Aqueous Soluble Single-Wall Carbon Nanotube

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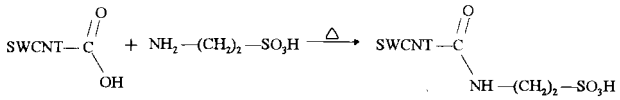
By condensation reaction with 2-aminoethanesulfonic acid (taurine), the end of single-wall carbon nanotube (SWCNT) was linked with sulfonic acid group, which enables much enhancement of the solubility of SWCNT in water.

Since the single-wall carbon nanotube (SWCNT) was first discovered by Iijima[1] and macroscopically prepared and purified,[2–5] it has attracted wide interests because of its peculiar chemical and physical properties. The SWCNT itself is insoluble in organic solvent or water, which limits its application in many fields. The ends of SWCNT are hexagon and pentagon rings of carbon, where chemical reaction can easily happen. Through oxidation, the ends of SWCNT can be turned into carboxylic groups, which enable many chemical reactions to be carried out between the ends of SWCNT and reagents. Liu and Smalley shortened SWCNT to the length of 150 nm–800 nm by oxidation with mixed concentrated H_2SO_4 and HNO_3.[6] Chen and his coworkers succeeded in modifying these shortened SWCNT through chemical reaction and prepared SWCNT that is soluble in common organic solvents. They added long-chain molecule octadecylamine and 4-tetradecylaniline to the open ends of shortened SWCNT via formation of the amide functionality.[7,8] Recently, Shi et al. prepared SWCNT colloids in polar solvents without attaching any additional functional groups to the SWCNT with carboxyl groups at the open end.[9] Y.-P. Sun et al. prepared the polymer-bound carbon nanotubes in homogeneous organic and aqueous solutions, and found these solubilized carbon nanotubes had strong luminescence properties.[10]

Here we report a method of attaching sulfonic acid groups at the open ends of shortened SWCNT by solid condensation reaction. The reaction product has a fine solubility in water. The characterization of the product shows the formation of amide functionality. The preparation of aqueous solution of SWCNT makes possible further study of their solution properties and potential applications.

The raw soot of SWCNT was produced by dc arc-discharge method and purified by filtration method.[5] Through filtration treatment, the purity of SWCNT is above 90%. After cutting by concentrated H_2SO_4 and HNO_3, long SWCNT was turned into shortened "fullerene pipe".[6] These SWCNT is terminated with carboxyl groups at their open ends. Then the product was filtered and dried. Finally the product was mixed with 2-aminoethanesulfonic acid (taurine), and the blend was made to slice. The slice was put into a sealed tube and heated at 300 °C for 6 h. Afterwards the product was dissolved in water. The turbid solution was first filtered by filter paper to remove a little precipitation, and then the black and clear solution was filtered by a ϕ 0.1 μm Super Membrane. After that the black product on Super Membrane was washed with water to get rid of adsorptive taurine and drying under vacuum. IR, laser scattering and STM were used to characterize the drying black product.

The solid state reaction between taurine and SWCNT with carboxyl groups under low temperature is impossible. But at slightly higher temperature, the condensation reaction between amine group of taurine and carboxyl group at the end of SWCNT is possible. The linkage of sulfonic acid groups to SWCNT considerably enhances its solubility in water. The sample easily became a black clear aqueous solution without any stirring or ultrasonication. The dilute solution is slightly brownish. The solubility is about 1.3 mg/mL in water at pH = 7. The reaction is as follows:



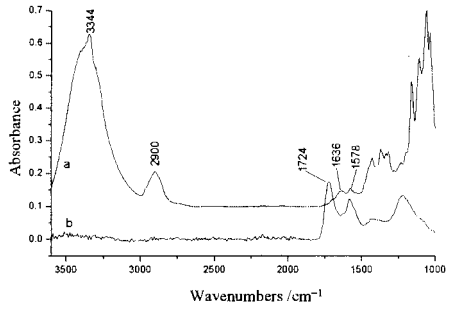


Figure 1. IR spectra of SWCNT reacted with taurine (a) and shortened SWCNT (b).

Figure 1 is the IR spectra of SWCNT sample before and after condensation reaction. The spectrum of the reaction product clearly indicated the formation of amide bond (1636 cm^{-1}) and the existence of $-SO_3H$ group (1038–1190 cm^{-1}, 1305–1390 cm^{-1}) in the sample. Absorption at 3344 cm^{-1} is due to N–H bending in the amide carbonyl group, while absorption at 2900 cm^{-1} is due to the C–H stretching modes in alkyl chain.

The hydrodynamic radius via laser scattering characterization can approximately estimate the tube length of SWCNT in solvents (Figure 2). Before reaction with taurine, SWCNT in water have a hydrodynamic radius in the range 35–410 nm with a mean of 121 nm, that is, the length of SWCNT ranges from 70 nm to 820 nm with a mean of 242 nm. After reaction, SWCNT in water have a hydrodynamic radius in the range 73–208 nm with a mean of 124 nm, that is, the length of SWCNT ranges from 146 nm to 416 nm with a mean of 248 nm. After reaction, the length of SWCNT did not change, but the length distribution became narrower. Strictly speaking, these solutions are not true solution, but colloid solution, like SWCNT colloids

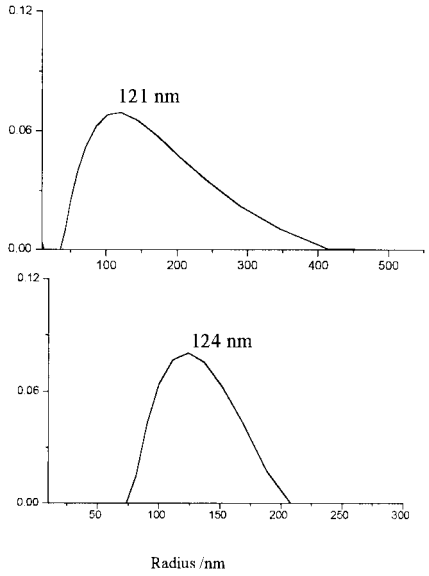


Figure 2. Hydrodynamic radius distribution of aqueous suspension of SWCNT after cutting by mixed acid (top) and aqueous colloid solution of SWCNT-SO_3H (bottom) (Measured Using 514.5 nm Laser-scattering).

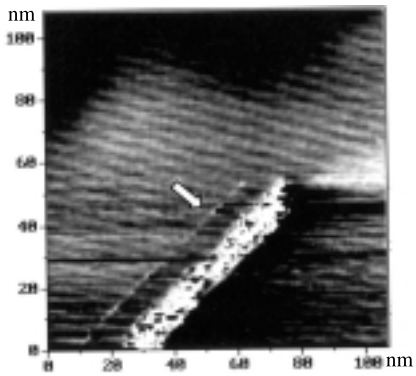


Figure 3. STM Images of SWCNT-SO_3H on graphite substrate.

in literature.[9]

The STM image of SWCNT-SO_3H is shown in Figure 3. There is a bundle of SWCNT in Figure 3. The length is about 270 nm. Near the bundle of SWCNT, there is an individual SWCNT (indicated by a white arrow).

In conclusion, the SWCNT sample can be linked with sulfonic acid group through condensation reaction with the formation of a product having fine solubility in water, which opens a new route to investigate solution behavior of SWCNT and organize SWCNT in aqueous solution.

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