Helicity Selective Separation of Zeolite-supported Single-walled Carbon Nanotubes Synthesized from Alcohol

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RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

ABSTRACT (Word Style "BD_Abstract").

Single-walled carbon nanotubes (SWNTs) synthesized by catalytic decomposition of an alcohol were purified by extraction. The purified SWNTs were characterized on the basis of visible-near infrared (vis-NIR) absorption, photoluminescence and Raman spectroscopic analyses, scanning electron microscopy (SEM) observation, and thermal analysis. Helicity selective separation of SWNTs was also achieved by the extraction condition.

Introduction

Many potential applications of single-walled carbon nanotubes (SWNTs) have been extensively investigated because of their excellent mechanical and electrical properties.[1,2] Many techniques for producing SWNTs in sufficient quantity and quality have been developed. The chemical vapor deposition (CVD) method attracts broad attention for one of possible low-cost and large-scale production.[3-9] The CVD method is advantageous because appropriate catalysts can be used and many of experimental parameters such as temperature and atmosphere are adjustable. Recently, a diameter selective synthesis of highly pure SWNTs has been achieved by temperature-controlled alcohol catalytic CVD (ACCVD) of an alcohol on metal supported Zeolite.[10,11] Purification and helicity selective separation of SWNTs is still an important challenge. Two methods for purification, removal of metal catalysts and Zeolite, of SWNTs produced by the ACCVD method were reported; (a) HF treatment and air oxidation and (b) NaOH treatment and air oxidation.[12,13] However, SWNTs may be damaged under these severe purification conditions. We report here simple purification of SWNTs, produced by the ACCVD method, under mild conditions. Moreover, helicity selective separation of SWNTs was also accomplished by simple extraction.

Experimental Section

SWNTs were produced according to the ACCVD method (ACCVD-SWNTs) in literature.[10]   A typical extraction procedure is as follows: 5 mg of ACCVD-SWNTs was added to 10 ml of a 1 M solution of octylamine in tetrahydrofuran (THF) and then sonicated for 2 hrs at 5-10°C (AP-ACCVD) followed by centrifugation (45,620 G, 12 hours). The solution-phase visible-near infrared (vis-NIR) absorption data were recorded on a Shimadzu UV-3150 spectrophotometer using a Pyrex cell with a path length of 10 mm. The fluorescence spectra were measured on a Horiba SPEX Fluorolog-3-11 spectrofluorometer with a liquid-nitrogen-cooled InGaAs near-infra red (NIR) detector. The slit widths and scan step were 10 nm and 5 nm for excitation and emission, respectively. Raman spectra were measured with a Horiba LabRAM HR-800 spectrophotometer by using excitation lasers with the wavelengths of 514.5 and 633 nm. Scanning electron microscope (SEM) observation was carried out with a JEOL JSM-6700FT field emission electron microscope (accelerating voltage: 5.0 kV; beam current: 10 μA). The specimen was fixed to the sample holder using a piece of adhesive carbon tape (DTM 9101, JEOL Datum). Thermo gravimetric analysis (TGA) was carried out on a Rigaku Thermo plus TG8120 at a heating rate of 10°C/min and dry air flow rate of 100 ml/min.

Results and Discussion

Figure 1 shows the vis-NIR absorption spectra of the ACCVD SWNTs in a THF solution containing octylamine (1 M, labeled by AP-ACCVD).   After centrifugation (labeled by ACCVD-O1), the characteristic SWNTs absorption bands were obtained in the vis-NIR region. The absorption peaks around 900-1400 and 550-900 nm are attributable to the first (S11) and second bands (S22) of semiconducting SWNTs (s-SWNTs) and peaks around 400-550 nm are attributable to the bands (M11) of metallic SWNTs (m-SWNTs).[14] We already reported that the dispersion efficiency of HiPco SWNTs was very sensitive to the structure and concentration of amine used.[15,16] To provide insight into the dispersion efficiency, we tested a series of amines in 1M THF solution; cyclohexylamine (ACCVD-C1), 1,2-diaminocyclohexane (ACCVD-D1), and propylamine (ACCVD-P1). Figure 1 shows that the vis-

NIR absorption intensity of ACCVD SWNTs indicating dispersibility depends on the sort of amines. O'Connell *et al*., reported that the absorption peaks of HiPco SWNTs dispersed in a D_2O solution of sodium dodecylsulfate (SDS) become sharper and shift towards the blue region after centrifugation because of the van der waals interaction between SWNTs.[17] In contrast to the S11 peaks in ACCVD-SDS, the S11 peaks in THF solutions containing various amines shifted to red and broadened. However, no clear difference was observed in S22 region. These results indicate strongly that SWNTs interact with SDS and amines. The difference of S11 peaks should reflect the difference of strength between SWNTs-SDS interaction and SWNTs-amine interaction. The SWNTs-amine interacation may include charge-transfer character. A further experiment may be necessary to clarify these interesting phenomena.

Figure 2 shows two-dimensional contour plots of the fluorescence mapping of ACCVD-O1 and ACCVD-SDS samples. The fluorescence peaks of ACCVD-O1 are shifted to red and broadened compared to those of ACCVD-SDS. The relative fluorescence intensity of SWNTs having a large diameter and a narrow band-gap in ACCVD-O1 increased as compared to that in ACCVD-SDS. Okazaki *et al*., reported that SDS dispersed SWNTs having a small diameter and a wide band-gap more selectively than sodium dodecylbenzene sulfonate (SDBS).[18] We already reported that amines interacted more strongly with m-SWNTs.[16,19] These are consistent with that SWNTs having large diameter and a narrow band-gap are dispersed effectively into THF containing amines.

The speed of rotation in centrifugation may be an important factor for extraction of SWNTs. Thus, the efficiency of the extraction in low-speed centrifugation (ACCVD-O1L, 14000g, 30min) was examined. Figure 3 shows that the extraction efficiency was not strongly dependent on rotation speed (cf. Fig. 1) and was increased with an increase of repetition of a dispersion-centrifugation cycle. Repetition of a dispersion-centrifugation cycle is effective for the SWNTs extraction. The SEM images of ACCVD-O1L, ACCVD-O1, and ACCVD-SDS show that Zeolite is completely removed by this simple extraction procedure under mild conditions, which do not involve the treatment using a strong acid or alkaline. We measured TGA to estimate the purity of samples. The weight-loss of AP-ACCVD

and SWNTs-O1L was 4.9 and 82 wt%, respectively. The residual material would be derived from metal catalysts. The purities after (a) HF treatment and air oxidation and (b) NaOH treatment and air oxidation were reported to be 95 and 63 wt%, respectively, though the damage of SWNTs was not mentioned.[12,13]

We have already reported a convenient amine-assisted dispersion and separation method, by which m-SWNTs were remarkably enriched.[16] The dispersion and separation efficiency of SWNTs strongly depends on the structure and concentration of amines used. To obtain m-SWNTs, ACCVD SWNTs were dispersed in a THF solution containing propylamine (3M and 5M) and then centrifuged (labeled by ACCVD-P3 and ACCVD-P5, respectively). Figure 5a shows that the amount of extracted SWNTs decreased with an increase of amine concentration. The absorption spectra of concentrated samples, normalized at 915 nm, show that the intensity of M11 bands in ACCVD-P3 and ACCVD-P5 increased with a decrease of that of the S11 and S22 bands. This strongly suggests that selective extraction of m-SWNTs was achieved.

SWNTs films were made of the extracted samples and Raman spectra of the films with excited at 514.5 and 633 nm were measured. The results are shown in Figure 6. From a detailed study of Raman spectra of SWNTs Kataura *et al*., proposed that the RBM peaks appear in the range around 260 cm^{-1} and 180 cm^{-1} when m-SWNTs were excited at 514.5 and 633 nm, respectively, while the peaks appear in the range around 200 cm^{-1} and 260 cm^{-1} when s-SWNTs were excited at 514.5 and 633, respectively.[20] The strong peaks assigned to m-SWNTs in ACCVD-P3 and ACCVD-P5 provide an additional evidence for the metal-semiconducting selective separation by our simple extraction method. The proportions of m-SWNTs area of ACCVD-P3 toward s-SWNTs area in RBM region with the excitation wavelengths of 514.5 and 633 nm were estimated 86% and 68%, respectively. (The proportions of m-SWNTs area of AP-ACCVD toward s-SWNTs; 514.5 nm: 85%, 633 nm: 42%) Especially, it was revealed that m-SWNTs having large diameter are efficiently enriched.

In order to establish effective and selective extraction of SWNTs, ACCVD-SWNTs were treated by 5M propylamine solution, and then extracted by 1M octylamine solution from its deposit (ACCVD-

P5O1). Absorption spectra show that multi-steps extraction is effective for selective purification due to electro properties of SWNTs.

Conclusions

Amines are effective to disperse and extract ACCVD-SWNTs in a THF solution. This purification process can be used for removal of Zeolite under mild conditions. The dispersion-centrifugation process makes m-SWNTs highly enriched in purification of ACCVD-SWNTs under the extraction conditions. The separation of m-SWNTs and s-SWNTs opens a new way in application of SWNTs.

Supporting Information Available: Vis-NIR spectra of HiPco SWNTs in amine solution in THF. TG data of ACCVD and ACCVD-O1L. Absorption spectra of ACCVD-P5 amd ACCVD-P5O1. This material is available free of charge via the Internet at http://pubs.acs.org.

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(1) (a) Iijima, S.; Ichihashi, T. Nature 1993, 363, 603. (b) Bethune, D. S.; Klang, C. H.; de Vries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. Nature 1993, 363, 605.

(2) Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen. R.; Itkis, M. E.; Haddon, R. C. Acc. Chem. Res. 2002, 35, 1105.

(3) Dai, H.; Rinzler, A. G.; Nikolaev, P.; Thess, A.; Colbert, D. T.; Smalley, R. E. Chem. Phys. Lett. 1996, 260, 471.

(4) Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. Chem. Phys. Lett. 1999, 313, 91.

(5) Bronikowski, M. J.; Willis, P. A., Colbert, D. T.; Smith, K. A.; Smalley, R. E. J. Vac. Sci. Technol. A 2001, 19, 1800.

(6) Colomer, J. –F.; Benoit, J. –M.; Stephan, C.; Lefrant, S.; Van Tendeloo, G.; Nagy, J. B. Chem. Phys. Lett. 2001, 345, 11.

(7) Zheng, B.; Li, Y.; Liu, J. Appl. Phys. A 2002, 74, 345.

(8) Alvarez, W. E.; Pompeo, F.; Herrera, J. E.; Balzano, L.; Resasco, D. E. Chem. Mater. 2002, 14, 1853.

(9) Harutyunyan, A. R.; Pradhan, B. K.; Kim, U. J.; Chen, G.; Eklund, P. C. Nano Lett. 2002, 2, 525.

(10) Maruyama, S.; Kojima, R.; Miyauchi, Y.; Chiashi, S.; Kohno, M. Chem. Phys. Lett. 2002, 360, 229.

(11) Miyauchi, Y.; Chiashi, S.; Murakami, Y.; Hayashida, Y.; Maruyama, S. Chem. Phys. Lett. 2004, 387, 198.

(12) Igarashi, H.; Murakami, H.; Murakami, Y.; Maruyama, S.; Nakashima, N. Chem. Phys. Lett. 2004, 392, 529.

(13) Okubo, S.; Sekine, T.; Suzuki, S.; Achiba, Y.; Tsukagoshi, K.; Aoyagi, Y.; Kataura, H. Jpn. J. Appl. Phys. 2004, 43, 396.

(14) Maruyama, S.; Miyauchi, Y.; Murakami, Y.; Chiashi, S. New J. Phys. 2003, 5, 149.

(15) Maeda, Y.; Kimura, S.; Hirashima, Y.; Kanda, M.; Lian, Y.; Wakahara, T.; Akasaka, T.; Hasegawa, T.; Tokumoto, H.; Shimizu, T.; Tokumoto, H.; Kataura, H.; Miyauchi, Y.; Maruyama, S.; Kobayashi, K.; Nagase, S. J. Phys. Chem. B 2004, 108, 18395.

(16) a) Maeda, Y.; Kimura, S.; Kanda, M.; Hirashima, Y.; Hasegawa, T.; Wakahara, T.; Lian, Y.; Nakahodo, T.; Tsuchiya, T.; Akasaka, T.; Lu, J.; Zhang, X.; Gao, Z.; Yu, Y.; Nagase, S.; Kazaoui, S. Minami, N.; Shimizu, T.; Tokumoto, H.; Saito, R. J. Am. Chem. Soc. 2005, 127, 10287. b) Maeda, Y.; Kanda, M.; Hashimoto, M.; Hasegawa, T.; Kimura, S.; Lian, Y.; Wakahara, T.; Akasaka, T.; Kazaoui, S. Minami, N.; Okazaki, T.; Hayamizu, Y.; Hata, K.; Lu, J.; Nagase, S. J. Am. Chem. Soc. 2006, 128, 12239.

(17) O'Connell, M. J.; Bachilo, S. M.; Huffman, C. B.; Moore, V. C.; Strano, M. S.; Haroz, E. H.; Rialon, K. L.; Boul, P. J.; Noon, W. H.; Kittrell, C.; Ma, J,; Hauge, R. H.; Weisman, R. B.; Smalley, R. E. Science, 2002, 297, 593.

(18) Okazaki, T.; Saito, T.; Matsuura, K.; Ohshima, S.; Yumura, M.; Iijima, S. Nano Lett. 2005, 5, 2618.

(19) Lu, J.; Nagase, S.; Maeda, Y.; Wakahara, T.; Nakahodo, T.; Akasaka, T.; Yu, D.; Gao, Z.; Han, R.; Ye, H. Chem. Phys. Lett. 2005, 405, 90.

(20) Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezu, I.; Suzuki, S.; Ohtsuka, Y.; Achiba, Y. Synth. Met. 1999, 103, 2555.
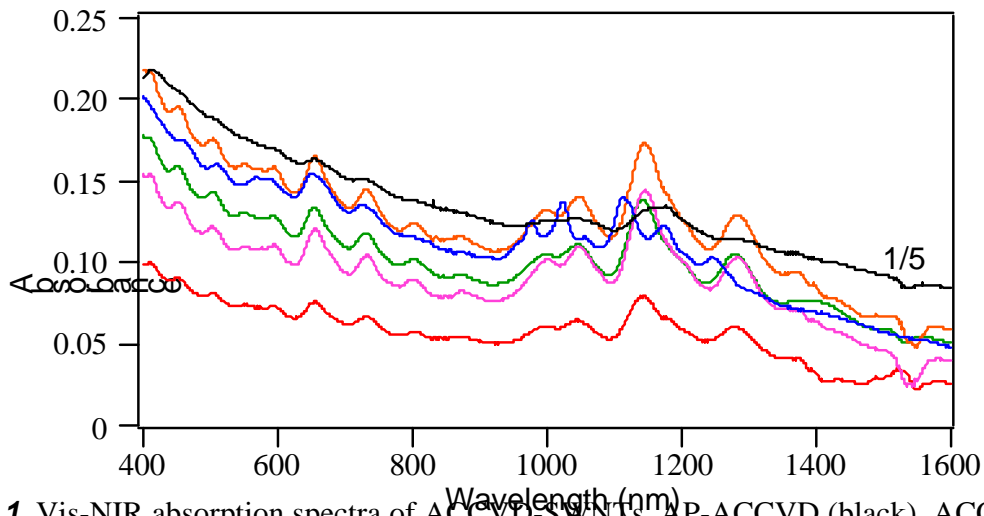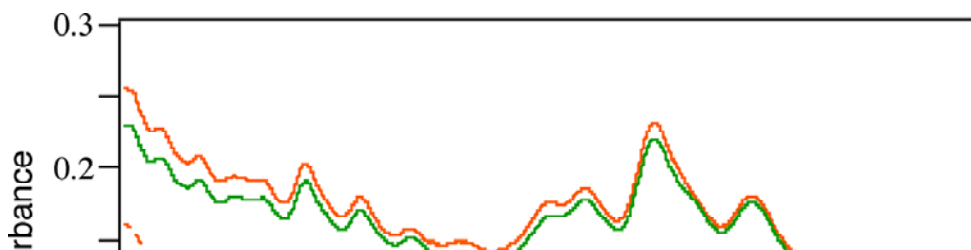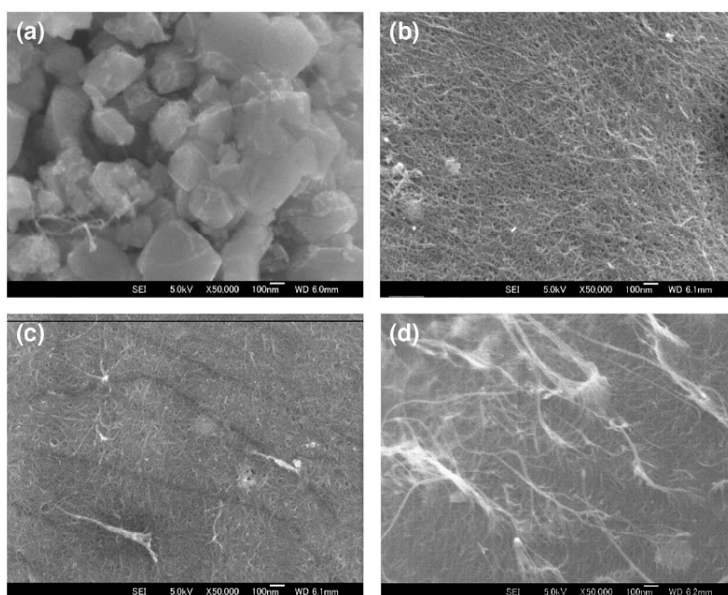
Figure 1. Vis-NIR absorption spectra of ACCVD-SWNTs. AP-ACCVD (black). ACCVD-SDS (blue). ACCVD-C1 (orange). ACCVD-O1 (green). ACCVD-D1 (pink). ACCVD-P1 (red).
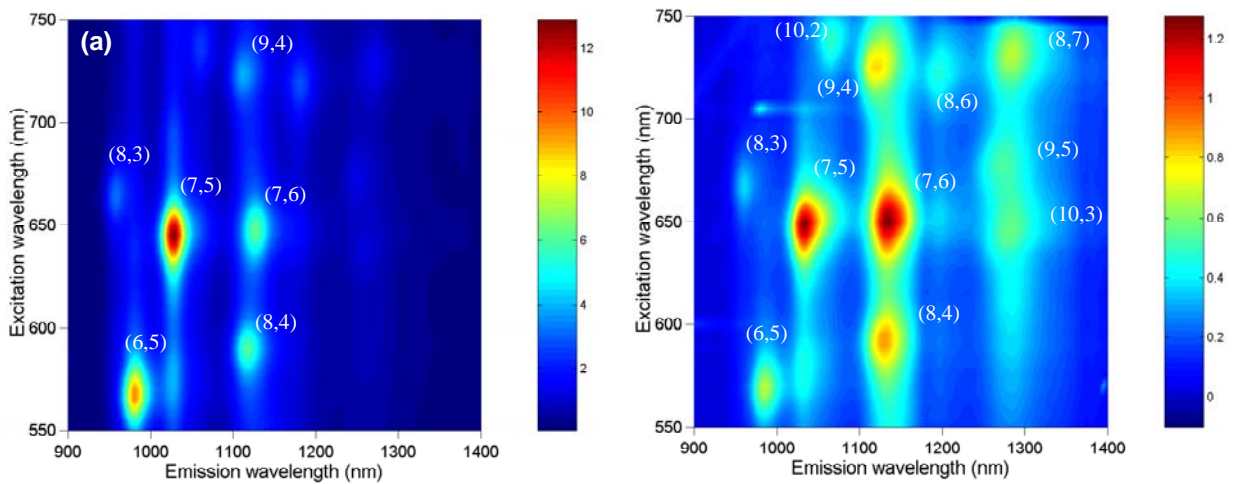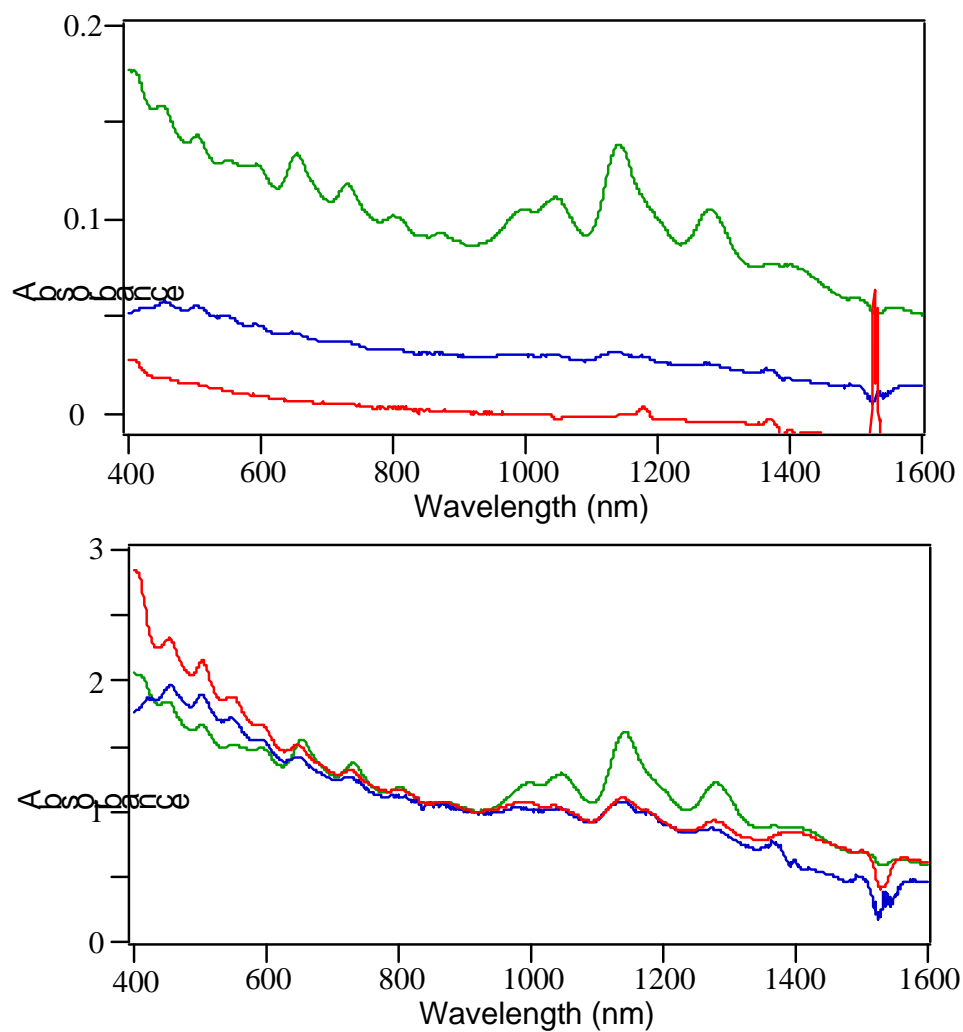

Figure 2. Two-dimensional contour plots of the NIR photoluminescence mappings of (a) ACCVD-SDS and (b) ACCVD-O1.
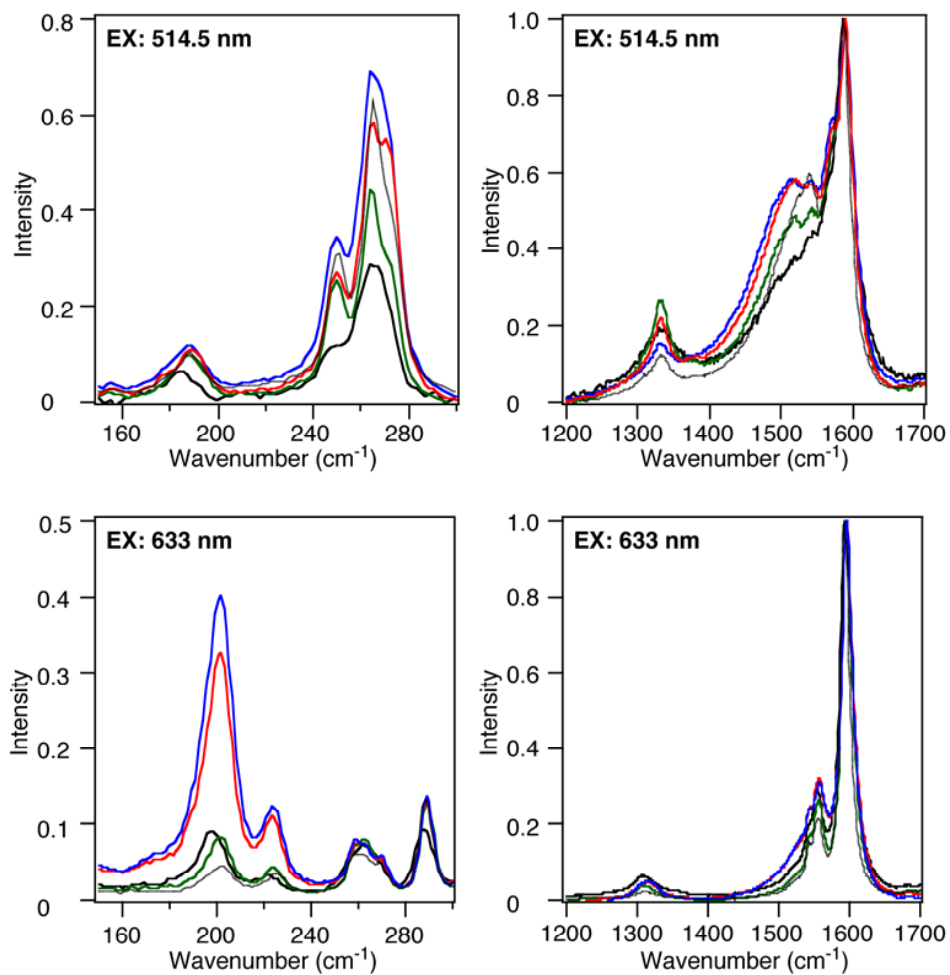
Figure 3. Vis-NIR absorption spectra of ACCVD-C1L (orange) and ACCVD-O1L (green). 1st extraction (solid line). 2nd extraction (dashed line). 3rd extraction (dotted line).
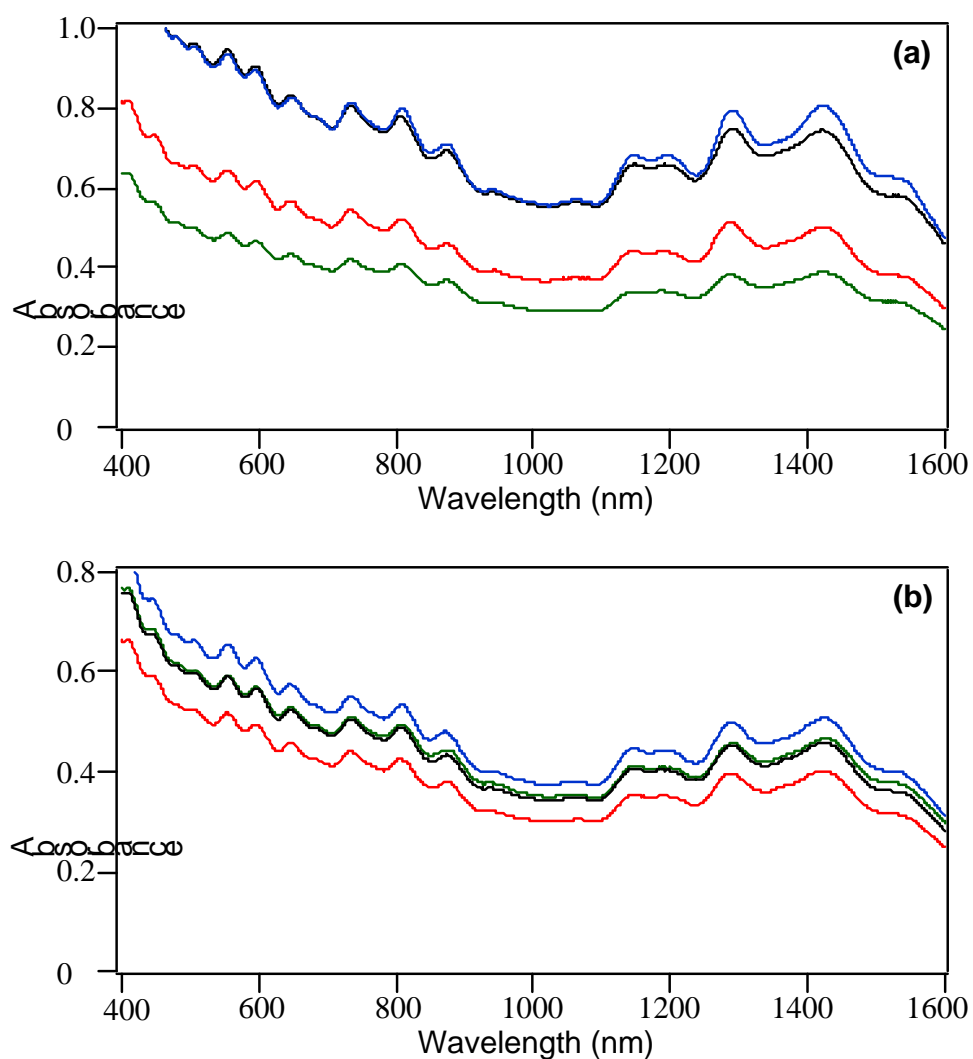

Figure 4. SEM images of SWNTs. (a) ACCVD-SWNTs. (b) ACCVD-O1L. (c) ACCVD-O1. (d) ACCVD-SDS.
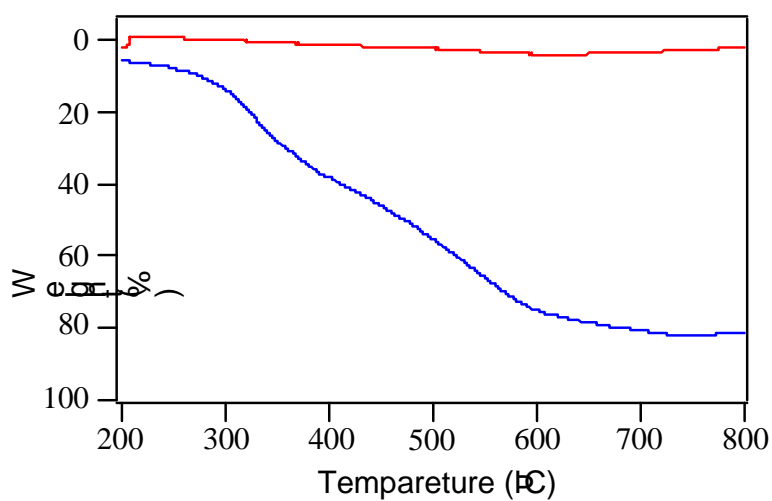
Figure 5. (a) Vis-NIR absorption spectra of ACCVD-O1 (green), ACCVD-P3 (blue), and ACCVD-P5 (red). (b) Vis-NIR absorption spectra of ACCVD-O1 (green), ACCVD-P3 (blue), and ACCVD-P5 (red) normalized at 915 nm.
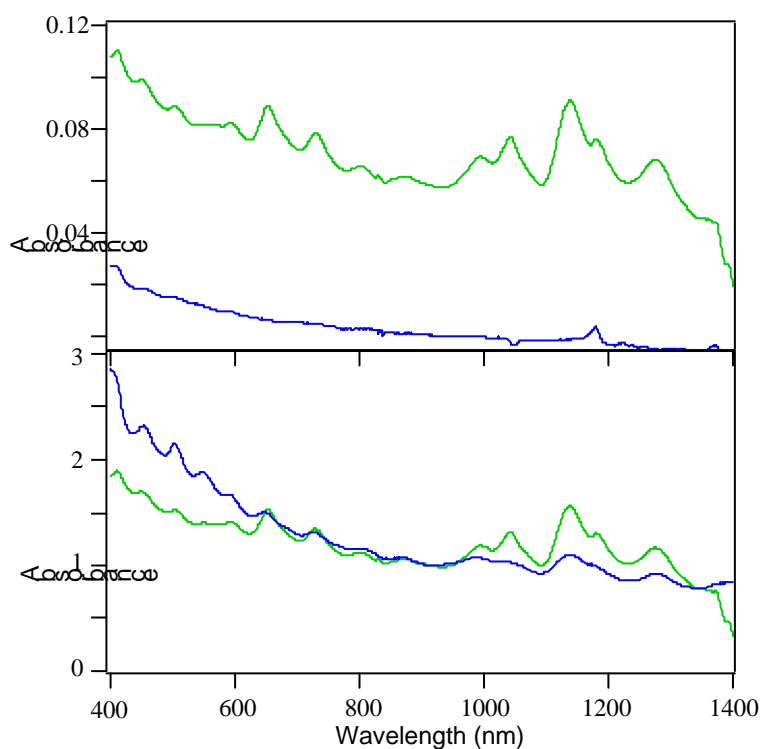
Figure 6. Raman spectra of AP-ACCVD (solid line), ACCVD-SDS (dashed line), ACCVD-O1 (green), ACCVD-P3 (blue), and ACCVDP5 (red).

Figure S1. Vis-NIR absorption spectra of HiPco-SWNTs. (a) 0.1 M solution. (b) 1 M solution. cyclohexylamine (black). octylamine (green). diaminocyclohexane (blue). propylamine (red).

Figure S2. TG curves of ACCVD (red) and ACCVD-O1L (blue).

Figure S3. (a) Vis-NIR absorption spectra of ACCVD-SWNTs. (b) Vis-NIR absorption spectra of ACCVD-SWNTs normalized at 915 nm. ACCVD-P5 (blue). ACCVD-P5O1 (green).