전기전도성 필름제조를 위한 탄소나노튜브 용해도 향상

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Enhanced Carbon Nanotube Dissolution for Electrically Conductive Films

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Abstract : Solubility of single wall carbon nanotubes (SWNTs) has been determined in various dispersing media by using the solvent parameters such as Kamlet-Taft parameter and 3-dimensional parameters. Nitric acid-treated SWNTs exhibit significantly improved solubility in hydrogen bondable solvents as well as in solvent mixtures. The forming bucky gel with ionic liquid allows for the new group of dissolving solvent. The dissolution behavior of SWNTs provides a route for SWNT dispersion/exfoliation in preparing electrically conductive films such as transparent electrode.
Key Words : Carbon Nanotubes, Dissolution, Electrically conductive film

1. Introduction

Transparent electrical conductors can serve as a critical component in displays, solar cells, lasers, optical communication devices, and solid state lighting.[1] Ultra-thin, transparent, optically homogeneous, and electrically conducting films of pure SWNTs have been prepared, which were transferred to various substrates for electrical coupling in photonic devices.[2] Single wall carbon nanotubes (SWNTs) typically exist in form of quasi-crystalline bundles containing hundreds of individual nanotubes. To achieve full potential, SWNTs must be exfoliated in a solvent or other organic media.[3] Up to date, there are several method to dissolve pristine SWNTs into organic media by using surfactants, ionic polyelectrolyte (salt), and functionalization on the opened ends or side walls.[4,5] Dispersion of SWNTs are origined from the studies of fullerene which were characterized by electron pair donicity (β), hydrogen bond donicity (α) and solvatochromic parameter (π*).[6] We recently have reported that carboxyl acid functionalized SWNTs can be dissolved in hydrogen bondable solvents which are known as poor solvents.[5] We report herein the solubility of SWNTs in various dispersing media by using the solvent parameters such as Kamlet-Taft parameter and 3-dimensional parameters.

2. Experimental

As purified HiPco SWNTs (containing about 1 wt% catalyst, from CNI Inc.) and carboxylic acid functionalized HiPco (f-) SWNTs have been used in this study. Nitric acid treatment of unpurified SWNTs (containing about 35 wt% catalyst, from CNI Inc.) was performed according to the previously reported procedure, and the solubility was measured by using optical spectra following the procedure previously described.[5] For measuring solubility, nanotube solutions was ultrasonificated for up to 96 hours in Fisher Scientific water bath sonicator (70W, 42KHz) maintained at 25-30°C. 1-butyl-3-methylimidazolium tetrafluloroborate ($BMIBF_4$) was used to form bucky gels with high purity SWNTs. Optical spectra were measured by UV-Vis-NIR spectrophotometry (Cary 5G, Varian) and a 10 mm quartz cell (Fisher Scientific) with baseline correction. All solvents were used as received and were obtained from Aldrich or Fisher Scientific.

3. Results and Discussion

With increasing sonication time, SWNTs debundle into smaller diameter ropes or as individuals and they partially re-aggregate into larger diameter ropes when sonication stops, unless they are surrounded by surfactant molecules. The solubility/dispersibility can depend on the type of nanotubes, their length as well as sonication time, temperature, power, and frequency. The optical absorptions of pristine purified SWNTs (20 mg/L) in N,N-dimethylformamide (DMF), a good SWNT solvent,[7] and that of f-SWNTs (25 mg/L) in 1-butanol as a function of sonication time are shown in Figure 1. The concentrations of 20 and 25 mg/L used in DMF and 1-butanol represents the solubility limits of the two types of tubes in the respective solvents. For pristine SWNT/DMF, the optical absorption increased up to 36 hours of sonication in the entire spectral range, while peak resolution increased noticeably in the 1200-1600 nm range. In the acid treated SWNT/butanol, there was little change in the absorption or peak resolution with sonication time. Absorbance changes as a function of sonication time shows that pristine SWNTs takes much longer to reach saturation.

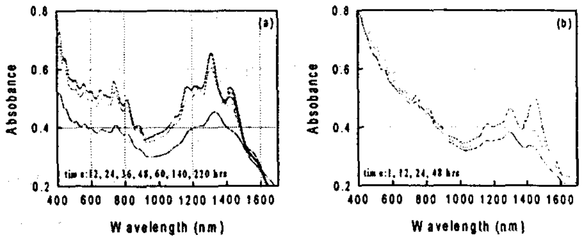

Figure 1. Optical absorptionspectra of (a) as-purified SWNTs/DMF (20 mg/L), (b) acid treated SWNTs/butanol (25 mg/L).

Organic solvents such as butanol, toluene and xylene are poor SWNT solvents. Nitric acid functionalizes SWNTs with carboxylic groups and enhances their hydrogen bonding ability, thus allowing broader solvent selection. Even the acid functionalized SWNTs are not soluble in toluene and xylene but exhibit good solubility when an alcohol such as butanol or ethanol is added. Figure 2 shows that solubility increased with increasing ethanol content, while pure xylene exhibited no solubility. On the other hand the pristine tubes are not soluble even in such solvent mixtures.

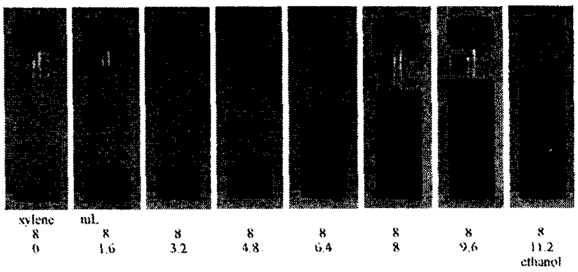

Figure 2. Solubility of acid-treated SWNTs in xylene/ethanol mixture. Top and bottom row indicate amount of xylene and ethanol in mL, respectively. One mg acid treated SWNTs were dispersed in 8 ml xylene and sonicated for 30 minutes and the dispersion was allowed to settle for 2 hours before taking a photograph. Subsequently, each time 1.6 ml ethanol was added followed by sonication (30 minutes) and settling (2 hrs).

By using small amount of ionic liquids, we found that resulting bucky gels with ionic liquids could be dissolved in different groups of solvents. Figure 3 shows the dispersion state of bucky gels in various solvents which have different solubility parameters.

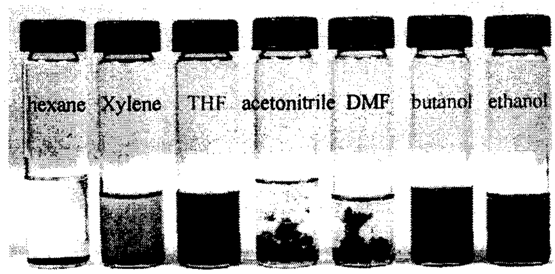

Figure 3. Solubility of SWNTs/RILs in various solvents.

The dispersion states show that nanotubes were dispersed or suspended well in specific group of solvents with certain polar and dispersive term of Hansen solubility parameter.

4. Conclusion

SWNT solubility has been determined using optical absorption. Nitric acid-treated SWNTs exhibit significantly improved solubility in hydrogen bondable solvents as well as in solvent mixtures. The dispersibility of SWNTs bucky gels with ionic liquid has been studied to various solvent systems, and correlated to solvent parameters. The use of a ionic liquid as the forming bucky gel allows for the new group of dissolving solvent for pristine SWNTs into organic solvents, which means the easy access to enhanced dispersion without surfactants and functionalizations. The dissolution behavior of SWNTs provides a route for SWNT dispersion/exfoliation in preparing electrically conductive films such as transparent electrode.

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