

Bath sonication for the scalable separation of semiconducting single walled carbon nanotubes

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Abstract—Commercially available single-walled carbon nanotubes (SWNTs) consist of a mixture of metallic (m-SWNTs) and semiconducting SWNTs (sc-SWNTs), and therefore cannot be used as they are for applications where pure semiconductors or metallic materials are needed. Hence, the separation of sc-SWNTs from pristine SWNT mixtures is an essential process that precedes the evaluation of SWNTs. The polymer wrapping method, which is one of the well-known methods for separating sc-SWNTs, can separate sc-SWNTs by forming a sc-SWNT/polymer complex in which sc-SWNTs are selectively wrapped with a conductive polymer over metallic SWNTs. This process is generally realized using a tip sonicator, which enables the polymer wrapping and dispersion for SWNTs. However, this conventional tip sonication has several drawbacks, such as difficulties with respect to mass production, contamination, and high cost of equipment. In this work, the selective dispersion and separation of sc-SWNTs were achieved using bath sonication, which can overcome the drawbacks related to conventional tip sonication process. It was confirmed that bath sonication can achieve a similar level of sc-SWNT dispersion efficiency to that of tip sonication. The variation in the dispersion efficiencies with respect to the dispersion time, SWNT concentration, SWNT types, polymer concentration, and solvent types and concentrations was investigated. Furthermore, the dispersion stability was compared by measuring the particle sizes of the sc-SWNT/conductive polymer composites obtained using the bath sonication and tip sonication methods via electrophoretic light scattering as a function of time.

Keywords: Bath Sonication, Semiconducting SWNT, Separation, Selective Dispersion, Poly(3-dodecylthiophene-2,5-diyl)

INTRODUCTION

Single-walled carbon nanotubes (SWNTs) have been studied extensively owing to their excellent electrical, physical and thermal properties [1–4]. They can be divided into two groups: metallic SWNTs (m-SWNTs) and semiconducting SWNTs (sc-SWNTs), based on their chiralities [5–7]. At present, there is no simple industrial manufacturing technique for the production of either pure sc-SWNTs or m-SWNTs. Given that as-prepared SWNTs, commercially produced, consist of a mixture of sc-SWNTs and m-SWNTs; when SWNTs are used in solid-state-devices such as field-effect-transistors, solar cells, and displays, where the presence of m-SWNTs could lead to the deterioration of the device performances due to short-circuits, a complex and time-consuming process of separating sc-SWNTs from pristine SWNTs should be preferentially carried out. To simplify the separation process for SWNTs, several researchers investigated different separation methods, including selective chemistry [8,9], density gradient ultracentrifugation (DGU) [10–12], gel separation [13–15], di-electrophoresis [16–18], and deoxy-ribonucleic acid (DNA)-assisted separation [19–21].

Polymer wrapping using polymers with high solubilities in solvents is one of the facile separation methods for SWNTs, given that sc-SWNTs can be easily separated over a short period of time

without additional surfactants. Polymers, such as Poly(3-dodecylthiophene-2,5-diyl) (P3DDT) and poly(tetradecyloctathiophene-*alt*-didodecylbithiazole) (P8T2Z-C12) having optimized density and length of hydrocarbon side chains, have been demonstrated to selectively wrap sc-SWNTs over m-SWNTs [22]. Given the successful demonstration of the selective dispersion of sc-SWNTs via polymer wrapping using tip sonication by Bao et al., similar studies were conducted to determine potential applications for the pure separated sc-SWNTs [22–25]. However, with respect to the separation of sc-SWNTs using the polymer wrapping method, there are limited reports on new processes that can solve the problems associated with tip sonication. Although tip sonication has the advantage of a short dispersion time, it also has several disadvantages. For example, i) there is significant solvent loss due to the inevitable exposure to air during dispersion; ii) a high risk of contamination due to the direct contact of the sample with the sonicator tip, and iii) the high cost of equipment. In addition, in tip sonication, the proper dispersion capacity is determined by the tip size, which makes it difficult to apply this method to large-scale separation. On the other hand, bath sonication overcomes these limitations, as it can minimize the decrease in the amount of solvent due to the dispersion condition with the closed-lid state. Moreover, it can disperse samples without direct contact with the vibrator, which minimizes the risk of contamination. Since dispersion efficiency is influenced by the dispersion temperature in the polymer wrapping method, it is advantageous that the temperature control function in a bath sonicator can accurately control the temperature. In addition, the

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equipment is low-cost and mass-separation is possible, which enables easy procurement of materials in the subsequent studies that require pure sc-SWNTs. Nevertheless, tip sonication has been exclusively used for sc-SWNT separation process in polymer wrapping process, because it has been thought that the sc-SWNT dispersion efficiency of bath sonicator is much lower than that of tip sonicator.

This study demonstrates that bath sonication can achieve a dispersion efficiency comparable with that of tip sonication using CoMoCAT as a model SWNT, and toluene as a solvent. Poly(3-dodecylthiophene-2,5-diyl) (P3DDT) was used as a dispersing polymer agent, which has the research result that its side chain length is very similar to the circumference of small diameter SWNTs, so that it is possible to effectively disperse sc-SWNTs [25,26]. In addition, the dispersion characteristics with respect to various parameters such as the dispersion time, the concentrations of SWNT and the polymer, and different types of SWNTs (HiPCO and Arc SWNT) and solvents (o-dichlorobenzene (ODCB)) were evaluated. It was confirmed that the SWNT/polymer composite obtained by bath sonication maintains its well-dispersed state for a longer period of time than the samples obtained by tip sonication.

EXPERIMENTAL

1. Materials

CoMoCAT SWNTs (Sigma-Aldrich, ≥ 95 wt% as carbon nanotubes), HiPCO SWNTs (Nanointegris, ≥ 65 wt%), Arc SWNTs (Hanwha Nanotech), P3DDT (Rieke Metals, regioregular), sodium dodecyl sulfate (SDS, Sigma-Aldrich, $\geq 98.5\%$), toluene (Sigma-Aldrich, 99.8%), and ODCB (Sigma-Aldrich, 99%) were used without further purification. Whatman Anodisc 25 with a pore size of $0.2\ \mu\text{m}$ was used as a vacuum filtration filter.

2. Selective Dispersion of sc-SWNTs

To separate sc-SWNTs from SWNTs, 10 mg of CoMoCAT SWNTs and 10 mg of P3DDT were mixed in 25 ml toluene and dispersed using two different sonication techniques. For tip sonication, the mixture was cooled to 0°C and dispersed at an amplitude of 70% for 30 min (Sonics ultrasonic processor 750 W). Moreover, in the case of bath sonication, the mixture was dispersed for 10 h at 50°C (Branson CPXH 3800). The dispersed SWNT solution was then centrifuged at 14,680 rpm (maximum rpm of benchtop) for 2 h (Eppendorf benchtop centrifuge 5424), and the supernatant was obtained for further evaluation. To obtain a control sample, 100 mg of carbon nanotubes (CNT) were mixed with 2 g of SDS dissolved in 100 mL of deionized water, followed by dispersion for 20 h at an amplitude of 30% (Sonics ultrasonic processor 750 W). The resulting solution was centrifuged at 32,000 rpm for 4 h (Beckman Coulter optima L-100 XP ultracentrifuge), and the supernatant was obtained for ultraviolet (UV) absorbance measurements, to observe the presence of m-SWNTs.

3. Preparation of sc-SWNT Film

For the preparation of the sc-SWNT film, 500 μL of supernatant obtained by centrifugation after the dispersion of the SWNTs was diluted with toluene (20 ml), for the preparation of the homogeneous film. Subsequently, the filtration was carried out using Whatman Anodisk 25 under reduced pressure, followed by thermal annealing at 450°C in Ar for 1 h, to obtain pure sc-SWNTs

(removal of P3DDT).

4. Sample Measurement

The dispersion efficiencies and the presence of m-SWNTs in the supernatant were characterized using a UV spectrophotometer (Perkin Elmer Lambda 750). The dispersion stability of the supernatant from each sonication method was compared by measuring the changes in the particle sizes of the sc-SWNT/P3DDT composites as a function of time using electrophoretic light scattering (ELS, Photal Otsuka electronic ELS-8000). Using Raman Spectroscopy (DM 500i, Dongwoo optron), the extent of SWNT defects generated during dispersion was compared for each dispersion method.

RESULTS AND DISCUSSION

1. Selective Dispersion of sc-SWNTs with P3DDT via a Bath Sonicator

Fig. 1(a) presents a schematic representation of the selective dispersion of CoMoCAT sc-SWNTs with P3DDT using a bath sonicator. Over the last decade, it was confirmed that the polymer wrapping behavior for the specific type of sc-SWNT is associated with the noncovalent interaction between the polymer side chain and sc-SWNT [27]. In a solvent with a low solubility for SWNTs, the SWNTs are not stable in the solvent, which results in the precipitation of a significant amount of SWNTs. Upon the addition of P3DDT as a dispersing agent that can be easily dissolved in a solvent, the polymers bind to sc-SWNTs to form sc-SWNT/P3DDT composites that can maintain their dispersed state in the solvent, due to the good solubility of the polymer with respect to the solvent. On the other hand, m-SWNTs were reported to have a polarizability stronger than that of sc-SWNTs by three orders of magnitude, and a tendency to form stronger temporal dipoles between the polymer and m-SWNTs than those of sc-SWNTs/polymer complexes [28]. Moreover, this easily leads to the aggregations of m-SWNTs and the polymer. The sc-SWNT/P3DDT composite stably remained in the supernatant after the strong centrifugation, whereas the m-SWNTs and other possible impurities could be easily precipitated and separated from sc-SWNT/P3DDT composites. The molecular structure of P3DDT used in the dispersion of the sc-SWNTs (Fig. 1(b)) contains a long side chain with 12 carbon atoms, which makes it possible to increase the contact area with the sc-SWNTs, and it facilitates the strong binding with sc-SWNTs. The dispersion temperature was set as 50°C based on the previous studies in which 50°C was reported as the optimal dispersion temperature condition, considering the efficient P3DDT winding for sc-SWNTs, due to the best flexibility of the P3DDT side chain [27].

The optical absorbance spectra of the sc-SWNTs supernatant obtained using different sonication methods (tip sonication and bath sonication) are presented in Fig. 1(c). Both samples exhibited the largest peaks at 1,030 nm, which indicates similar dispersion efficiencies for the tip and bath sonication methods. However, the tip sonication method resulted in a large solvent loss ($\sim 12\%$) during the short dispersion time-period of 30 min, whereas the loss of solvent in the bath sonication was less than $\sim 1.5\%$ during the long dispersion time-period of 10 h. To confirm the successful selective

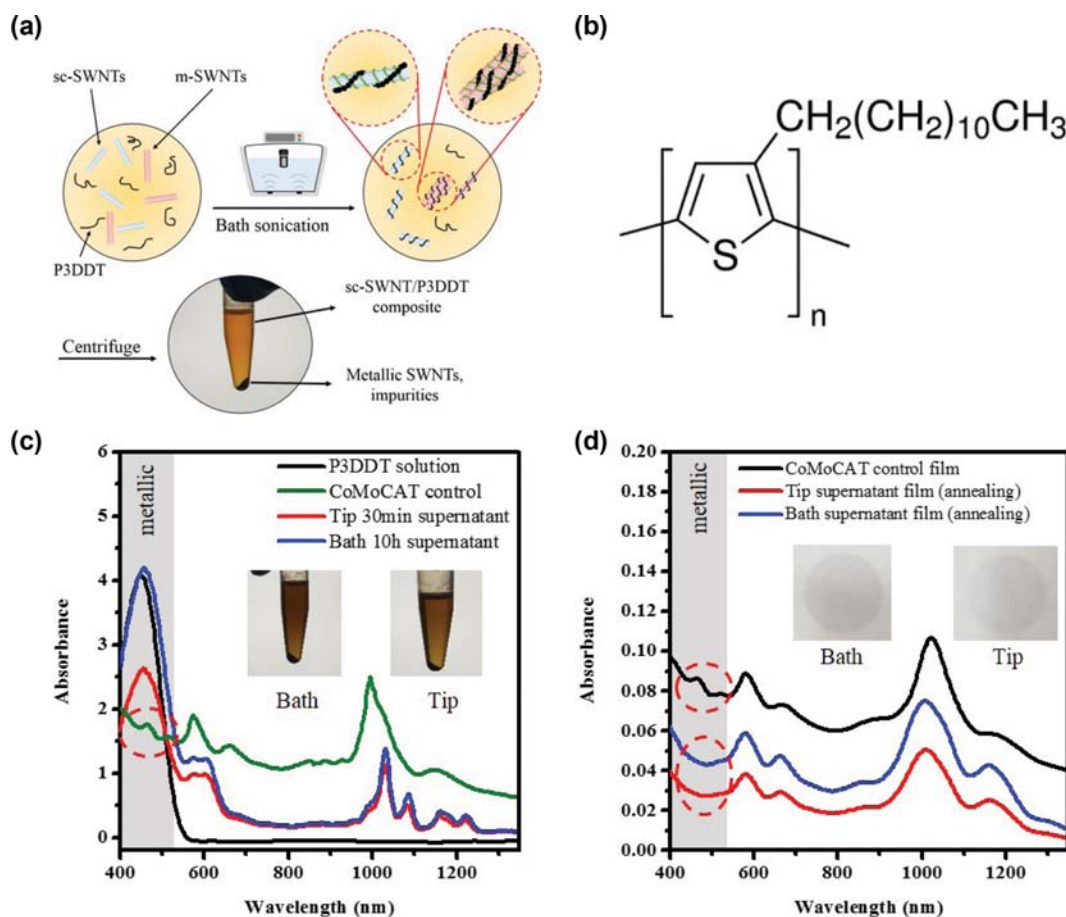


Fig. 1. Experimental overview and dispersion results using different sonication methods (bath sonication and tip sonication): (a) Schematic diagram of polymer wrapping process using bath sonication, (b) chemical structure of P3DDT, (c) absorbance spectrum of CoMoCAT SWNT supernatants with different dispersion methods, and (d) film (containing only CoMoCAT sc-SWNTs) after annealing the supernatant.

dispersion for sc-SWNTs, the removal of m-SWNTs (peaks located between 400 nm and 540 nm) should be verified. However, it is difficult to confirm the elimination of absorption peaks from the m-SWNTs due to a large peak from P3DDT at 370–540 nm, which overlaps the peak (400–540 nm) from the m-SWNTs. Accordingly, to accurately confirm the complete removal of m-SWNTs in the dispersed SWNT solution using P3DDT, the selective removal of P3DDT should be carried out.

Fig. 1(d) presents the optical absorbance spectra for the film that was prepared by the filtration of the supernatant, followed by thermal annealing, for the selective removal of P3DDT. The results in Fig. 1(d) reveal that all the m-SWNTs peaks were completely disappeared, regardless of the sonication methods used, which suggests that bath sonication is a good alternative to tip sonication. The results also imply that once the dispersion of SWNTs is confirmed (e.g., from the peak at ~1,000 nm) using a bath sonicator, the separation of sc-SWNTs can be guaranteed without removing the P3DDT by thermal annealing in the subsequent processes. In the case of the CoMoCAT control film sample, 1,022 nm peaks were red-shifted relative to the peaks of the tip and bath sonication supernatant film samples, which is attributed to the different degrees of SWNT aggregation [29].

2. Effects of Sonication Time and Concentration of SWNT and P3DDT on the sc-SWNT Dispersion

Fig. 2(a) presents the differences in dispersion efficiencies with respect to the dispersion time. The most pronounced peak at ~1,012 nm can be used as the criterion for the evaluation of the dispersion efficiency. The dispersion efficiency increased by 288.4% when the dispersion time increased from 1 h to 5 h. The dispersion efficiencies increased by 53.6% and 55.4% when the dispersion time increased from 5 h to 10 h and from 10 h to 15 h, respectively. Fig. 2(b) shows the results of Raman analysis for the supernatant obtained by the tip sonication method for 30 min and the bath sonication method for 10 and 15 h. The comparison of the intensity ratio (I_D/I_G) between D-band and G-band for the samples under 30 min tip sonication and 10 h bath sonication reveals almost identical values regardless of the sonication method, indicating that defect densities in CoMoCAT SWNTs are independent of the sonication method. Moreover, even if the sonication time was increased from 10 h to 15 h, I_D/I_G value also remained unchanged. This result further shows that the defect densities in SWNTs do not increase with the extension of bath sonication time, which means the application of prolonged bath sonication time could yield negligible effect on defect density for SWNTs.

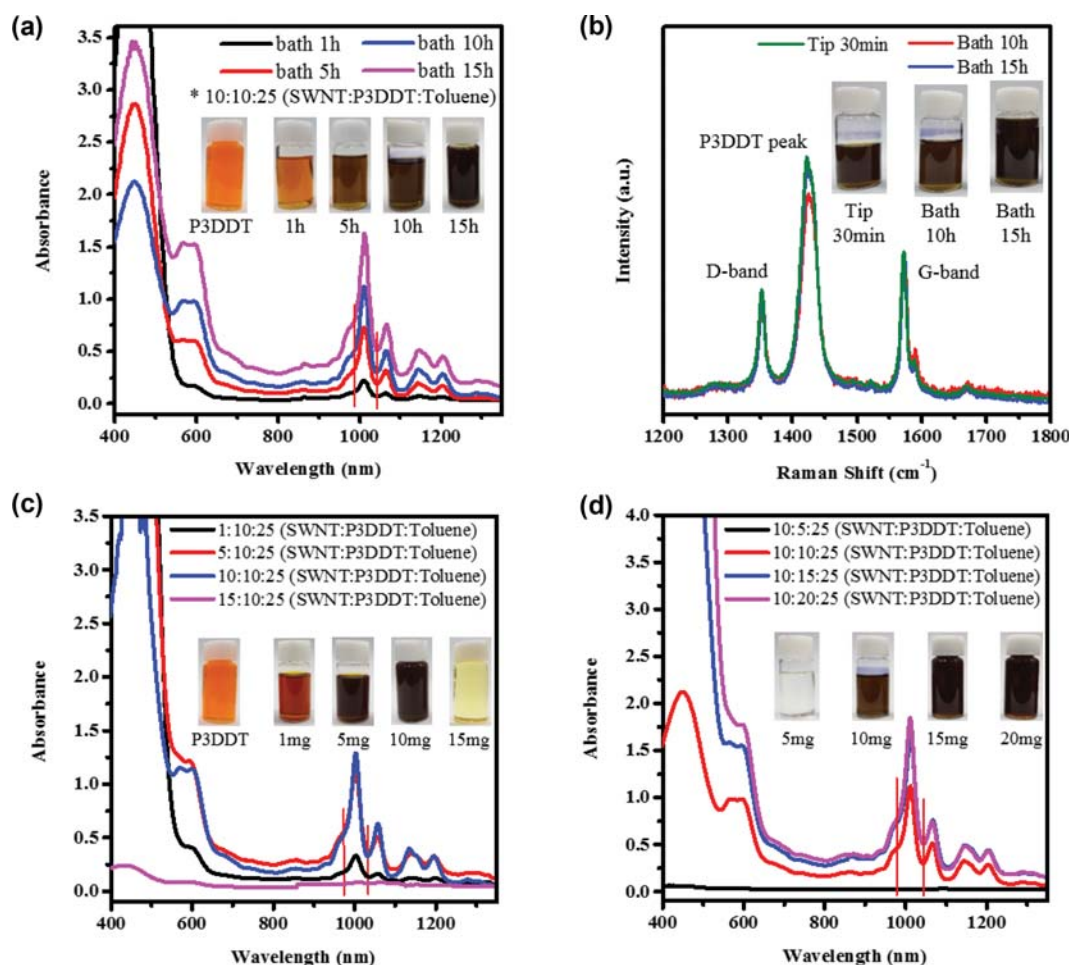


Fig. 2. (a) The absorbance spectra of CoMoCAT SWNTs/P3DDT dispersed in toluene using bath sonication with different dispersion time, (b) comparison of Raman spectra of CoMoCAT SWNTs/P3DDT between bath (10 and 15 h) and tip sonication. The absorbance spectra of SWNTs/P3DDT dispersed using bath sonication under the effect of different (c) SWNTs content and (d) P3DDT content. Sonication time and solvent for (c) and (d) are 10 h and toluene, respectively.

Fig. 2(c) presents the changes in the absorbance spectrum as a function of the SWNT concentration. Based on the peak at 1,002 nm, when the amount of SWNTs was initially increased by a factor of 5 (from 1 mg to 5 mg), the dispersion efficiency increased by a factor of ~ 5 (from black to red). Moreover, the dispersion efficiency increased by a factor of ~ 1.1 when the amount of SWNTs was increased from 5 mg to 10 mg (from red to blue). However, when the SWNT amount was increased from 10 mg to 15 mg (from blue to pink), the dispersion efficiency decreased significantly. This phenomenon occurs when SWNTs are excessively present, when compared with the given P3DDT content where all the P3DDT was consumed in the SWNT wrapping, which can be confirmed by the disappearance of the peak in the range of 400–500 nm. Similar trends were observed with respect to the P3DDT concentration. When the P3DDT concentration was excessively low (5 mg, black in Fig. 2(d)), SWNTs were not dispersed, due to the lack of P3DDT. However, a further increase in the P3DDT concentration increased the dispersion efficiency. For example, the dispersion efficiency of SWNTs using 15 mg of P3DDT (blue in Fig. 2(d)) was higher than that with 10 mg of P3DDT (red in Fig. 2(d)) by a fac-

tor of 1.8, based on the peak at $\sim 1,012$ nm.

3. Effects of SWNT Type and Solvent on the sc-SWNT Dispersion

The feasibility of the proposed approach (dispersion and separation of sc-SWNTs using a bath sonicator) was evaluated using different types of SWNTs (HiPCO SWNTs and Arc SWNTs) and a different solvent (ODCB). Fig. 3(a) presents a comparison of the absorbance spectrum of the HiPCO SWNT film between bare SWNTs (mixture of sc-SWNTs and m-SWNTs) and supernatant (sc-SWNT wrapped by P3DDT). For the supernatant film, the disappearance of the peak below ~ 540 nm was clearly observed, which indicates that the m-SWNTs in the HiPCO SWNTs were completely removed (Fig. 3(a)). In the case of the Arc SWNTs supernatant, neither m-SWNTs nor sc-SWNTs were present, given that the peak of the m-SWNTs at ~ 680 nm and the sc-SWNT peaks at ~ 970 nm disappeared after the centrifugation; whereas the Arc SWNT control sample clearly exhibited these two distinct peaks (Fig. 3(b)). In particular, only bare P3DDT remained in the supernatant when the Arc SWNTs were dispersed, which can be confirmed by a comparison of the images of the bare P3DDT (left inset

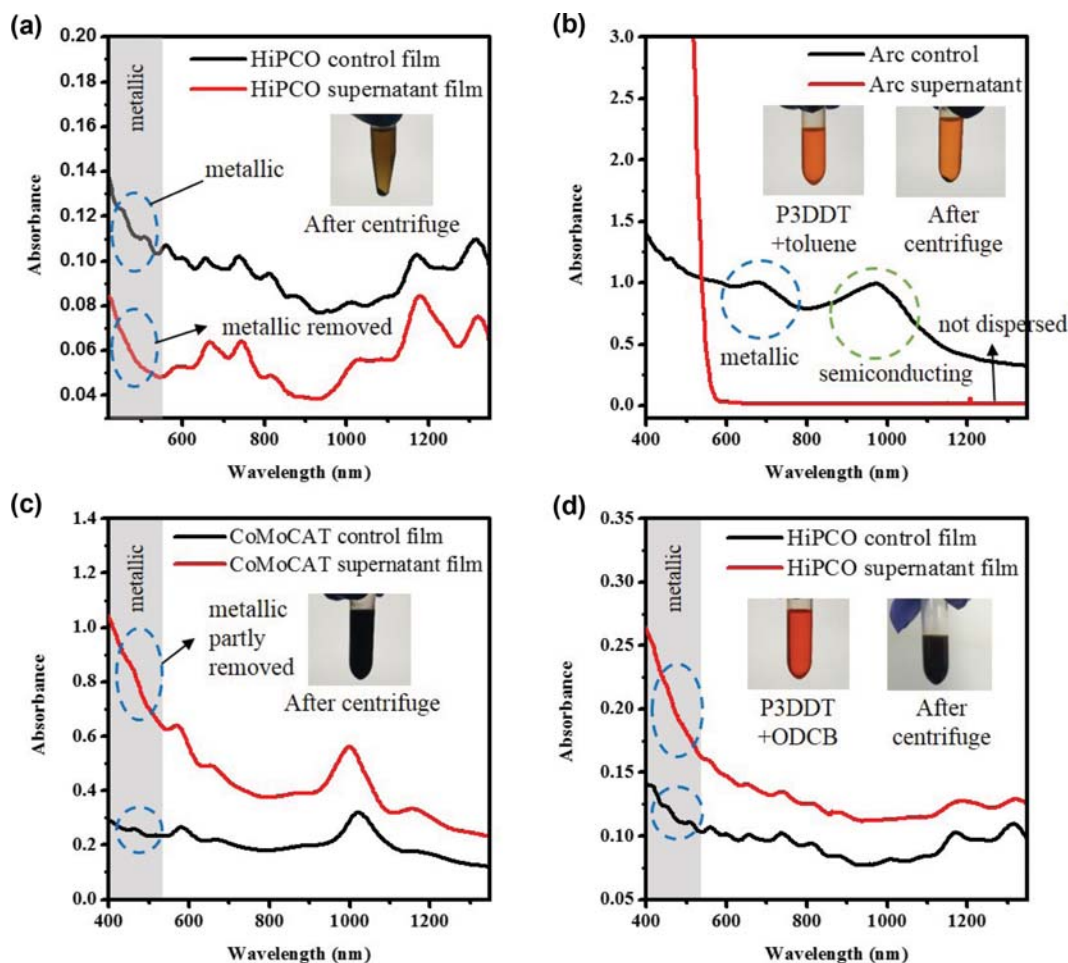


Fig. 3. The absorbance spectrum of samples using (a) HiPCO, (b) Arc SWNTs with P3DDT dispersed in toluene; and samples using (c) CoMoCAT SWNTs and HiPCO SWNTs with P3DDT dispersed in ODCB.

in Fig. 3(b)) and supernatant (right inset in Fig. 3(b)). The results indicate that the sc-SWNT/P3DDT composite was not formed in the dispersion of Arc SWNTs using a bath sonicator. The difference in the results for the HiPCO and Arc SWNTs can be attributed to their difference in diameters. Moreover, SWNTs with a relatively small diameter (less than 1 nm) for CoMoCAT and HiPCO can be easily encapsulated by the side chain (12 carbons) of P3DDT, whereas Arc SWNTs with diameters of ~ 1.2 nm are not completely wrapped by the side chain of P3DDT [26]. Consequently, SWNTs with several chiralities cannot be dispersed with P3DDT, as they cannot easily form a complex with P3DDT.

Fig. 3(c) and 3(d) present the dispersion results for the CoMoCAT and HiPCO SWNTs (e.g., SWNTs for which the dispersion and separation of sc-SWNTs were confirmed) when a different solvent (ODCB) was used. Both CoMoCAT and HiPCO SWNTs exhibited m-SWNT peaks in the supernatant, although the concentrations of m-SWNT were slightly reduced in their supernatants. According to Bao et al., for the effective dispersion of SWNTs, first, the solubility of the solvent should be high for the polymer and low for the SWNTs. Second, the density of the solvent should be lower than that of the SWNTs [28]. Table 1 presents the density of the SWNTs and solvent, in addition to the solubility of the

Table 1. Density, SWNT solubility of solvents, and SWNTs used in the experiments [30]

	Material	Density (g/cm ³)	SWNT solubility (mg/L)
Solvent	Toluene	0.867	<1
	o-Dichlorobenzene	1.3	95
	HiPCO	1.6	-
SWNT	CoMoCAT	1.7-1.9	-
	Arc	1.7-1.9	-

SWNTs used in the experiment. Toluene has a poor solubility with respect to SWNT, and a significantly lower density when compared with those of the HiPCO or CoMoCAT SWNTs. Hence, a small amount of sc-SWNTs that are not bound to P3DDT, in addition to m-SWNTs aggregated by the dipole between P3DDT and m-SWNTs in toluene, can be easily be precipitated through centrifugation. On the other hand, the density of ODCB is slightly smaller than those of the SWNTs, and the solubility of ODCB is extremely high for SWNTs. Therefore, if there are SWNTs that are not bound to P3DDT, they can be easily dispersed in the ODCB

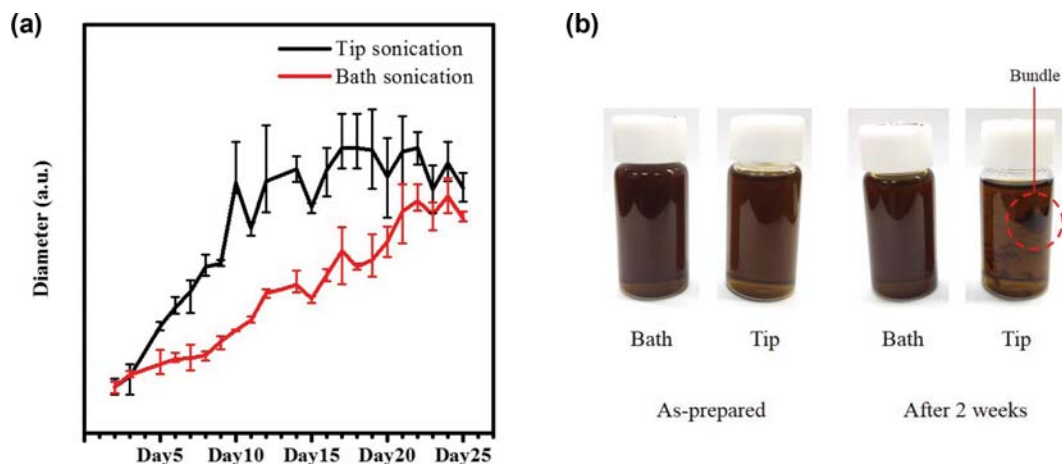


Fig. 4. (a) Variation in hydrodynamic particle size of supernatant samples (CoMoCAT SWNTs wrapped with P3DDT in toluene) prepared by tip and bath sonication, (b) the photographs of dispersed samples (as-prepared and after 2 weeks).

solvent. In this case, it is difficult to separate the sc-SWNTs from pristine SWNTs; thus, all the SWNTs remain in the supernatant after centrifugation, regardless of the sc-SWNTs and m-SWNTs. Despite the high solubility of ODCB for SWNTs, several precipitates were formed after the centrifugation, which can be confirmed by the decrease in the m-SWNT peak (dotted circles in Fig. 3(c) and 3(d)). However, the separation efficiency was expected to be insufficiently low when using ODCB as a solvent. These results suggest that the selective dispersion of sc-SWNT over m-SWNT can be realized only when all the conditions (side chain length of polymer compared to the diameter of the SWNT, and appropriate solubility of the solvent for both polymer and SWNT) are satisfied.

4. Dispersion Stability between Tip and Bath Sonication

The stability of SWNT dispersion is essential for the separation of sc-SWNTs, as it is directly related to the separation efficiency with respect to time. To better understand the dispersion stability of the supernatant samples (CoMoCAT SWNT with P3DDT and toluene) prepared using different methods (tip and bath sonication), the hydrodynamic particle sizes of the sc-SWNT/P3DDT composites were measured using ELS as a function of time. To estimate the average and error, the size at a given time was repeatedly measured three times. As shown in Fig. 4(a), although the particle sizes gradually increase with increase in time in both cases, they were consistently smaller for the samples prepared by bath sonication, which suggests that aggregation progressed relatively slowly for the samples prepared by bath sonication. The results demonstrate the superiority of bath sonication over tip sonication with respect to dispersion stability. The difference of dispersion stability can be also confirmed by macroscopic observation, as shown in Fig. 4(b), where the distinct SWNT bundles are clearly seen for the sample prepared by tip sonication, whereas they cannot be found for the samples obtained by bath sonication. Thus, as shown in Fig. 4(b), it was confirmed that the dispersion state was still maintained for the samples prepared by bath sonication, while the bundle was visually observed in the supernatant obtained by tip sonication.

CONCLUSION

Bath sonication has many advantages over tip sonication, such as its cost-effectiveness, low risk of contamination during dispersion, and higher dispersion capacity. However, at present, it is only regarded as a pre-treatment method to increase the efficiency of tip sonication for the selective separation of sc-SWNTs using polymers. It was confirmed that bath sonication can replace the tip sonication method by achieving a dispersion efficiency similar to that of tip sonication. Using several experiments with the application of different dispersion times and SWNTs-polymer ratios, the appropriate dispersion time and SWNT/polymer ratio for the efficient dispersion and separation of sc-SWNTs were determined. Moreover, several criteria were found for the type of SWNT and solvent, to ensure the successful dispersion of SWNTs, i.e., the appropriate diameter of the SWNTs for the given dispersing polymer agent, and the solubility and density of the solvent for the given SWNTs. Finally, it was found that an SWNT solution dispersed using the bath sonication method has an additional merit in that the stability of dispersion is maintained longer than the case wherein tip sonication is used. This was confirmed by comparing the variation in the hydrodynamic particle size using ELS. Overall, bath sonication presents a facile and scalable platform process for the separation of sc-SWNTs from pristine SWNTs, which will be utilized in the manufacture of improved electronic devices that require pure separated sc-SWNTs.

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