bundles being well ground. The SWCNT bundles were disassembled into their constituent elements as the dipole/dipole interactions take place (Figure 3). After the bundles are being disassembled, a cylindrical SAZM has further been created with the unbundled SWCNTs being acting as kernels.

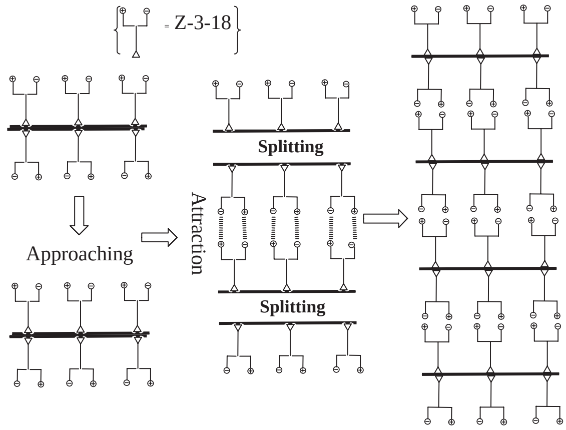


**Figure 3.** Schematic representation of the method for disassembling (splitting) SWCNT bundled into individual tubes using dipole/dipole interactions.

$\kappa$-Carrageenan is a typical poly-sulfonate. This type of anions shows high propensities to repel the zwitterionic surfactants.[11] The zwitterionic surfactants have to stay with SWCNTs and as a result, a self-assembled zwitterionic monolayer of high stability was obtained.

A simple yet powerful method for producing large quantities of unbundled SWCNTs has been established. The unbundled SWCNTs obtained using this method can be used directly for developing SWCNT-composites of high-strengths. Preparation of SWCNT-embedded open-celled flexible polyurethane foams by adding the unbundled SWCNTs into the host medium is undertaken by our group.

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