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Facile and Scalable Route for Highly Efficient Enrichment of Semiconducting Single-Walled Carbon Nanotubes

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Abstract: Purely semiconducting single-walled carbon nanotubes (s-SWNTs) with a narrow diameter distribution have been produced for HiPco SWNTs. A facile technique combining microwave irradiation with mixed-acid-assisted dispersion has proven efficient for enrichment of s-SWNTs. Using this process, both electronic type-dependent (metallic versus semiconducting) and diameter-dependent separation of SWNTs were simultaneously realized. By mildly controlling experimental conditions, metallic single-walled carbon nanotubes (m-SWNTs) and smaller s-SWNTs were preferentially removed, yielding purely diameter distribution-narrowed semiconducting nanotubes. Furthermore, the chemical structure of carbon nanotubes was restored after thermal annealing, as indicated by Raman and UV absorption investigations. The dual effects of semiconducting enrichment and diameter distribution narrowing, along with facile procedures, make this method promising for large-scale separation of SWNTs and therefore for industrial fabrication of nanotube-based electronics.

Introduction

Sixteen years after their discovery, SWNTs continue to fascinate the scientific community, mostly because of the unique electronic properties of s-SWNTs.[1−4] However, no pure s-SWNTs over metallic counterparts have been obtained directly from any synthetic procedure. That shortcoming of present technologies extremely hinders further studies and especially limits the scalable applications for promising electronics that are widely believed to be the best candidates to surpass modern silicon devices. Recently, efforts have particularly been undertaken to examine separation of carbon nanotubes with the aim of obtaining SWNTs of a single type through selective removal of either metallic or semiconducting nanotubes based on the small differences in their chemical structures. These studies typically involve covalent or noncovalent chemical functionalizations[5−13] and physical techniques.[14−18] Unfortunately, these methods suffer from shortcomings of introducing additional unwanted contamination, complex operating procedures, unscalability, or poor feasibility, which render them useless for achieving large-scaled separation of SWNTs required in practical applications. A more facile and easily scalable approach aimed at achieving full semiconductor yield and optimum-diameter nanotubes is needed and desired.

Because of the advantages it presents over conventional chemical approaches, a microwave-induced technique has been introduced into carbon nanotube chemistry, by which products with a high yield and purity have been obtained by virtue of a rapid reaction rate and a small amount of solvent used.[19−23] Nevertheless, few reports in the relevant literature describe separa-

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(1) Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature* **1998**, *393*, 49–52.
(2) Rosenblatt, S.; Yaish, Y.; Park, J.; Gore, J.; Sazonova, V.; McEuen, P. L. *Nano Lett.* **2002**, *2*, 869–872.
(3) Javey, A.; Guo, J.; Wang, Q.; Lundstrom, M.; Dai, H. J. *Nature* **2003**, *424*, 654–657.
(4) Appenzeller, J.; Lin, Y. M.; Knoch, J.; Chen, Z. H.; Avouris, P. *IEEE Trans. Electron Devices* **2005**, *52*, 2568–2576.
(5) Strano, M. S.; Dyke, C. A.; Usrey, M. L.; Barone, P. W.; Allen, M. J.; Shan, H. W.; Kittrell, C.; Hauge, R. H.; Tour, J. M.; Smalley, R. E. *Science* **2003**, *301*, 1519–1522.
(6) An, K. H.; Park, J. S.; Yang, C. M.; Jeong, S. Y.; Lim, S. C.; Kang, C.; Son, J. H.; Jeong, M. S.; Lee, Y. H. *J. Am. Chem. Soc.* **2005**, *127*, 5196–5203.
(7) Menard-Moyon, C.; Izard, N.; Doris, E.; Mioskowski, C. *J. Am. Chem. Soc.* **2006**, *128*, 6552–6553.
(8) Chattopadhyay, D.; Galeska, L.; Papadimitrakopoulos, F. *J. Am. Chem. Soc.* **2003**, *125*, 3370–3375.
(9) Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. *Nat. Nanotechnol.* **2006**, *1*, 60–65.
(10) Hwang, J. Y.; Nish, A.; Doig, J.; Douven, S.; Chen, C. W.; Chen, L. C.; Nicholas, R. J. *J. Am. Chem. Soc.* **2008**, *130*, 3543–3553.
(11) Zheng, M.; Jagota, A.; Strano, M. S.; Santos, A. P.; Barone, P.; Chou, S. G.; Diner, B. A.; Dresselhaus, M. S.; McLean, R. S.; Onoa, G. B.; Samsonidze, G. G.; Semke, E. D.; Usrey, M.; Walls, D. J. *Science* **2003**, *302*, 1545–1548.
(12) Maeda, Y.; et al. *J. Am. Chem. Soc.* **2005**, *127*, 10287–10290.
(13) Maeda, Y.; Kanda, M.; Hashimoto, M.; Hasegawa, T.; Kimura, S.; Lian, Y. F.; Wakahara, T.; Akasaka, T.; Kazaoui, S.; Minami, N.; Okazaki, T.; Hayamizu, Y.; Hata, K.; Lu, J.; Nagase, S. *J. Am. Chem. Soc.* **2006**, *128*, 12239–12242.
(14) Collins, P. C.; Arnold, M. S.; Avouris, P. *Science* **2001**, *292*, 706–709.
(15) Krupke, R.; Hennrich, F.; von Lohneysen, H.; Kappes, M. M. *Science* **2003**, *301*, 344–347.
(16) Zhang, G. Y.; Qi, P. F.; Wang, X. R.; Lu, Y. R.; Li, X. L.; Tu, R.; Bangsaruntip, S.; Mann, D.; Zhang, L.; Dai, H. J. *Science* **2006**, *314*, 974–977.
(17) Song, J. W.; Seo, H. W.; Park, J. K.; Kim, J. E.; Cho, D. G.; Han, C. S. *Curr. Appl. Phys.* **2008**, *8*, 725–728.
(18) Priya, B. R.; Byrne, H. J. *J. Phys. Chem. C* **2009**, *113*, 7134–7138.

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tion of SWNTs using microwave-assisted technique. Recently, selective destruction of m-SWNTs was achieved by microwave-irradiating a randomly networked SWNT film based on the different dielectric constants of m-SWNTs and s-SWNTs.[17,18] The studies seem capable of destroying m-SWNTs, however, because of the strong aggregation of nanotube bundles comprising both m-SWNTs and s-SWNTs, the incomplete removal of m-SWNTs, and damage to s-SWNTs neighboring heated m-SWNTs during irradiation are unavoidable. That shortcoming has become a major roadblock to the fabrication of nanodevices based on pure s-SWNTs with chemical and electrical integrities.

To overcome this intractable problem, exfoliation of SWNT bundles and homogeneous dispersion of SWNTs of different types are crucial. As a popular chemical reagent, acid mixtures typically composed of nitric acid and sulfuric acid with different ratios in volume have played a significant role in improving the dispersibility and solubility of carbon nanotubes, as studies of carbon nanotube chemistry have widely investigated.[24] Unfortunately, little attention to date has been given to understanding the effectiveness of the acids in separating SWNTs deliberately, except for reports explaining the stronger chemical reactivity of metallic tubes toward nitric acid.[25] We herein demonstrate a method of subtly integrating mixed acids-assisted dispersion and microwave irradiation, which exhibits a high effectiveness in enriching semiconducting carbon nanotubes. Through our study, the high efficiency of the proposed method in obtaining enriched s-SWNTs was clarified for the first time. The retained product contains nearly 100% s-SWNTs and has a much narrower diameter distribution than the starting material. More importantly, the resultant material exhibits distinct characteristics of SWNTs after thermal annealing, indicating better chemical and electrical integrity. Both are important for high-performance electronics. These findings demonstrate that the microwave irradiation-acids dispersion assisted method is useful for effective enrichment of s-SWNTs. Its simplicity and high efficiency make it promising for realizing industrial fabrication of nanotube-based electronics.

Experimental Section

Microwave irradiation was done in a modified microwave oven (500 W, 2450 MHz) with a water-cooling system and a water-bath isothermal setup. For safety reasons, the microwave oven was placed and operated within a fume hood. The water bath was used to maintain the temperature of reactions to be performed under a mild condition (100 °C) instead of running in a refluxing manner as done for functionalizing or cutting nanotubes reported previously, which played a key role in minimizing damage to s-SWNTs during treatment.

The starting SWNTs prepared by the high-presure carbon monoxide chemical vapor deposition method (HiPco) were obtained commercially from Carbon Nanotechnologies, Inc. Both the sulfuric acid and nitric acid were purchased from Wako Pure Chemical Industrial, Ltd. All chemical reagents were used as received, unless otherwise stated. In a typical reaction, 97% H_2SO_4 and 60% HNO_3 were slowly mixed in a 1:1 volume ratio with stirring in an ice bath so as to maintain the temperature close to room temperature. (The acid mixture is highly corrosive and strongly oxidative. Extreme care should therefore be exercised during handling.) Subsequently, 3 mg of pristine SWNTs were added into a flask containing 30 mL of the aforementioned acid mixture. The solution was ultrasonicated for 10 min at room temperature in which SWNTs were well dispersed and debundled; then the flask loading the solution was placed in a preheated water bath (nearly boiling) and subjected to microwave irradiation in the microwave oven for a series of 5 min intervals of 0−30 min. The solution treated for a different time was then carefully diluted with copious amounts of deionized (DI) water while being cooled by an external ice bath, and vacuum filtered through a 0.45 μm HA filter (Millipore Corp., Ireland). This process was repeated a few times until the filtrate was neutral. To obtain free-standing flexible SWNT films, the solid was resuspended in methanol by ultrasonication, and vacuum filtered with a 0.2 μm poly(tetrafluoroethylene) (PTFE) filter. After the buckypaper-like SWNTs were obtained by peeling the PTFE filter off atomatically with the slow vacuum filtration, they were dried overnight at room temperature in vacuum. As a final step, thermal annealing treatments were conducted at 900 °C under Ar atmosphere for 1 h, and at 350 °C in air for 30 min, respectively, to eliminate any remaining absorbate. Hereto, the samples were prepared for characterization measurements as discussed below.

Raman spectra for films made of the treated carbon nanotubes by filtration in vacuum were recorded using a spectrophotometer (LabRAM HR-800; Horiba Ltd.) with laser excitations of 514.5 and 632.8 nm. The solution-phase optical absorption data of SWNTs dispersed in THF were recorded using a spectrophotometer (UV-3150; Shimadzu Corp.) with a 10-mm path length Pyrex cell. Scanning electron microscope (SEM) observations were conducted using a field emission electron microscope (accelerating voltage, 5.0 kV; beam current, 10 μA, S-4800; JEOL) by fixing specimens to the sample holder with a piece of adhesive carbon tape (DTM 9101; JEOL Datum). The $I-V$ characteristics of SWNT membranes were recorded by the two tungsten-probes using a parameter analyzer (E5270B; Agilent Technologies Inc.). For better comparing and analyzing the results, all of the nanotube membranes were clipped into the same size of 20 × 20 mm^2, and fixed onto the sample stage for the following measurement. The sheet resistance (R_s) was estimated in the low-current-low-bias linear regime. The average SWNT membrane thicknesses (t) were measured using a surface profiler (Alpha-Step IQ; KLA Tencor Corp.).

Results and Discussion

To determine whether a mixture contains m-SWNTs or s-SWNTs, Raman scattering is a powerful tool by which both the diameter-dependent resonance radial-breathing mode (RBM) located at a lower frequency and the tangential mode (G-band) at a higher frequency can provide important data related to nanotube characteristics.[26−28] Known as a Kataura plot, both metallic and semiconducting HiPco SWNTs can be probed

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(19) Delgado, J. L.; de la Cruz, P.; Langa, F.; Urbina, A.; Casado, J.; Navarrete, J. T. L. *Chem. Commun.* **2004**, *15*, 1734–1735.

(20) Liu, J.; Zubiri, M. R. I.; Vigolo, B.; Dossot, M.; Fort, Y.; Ehrhardt, J. J.; McRae, E. *Carbon* **2007**, *45*, 885–891.

(21) Brunetti, F. G.; Herrero, M. A.; Munoz, J. D.; Diaz-Ortiz, A.; Alfonsi, J.; Meneghetti, M.; Prato, M.; Vazquez, E. *J. Am. Chem. Soc.* **2008**, *130*, 8094–8100.

(22) Umeyama, T.; Tezuka, N.; Fujita, M.; Matano, Y.; Takeda, N.; Murakoshi, K.; Yoshida, K.; Isoda, S.; Imahori, H. *J. Phys. Chem. C* **2007**, *111*, 9734–9741.

(23) Wang, Y. B.; Iqbal, Z.; Mitra, S. *J. Am. Chem. Soc.* **2006**, *128*, 95–99.

(24) Liu, J.; Rinzler, A. G.; Dai, H. J.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y. S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253–1256.

(25) Bergeret, C.; Cousseau, J.; Fernandez, V.; Mevellec, J. Y.; Lefrant, S. *J. Phys. Chem. C* **2008**, *112*, 16411–16416.

(26) Rao, A. M.; Richter, E.; Bandow, S.; Chase, B.; Eklund, P. C.; Williams, K. A.; Fang, S.; Subbaswamy, K. R.; Menon, M.; Thess, A.; Smalley, R. E.; Dresselhaus, G.; Dresselhaus, M. S. *Science* **1997**, *275*, 187–191.

(27) Pimenta, M. A.; Marucci, A.; Empedocles, S. A.; Bawendi, M. G.; Hanlon, E. B.; Rao, A. M.; Eklund, P. C.; Smalley, R. E.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. B* **1998**, *58*, 16016–16019.

(28) Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A.; Souza, A. G.; Saito, R. *Carbon* **2002**, *40*, 2043–2061.

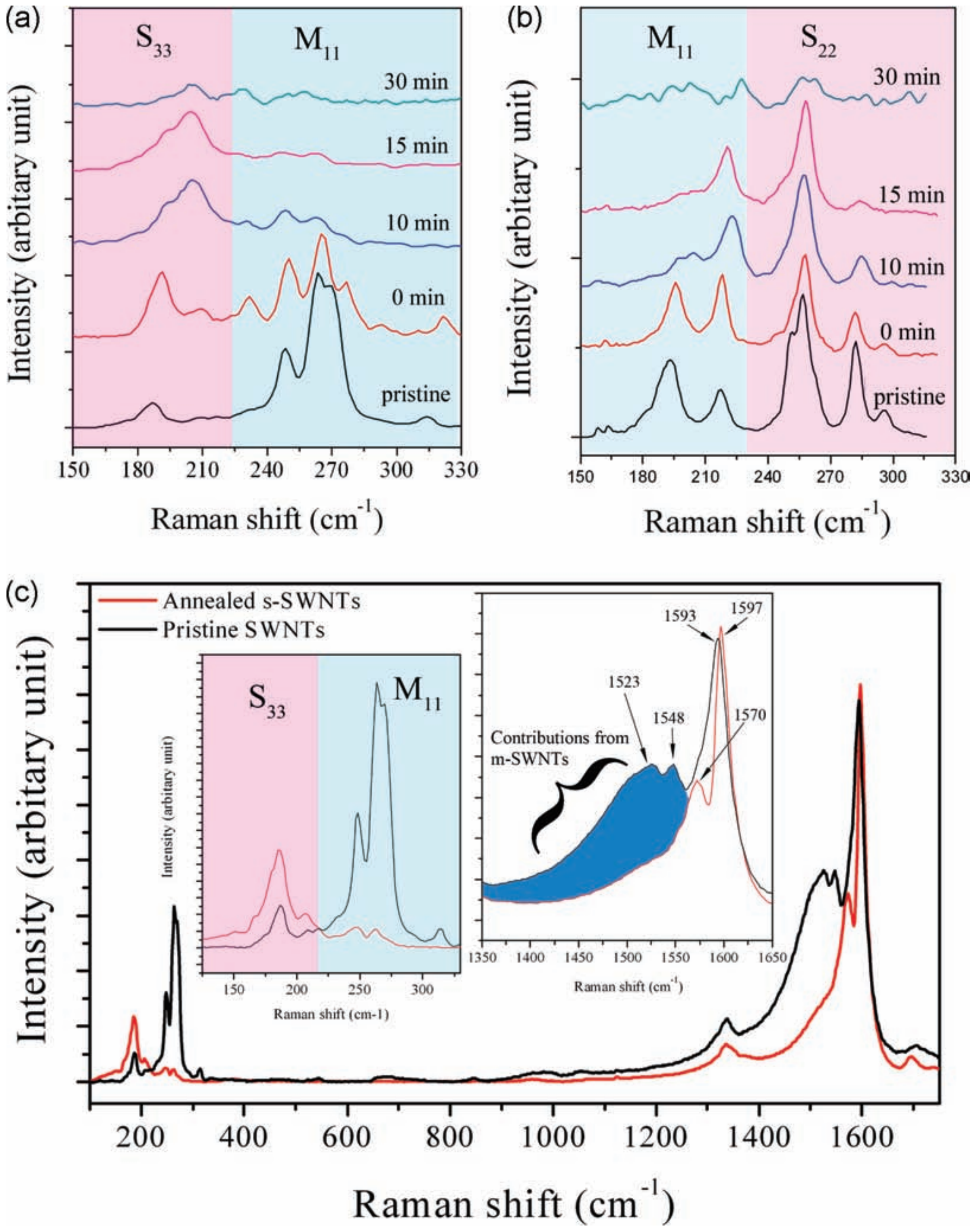

Figure 1. RBMs of Raman spectra for the treated and pristine samples obtained respectively at a 514.5 nm (a), and a 632.8 nm excitation wavelength (b). Raman spectra for the pristine and annealed s-SWNTs measured at a 514.5 nm wavelength (c). The inset shows magnified RBMs with the semiconducting (pink) and the metallic (blue) regions.

simultaneously using 514.5 and 632.8 nm excitations.[29,30] The semiconducting and metallic types of nanotubes are, respectively, in resonance around 150−220 cm^{-1} and 220−300 cm^{-1} with a 514.5 nm excitation. In contrast, lower RBMs correspond to m-SWNTs and higher ones to s-SWNTs with a 632.8 nm excitation. Figure 1a presents RBMs of the Raman spectra for pristine and resultant materials, as measured using laser excitation of 514.5 nm. The well-defined Raman peaks immediately after short-duration sonication and without microwave irradiation yet (0 min) demonstrate highly dispersed and less-bundled SWNTs in acid solutions. Nevertheless, it is apparent that, with increasing treatment time, Raman peaks located in higher RBMs are gradually depressed, and even vanish completely, while the lower peaks are better retained, compared to the RBMs for pristine SWNTs shown at the bottom of the figure. The disappearance of peaks related to m-SWNTs in higher RBMs and the intensification of features for s-SWNTs at lower frequencies strongly indicate the preferential elimination of m-SWNTs and the consequent enrichment of s-SWNTs during the treatment. It is also observed that the lower peaks from s-SWNTs were upshifted slightly. This is expected to result from the charge transfer between carbon nanotubes and the absorbed ions, as confirmed by the fact that the peak shift was recovered

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(29) Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezu, I.; Suzuki, S.; Ohtsuka, Y.; Achiba, Y. *Synth. Met.* **1999**, *103*, 2555–2558.

(30) Weisman, R. B.; Bachilo, S. M. *Nano Lett.* **2003**, *3*, 1235–1238.

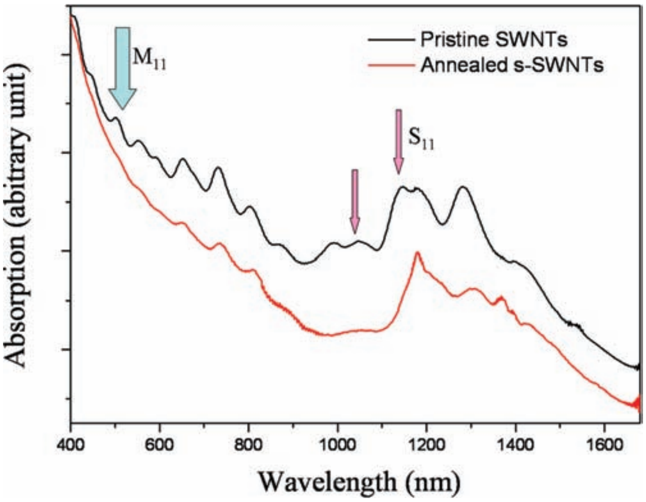

Figure 2. Optical absorption spectra of the pristine (black) and annealed s-SWNTs (red) both suspended in tetrahydrafuran.

after the removal of absorbates by heat treatment (see Figure 1c). Additionally, the enrichment of s-SWNTs is evidenced by line shape changes of the G-bands in the Raman spectra for the pristine and the annealed s-SWNTs obtained after 15-min microwave irradiation and thermal treatment at 900 °C in Argon, as shown in Figure 1c. By contrast, the broad and asymmetric G-band described as a Breit−Wigner−Fano (BWF) line shape attributed to m-SWNTs shown for the pristine SWNTs (black line) is absent from the treated sample (red line). A much narrower G-band with a 4 cm^{-1} upshift is present instead, providing further evidence of the substantial enrichment of s-SWNTs in the resultant material.[28,31] The same conclusion can be validated by Raman spectra recorded at 632.8 nm, as portrayed in Figure 1b. It is particularly interesting that, aside from the absence of m-SWNT peaks at lower frequencies, with increased treatment time, the smaller diameter s-SWNTs resonated at high frequencies become gradually featureless, while the larger s-SWNTs survived. This implies that smaller s-SWNTs could be destroyed preferentially over larger ones by prolonging reaction times during the treatment because of the higher radius of curvature and strain in the C−C bonding configuration. Raman spectra lend firm credence to the fact that s-SWNTs with much narrower diameter distribution have been enriched with the destructive removal of m-SWNTs and the highly reactive small s-SWNTs using the proposed method.

Optical absorption spectra of the pristine and the annealed s-SWNTs suspended in THF were measured to characterize the electronic states of the enriched s-SWNTs. Figure 2 presents the UV−vis−NIR absorption spectrum of the pristine SWNTs (black curve). In accordance with previous reports, it displays the energy transitions between the van Hove singularities of the density of states, typically the first transition of s-SWNTs (S_{11}) around 1000−1600 nm, the second (S_{22}) in 550−1000, and the first metallic transition (M_{11}) in 450−650.[30,32] The functionalization of SWNTs is known to always cause a great loss of their original electronic properties because of the saturation of double bonds induced by additions, especially in the case of heavy functionalization, showing no characteristic in absorption spectra.[23,33−35] Unlike those functionalizations of SWNTs, the mild experimental condition applied in our study aiming at effective enrichment of s-SWNTs over metallic ones makes the intrinsic electronic structure of the treated SWNTs restored just followed a high temperature annealing step, as is evidenced by the pronounced characteristic absorption peaks shown in Figure 2 (red curve). In comparison with the spectrum of pristine SWNTs, however, the absence of M_{11} transition of the annealed s-SWNTs points to significant elimination of m-SWNTs during processing. Another interesting observation is the weakness of the peaks indicated by pink arrows and the slight up-shifts of the S_{11} semiconducting transitions in the absorption spectrum of the annealed s-SWNTs, indicating that the diameter-distribution narrowing of s-SWNTs has indeed occurred with the selective removal of smaller s-SWNTs. What the absorption spectra demonstrated substantially accords with the Raman data discussed above.

Additionally, two-point probe conductivity measurements of membranes made up of the annealed and unannealed enriched s-SWNTs, as well as the corresponding annealed pristine SWNTs were performed to prove the effectiveness of the enrichment further. Figure 3 depicts the current−voltage (I−V) traces for those membranes. The measured membranes' thicknesses were normalized to 60 μm for comparison. The conductivities of the enriched s-SWNT films are greatly reduced (red curve), compared to the annealed pristine film (black curve). After annealing, the conductivity was increased slightly (blue curve), indicating the removal of absorbed impurities and integrity of nanotube structures. The calculated resistance of the annealed s-SWNTs is about 1670 Ω, which is 8 times larger than that of the pristine SWNTs (resistance of about 195 Ω). Although some experimental process might increase the resistance, the great loss in conductivity measured for these samples, to some extent, validates elimination of m-SWNTs and the enrichment of s-SWNTs during treatment, which qualitatively agrees with the Raman and UV−vis−NIR results described above.

Results of this study underscore the effectiveness of the proposed method in enriching narrow diameter distribution s-SWNTs. We attribute the preferential elimination of m-SWNTs and small s-SWNTs to the joint employment of acid mixture and microwave irradiation performed under mild conditions. As reported previously, the acid mixture was the most commonly used reagent for obtaining highly dispersed and debundled SWNTs.[24] It was also capable of destroying chemically reactive nanotubes with small diameters.[36] Alternatively, the microwave technique exhibited the selective destruction of m-SWNTs.[17,18] In this study, the acid mixture promoted the dispersion and exfoliation of the bundled nanotubes immediately following a few minutes' sonication. Long-duration sonication should be avoided in order not to introduce more defects to the carbon walls and consequently cut nanotubes into short ones. When microwave irradiation was applied to the homogeneous solution containing less aggregated SWNTs, both m-SWNTs and s-SWNTs were discriminated sufficiently. To realize the highly efficient enrichment of s-SWNTs with fewer defects, however, the mild experimental condition conducted in the study is crucial because

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(31) Piscanec, S.; Lazzeri, M.; Robertson, J.; Ferrari, A. C.; Mauri, F. *Phys. Rev. B* **2007**, 75.

(32) Bahr, J. L.; Mickelson, E. T.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *Chem. Commun.* **2001**, *2*, 193–194.

(33) Bahr, J. L.; Yang, J. P.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6536–6542.

(34) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124*, 760–761.

(35) Kamaras, K.; Itkis, M. E.; Hu, H.; Zhao, B.; Haddon, R. C. *Science* **2003**, *301*, 1501–1501.

(36) Ziegler, K. J.; Gu, Z. N.; Peng, H. Q.; Flor, E. L.; Hauge, R. H.; Smalley, R. E. *J. Am. Chem. Soc.* **2005**, *127*, 1541–1547.

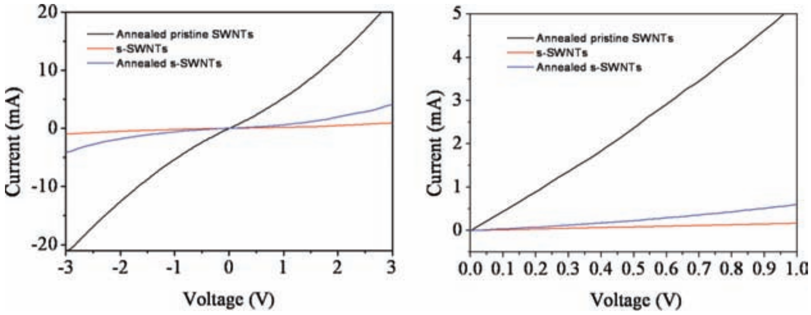

Figure 3. Current vs voltage ($I-V$) characteristics of SWNT membranes with a normalized thickness of 60 μm.

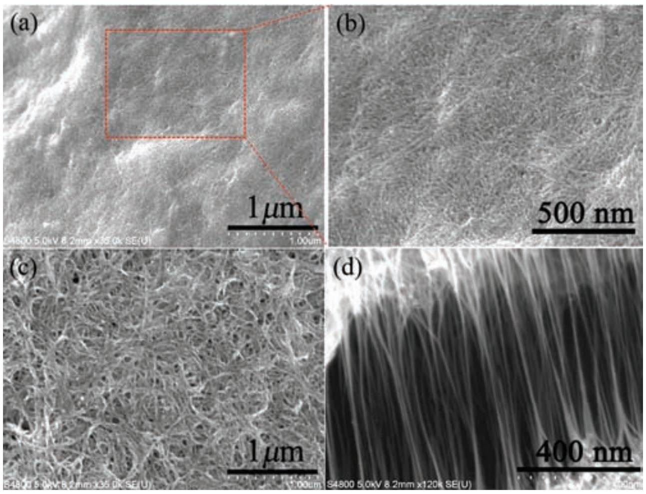

Figure 4. Typical FE-SEM images of SWNT membranes: (a) the thermally annealed s-SWNTs, (b) high magnification of the indicated area in (a), (c) the pristine SWNTs obtained by filtering their methanol solution, and (d) the well-aligned s-SWNTs showing an excellent mechanical characteristic.

it plays a key role in the resultant products. For functionalization of SWNTs, the characteristic peaks in RBMs of Raman spectra were only slightly observed because of the introduction of functional groups and loss of intrinsic properties of nanotubes resulting from the microwave irradiation applied under high-temperature conditions, even though the reaction proceeded for a short time.[23] Consequently, neither SWNT type-preferential separation nor diameter-dependent elimination was observed. Using an isothermal setup in the present case, the reactions occurred mildly at lower temperatures and for longer treatment times, which allowed carbon nanotubes of different types to be well dispersed in acid solutions. They were therefore sufficiently discriminated. After 15 min exposure of microwave irradiation, which was found to be the optimum time for the reaction considering both the yield and purity of the resulting s-SWNTs, nearly all m-SWNTs were destroyed selectively into graphitic fragments showing no SWNT characteristics. Meanwhile those smaller s-SWNTs with highly chemical reactivity were also attacked preferentially over the larger ones. Therefore, the survived s-SWNTs were diameter-narrowed and retained with minimal damage and maximal yield. Following simple filtration and thermal annealing steps, highly enriched s-SWNTs were finally obtained, exhibiting both electronic and mechanical properties as the pristine SWNTs do. Figure 4 presents typical SEM images of the pristine (Figure 4c) and obtained s-SWNTs (Figure 4a), both of which were measured at the same magnification for better comparison. As shown in Figure 4a, we can find few distinct nanotubes or their bundles at such a low magnification and resolution level of the device. In the further magnified image of the area shown in Figure 4a, however, well-defined nanotubes are visible (see Figure 4b). The sizes of the nanotube bundles were much smaller than those of the pristine SWNTs shown in Figure 4c, revealing not only the occurrence of the homogeneous dispersion and the disaggregation of SWNTs during the treatment. The size also suggests the high efficiency of separating s-SWNTs from the metallic counterpart. The excellent mechanical property is demonstrated by attempting to rip apart the s-SWNTs bulky membrane with tweezers, as revealed in Figure 4d. The well-aligned nanotubes without disconnection under external tensile force evidently validate that the enriched s-SWNTs obtained using the proposed method retain the intrinsic properties of carbon nanotubes, indicating the reliability and feasibility of the method in enriching s-SWNTs.

Conclusions

In summary, microwave-assisted treatment of as-received HiPco SWNTs suspended in mixed acids has proven to be an effective method for enriching s-SWNTs through preferential elimination of m-SWNTs. To the best of our knowledge, this is the first report clarifying the effectiveness of this method for SWNT separation. By applying microwave irradiation to an acid-mixture containing highly dispersed SWNTs, not only nanotube-type dependent separation, the enrichment of s-SWNTs, but also diameter-dependent sorting, the diameter-distribution narrowing, can be achieved simultaneously using a simple step, making this method much more viable for scaled-up future applications. More importantly, the mild condition employed minimized damage to the carbon nanotube sidewalls induced during the treatment. It simultaneously improved the separation efficiency: the enriched s-SWNTs retain good chemical and electrical integrity. Accordingly, the proposed method integrating the enrichment of s-SWNTs and the diameter distribution narrowing into one procedure is the most promising technique for future s-SWNT-based electronics.

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Supporting Information Available: Complete ref 12, Raman spectra of the pristine and annealed s-SWNTs recorded at 633 nm excitation, and the cross-sectional profiles of SEM images of unannealed s-SWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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