Growth of Single-Walled Carbon Nanotubes on a Nanorough Surface

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Received: February 9, 2007; In Final Form: April 24, 2007

We compare the growth of single-walled carbon nanotubes (SWNTs) on rough and smooth surfaces. Individual raw HiPco (high-pressure CO) SWNTs are deposited onto porous oxide nanoparticles on a silicon or quartz substrate. The HiPco SWNTs are shown to retain their original catalyst particles that are carbon coated as a result of arrested growth due to bundle formation in the HiPco reactor. Overcoated catalysts are activated with O₂ oxidation and SWNTs grown at 900 °C in the presence of CO and H₂. The typical length of the SWNTs is more than 10 μm when grown on nanorough surfaces such as fumed silica. This is much longer than the original HiPco SWNTs where the average length is approximately 0.5 μm. They are also much longer than SWNTs grown from the same source material with the same growth conditions on a flat silicon oxide surface. These results support the general impression that extensive interaction of both the nanotube and the catalyst particle with an adjacent surface greatly retards growth.

In recent years, single-walled carbon nanotubes (SWNTs) have been intensively studied both theoretically and experimentally. For SWNTs to achieve their potential as a new material, they must be synthesized as specific types. We have taken the approach of growing SWNT seeds as the most likely method of achieving single-type SWNT growth. As part of our investigations of seed growth we have investigated the extended growth of HiPco SWNTs. Here, we refer to it as “the regrowth of raw SWNTs” since the raw SWNT is used as an SWNT seed, which is different from “continued growth” where new SWNT growth is from SWNT seeds which were made by attaching a new catalyst to a prepurified SWNT. The big advantage of “regrowth” is avoiding the size match between the new catalyst and the SWNT, since we know that it is difficult to attach a correctly sized new catalyst to a SWNT.

Initial studies were carried out to confirm the presence of iron catalyst particles on the ends of the HiPco SWNTs. It has been stated that the stoppage of growth in the HiPco reactor is due to increasing metal nanoparticle size by continued addition of metal atoms up to the point where they no longer act as a source of carbon for nanotube growth and instead overcoat with carbon. Alternatively, stoppage of growth may be caused by nanotube bundling as the nanotube concentration builds up in the reaction zone of the HiPco reactor. Bundling of SWNTs can stop growth if metal catalyst particles at the ends of the growing tubes form carbon bridge bonds to neighboring nanotubes in a bundle. When neither the nanotube nor the catalyst is free to move, carbon coating of the metal catalyst is expected. To investigate whether catalysts remain attached to HiPco SWNTs and also their size relative to the attached nanotube, we have carried out TEM studies of SWNTs dispersed on nanorough surfaces of fumed silica.

Raw HiPco SWNTs were functionalized via reductive alkylation by using lithium and alkyl halides in liquid ammonia. This method provided SWNTs exhibiting high solubility in chloroform. Any carbon-coated large catalyst particles that are also present in raw HiPco SWNTs and that have also been made soluble were removed by filtering through a 100 nm filter paper. Figure 1 is a TEM image of chloroform-solubilized SWNTs deposited on a carbon thin film of a copper TEM grid. One clearly sees that the majority of SWNTs still retain their metal catalysts, where the size of the catalyst remains similar to the size of the attached nanotube.

To avoid the aggregation of SWNTs during the drying process, we have deposited a low concentration of chloroform-soluble SWNTs onto porous silicon oxide nanoparticles. Parts a and b of Figure 2 show a schematic of SWNTs on the nanoporous SiO₂ and a TEM image of individual SWNTs embedded into the nano-SiO₂ oxide network. TEM images were obtained with a JEOL 2010 transmission electron microscope at 200 kV.

Five steps were used to prepare raw HiPco SWNTs for regrowth: (1) individual SWNTs were functionalized and dissolved in chloroform; (2) SWNTs were dispersed at low concentrations onto porous methylated silicon oxide nanoparticles in chloroform; (3) the mixture of SWNTs and nanoparticles was spin coated onto a silicon or quartz substrate; (4) the carbon-overcoated catalysts were activated by heating in an oxidizing environment; (5) the activated HiPco SWNTs were heated to 900 °C in the presence of a carbon feedstock.

To activate “dead” catalysts overcoated with carbon, the carbon must be etched away without completely etching away the SWNTs. Figure 3 shows thermal gravimetry analyses of raw HiPco SWNTs in air, N₂/H₂O, H₂, and CO₂ as a function of the temperature during heating. All raw HiPco material is oxidized to CO₂ at 325 °C in air. It is hydrogenated to form CH₄ at 600 °C in H₂. It is oxidized to form CO and H₂ at 890 °C in H₂O. The catalytic effect of iron or iron oxide on nanotube etching is required for these etching reactions. Raw HiPco material is oxidized slowly in CO₂ when the temperature is above 900 °C. Etching temperatures clearly depend on the choice of the etching gases. For example, one can activate the catalyst in air at 300 °C, in H₂O at 875 °C, or in H₂ at 550 °C.

After activation of the catalyst by heating in air at 300 °C for 5 min, the activated HiPco SWNTs were heated to 900 °C in the presence of 900 mL/min of CO and 100 mL/min of H₂.
at atmospheric pressure for 10 min to induce the growth of SWNTs. SEM was used to characterize the regrowth of raw HiPco SWNTs. Figure 4a shows SWNT seeds deposited on a quartz substrate before the air activation treatment and regrowth. Since the normal length of raw HiPco SWNTs is less than 400 nm, it is difficult to observe them in an SEM image. However, after the regrowth process, many SWNTs with lengths of several µm appear, as shown in Figure 4b. Regrown SWNTs are shown lying on the top of the nanorough surface and are much longer than the original raw HiPco SWNTs. Raman was used to follow the oxidation and regrowth steps, as shown in Figure 5. It is clear that the oxidation step did not etch all of the original SWNTs away. Unfortunately, because it is difficult to image the specific SWNTs after the oxidation step and regrowth step by SEM, one cannot be sure that the longer SWNTs result from the original SWNTs or catalyst particles left by etching away some of the original SWNTs during the oxidation step.

However, it is of interest to compare the growth of SWNTs on a nanorough surface to that on a smooth surface. Parts a and b of Figure 6 show AFM and SEM images of fumed methylated SiO₂ nanoparticles in chloroform solution spin coated onto a substrate. Parts c and d of Figure 6 compare growth on a nanorough surface with growth on a flat SiO₂ surface for the

Figure 1. TEM image of raw dodecylated SWNTs and fumed methylated SiO₂ in CHCl₃ dropped dry onto a carbon thin film of the copper TEM grid.

Figure 2. (a) Schematic description and (b) TEM image of raw dodecylated SWNTs impregnated with fumed methylated SiO₂ in CHCl₃. In (a) the green line represents a single-walled carbon nanotube. The light blue balls are oxide nanoparticles. The red ball is a metal catalyst.

Figure 3. TGA of raw HiPco tubes heated in different gases: (a) air; (b) H₂; (c) H₂O; (d) CO₂ (heating rate 5 °C/min).
same starting material and reaction conditions as those in Figure 4. One clearly sees a large difference between the lengths of SWNTs that grew on the nanorough surface and the smooth SiO₂ surface. We conclude that simultaneous interactions of the nanotube and catalyst particle can greatly retard the growth of a nanotube. In the case of a nanorough surface, tip growth of the SWNT where the catalyst particle is largely free to move and grow the nanotube is likely responsible for the extended growth. Thus, we suggest that future growth of SWNT seeds is most likely to succeed on nanorough surfaces.

In summary, decreasing the contact between the SWNT and the surface or the SWNT and the SWNT is expected to make SWNTs grow more freely. The cage structure formed by porous oxide nanoparticles can form a porous and rough surface for SWNT growth. Impregnating individual SWNTs in the porous cage structures can avoid forming SWNT bundle structures in which the strong van der Waals interactions between SWNTs prevent movement of the nanotube and carbon bridges to neighboring SWNTs from catalyst particles and retard movement of the catalyst. Catalysts located on a nanorough surface have a high probability of escaping the surface due to its highly localized curvature, thus allowing free tip growth, which is known to give the highest rates of growth and produce the longest nanotubes.

Acknowledgment. We thank the late Prof. Richard E. Smalley for his support and encouragement and Dr. Liang for the preparation of individual SWNTs in chloroform. We also thank the Robert A. Welch Foundation, Department of Energy, AFOSR, and NASA for their support of this research.

Figure 4. SEM images: (a) raw HiPco SWNTs and (b) regrown SWNTs sticking to oxide nanoparticles on the quartz substrate.

Figure 5. Raman spectra of raw HiPco SWNTs before the oxidation step (a), after the oxidation step (b), and after the regrowth step (c).
Figure 6. (a) AFM image and (b) SEM image of the nanorough surface formed by fumed methylated SiO$_2$. SEM images of the regrowth of raw SWNTs on the nanorough surface (c) and on the smooth surface (d).

References and Notes

(11) Fumed silica (CAB-O-SIL TS-530) was bought from Cabot Corp.