NANO LETTERS

2008
Vol. 8, No. 1
237−240

Synthesis and Isolation of Molybdenum Atomic Wires

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Received October 1, 2007; Revised Manuscript Received November 20, 2007

ABSTRACT

One of the main challenges in nanoscience and nanotechnology consists in the production and isolation of metallic atomic-scale nanowires (Benzryadin, C. N.; Lau, A.; Tinkham, M. Q. *Nature* 2000, *404*, 971–974; Zach, M. P.; Ng, K. H.; Penner, R. M. *Science* 2000, *290*, 2120–2123; Nilius, N.; Wallis, T. M.; Ho, W. *Science* 2002, *297*, 1853–1856.). Here we report a unique and controllable way of isolating individual atomic molybdenum (Mo) chains by their encapsulation inside double-walled carbon nanotubes, exhibiting inner diameters ranging from 0.6 to 0.8 nm. We have found that these individual atomic chains form spontaneously within the hollow core of tubes in the absence of any reducing agent. We believe that these atomic-scale nanowires could now be studied without suffering oxidation, so that their physical and chemical properties are elucidated.

The inner hollow of carbon nanotubes is known to be an extremely small confined nanospace with unique properties. Wide varieties of low-dimensional crystals have been synthesized by introducing atomic arrays and molecules inside carbon nanotubes.[4−8] However, the introduction of individual atomic metallic chains into carbon nanotubes is quite challenging, and to the best of our knowledge the successful introduction of linear metallic atomic chains has not been reported hitherto. Recent studies showed that low-dimensional materials such as atomic chains exhibited novel transport and mechanical properties that the bulk metals do not have.[1−3,9] Therefore, the encapsulation of metal atoms inside narrow carbon nanotubes appears to be an efficient way to isolate and stabilize linear metal chains so that they can be studied further avoiding their oxidation.

In our process, we have used catalytically grown double-walled carbon nanotubes (DWNTs) as templates to obtain Mo atomic-scale chains. Highly pure and crystalline DWNTs (see Figure 1a,b) were successfully prepared by a catalytic chemical vapor deposition method[10,11] and the subsequent oxidative purification process, as detailed in our previous report.[12] To prepare self-assembled Mo chains inside DWNTs, a two-step process was followed. Air-oxidation at 550 °C for 1 h was carried out to remove amorphous carbon, chemically active single-walled carbon nanotubes, and defective multiwalled carbon nanotubes; the method also opened the ends of DWNTs. Subsequently, air-oxidized tubes (1.5 g) and hexaammonium heptamolybdate tetrahydrate (0.8 g) were chemically treated in hydrochloric acid (18 wt %) solution at 100 °C for 24 h and then oxidized in air at 500 °C for 30 min. This process appeared to be crucial in forming single atomic Mo wires within the hollow core of DWNTs. Detailed high-resolution transmission electron microscopy (HRTEM) (JEOL2010FEF) and scanning electron microscopy (JSM6335Fs) observation of both pure DWNTs and Mo-filled DWNTs revealed that the tubes possess bundle structures, noting that both iron catalysts and molybdenum particles were notably absent on the exterior of the tubes and bundles.

Energy-dispersive X-ray spectroscopy (Figures 2a−c) and high-angle annular dark-field analysis (HAADF) (Figure 2d) confirm the presence of Mo atoms located in the interior of DWNTs. The absence of the K-edge in the oxygen spectra located at ca. 550 eV (by electron energy-loss spectroscopy; Figure 2e) confirms the formation of pure Mo inside the tubule. Typical TEM images of narrow DWNTs containing long and stable atomic-scale Mo chains are shown in Figures 2f−j. Clearly, black contrast dots observed inside the DWNTs correspond to the Mo chains (Figure 2j), which is also in good agreement with TEM simulation images (Figure 2k). In addition, we found high similarity in their corresponding line scan profiles (see insets in Figures 2j,k). The interatomic distance measured between Mo atoms was not

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10.1021/nl0725188 CCC: $40.75
Published on Web 12/11/2007

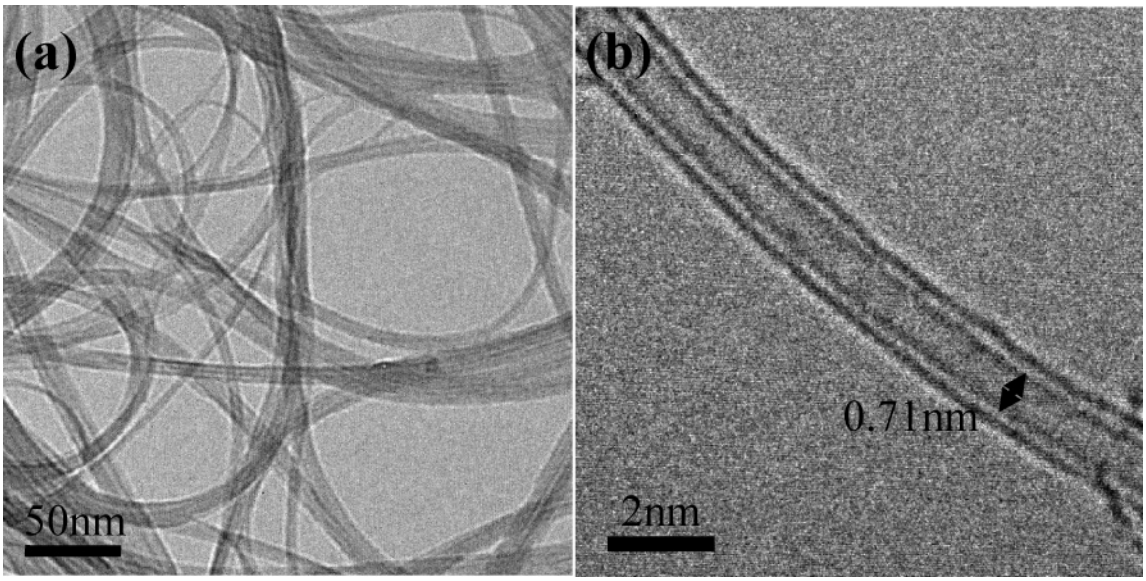

Figure 1. (a) Low- and (b) high-resolution TEM images of highly pure and crystalline DWNTs.

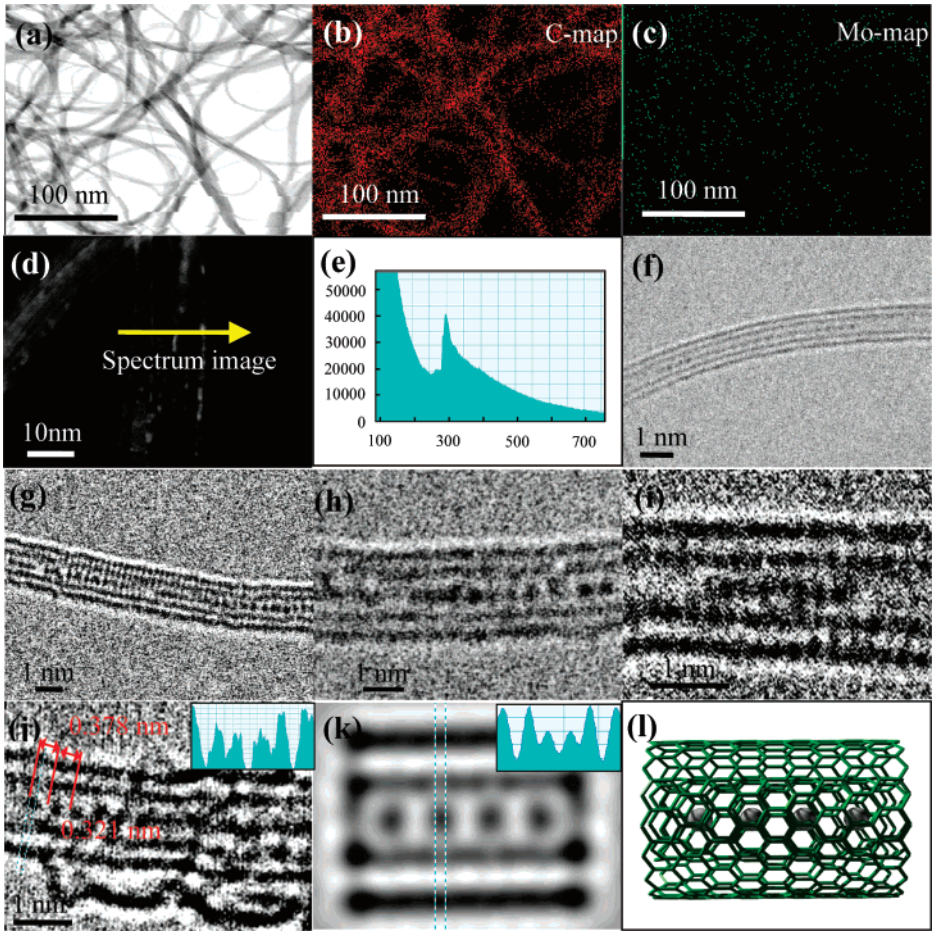

Figure 2. (a) TEM image of the bundled DWNTs and (b,c) its corresponding elemental maps of carbon and molybdenum. (d) HAADF image of DWNTs including Mo. White contrast along with tube length is due to Mo atoms. (e) Electron energy loss spectra taken from allowed line reveals that the included Mo inside DWNTs is not oxidized. (f,g) Typical TEM images of DWNTs including long molybdenum chains. (h−j) HRTEM images exhibiting explicitly resolved quantum Mo chains. Their corresponding (k) TEM-simulated image and (l) structural model. Note that the line scan profile of double-walled carbon nanotubes containing atomic chains of molybdenum (see inset in panel j) is consistent with that of the TEM-simulation image (inset in panel k).

constant and ranged from 0.32 to 0.38 nm, which is slightly larger than their interatomic distance in crystalline Mo in crystal (0.315 nm). When the inner tube diameter of DWNTs becomes larger than 0.9 nm, Mo atoms inside the nanotube

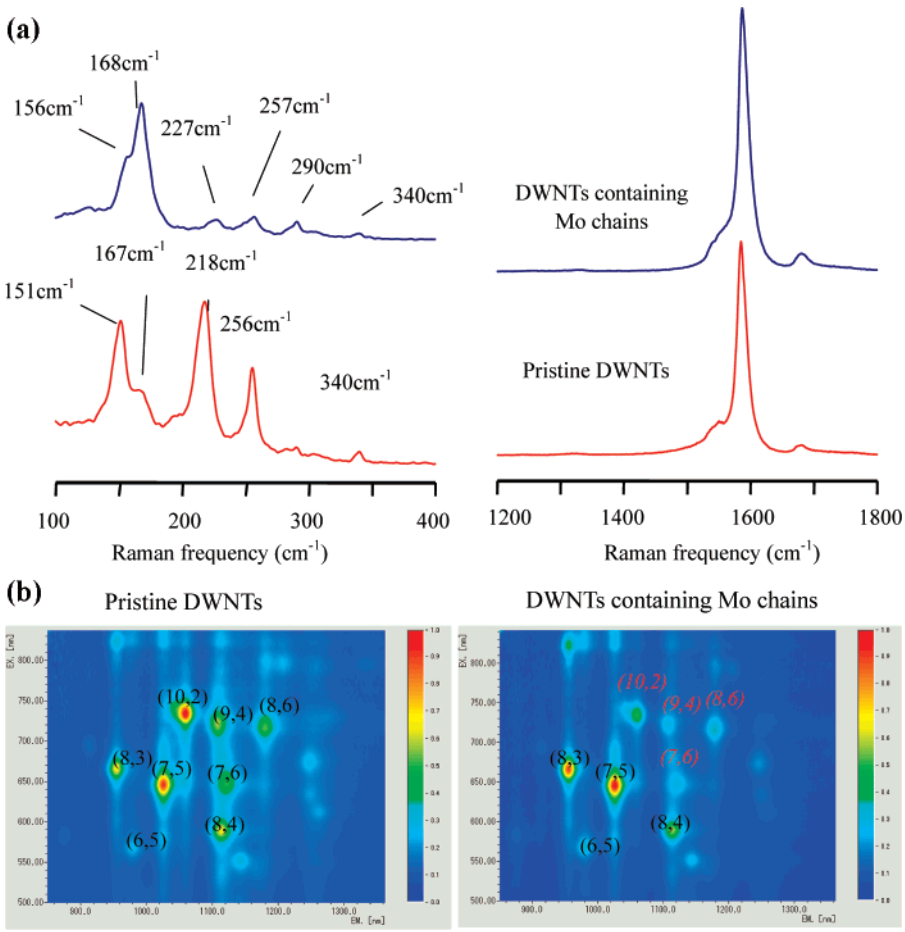

Figure 3. (a) Raman spectra taken from 633 nm laser line excitation. Note that radial breathing modes between 200 and 270 cm^{-1} corresponding to the inner tubes of the DWNTs are highly depressed by including Mo chains. (b) Contour plots of fluorescence spectra versus excitation and emission wavelength for the DWNTs and Mo containing DWNTs, respectively. Note that the intensity from DWNTs with chiralities of (10, 2), (9, 4), (8, 6), (7, 6) were highly quenched through a interaction with atomic-scale Mo chains.

start to form three-dimensional nanowires. The unique confined space inside DWNTs (from 0.6 to 0.8 nm) acts as a template for the formation of linearly isolated atomic-scale metallic wires. Long atomic chains are critical to evaluate their transport and mechanical properties. On the basis of our experimental results, the encapsulated Mo chains range from several to several tens of nanometers, even though the length is also strongly depending on the inner diameters of our DWNTs. We believe that the formation of metallic chains occurs through a direct redox reaction between nanotubes and metal ions, as described in ref 13. More specifically, molybdenum chloride ions reduce to metal atoms by acquiring electrons from nanotubes, and consequently Mo atoms are inserted (possibly by capillary action) inside the hollow cores of the tubes and form the wires. In the future, the electronic properties of Mo-filled DWNTs could be studied using various techniques.

Also to confirm the presence of charge transfer between the Mo atomic chains and the concentric carbon nanotubes, we used Raman spectroscopy (Figure 3a) and photoluminescence (Figure 3b) techniques to monitor the modified electronic structure of carbon nanotubes. We observed a large quenching at above 200 cm^{-1}, which corresponds to the signals arising from the inner shells of DWNTs. Specifically, the Raman peaks located at 218 and 256 cm^{-1} were highly depressed due to the encapsulation of Mo atoms, indicating the strong interaction between the metallic DWNT inner shells and the Mo atoms. In addition, the enhanced Raman peak at about 167 cm^{-1}, which corresponds to the radial breathing mode of the outer tube, could indicate the modified electric structure by the wall−wall interaction between the inner and outer shells. However, we could not observe any obvious spectral change at 290 and 340 cm^{-1} from the semiconducting inner tubes in spite of the insertion of atomic chains of Mo, consistent with prior Raman studies on DWNTs with different metallic and semiconducting tube configurations.[14−16]

Fluorescence spectra reveal the quenching of excitation spectra caused by the insertion of Mo atoms. Especially, the specific inner tubes having ((10, 2), (9, 4), (8, 6) and (7, 6)) were strongly depressed by the Mo inclusion, which indicates a strong interaction between inner tubes and Mo atoms possibly due to the charge-transfer effects. From these Raman and fluorescence results, we could claim that the electronic structure of the inner tubes was modified due to the interaction between the Mo atomic chain and inner tubes.

We have described here, for the first time, the synthesis atomic chains of Mo that are stabilized inside DWNTs. We

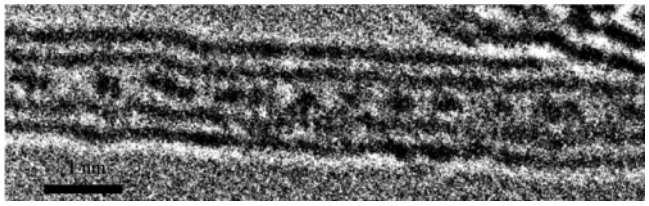

Figure 4. A typical TEM image of a singular DWNT containing atomic Pt chains.

believe the DWNTs including Mo could be extremely useful in experimental determination of the electronic, catalytic, and mechanical properties of atomic Mo chains. The method reported here allows the formation of other metallic atomic chains (e.g., Au, Pt, Ni, Fe, etc.) inside DWNTs (see Pt nanowire encased in the hollow core of a DWNT in Figure 4). We envisage that the electronic and magnetic properties of such atomic chains are different when compared to the known materials up to date. Finally, this report opens up the possibility of developing this technique further toward the fabrication of atomic chains of any metal confined within high purity DWNTs.

Acknowledgment. H.M. received support by the JSPS Research Fellowships for Young Scientists. This work was partially supported by the CLUSTER (the second stage) (M.E., T.H.) and Gran-in-Aid for Specially Promoted Research (No. 19002007) (M.E., Y.A.K.) of Ministry of Education, Culture, Sports, Science and Technology of Japan. The authors thank Dr. Okunishi (JEOL. Ltd) for his valuable discussion. This work was supported in part by CONACYT-México Grants 56787 (Laboratory for Nanoscience and Nanotechnology Research-LINAN), 45772 (M.T.), 41464-Inter American Collaboration (M.T.), 2004-01-013/SALUD-CONACYT (M.T.), and PUE-2004-CO29 Fondo Mixto de Puebla (M.T.). The work was also supported in part by NSF/DMR 07-04197 (M.S.D.).

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NL0725188