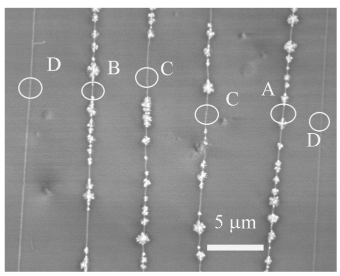
JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

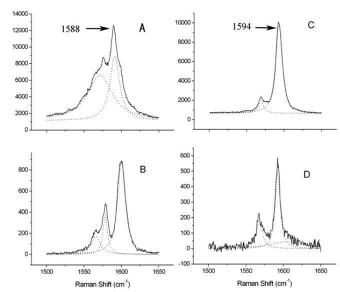
Communication

Identification of the Structures of Superlong Oriented Single-Walled Carbon Nanotube Arrays by Electrodeposition of Metal and Raman Spectroscopy

Shaoming Huang, Yong Qian, Jiangying Chen, Qiran Cai, Li Wan, Shun Wang, and Wenbing Hu

J. Am. Chem. Soc., **2008**, 130 (36), 11860-11861 • DOI: 10.1021/ja803682j • Publication Date (Web): 15 August 2008





More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

ACS Publications
High quality. High impact.

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

J|A|C|S
COMMUNICATIONS

Published on Web 08/15/2008

Identification of the Structures of Superlong Oriented Single-Walled Carbon Nanotube Arrays by Electrodeposition of Metal and Raman Spectroscopy

Shaoming Huang,*,† Yong Qian,†,‡ Jiangying Chen,† Qiran Cai,† Li Wan,† Shun Wang,† and Wenbing Hu‡

Nanomaterials & Chemistry Key Laboratory, Wenzhou University, Wenzhou, 325027, P. R. China, and School of Chemistry & Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China

Received May 30, 2008; E-mail: smhuang@wzu.edu.cn

Single-walled carbon nanotubes (SWNTs) can be metallic or semiconducting and generally coexist with $^{1}/_{3}$ metallic SWNTs (M-SWNTs) and $^{2}/_{3}$ semiconducting SWNTs (S-SWNTs) in as-grown materials. One of the main challenges is to generate pure S-SWNTs or M-SWNTs. Particularly for SWNT-based field effect transistor (FET) application, in situ growth of well-oriented S-SWNTs with high density are required. Superlong SWNTs with the same chirality and diameter will provide an opportunity to fabricate millions of multi-devices with consistent performance, which is one of the important issues for real nanoelectronics applications. Many efforts have been put into the generation of aligned long nanotubes by various methods,[1–3] and pure S-SWNTs or M-SWNTs as well.[4–8] Several techniques including FET,[5] Raman microscopy,[9] fluorescence spectroscopy,[10] and UV−vis−NIR[4] have been applied to identify the structures of SWNTs. However using FET one needs to fabricate the devices and measure their transportation characteristics. Using Raman spectroscopy to identify individual nanotubes is often hampered by the poorly defined position and orientation of the nanotubes. Furthermore, a facile and effective method needs to be developed to evaluate the structural uniformity along the length of the SWNT. In this paper, we demonstrate that centimeter-long oriented SWNT arrays on a SiO_2/Si wafer with a low percentage of M-SWNTs (∼5%) can be generated by CVD using Fe/Mo nanoparticles as catalyst and ethanol as carbon source. A simple approach, electrodeposition of silver on long oriented SWNT arrays, has been developed to identify the structure and to evaluate the structural uniformity of an individual long SWNT, as well by using Raman spectroscopy.

The superlong oriented SWNT arrays on silicon wafer (with 1 μm oxide layer) were grown by CVD using Fe/Mo nanoparticles as catalyst and ethanol as carbon feedback.[2](detailed experiment in Supporting Information). One side of the wafer (catalyst side) was coated with silver conducting adhesive or Au layer as an electrode. The electrodeposition of Ag was performed under the condition of 0.1 mM $AgNO_3$ and 10 mM KNO_3 aqueous solution. The Raman spectra were taken under ambient conditions by using a laser excitation of 514.5 nm (2.41 eV) and 632.8 nm (1.96 eV) from an air-cooled Ar^+ laser and He−Ne laser, respectively. Figure 1 is the typical SEM image of as grown superlong well-oriented SWNT arrays on the wafer. The inset is a high magnification image showing the straight and parallel structure of the arrays. The length of the wafer is about 1.2 cm. Most of the nanotubes can grow from one side to another side of the wafer, indicating the length of the SWNT arrays in centimeter scale. Such parallel nanotube arrays make it possible for us to connect all the nanotubes with conducting metal, which can be used as a electrode for electrochemical deposition of metals. Figure 1b is the SEM image of the nanotubes after electrodeposition for 10 s in 0.1 mM $AgNO_3$ solution at −0.6 V. It can be seen from that after electrodeposition the nanotubes are much brighter than the original ones because of the deposition of silver particles on the sidewalls of the SWNTs (Figure 1b). The line as indicated by arrow in the Figure 1b is the solution boundary. After careful check by SEM it is interesting to find that no Ag particles can be found on some of the long nanotubes surface as shown in Figure 1c, in which 7 of 12 have Ag particles (inserted is the high magnification of nanotubes with and without Ag particles on surface). As shown in Figure 1d it is also found that when the nanotubes were cut (indicated by the arrows) before electrodeposition Ag particles were only deposited on the nanotubes which connected to the electrode. Note no Ag particles deposit on the surrounding SiO_2 substrate. It is also noted that Ag can be also deposited on the short nanotubes which do not connect to the electrode but connect to long oriented nanotubes. This experimental observation indicates that the connection of the nanotubes to the electrode is necessary for deposition of Ag on their surface. The selective deposition of Ag on some of the long SWNTs is believed to be related to their electronic structures.

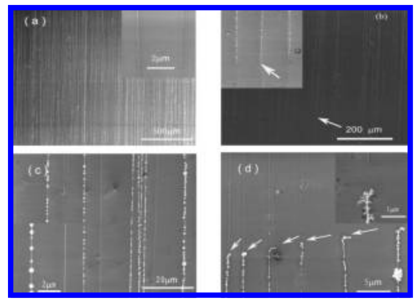


Figure 1. SEM images of well-oriented SWNT arrays on silica wafer (a) after electrodeposition of Ag for 10 s at −0.6 V. The bright line as indicated by the arrows is the solution boundary (b) (bottom is the electrode side). Some of the nanotubes were found not to be deposited with Ag particles (c); no Ag particles were deposited on physically cut SWNT arrays (without connection to the electrode) (d).

As reported earlier, Au and Pt can be electrolessly deposited on SWNTs[11] and metals such as Ag, Au, Pd, etc. can be deposited electrochemically onto short random SWNTs on substrate.[12] The difference between the long oriented SWNT arrays and short random SWNTs is that all the parallel long SWNTs can be connected to an electrode and they are distinguishable, while short random SWNTs do not. It is easy to identify that whether Ag particles are deposited on their surface. After careful examination of total 1832 long oriented SWNTs on three different samples, we find that 586 nanotubes (32%) have no Ag particles after 10 s deposition at −0.6 mV. As mentioned above, Raman spectroscopy is a powerful tool and has also been intensively used to characterize the structures of SWNTs. In the Raman spectrum of a single nanotube, the G-band between 1500−1600 cm^{-1} is related to the Raman-allowed tangential G-mode of graphite that occurs at about 1582 cm^{-1}. The G-mode can be used to identify the semiconducting or metallic structure of a SWNT. M-SWNT has broadened line shape fitting with Breit−Wigner−Fano (BWF) line

† Wenzhou University.
‡ Nanjing University.

10.1021/ja803682j CCC: $40.75

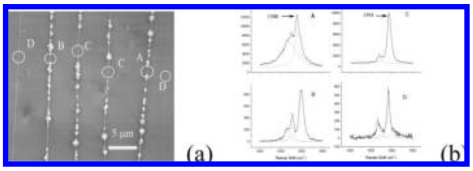


Figure 2. SEM image (a) and typical Raman spectra (type A, B, C, and D) from isolated individual SWNTs (b).

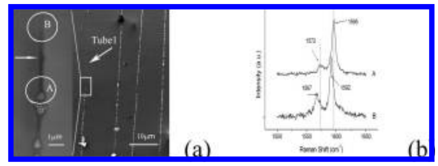


Figure 3. SEM image of well-oriented SWNT arrays with kink structure (a); Raman spectra of nanotube pigments before and after kink (b).

and S-SWNT has Lorentzian line shape. Although many research work has been done on individual SWNTs, to achieve the Raman spectrum of individual SWNTs on a surface is still very difficult because of the poorly defined position and orientation. The deposition of Ag on long well-oriented nanotubes makes it possible to know the precise position of the nanotubes because of their visibility under optical microscopy (see Supporting Information). The density of the parallel arrays of long SWNTs is around 4∼5 nanotubes/20 μm in our samples. The spot size of the laser is around 2 μm. Suitable density and visibility or identical position of the nanotubes make it possible to acquire Raman spectrum from isolated individual SWNTs. The nanotubes without Ag particles are also easy to find by using the nearby nanotubes which has Ag particles and the edge of the electrode as reference with the help of SEM observation. We exam 98 individual long nanotubes among which 28 nanotubes have no Ag particles by Raman using $E_{laser} = 2.41$ eV (20mw) and find four types of G-band, type A, B, C, and D. Type A, B, and C are acquired from SWNTs with Ag deposition and type D from nanotubes without Ag deposition. Only four nanotubes (4.1%) are type A which are typical metallic nanotubes with broadened BWF and a Lorentzian peak around 1588 cm^{-1} (small shift for different nanotubes) and 61 nanotubes (62.3%) are typical S-SWNTs having strong sharp peaks at around 1594 cm^{-1} with a small peak at 1570 cm^{-1} (type C). There is a very small amount of type B (5 nanotubes, 5.1%) which is different either from metallic or semiconducting. It is believed that type B corresponds to the so-called quasimetallic nanotube (or small band gap semiconducting nanotube) as Dai reported.[13] What is interesting to find is that type D has relatively weak Raman scattering signals compared with the other three types. The ratio of I_{1570}/I_{1594} increases compared with typical S-SWNTs. These kinds of nanotubes have possibly more defects along the nanotubes and behave as having an insulator character. The selective deposition of Ag on SWNTs could relate to their electrical conductivity. We call them quasi-insulator nanotubes. Although the high power of the 514.5 nm laser was used, it is still necessary to use a multiple laser line to identify the structures of the SWNTs, particularly for M-SWNT. An $E_{laser} = 1.96$ eV (632.8 nm, 3 mw) laser was then used to collect the G-band from the SWNTs and similar results were obtained; 5 out of 83 long nanotubes with Ag deposition are M-SWNTs. Thus, the low percentage of M-SWNTs (∼5%) in long well-oriented SWNTs is further confirmed. This is believed to be related with their tip-growth mechanism and long length.[14,15]

The deposition of Ag along the nanotubes may also provide a facile and effective probe to identify the structural uniformity. It is noted that for most of the nanotubes Ag can be deposited on whole nanotubes (except without Ag deposition), even if the nanotubes are a centimeter away from the electrode, indicating most of the nanotubes have electronic and structural uniformity, which is very important for the consistency of the performance of the multidevices fabricated on one long nanotubes. However, as the similar situation was observed from random nanotubes, the density of the Ag particles decreases along the nanotubes away from the electrode and depends on the deposition voltage and time (Supporting Information). It is also observed in some nanotubes that the Ag particles only deposit on part of the nanotube as shown in Figure 3a (nanotube 1). Careful observation by SEM shows that a kink structure indicated by the arrow in the inserted image is found. Raman spectra taken from the position before and after the kink (Figure 3b) reveal the change of the structure. Before the kink it has typical semiconducting character (A) while after kink (B) it appears type D-like. This change is believed to be due to the defects caused by the kink structure. This also provides the evidence for a high percentage (32%) of type-D nanotubes because of the defects caused during the prolong growth time, which affects the electronic characteristics of the SWNTs.[15,16]

In summary, we have developed a facile and effective method to identify the structure of superlong well-aligned SWNTs by the combination of electrodeposition of Ag on the SWNTs with Raman spectroscopy. The suitable density and the visibility of the Ag-deposited long nanotubes make it possible to acquire Raman spectra from isolated individual long nanotubes very easily. The results reveal that the well-oriented SWNT arrays on SiO_2/Si wafer fabricated by EtOH-CVD using Fe/Mo nanoparticles as catalyst exhibit a lower percentage of M-SWNTs (∼5%). Among other SWNTs, ∼62% are S-SWNT and ∼32% are so-called quasi-insulators, a characteristic which is caused inevitably by the defects during growth. Small amount of nanotubes are quasimetallic. Furthermore, the structural uniformity of the long SWNTs can be also evaluated by the deposition of Ag along the length and Raman spectroscopy. This method also provides an approach to deposit other metal on long SWNTs which could have various potential applications such as sensors, etc. More importantly, this facile method can be applied to long SWNT arrays fabricated from other different catalytic systems so that the relationship between the growth conditions and the structures of SWNTs can be expected to be ruled out.

Acknowledgment. The work was supported in part by grants from NSFC (50772076), MOST(2007CB616901, 2006AA02Z111), ZJST (2006C24010), and WZST (H2005B022).

Supporting Information Available: Experimental details, SEM images of the superlong well-oriented SWNT arrays with and without Ag deposition, the Raman spectra of the individual SWNTs as well as optical photo. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Ural, A.; Li, Y. M.; Dai, H. J. *Appl. Phys. Lett.* **2002**, *81*, 3464.
(2) Huang, S.; Cai, X.; Liu, J. *J. Am. Chem. Soc.* **2003**, *125*, 5636.
(3) Kocabas, C.; Shim, M.; Rogers, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 4540.
(4) Li, X.; Tu, X.; Zaric, S.; Welsher, K.; Seo, W. S.; Zhao, W.; Dai, H. *J. Am. Chem. Soc.* **2007**, *129*, 15770.
(5) Collins, P.; Arnold, M.; Avouris, P. *Science* **2001**, *292*, 706.
(6) Krupke, R.; Hennrich, F.; v. Löhneysen, H.; Kappes, M. M. *Science* **2003**, *301*, 344.
(7) An, L.; Fu, Q.; Lu, C. G.; Liu, J. *J. Am. Chem. Soc.* **2004**, *126*, 10520.
(8) Zhang, G.; Qi, P.; Wang, X.; Lu, Y.; Li, X.; Tu, R.; Bangsaruntip, S.; Mann, D.; Li, Z.; Dai, H. *Science* **2006**, *314*, 974.
(9) Brown, S. D. M.; Jorio, A.; Corio, P.; Dresselhaus, M. D.; Dresselhaus, G.; Saito, R.; Kneipp, K. *Phys. Rew. B* **2001**, *63*, 155414.
(10) Miyauchi, Y.; Chiashi, S.; Murakami, Y.; Hayashida, Y.; Maruyama, S. *Chem. Phys. Lett.* **2004**, *387*, 198.
(11) Choi, H. C.; Shim, M.; Bangsaruntip, S.; Dai, H. *J. Am. Chem. Soc.* **2002**, *124*, 9058.
(12) Day, T. M.; Unwin, P. R.; Wilson, N. R.; Macpherson, J. V. *J. Am. Chem. Soc.* **2005**, *127*, 10639.
(13) Cao, J.; Wang, Q.; Dai, H. *Phys. Rev. Lett.* **2003**, *90*, 157601.
(14) Huang, S.; Woodson, M.; Smalley, R.; Liu, J. *Nano Lett.* **2004**, *4*, 1025.
(15) Doorn, Stephen K.; O'Connell, Michael J.; Lianxi, Z. 1; Yuntian, T. Z.; Huang, S.; Liu, J. *Phys. Rev. Lett.* **2005**, *94*, 016802.
(16) Chakrabarti, S.; Gong, K.; Dai, L. *J. Phys. Chem. C* **2008**, *112*, 8136.

JA803682J