Communication

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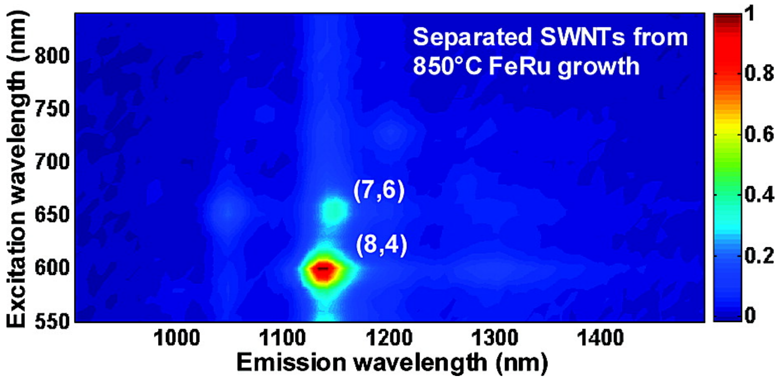
J. Am. Chem. Soc., **2007**, 129 (51), 15770-15771 • DOI: 10.1021/ja077886s



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Selective Synthesis Combined with Chemical Separation of Single-Walled Carbon Nanotubes for Chirality Selection

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Received October 15, 2007; E-mail: hdai@stanford.edu

Single-walled carbon nanotubes (SWNTs) are potential materials for future nanoelectronics.[1,2] Since the electronic and optical properties of SWNTs strongly depend on tube diameter and chirality, obtaining SWNTs with narrow (*n*,*m*) chirality distribution by selective growth[3−5] or chemical separation[6−8] is important. Progress has been made on selective growth of (6,5) SWNTs by chemical vapor deposition (CVD) of CO on a CoMo catalyst (CoMoCAT)[3] and by ethanol CVD to a certain degree.[4] Methane CVD has been widely used for SWNT synthesis in bulk and on substrates for basic physics studies and device integrations,[9,10] but the nanotubes tend to exhibit wide diameter distribution in the ∼1−3 nm range. SWNT growth in the $d \sim 1$ nm range with high diameter or chiral selectivity has been difficult by methane CVD thus far.

Here, we demonstrate that a new, bimetallic FeRu catalyst can afford SWNT growth with narrow diameter and chirality distribution in methane CVD. At 600 °C, methane CVD on FeRu catalyst produced predominantly (6,5) SWNTs according to UV−vis−NIR absorption and photoluminescence excitation/emission (PLE) spectroscopic characterization. At 850 °C, the dominant semiconducting species produced are (8,4), (7,6), and (7,5) SWNTs, with much narrower diameter distributions than previous methane CVD-grown SWNTs. Further, we show that narrow diameter growth by methane CVD combined with chemical separation by ion exchange chromatography (IEC) facilitates achieving highly single-chirality enriched SWNT samples. This is demonstrated by obtaining SWNT samples highly enriched in the (8,4) tube and free of metallic species.

Methane CVD synthesis was preformed at various temperatures between 600 and 850 °C on a new silica-supported FeRu bimetallic catalyst (see Supporting Information). We purified and suspended the synthesized SWNTs in surfactant solutions for characterizations. The UV−vis−NIR optical absorbance spectra (Figure 1) of our FeRu SWNTs grown at various temperatures showed one or several dominant peaks in the first van Hove E_{11} range (900−1400 nm) corresponding to SWNTs in the $d \sim 1$ nm region (see Figure S2 for atomic force microscopy images). Photoluminescence excitation/emission (PLE) spectroscopy was used to assign (*m*,*n*)[11] of SWNTs grown from the FeRu catalyst. The 600 °C growth produced the narrowest (*m*,*n*) distribution with a dominant single peak corresponding to the (6,5) tube (Figure 2a). Higher growth temperature led to larger diameter tubes and wider (*m*,*n*) distribution of semiconducting tubes (Figure 2b,c). Growth at 700 °C produced mainly (6,5), (7,5), and (8,4) SWNTs (Figure 2b), while 850 °C growth produced mainly (8,4), (7,5), (7,6), with few (6,5) tubes (Figure 2c). Metallic SWNTs existed in the as-grown materials evident from the metallic E_{11} absorption peaks in the 400−600 nm region (Figure 1).

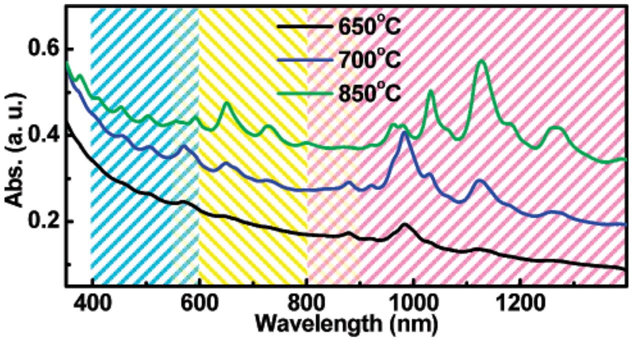

Figure 1. UV−vis−NIR spectra of cholate suspended SWNTs grown by methane CVD on FeRu catalysts at various temperatures. The wavelength ranges of lowest energy semiconducting, second lowest semiconducting, and lowest metallic absorption peaks are shaded pink, yellow, and blue, respectively.

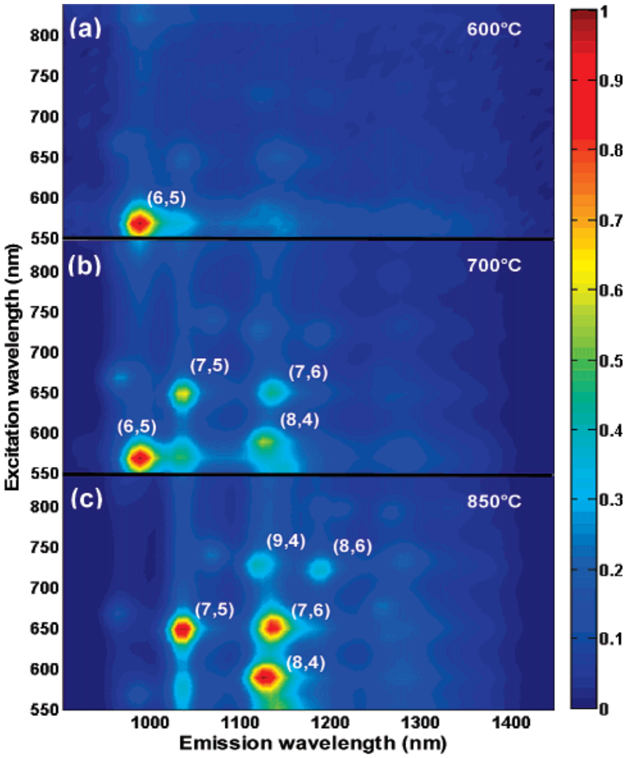

Figure 2. Contour plots of normalized photoluminescence emission intensities under various excitations for the Fe−Ru SWNTs grown at various temperatures; (*m*,*n*) is labeled at the right corner of each peak.

The FeRu SWNTs grown at 600 °C are enriched in the (6,5) tube with high photoluminescence (PL) (Figure 2a) and weak signals from (*m*,*n*) = (7,6), (7,5), and (8,4) tubes (Figure 2a). It is difficult to analyze the absolute percentages of (6,5) tubes in the material due to the unknown optical absorption cross section and quantum yields for various (*m*,*n*) SWNTs.[12−14] Note that recent

10.1021/ja077886s CCC: $37.00

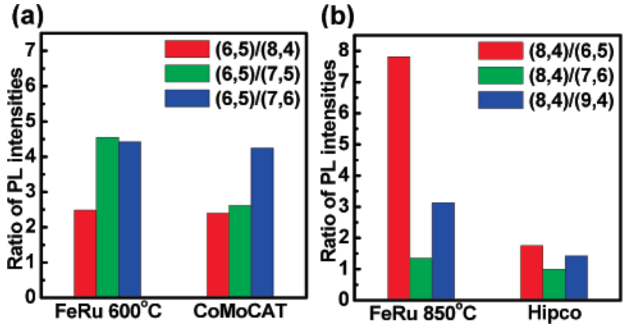

Figure 3. (a) PL intensity ratios between the (6,5) SWNT and the (8,4), (7,5), and (7,6) tubes in 600 °C grown FeRu tubes versus commercial CoMoCAT tubes. (b) PL intensity ratios between the (8,4) SWNT and (6,5), (7,6), and (9,4) tubes in 850 °C grown FeRu tubes versus Hipco tubes.

experiments suggested no drastic chirality dependence for the PL brightness of SWNTs.[14] In a relative sense, we compared our material with CoMoCAT SWNTs known to be highly selective to the (6,5) tube.[3] We analyzed the (6,5)/(m,n) [for (m,n) = (7,6), (7,5), and (8,4), respectively] PL intensity ratios for both materials (Figure 3a and Figure S1 for CoMoCAT) and found that the FeRu 600 °C SWNTs are similarly enriched in the (6,5) SWNT relative to other (m,n)'s tubes compared to CoMoCAT.

For FeRu SWNTs grown at 850 °C, the (8,4) SWNT exhibited the highest PL intensity over other (m,n)'s (Figure 2c). We compared this material with Hipco SWNTs known to be broad in (m,n) distribution. We found much higher (8,4)/(6,5) and (8,4)/(m,n) [(m,n) = (7,6), (9,4)] PL intensity ratios for FeRu 850 °C material than for Hipco (Figure 3b and Figure S1 for Hipco). This suggested that, compared to Hipco, the 850 °C FeRu grown SWNTs are more selective to (8,4) SWNT than to (6,5), (7,6), and (9,4) SWNTs. Note that we compared the (8,4) tube to (7,6) and (9,4) tubes due to their similar diameters and E_{11} emission peak positions (Figure 2c). Thus, the 850 °C FeRu methane CVD produced abundant chiral (8,4) SWNTs (chiral angle = 19.2°) away from the arm-chair configuration. These growth results of narrow diameter distribution differ from typical previous methane CVD growth, suggesting that the FeRu catalyst, used here for the first time for CVD of nanotubes, might be unique and responsible for the growth results.

For the same methane CVD growth condition with other catalysts such as Fe/silica and FeMo/silica, SWNTs with 1−3 nm diameters are produced with little selectivity in diameter and chirality.[10] The current Fe−Ru/silica catalyst produces SWNTs with a diameter less than ~1.2 nm (Figure S2) and certain chiral selectivity. We suggest that the FeRu catalyst is unique owing to the low Fe−Ru eutectic temperature (~600−650 °C).[15] The intimate alloying of FeRu and strong Fe−Ru interactions afford small catalytic nanoparticles stable against high-temperature sintering for producing small diameter SWNTs. Indeed, transmission electron microscopy revealed much smaller FeRu alloy particles (average size <2 nm), smaller than particles in pure Fe or Fe/Mo catalysts after CVD growth. The large populations of FeRu nanoclusters in the 1−2 nm range are stable under the methane CVD conditions and are responsible for the observed growth results. Diameter and chirality distributions generally widen and shift to larger size at higher temperatures as found by various methods.

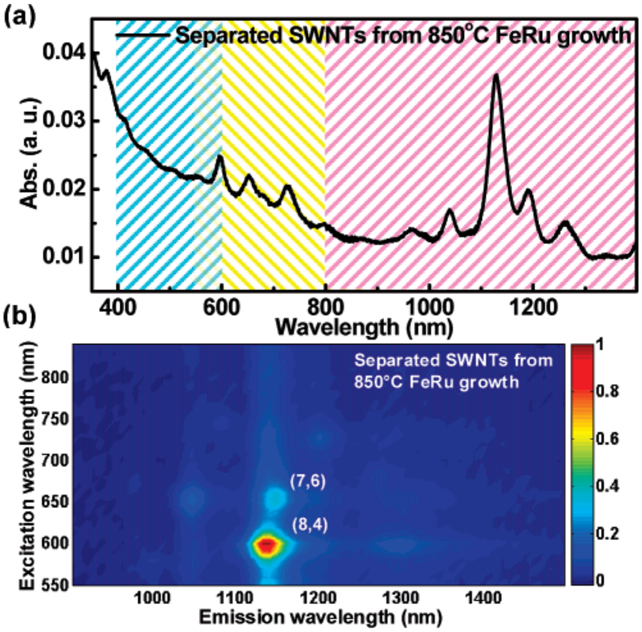

Figure 4. (a) UV−vis−IR and (b) PLE spectra of ion exchange chromatography separated SWNTs from 850 °C FeRu growth.

For the 850 °C grown SWNTs by FeRu with (8,4) SWNT enrichment, we carried out DNA functionalization and then ion exchange chromatography (IEC) separation (see Supporting Information) known to give diameter separated semiconducting SWNTs.[7] We obtained a fraction with the (8,4) SWNT as the dominant species (Figure 4b) with few metallic tubes (few peaks in the 400−600 nm range in Figure 4a). Compared to the as-grown material, the smaller diameter (6,5) and (7,5) tubes were eliminated by 3- and 5-fold, respectively, and the similar diameter (7,6) and (9,4) tubes were reduced by 2- and 3-fold, respectively. Thus, narrow diameter distribution growth and chemical separation combined facilitated obtaining highly enriched single chirality SWNT samples.

In summary, we developed a unique FeRu catalyst for selective growth of SWNTs. This combined with chemical separation of the as-grown materials led to nearly single chirality SWNT materials.

Acknowledgment. We thank MARCO MSD, Intel, and Stanford GCEP for support.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Dai, H. J. *Surf. Sci.* **2002**, *500*, 218.
(2) Javey, A.; Guo, J.; Wang, Q.; Lundstrom, M.; Dai, H. *Nature* **2003**, *424*, 654.
(3) Bachilo, S. M.; Balzano, L.; Herrera, J. E.; Pompeo, F.; Resasco, D. E.; Weisman, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 11186.
(4) Miyauchi, Y.; Chiashi, S.; Murakami, Y.; Hayashida, Y.; Maruyama, S. *Chem. Phys. Lett.* **2004**, *387*, 198.
(5) Wang, B.; Patrick Poa, C. H.; Wei, L.; Li, L. J.; Yang, Y. H.; Chen, Y. *J. Am. Chem. Soc.* **2007**, *129*, 9014.
(6) 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.
(7) Zheng, M.; Semke, E. D. *J. Am. Chem. Soc.* **2007**, *129*, 6084.
(8) Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. *Nat. Nanotechnol.* **2006**, *1*, 60−65.
(9) Kong, J.; Soh, H. T.; Cassell, A.; Quate, C. F.; Dai, H. *Nature* **1998**, *395*, 878.
(10) Cassell, A.; Raymakers, J.; Kong, J.; Dai, H. *J. Phys. Chem. B* **1999**, *103*, 6484.
(11) Bachilo, S. M.; Strano, M. S.; Kittrell, C.; Hauge, R. H.; Smalley, R. E.; Weisman, R. B. *Science* **2002**, *298*, 2361.
(12) Reich, S.; Thomsen, C.; Robertson, J. *Phys. Rev. Lett.* **2005**, *95*, 077402.
(13) Oyama, Y.; Saito, R.; Sato, K.; Jiang, J.; Samsonidze, G. G.; Gruneis, A.; Miyauchi, Y.; Maruyama, S.; Jorio, A.; Dresselhaus, G.; Dresselhaus, M. S. *Carbon* **2006**, *44*, 873.
(14) Tsyboulski, D. A.; Rocha, J. R.; Bachilo, S. M.; Cognet, L.; Weisman, R. B. *Nano Lett.* **2007**, *7*, 3080.
(15) Massalski, T. B. *Binary alloy phase diagrams*; American Society for Metals: Metals Park, OH, 1990.

JA077886S