Review

Centrifugal purification of chemically modified single-walled carbon nanotubes

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Abstract

A wet chemistry procedure which couples chemical functionalization and a dispersion–centrifugation cycle was applied to the dissolution and purification of as-prepared electric-arc produced single-walled carbon nanotubes (SWNTs). It is validated that K2S2O8 treatment generates hydrophilic groups such as carboxyl and hydroxyl on the surfaces of varying carbons, whereas such treatment also causes no severe destruction on the structure of SWNTs. Amidation of the K2S2O8-treated and mixed acids shortened SWNTs leads them largely soluble in tetrahydrofuran (THF) or other organic solvents. The soluble sample was fractionated via a dispersion–centrifugation cycle and highly pure and well-separated SWNTs were successfully obtained in the middle fractions. The purity of the centrifugally fractionated samples is qualitatively estimated with Raman spectroscopy, scanning electron microscope (SEM), and atomic force microscopy (AFM). Quantitative optical absorption spectroscopy and thermogravimetric analysis show that about 60% nanotubes in the starting material are transferred into liquid phase and the carbonaceous purity reaches as high as 129% of a reference sample R2, an ‘impurity-free’ fragment of soot directly from the arc chamber.

Keywords: Carbon nanotubes; Chemical modification; Purification; Dispersion; Centrifugation; Absorption spectroscopy

1. Introduction

Single-walled carbon nanotubes (SWNTs) exhibit several excellent properties such as high surface area, good chemical stability, electrical conductivity, and extremely high mechanical strength, etc. [1], and they are proposed for many promising applications in the field of nanoelectronics, nanorobes, nanostructural composites, field-emission displays, etc. [2].
chemical sensors, etc. [1,2]. However, the current methods for large-scale production of SWNTs generate significant amounts of carbonaceous impurities such as amorphous carbon, fullerene, turbostratic graphite (TSG), and polyhedral carbon nanoparticles (PCNs) along with transition metals that were introduced as catalysts in the growth of nanotubes [3–5]. To get rid of the disturbance of those impurities on the intrinsic properties and the technological potentials of the unique one-dimensional structural materials, a highly efficient purification procedure must be developed.

During the past decade, much effort has been directed toward improving the purity as well as the quality of as-prepared SWNTs materials and several techniques including chemical acid or gas oxidation, filtration, chromatography, capillary electrophoresis, and field-flow fractionation, etc. have been applied. In general, carbonaceous impurities are removed by refluxing as-prepared samples in boiling nitric acid or burning them in air under a relatively high temperature [6,7]. Though amorphous carbon can be etched away to some extent in this process, other carbonaceous impurities such as TSG and PCNs could not be removed in this stage because of their higher stability than that of SWNTs [8]. Moreover, large numbers of SWNTs are also etched away along with amorphous carbon. Therefore, such treatment encounters problems of both very low purification yield and high degree destruction to the target material [8,9]. The metal catalysts are usually dissolvy by inorganic acids such as concentrated HCl with the assistance of sonication and filtration [10]. Since metal catalytic particles are always found encapsulated in PCNs, the accessibility of acids to them is a severe problem. It has been reported that exposure to moist air or wet Ar/O2 mixture [11], ultrasonic suspension with inorganic nanoparticles [12], ozone oxidation [13], and microwave treatment [14,15] can breach the surrounding carbon shell to some degree. But, under these severe conditions further damage on the remaining walls of SWNTs inevitably took place. Furthermore, the residues of cracked-open carbon shells are also hard to be gotten rid of because they are always strongly bonded to SWNTs.

Recently, researchers paid much attention to the wet chemistry of nanotubes, in which SWNTs have been dissolved in different solvents via surfactant-assisted dispersion [16], noncovalent modification [17–19], or covalent functionalization [20,21]. Such dissolution not only provides an effective approach to bundle exfoliation and chemical maneuverability of SWNTs, but also allows the removal of varying impurities from nanotubes by microfiltration [16], capillary electrophoresis separation [17], and chromatographic isolation [22]. In the case of covalent functionalization, the amidation or esterification of the carboxylic acid groups of oxidized SWNT material and adding reactive groups onto the sidewalls were proposed [20]. It has been reported that sidewall modification is applicable to the purification of HiPco™ carbon nanotubes (Nanotechnologies, Inc.) [23]. However, it has disadvantage in that significant modification would drastically affect the solution-phase absorption spectroscopy, leading to a complete loss of optical features, which makes it impossible to monitor the purity as well as the dispersibility of purified nanotube samples.

In this review, we will summarize our recent researches on chemical modification and centrifugal purification of the as-prepared electric-arc produced SWNTs.

2. Chemical modifications of SWNTs

2.1. K2S2O8 oxidation

We found that K2S2O8 is a proper oxidant to differentiate the varying oxidized extent among the carbon materials existing in as-prepared SWNTs (CarboLex, Carbon Solution, Inc.) [24]. Though its oxidative ability is stronger than that of KMnO4, K2S2O8 is still a mild chemical to carbon materials, owing to its usual low chemical reaction rate. After treatment by K2S2O8 in dilute H2SO4 solution, a black sample quite easily dispersed in water, DMF, and other polar solvents was obtained. In contrast, when treated with KMnO4 in acid solution nearly all of the carbon materials were devastated.

From the good dispersibility in water, we could conclude that hydrophilic groups such as carboxyl and hydroxyl are generated on the surface of the K2S2O8-treated carbons and SWNTs are unbundled to some extent. Since amorphous carbon has larger surface areas and higher reactivity, it should be oxidized to a much heavier degree under our experimental conditions than SWNTs. On the other hand, carbon particles are less modified than SWNTs because of their multilayered structures and chemical inertness. Therefore, K2S2O8 oxidation makes it possible to centrifugally fractionate carbonaceous impurities by virtue of gradation in solubility and density.

Moreover, K2S2O8 oxidation is a nondestructive process to the structure of SWNTs. From Fig. 1, we observe that the

![Fig. 1. A representative AFM image of the K2S2O8-treated CarboLex SWNT sample dispersed in DMF on freshly cleaved mica surface observed in the tapping-mode of operation [26].](image-url)
surface of tube bundles is coated with some amorphous carbon and length of these SWNTs remains nearly the same as in the pristine material. Therefore, after the K$_2$S$_2$O$_8$ treatment the highly oxidized amorphous carbon is deposited on the surface of SWNTs which keeps SWNTs from severe destruction.

Thermogravimetric analysis (TGA) provides further support to such assumption. Fig. 2 shows the TGA and differentiated TGA (DTG) curves of the as-prepared and K$_2$S$_2$O$_8$-treated CarboLex SWNTs samples measured in air. The weight loss during 100 and 400 °C in Fig. 2b is owing to the removal of hydrophilic groups. There are three stepwise weight losses observed in Fig. 2a. In contrast, only one is detected in Fig. 2b. Thus, varying carbon components are simultaneously burned after K$_2$S$_2$O$_8$ treatment. This is a result of the evenly dispersed amorphous carbon on the surfaces of SWNTs and carbon particles. It should be noted that the burning temperature of the K$_2$S$_2$O$_8$-treated CarboLex SWNTs sample increases in comparison with the starting materials. This is a result of partial removal of metal catalysts [11] as verified by the smaller amount of residue at 900 °C than that of the as-prepared SWNTs sample. In summary, K$_2$S$_2$O$_8$ oxidation plays roles in modifying, unbundling and coating SWNTs, along with partial removal of amorphous carbon and metal catalysts.

The reaction between the oxidized SWNTs, ODA and DCC could be expressed as Eq. (2):

$$
\text{SWNT-COOH} + \text{NH}_2(\text{CH}_2)_7\text{CH}_3 + \overset{\text{O}}{\text{N}}=\text{C}=\overset{\text{O}}{\text{N}} \rightarrow \overset{\text{O}}{\text{O}} \overset{\text{O}}{\text{S}}\text{WNT-C-NH}(\text{CH}_2)_7\text{CH}_3 + \overset{\text{O}}{\text{N}}=\text{C}=\overset{\text{O}}{\text{N}} \quad (2)
$$

Long alkyl chains are covalently attached to SWNTs by the condensation reaction between the amine group of ODA and the carboxyl group at the ends as well as the sidewall of SWNTs [27]. DCC plays a role of condensing agent, which combines with water to form N,N-dicyclohexylurea. The attachment of long alkyl chains leads to the unbundling and solubilization of SWNTs in THF and other organic solvents.

### 3. Dispersion–centrifugation cycle

The reaction mixture of amidated SWNTs was ultrasonically dispersed in THF and then subjected to centrifugation at 20,000 rpm for 6 h (TOMY SRX-201 High Speed Refrigerated Centrifuge). The upper suspension was carefully decanted and monitored by UV–vis–NIR spectrum (Shimadzu UV-3150 spectrophotometer). The sludge thus obtained was dispersed in a proper amount of THF with the help of ultrasonic, and then subjected to further centrifugation. The dispersion/centrifugation process, shown in Fig. 3, was repeated till no obvious absorptions from SWNTs were observed in the decanted suspension. After 10 times of dispersion/centrifugation cycles, about half of the starting material is left as residue, which cannot easily be dispersed in THF anymore. We refer to the samples thus obtained as Dispersions 1, 2, 3, …, and 10, according to the times of dispersion–centrifugation cycles.

### 3.1. Shortened CarboLex SWNTs

As a second modification step, the K$_2$S$_2$O$_8$-oxidized SWNTs were shortened and polished by successive sonication in the mixtures of H$_2$SO$_4$/HNO$_3$ (3:1) and H$_2$SO$_4$/H$_2$O$_2$ (4:1) according to the reference [25]. The sample after H$_2$SO$_4$/H$_2$O$_2$ treatment was completely washed with water to remove any physically adsorbed chemicals and heated in a vacuum at 120 °C overnight.

### 2.3. Amidation of the oxidized SWNTs

The K$_2$S$_2$O$_8$-treated and the mixed acids shortened SWNT samples were finally modified with octadecylamine (ODA) with the assistance of dicyclohexylcarbodiimide (DCC). We carried out this reaction in two ways. Firstly, the mixture was dispersed in tetrahydrofuran (THF) ultrasonically, then was stirred with a magnetic stirrer and refluxed in THF for 3 days [24]. Secondly, the oxidized SWNTs samples were functionalized with a solvent-free process. The reactants were ground and evenly mixed in a mortar, then were heated to 140 °C and stirred by a magnetic stirrer under Ar atmosphere for a week. After a proper amount of DCC was added, the reaction mixture was further heated at the temperature of ~ 130 °C [26].

The reaction mixture of amidated SWNTs was dispersed in THF and then subjected to centrifugation at 20,000 rpm for 6 h (TOMY SRX-201 High Speed Refrigerated Centrifuge). The upper suspension was carefully decanted and monitored by UV–vis–NIR spectrum (Shimadzu UV-3150 spectrophotometer). The sludge thus obtained was dispersed in a proper amount of THF with the help of ultrasonic, and then subjected to further centrifugation. The dispersion/centrifugation process, shown in Fig. 3, was repeated till no obvious absorptions from SWNTs were observed in the decanted suspension. After 10 times of dispersion/centrifugation cycles, about half of the starting material is left as residue, which cannot easily be dispersed in THF anymore. We refer to the samples thus obtained as Dispersions 1, 2, 3, …, and 10, according to the times of dispersion–centrifugation cycles.
H₂SO₄/HNO₃ and polishing with H₂SO₄/H₂O₂, and then amidation. Shown in Fig. 4 are the absorption spectra of Dispersions 1–10 in the visible and near-infrared ranges, with shortened CarboLex SWNTs as starting material. To account for the difference in tube concentration, all of the plots were normalized at 1360 nm.

From Fig. 4, three characteristic absorption bands are observed at approximately 1800, 1000, and 700 nm, respectively. The first two bands are attributed to electronic transitions between the first and second pairs of the van Hove singularities (VHSs) of the density of states in semiconducting (sem-) SWNTs, and the last one to the first pair of VHSs in metallic (met-) SWNTs [28]. The steplike change of absorption at around 835 nm is an artifact from the spectrophotometer, and the shoulders around 1920 and 1180 nm and the broad absorption bands at 1382 nm are due to the absorbed water in the THF solution. It is obvious that the spectral resolution and the absorptive intensity of the characteristic features from SWNTs improve gradually from Dispersions 1 to 6, corresponding to gradual decrease of fine functionalized impurities. In contrast, the resolvability of optical absorption spectra gets lower and lower from Dispersions 6 to 10, indicating that more impurities and larger bundle of SWNTs transform into the liquid phase. Therefore, Dispersion 6 displays the most pronounced features among the 10 soluble samples. Detailed study of them leads us to a better understanding of the diameter and chirality distributions in the electric-arc-produced SWNTs [24].

Very recently, Haddon et al. [29] proposed a spectroscopic approach to quantitatively evaluate the purity of SWNTs. We attempt to apply this method to estimate the purity of the shortened SWNTs. Fig. 5 shows the solution-phase NIR absorption spectra of sample Dispersion 6 in the range of 850–1290 nm, corresponding to the second optical absorption bands originating from semiconducting SWNTs (S₂₂). To estimate the real purity of our purified sample, a reference is necessary. Though a 100% pure SWNT sample is unavailable, we could estimate the purity of our functionalized full-length SWNTs with respect to the reference sample R2 in Ref. [29], which is an ‘impurity-free’ fragment of soot directly from the arc chamber. By referencing to the documented datum A(S₂₂,R2)/A(T,R2)=0.141, we could conclude that the relative purity of our functionalized shortened SWNTs is 129% (0.1818/0.141). This means that the present procedure generates SWNTs with a purity much higher than that of the reference sample R2. On the other hand, our data also prove that reference R2 is still far from 100% pure SWNTs.

Further support for the purity as well as dispersibility of our functionalized nanotubes comes from AFM measurement. Shown in Fig. 6 is a typical AFM image of Dispersion 6, in which well-separated SWNTs with clean surfaces are observed.
Typically, the raw CarboLex SWNTs contains catalyst metal particles, metal clusters encapsulated in graphite layers, amorphous carbon, and in some cases fullerenes, with a 30-wt% abundance of carbon nanotube ropes. In our wet chemical process, most of the SWNT ropes are unbundled and well dispersed in THF solution. Large tube bundles, aggregates of nonnanotube carbon structures, and residual catalyst are removed as sediment by repeating dispersion/centrifugation. Fine functionalized amorphous carbon and few metal clusters encapsulated in graphite layers are more soluble than functionalized SWNTs, and most of them are fractionated into the samples before Dispersion 6. The UV–vis–NIR spectra of Solutions 1–10 (Fig. 4) support such an assumption.

3.2. Full-length CarboLex SWNTs

A two-step wet chemistry procedure was applied in this work. The as-prepared CarboLex SWNTs were firstly modified with K$_2$S$_2$O$_8$ in dilute aqueous H$_2$SO$_4$ solution, and then subjected to alkyl amidation through a solvent-free functionalization process. After 10 times of dispersion–centrifugation cycles, about half of the starting material is left as sediment 10, which cannot easily be dispersed in THF anymore. Dispersion 1 and the mixture of Dispersions 2,3,…,10 were filtered with 0.1 μm PTFE microfilm, and the solid samples were dried for 8 h at 100 °C in a vacuum and weighted.

Raman spectroscopy is a powerful tool to characterize SWNTs. The characteristic peaks, the radial breathing mode (RBM), disordered carbon mode (D band), the tangential Raman mode (split G band), and the combination mode, usually appear in the wavenumber ranges in approximately 100–250, 1320–1370, 1530–1610, and 1680–1830 cm$^{-1}$, respectively [30]. Shown in Fig. 7 are the Raman spectra of Dispersion 1, Dispersions 2–10 and Residue. It can be seen that none of the characteristic Raman peaks of SWNTs are observed in Fig. 7a. We argue that Dispersion 1 is composed of highly functionalized amorphous carbon. It is suggested that the area ratios of the Raman peaks (G/D) are proportional to the in-plane crystallite size and inversely proportional to the amount of ‘unorganized’ carbon in graphitic materials [31]. As shown in Fig. 7b and c, the disorder Raman (D) peaks are extremely weaker for Dispersions 2–10 and Residue than that of the as-prepared SWNTs with respect to their corresponding prominent split G bands, implying that they are well crystallized. Moreover, the Raman intensity of Dispersions 2–9 is observed about 10 times higher in the RBM, and four times higher in the split G band than those of Residue. Therefore, we ascribe Dispersions 2–9 as purified SWNTs and sample Residues as TSG and PCNs along with few large SWNT bundles.

In comparison with the Raman data of the as-prepared SWNTs shown in Fig. 7d, we observed a large increase in integrated ratio of the Raman peaks (G/D), a reduction in G peak width, and a prominent combination peak near 1744 cm$^{-1}$ in Fig. 7b, indicating a dramatic improvement in the SWNT purity of Dispersions 2–9 with respect to the starting material. Moreover, it is well known that the RBM modes could be used to estimate the diameters and to identify the type (metallic or semiconducting) of SWNTs when resonantly enhanced [30]. As shown in Fig. 7b–d, no observable variance is detected in the distribution of the RBM modes among the starting material, Dispersions 2–9 and Residue. Therefore, we conclude that our chemical processes have no or little damage to the structure of SWNTs. Further support comes from the AFM image shown in Fig. 8, which does not stand for the whole sample, but has been picked up to show the length of soluble nanotubes. Here, we observed a well-separated thin bundle with length as long as...
2.8 μm, which is one order longer than those mixing acids shortened ones [25].

The morphologies of Dispersion 1, Dispersions 2–10, and Residue are observed and the SWNTs purity is qualitatively estimated with a scanning electron microscope (SEM). Fig. 9 shows the SEM images of as-prepared SWNTs, Dispersion 1, Dispersions 2–10, and Residue. Only irregular agglomerates of amorphous carbon are seen in Fig. 9b. In contrast, high-density SWNTs are observed in Fig. 9c without catalytic metal particles, TSG, or PCNs. From Fig. 9d, the SEM image of Residue, a large number of agglomerates of larger particles with a small amount of SWNTs are detected. These particles are due to metal catalysts, TSG, and PCNs. Of interest to note is that SWNTs in the sample anchor to larger particles through one or both of their ends. They also show cleaner surfaces and larger bundles than those found in Fig. 9c, indicating their low degree of functionalization. In comparison with the SEM image of the as-prepared sample (see Fig. 9a), high-purity SWNTs are effectively separated with metal catalysts and varying carbon impurities via chemical functionalization and centrifugation.

Shown in Fig. 10 are the absorption spectra of Dispersion 1, Dispersions 2–9 and Residue in the visible and near infrared ranges. No optical absorption features of SWNTs are detectable in Fig. 10a, suggesting that no SWNTs exist in Dispersion 1. Comparing with those observed in Fig. 10b, the optical absorption features of Residue are very weak. Moreover, fine structure is also resolved in the visible range of Fig. 10b. The features at 644, 675, 699, 735, and 784 nm are ascribed to the electronic transitions between the first pair of VHSs in metallic SWNTs, and those at 466, 553, and 584 nm to the third pairs of VHSs in semiconducting SWNTs. The resolution improvement in optical adsorption spectra is indicative of good dispersibility and high purity of SWNTs. Therefore, the optical absorption data are consistent with the above Raman results in assigning Dispersion 1, Dispersions 2–10 and Residue as highly functionalized amorphous carbon, well-dispersed pure SWNTs and low-grade modified aggregates of nonnanotube carbon structures such as TSG and PCNs and residual catalyst along with few large tube bundles, respectively.

Fig. 11 shows the solution-phase NIR absorption spectra of the reaction mixture, Dispersions 2–10 and Residue in the range of 850–1290 nm, corresponding to the second optical absorption bands originating from semiconducting SWNTs (S22). Purity calculations reveal that the relative purities of Dispersions 2–10 and Residue with respect to the reaction mixture are 5.1 and 1.1, respectively. This means that a 5-fold improvement in the purity of functionalized SWNTs is obtained with the dispersion–centrifugation recycles. By
referencing to the documented reference sample R2, the relative purity of our functionalized full-length SWNTs is 96% (0.135/0.141). Thus, a SWNTs sample with a purity at the same level as that of the reference sample R2 is obtained.

TGA was used to determine the functionalization degree and the total amount of residual metals in the samples. Fig. 12 shows the TGA–DTG curves of Dispersion 1, Dispersions 2–10, and Residue measured in argon atmosphere. It is obvious that the TG and DTG curves of the three samples show similar shapes in the same weight-loss temperature range, implying that the same component was lost during the heating process. We ascribe the weight loss to the destruction of functionalities attached on SWNTs. When heated to 500°C, Dispersion 1, Dispersions 2–10, and Residue undergo weight losses of 42, 32 and 26%, respectively, which offers a direct evidence for the different functionalization degree of the varying carbons presented in the starting material.

The samples that survived from heating in argon were successively subjected to thermogravimetric analysis in air atmosphere. As shown in Fig. 13, the weight starts to loss near 350°C and a large stepwise weight-loss along with a small one. In contrast, only one stepwise weight-loss was observed for Dispersions 2–10, corresponding to the burning of SWNTs. From the DTG curve of Residue, at least three peaks are observed. The narrow peak at 490°C is assumed to be owing to SWNTs. The broad peak around 730°C and the small peak near 520°C might be because of varying crystalline graphite materials such as TSG and PCNs, etc. The burning temperature of the SWNTs in Residue is lower than that in Dispersions 2–10. This is a result of the presumably metal-catalyzed oxidation process [11]. Almost all carbon materials in these samples are burned near 900°C and the remaining residues are the oxidized transition metals, which are 3%, 6% and 42 wt% for Dispersion 1, Dispersions 2–10 and Residue, respectively. The much lower content of metal residue in Dispersions 2–10 than that in Residue suggests an effective removal of metal catalysts from SWNTs.

With the optical absorption spectroscopic and thermogravimetric data outlined above, we can estimate the SWNTs purity in Dispersions 2-10 (PNT) and Residue (PR), and then the purification efficiency factor (FPE) of the present procedure.

\[
P_{\text{NT}} = 96\% \times (1 - 0.785 \times 6\%) = 91.5\% \quad [26]
\]

\[
P_{\text{R}} = 96\% \times 1.151 \times (1 - 0.785 \times 42\%) = 13.9\% \quad [26]
\]

3.3. Full-length UT SWNTs

The as-prepared SWNTs were produced by an electric arc-discharge method [3] in University of Tsukuba. A graphite rod, drilled and filled with powder of graphite and catalyst particles (Ni:Y:C/2:1:10 atomic ratio), is vaporized by an 80 A current under a helium atmosphere of 650 Torr. The sticky cotton-like
soot collected on the top of the furnace chamber was referred as UT SWNTs.

The UT SWNTs were treated with the same procedure used for full-length CarboLex SWNTs to test the applicability of our purification method. Fig. 14 shows the TGA and DTG curves of the as-prepared and K2S2O8-treated UT SWNTs measured in air. There are two stepwise weight losses observed in Fig. 14a, which are ascribed to the burning of amorphous carbon and SWNTs, respectively. In comparison with Fig. 2a, we here observed higher burning temperature, fewer weight-loss steps, and less amount of residues. This means that UT SWNTs have advantages over CarboLex SWNTs in fewer metal particles and fewer TSG and PCNs. Comparing with Fig. 14a, we also see the higher burning temperature and less amount of residue in Fig. 14b, indicating the effect of K2S2O8 treatment on as-prepared UT SWNTs. It should be noted that three peaks can be observed from 450 to 500 °C in Fig. 14b. Such narrow weight-loss temperature also supports that amorphous carbon and other carbonaceous material were coated on the surfaces of SWNTs.

Shown in Fig. 15 are the SEM images of the as-prepared and the K2S2O8-treated UT SWNTs, which display that the length of the K2S2O8-treated UT SWNTs is at least several micrometers, indicating K2S2O8 oxidation is nondestructive to the structure of UT SWNTs. Moreover, Fig. 15b also shows clearly that the surfaces of the oxidized SWNTs are evenly coated with highly functionalized amorphous carbon.

Therefore, the roles played by K2S2O8 oxidation in modifying, unbundling and coating CarboLex SWNTs along with partial removal of amorphous carbon and metal catalysts are also verified with the UT SWNTs.

Fig. 12. TGA–DTG curves of samples (a) Dispersion 1, (b) Dispersions 2–10, and (c) Residue heated in argon atmosphere (ramp rate: 10 °C; Ar flow rate: 300 cm³/min) [26].

Fig. 13. TGA–DTG curves of (a) Dispersion 1, (b) Dispersions 2–10, and (c) Residue heated in air atmosphere (samples have been heated on Ar; ramp rate: 5 °C; air flow rate: 100 cm³/min) [26].

Fig. 14. The TGA–DTG curves of (a) the as-prepared and (b) the K2S2O8-treated UT SWNTs samples (Ramp rate: 5 °C; Air flow rate: 100 cm³/min).
The \( \text{K}_2\text{S}_2\text{O}_8 \)-treated UT SWNTs were subjected to dispersion–centrifugation recycles after amidation, and then were fractionated to 10 dispersions. From Fig. 16, three characteristic absorption bands are observed at the same regions as CarboLex SWNTs, indicating a similar diameter distribution between these two SWNTs. It is clearly seen that the spectral resolution and the absorptive intensity of the characteristic features from SWNTs get higher and higher from Dispersions 1 to 5, indicative of the improvement in SWNTs purity. However, they decrease gradually from Dispersions 5 to 10, suggesting that more carbonaceous impurities transfer into these dispersions.

The amount of SWNTs distributed among the above 10 dispersions could be extracted by analyses of the \( S_{22} \) interband transition. The relative purity of SWNTs to reference \( R_2 \) [29] in a dispersion is obtained by comparing the relative ratio of the aerial absorption after baseline subtraction and the total aerial absorption in the \( S_{22} \) interband transition. Table 1 shows the relative carbonaceous purity \( [A(S_{22},D)/A(T,D)]/[A(S_{22},R2)/A(T,R2)] \) of the Dispersions 1–10, similar to the case of full-length CarboLex SWNTs, the middle fractions (Dispersions

| Dispersion | \( A(S_{22},D)/A(T,D) \) | \( [A(S_{22},D)/A(T,D)]/[A(S_{22},R2)/A(T,R2)] \) (%) |
|-----------|----------------|-----------------------------------------|
| 1         | 0              | 0                                      |
| 2         | 0.0635         | 45.1                                   |
| 3         | 0.1122         | 79.58                                  |
| 4         | 0.16497        | 117                                    |
| 5         | 0.17808        | 125.3                                  |
| 6         | 0.1479         | 104.9                                  |
| 7         | 0.1167         | 82.8                                   |
| 8         | 0.08897        | 63.1                                   |
| 9         | 0.0791         | 56.1                                   |
| 10        | 0.0659         | 46.8                                   |

![Fig. 15. SEM images of (a) the as-prepared and (b) the \( \text{K}_2\text{S}_2\text{O}_8 \)-treated UT SWNTs.](image)

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The \( \text{K}_2\text{S}_2\text{O}_8 \)-treated UT SWNTs were subjected to dispersion–centrifugation recycles after amidation, and then were fractionated to 10 dispersions. From Fig. 16, three characteristic absorption bands are observed at the same regions as CarboLex SWNTs, indicating a similar diameter distribution between these two SWNTs. It is clearly seen that the spectral resolution and the absorptive intensity of the characteristic features from SWNTs get higher and higher from Dispersions 1 to 5, indicative of the improvement in SWNTs purity. However, they decrease gradually from Dispersions 5 to 10, suggesting that more carbonaceous impurities transfer into these dispersions.

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![Fig. 16. Absorption spectra of Dispersions 1–10 (D1,D2,..,D10). The spectra are normalized at 1360 nm. Absorption spectra of Dispersions 1–10 with shortened CarboLex SWNTs as starting material (SD1,SD2,..,SD10). To account for the difference in tube concentration, all of the plots were normalized at 1360 nm.](image)

Fig. 16. Absorption spectra of Dispersions 1–10 (D1,D2,..,D10). The spectra are normalized at 1360 nm. Absorption spectra of Dispersions 1–10 with shortened CarboLex SWNTs as starting material (SD1,SD2,..,SD10). To account for the difference in tube concentration, all of the plots were normalized at 1360 nm.

![Fig. 17. SEM images of Dispersion 4 (a) before and (b) after heating in argon atmosphere to 900 °C (ramp rate: 10 °C; Ar flow rate: 300 cm³/min).](image)

Fig. 17. SEM images of Dispersion 4 (a) before and (b) after heating in argon atmosphere to 900 °C (ramp rate: 10 °C; Ar flow rate: 300 cm³/min).
4–6) are of the highest purity. Moreover, we ascribe the main impurity in the early fractions to highly functionalized amorphous carbon, whereas the main impurity in the later fractions comes from those lightly functionalized TSG, PCNs, and metal catalysts.

We also checked out the purity of the centrifugally fractionated dispersions by SEM. Shown in Fig. 17 are the SEM images of Dispersion 4 before and after heating in argon atmosphere. In comparison with those observed in Fig. 15, we found very pure SWNTs with their surface coated with amorphous alkyl amine in Fig. 17a. After heating in argon atmosphere, those coated amorphous materials are disappeared and clean surface of SWNTs along with a few very fine white dots are observed in Fig. 17b. Those white dots might originate from ODA disassociation or catalyst metal residues. SEM observation also proves the validity of centrifugal fractionation in purification of SWNTs.

4. Conclusions

In summary, we developed a procedure for nondestructive and high-yield purification of as-prepared electric-arc produced SWNTs. In our wet chemical process, most of the SWNTs ropes are unbundled and well dispersed in organic solvent. Large tube bundles, aggregates of nonnanotube carbon structures, and residual catalyst are removed as sediment by a dispersion–centrifugation cycle. Heavily functionalized amorphous carbon is more soluble than functionalized SWNTs, and are fractionated into early centrifugal fractions, whereas the lightly functionalized fine graphite, carbon nanoparticles, metal clusters encapsulated in graphite layers are fractionated to the latter centrifugal fractions. Therefore, highly pure SWNTs are obtained in the middle centrifugal fractions. The results of Raman and optical spectroscopies, AFM and SEM observations, and TGA analyses strongly support the validity of our proposed purification method. We believe that the nanotube purity and recovery yield could be further improved by repeating the present purification procedure on these centrifugally fractionated dispersions.

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