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Communication

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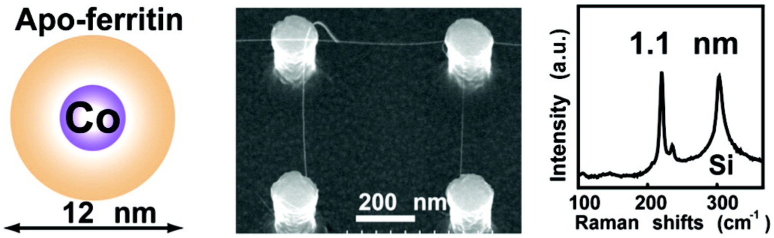

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COMMUNICATIONS

Cobalt-Filled Apoferritin for Suspended Single-Walled Carbon Nanotube Growth with Narrow Diameter Distribution

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Many attempts to control the electronic properties of single-walled carbon nanotubes (SWNTs)[1] have been made via several growth techniques, surface functionalization, and doping with foreign species. In any methodology, diameter-controlled SWNT growth is recognized as the primary and ultimate goal because the electronic properties of SWNTs depend on tube diameter and chirality.[2] Among growth techniques, a chemical vapor deposition (CVD) is widely used to grow SWNTs for its versatility in the growth process.

Electron beam deposition has been used as a dry process for catalyst preparation. With this approach, we cannot know the actual size of the catalyst because the catalytic thin film is changed to various sized nanoparticles by thermal pretreatment. Therefore, it becomes very difficult to investigate the size relationship between catalysts and the resultant nanotubes. On the other hand, wet catalysts, such as ferritins,[3] dendrimers,[4] and various metal nanoparticles,[5] have recently been used for diameter-controlled growth because of their fixed diameter. Up to now, most experiments have been performed using a flat surface, where the nanotubes are confined by substrates. Suspended SWNTs are useful for elucidating fundamental properties (especially optical ones) because of their lack of interaction with substrates.[6] In addition, the successful synthesis of diameter-specified suspended SWNTs will lead to the development of carbon-nanotube-based nanoelectronics. For this reason, we tried to grow the diameter-controlled suspended SWNTs using wet catalysts, which have a predetermined and refined size. In this communication, we report the facile growth of suspended SWNTs using cobalt-filled apoferritin (Co−ferritin) for diameter-controlled SWNTs growth.

Co−ferritin prepared by converting iron particles to Co particles in commercial horse spleen ferritin (Sigma Aldrich) was selected because of the low diffusion coefficient of cobalt compared with that of iron in ferritin. Co nanoparticles were uniformly distributed on substrates by spin-coating and successive calcination of the Co−ferritins. The presence of the Co was confirmed by energy dispersive spectroscopy (Supporting Information 1). The catalyst preparation and nanotube growth are described in detail in Supporting Information 2. Two-dimensional pillar-structured Si substrates (height 360 nm; pitch 500−800 nm) were hydrophilically treated using H_2SO_4 and H_2O_2. Thermal CVD with methane was performed at 500 Torr for 5 min to grow suspended SWNTs. Scanning and transmission electron microscopes (SEM and TEM) were used for structural characterization. An atomic force microscope (AFM) operated in the tapping mode was mainly used for diameter estimation of the Co−ferritin before and after calcination. Micro-Raman scattering spectroscopy (Renishaw 1000, 785 nm excitation wavelength) was also used for SWNT diameter determination by comparing the peaks in the radial breathing mode (RBM), which is a unique signal of SWNTs.[2]

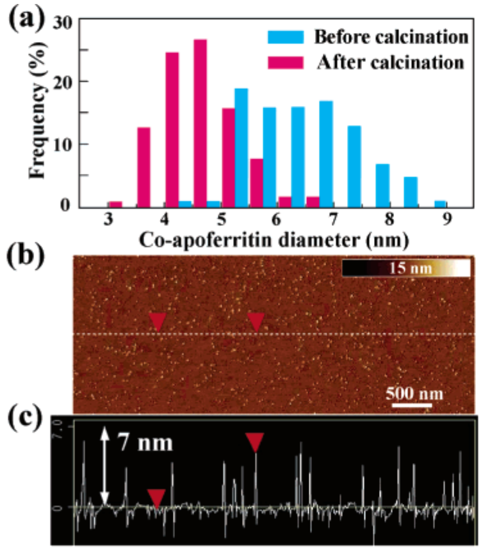

Figure 1. (a) Histogram showing diameter distribution change of cobalt-filled apoferritins before (blue) and after (red) calcination. (b) AFM topographic image (5 μm width) showing that cobalt nanoparticles are uniformly distributed over a large area. (c) AFM height profile along the white dotted line in (b); the typical height difference designated by the two red arrows is around 4.8 nm.

Figure 1a shows the AFM-estimated diameter change of Co−ferritin (blue column) and corresponding Co nanoparticles (red column). Here, hydrophilically treated SiO_2 flat substrates were used for precise diameter evaluation. Graphs b and c of Figure 1 are typical AFM topographic images, which show uniformly distributed nanoparticles in a large area and the corresponding height scan profile, respectively. The average diameter of the Co−ferritins was found to be 6.4 ± 1.0 nm, and it changed to 4.7 ± 0.7 nm after calcination by the removal of the protein shell of the ferritins.

Panels a and b of Figure 2 show SEM images of suspended SWNTs grown at 900 and 1000 °C, respectively. Most of the suspended nanotubes grown at 900 °C were relatively short and reached adjacent pillars. In contrast, long suspended nanotubes were grown and reached second- or third-neighboring pillars, as well as first-neighboring ones in the 1000 °C growth. Some of the tubes fell to the substrate, and some wound around one another, yielding junction structures with an X or Y shape. Suspending yield at 1000 °C was more than 90%. For comparison, we investigated the effect of growth temperature using a SiO_2 flat surface (Supporting

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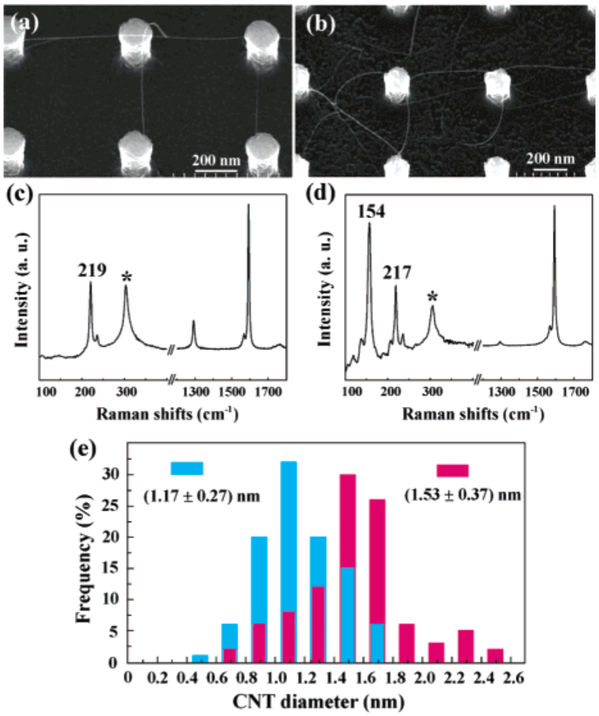

Figure 2. SEM images and corresponding Raman spectra from the suspended SWNTs obtained at different growth temperatures; (a and c) 900 °C and (b and d) 1000 °C. Peaks indicated by asterisks in each spectrum are from the substrate. (e) Histogram showing the diameter distribution change of SWNTs grown on flat surface at 900 (blue) and 1000 °C (red).

Information 3) and found the minimum growth temperature was less than 850 °C. This value was slightly higher than our previous result and will be calibrated.[7] Directional growth, such as along the gas flow, was not observed in the present flow condition (300 cm^3/min).

Panels c and d of Figure 2 are typical Raman results for the same samples in panels a and b of Figure 2, respectively. We can understand the 1000 °C samples are less defective than are the 900 °C samples from the G/D ratio comparison in the Raman spectra. The relation $d = 248/\omega$, where d is tube diameter (nm) and ω the Raman frequency (cm^{-1}), was used for tube diameter estimation.[8] Peaks indicated by asterisks in each spectrum are from the substrate. In Figure 2c, the single peak at 219 cm^{-1} corresponds to SWNTs with 1.13 nm diameter. On the other hand, several peaks were obtained around 154 and 217 cm^{-1}, which correspond to 1.61 and 1.14 nm, respectively (Figure 2d). In Raman measurements, it is necessary to utilize various excitation wavelengths to draw exact diameter distribution. Even if limited nanotubes are detected here, however, we can estimate that the 900 °C samples have a narrower diameter distribution than that of the 1000 °C samples when we assume the uniform chirality distribution of carbon nanotubes. Actually, we obtained the same tendency from the flat substrate case. Figure 2e, which shows the results of AFM measurement, shows that the diameter distribution was changed by the growth temperatures. Average tube diameter decreased from 1.53 ± 0.37 to 1.17 ± 0.27 nm by lowering the growth temperature from 1000 to 900 °C. We think the main reason is clustering of the Co nanoparticles. From these results, we can understand that the agglomeration of discrete nanoparticles should be suppressed for narrow diameter tube growth.

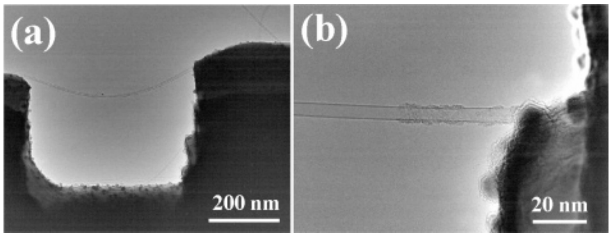

Figure 3. (a) Typical TEM image of suspended SWNTs grown at 1000 °C and (b) an individual SWNT with a large diameter of 4.8 nm.

Figure 3a shows a typical TEM image of a 1000 °C sample. Although SWNTs with a large diameter were sometimes observed by partial aggregation of Co nanoparticles (Figure 3b), the majority of the suspended SWNTs have similar narrow tube diameters. Using the same growth condition, we observed severe aggregation of the iron nanoparticles in the case of ferritins (Supporting Information 4).[3]

To apply SWNTs in electronic devices, not only diameter control but also growth direction control is essential. Here, it was found that growth features may depend on the sites of Co nanoparticles. For instance, nanotubes grown from the sidewalls or edges of pillars preferentially grow parallel to the substrate. However, nanotubes grown from the top surface of pillars extend upward and eventually fall onto other pillars or the substrate and have long and arch-shaped nanotubes. Therefore, site-selective distribution of Co−ferritins using such as hydrophilic/hydrophobic interaction will be required for site-specified nanotube growth.

In summary, we have demonstrated a facile growth of suspended networks of SWNTs using Co-filled apoferritins. The suspended SWNTs showed narrow diameter distribution with a relatively good structural completeness. By virtue of low diffusion coefficient of cobalt, Co−ferritin might be more useful for SWNTs growth with narrow diameter distribution rather than ferritins, which encase iron particles.

Supporting Information Available: EDS result of Co−ferritin, description of experimental procedure, temperature dependence of SWNTs growth, and 1000 °C growth feature in ferritin case. This material is available free of charge via the Internet at http://pubs.acs.org.

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