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Multibranching Carbon Nanotubes via Self-Seeded Catalysts

Joseph F. AuBuchon, Li-Han Chen, Chiara Daraio, and Sungho Jin*

Materials Science and Engineering Program, Mechanical and Aerospace Engineering Department, University of California, San Diego, La Jolla, California 92093-0411

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ABSTRACT

A novel multibranching carbon nanotube (CNT) structure is synthesized by direct current plasma enhanced chemical vapor deposition. The structure consists of aligned CNTs which have branches of smaller diameters growing aligned along a direction perpendicular to the original CNT. The mechanism of branching is explained in terms of a self-seeding of Ni catalyst which is transferred by sputtering from the original catalyst particles in the backbone CNTs to the walls of those CNTs. It is also shown that the branching induced a large increase in surface area and total nanotube length and can be beneficial in supporting very fine Pt nanoparticles for fuel cell and other catalytic applications. Such an array of Y-junction nanostructures could be useful for the fabrication of a high-density array of nanoelectronics switches and transistors.

Miniaturization of devices has allowed great advances in semiconductor technology over the past few decades. While demands push for a continuation of these advances, the cost and feasibility of miniaturization on the nanoscale are increasingly becoming more problematic. The exceptional electrical and mechanical properties of carbon nanotubes (CNTs)[1,2] have drawn considerable attention for researchers seeking to find a different way to continue the push for miniaturization. A subset of CNTs attracting great attention is CNT branchings such as Y-junctions. Recently, sharp electronic switching[3] and differential current gain[4] have been demonstrated using one of the three branches as an in situ control gate. An array of such carbon nanotube Y-junctions formed by multiple branchings from a single CNT would be beneficial for more complex devices, and it would be desirable if such an array could be constructed on existing carbon nanotubes which can be patterned and positioned on a substrate. Here we show how such an array of multibranching CNTs can be fabricated.

To utilize CNTs as device components and for other applications, good control over their growth morphology is required. The growth of vertically aligned CNTs has been demonstrated by several groups using plasma-enhanced chemical vapor deposition (PECVD).[5−7] These results all had CNTs aligned perpendicular to a substrate surface due to the applied field or electrical self-bias field created by the plasma environment. Recently, we have demonstrated the ability to grow CNTs aligned at angles not perpendicular to a substrate containing sharp bends with radii of curvature less than 25 nm by manipulating the electric field directions in the CNT growth regions.[8] This adds great potential to CNTs as interconnections or devices since using only straight CNTs would limit device geometries considerably.

Stable CNT Y-junctions have been produced by various methods. Some of the early ones were synthesized by arc discharge,[9] while slightly later individual Y-junction CNTs were grown in large and uniform quantities through a CVD process in Y-branched nanochannel alumina templates.[10] Another method is to grow CNTs in a CVD process and, during the growth processing, add precursors containing a catalyst metal suitable for CNT growth which can attach to the growing CNTs and nucleate a branch.[11] Y-junctions in single-walled CNTs (SWNTs) have been reported by means of thermal decomposition of fullerene in the presence of various transition metals[12] and also by welding together separate SWNTs using an electron beam in a high acceleration voltage transmission electron microscope (TEM).[13] The electronic properties of CNT Y-junctions have been modeled theoretically,[14] and measurements have been achieved[3−4,15] showing great potential of CNT Y-junctions as elements in simple nanoelectronic devices.

In this work, the growth of aligned arrays of CNTs was carried out by a dc plasma enhanced chemical vapor deposition (PECVD) process using Ni catalyst particles with a tip-growth mechanism, which is described in detail elsewhere.[8] Briefly, A mixed gas of ammonia (NH_3) and acetylene (C_2H_2) was used for the CVD growth. The main CNT backbone arrays had a density of $\sim 2 \times 10^9$ CNTs/cm^2. They were fabricated by first sputter depositing a 50−100 Å thick Ni film over the surface of an n-type Si(100) substrate. The substrates were then transferred (in air) to the CVD chamber. Upon heating to ~700 °C in a low-pressure

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* To whom correspondence may be addressed: e-mail, jin@ucsd.edu; fax, 858-534-5698.

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hydrogen atmosphere, the Ni film breaks up into islands with the majority having diameters ranging from 30 to 60 nm. After catalyst island formation, the atmosphere was changed to NH_3 flowing at 150 sccm. A dc bias of 550 V was applied between an anode above the sample and a cathode just below the sample. Under the applied voltage, plasma formed and C_2H_2 was added to the chamber flowing at 30 sccm with the total NH_3 and C_2H_2 pressure held at 3 Torr. For microstructural analysis, field emission scanning electron microscopy (SEM) was performed using a Phillips ESEM operated at 30 kV. TEM images were obtained using a JEOL 3010 operated at 300 kV.

After the main CNTs have been grown, the experimental setup was then changed to cause the subsequent growth stage to occur aligned along a different direction. The continued growth and bending of the CNTs was achieved by inducing strong changes in the direction of the electric field in the growth region of the CNTs.[16] In our previously reported results, the goal was to grow CNTs with sharp bends where we had control of both bend angles and locations. In contrast, here we used modified conditions to cause the creation of multiple CNT branches along the side of the original CNT "backbone" all aligned with the direction that the CNT growth was continued in.

Images both after the initial CNT growth but before branching and after the growth of the aligned branches (Figure 1) show a dramatic change in the structure. The many branches that form from each of the initial backbone CNTs are much smaller in diameter than the original CNTs. The branches have a range of diameters, with only the larger branches clearly visible in the scanning electron microscopy (SEM) images of Figure 1. High-resolution TEM images of CNTs shown in Figure 1 are presented in Figure 2. In the CNTs shown before branching, we can clearly see the herringbone structure associated with CNTs grown by dc PECVD processes. The only metal particle that can be seen is the Ni catalyst particle residing at the tip end of the CNT (Figure 2a). After the branching growth (Figure 2b), we see many new CNTs with the majority of the diameters 5−10 nm. Each of these new smaller CNT branches has its own equally small catalyst particle at its tip which lets us conclude that they grew under a tip growth mechanism just as the initial CNTs that support them were. The side of the backbone CNT that faces the direction of the branch growth has a much more complicated surface than the side facing the opposite direction. There are not only the beginnings of many more CNT branches but also small Ni particles and damaged graphene plane ends. The CNT branches shown in the TEM images of Figure 2b do not appear to be as aligned as those in the SEM image in Figure 1b. This is likely due to the fact that these very small diameter CNTs can be easily disturbed during sample preparation to obtain the TEM samples such as during the sonication process for CNT distribution on a TEM grid.

The basic CVD conditions that result in this novel structure are similar to those that enabled continuing the growth of the CNTs in a new direction;[16] however, some of the different processing conditions employed here resulted in clearly distinct growth morphologies. We believe that the critical factor was the energy of the ions in the plasma. It is clear from the TEM images in Figure 2b that every branch was grown from a Ni catalyst particle under a tip-growth mechanism. Since the Ni was confined to the main catalyst particles at the tips of each of the initially grown CNT backbones (Figure 2a), the Ni catalyst particles that form the CNT branches must somehow form during the plasma processing. Although our CVD chamber is not 100% contamination free, there are no Ni parts inside of it and we have not observed neither Ni nor any other metal particle contamination moving into our CNT samples during growth processing. Therefore, we conclude that these new smaller Ni catalyst particles originate from the only accessible source of Ni, the main catalyst particles of the original backbone CNTs.

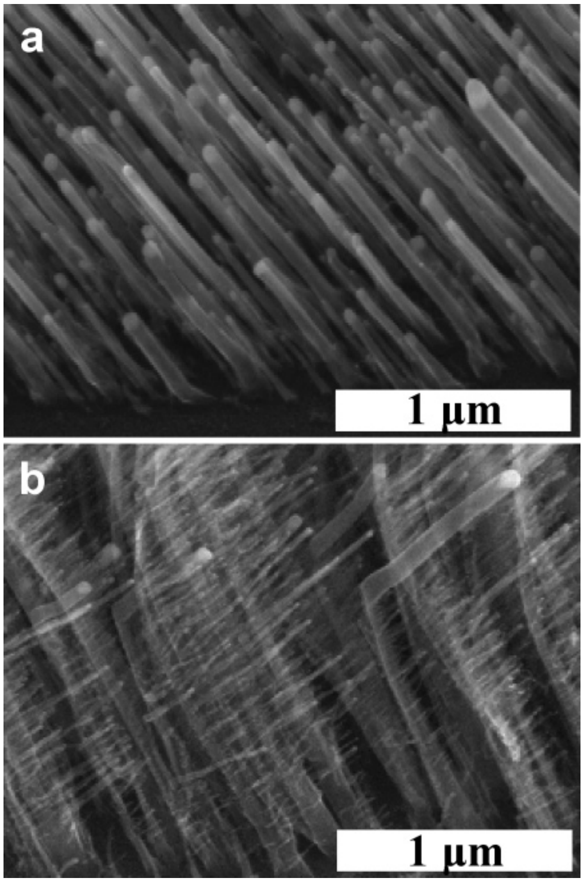

Figure 1. Scanning electron microscopy (SEM) images taken of CNTs (a) after their initial growth stage and (b) after the second growth stage results in the aligned multibranched structure. The insert data bars in both panels are 1 μm.

We have observed that the Ni catalyst particles can break up during growth and that some of these particles can become trapped in the CNT.[17] We have also seen that under the right plasma conditions that the Ni catalyst particle can be reduced in size by sputtering.[5,18] Both of these result in the redistribution of Ni from the initial catalyst particle. The breaking up of the Ni catalyst particle does not appear to be occurring in this work since in our previous observations it occurred during the growth of the CNT and here we do not see any Ni particles attached along the length of the initially grown

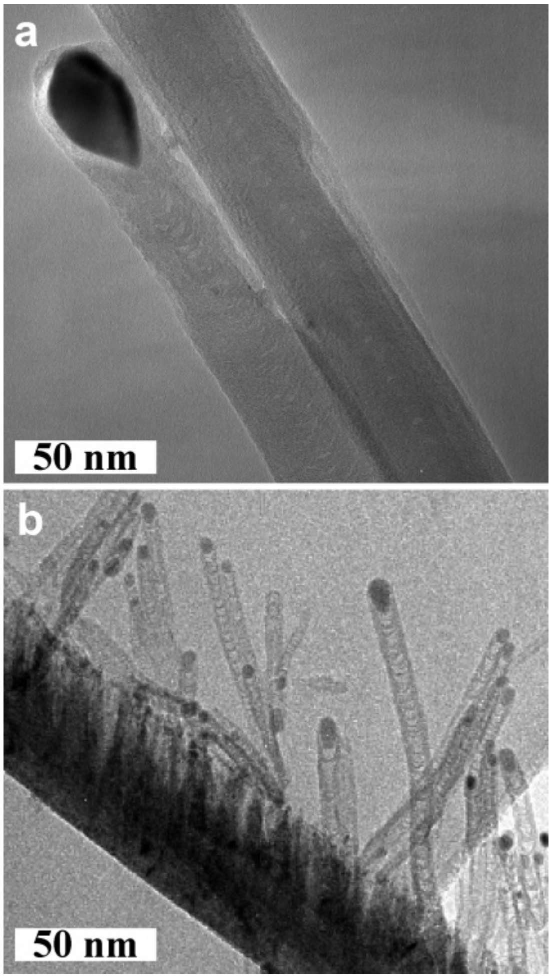

Figure 2. (a) TEM images of as initially grown CNTs showing Ni only present in the main catalyst particles. (b) Branched CNTs with much smaller Ni catalyst particles present at the tips of each branched CNT. Alignment of the very small diameter branches was likely disturbed during TEM sample preparation. The data bars are 50 nm in both panels.

CNTs. It is also unlikely that after growth, larger chunks of Ni would break off of the large catalyst particle and attach to the sides of the CNTs in relatively uniform size and distribution. The second option, sputtering of the Ni catalyst particle, does appear to be a strong possibility. We would expect that if sputtering were occurring, a small amount of Ni would be deposited in thin film form on the surfaces of the CNTs near each of the catalyst particles that was being sputtered. This processing is being carried out at an elevated temperature with the substrate above 700 °C and the actual temperature near the tips of the CNTs locally much higher due to ion bombardment from the plasma. At these temperatures, a thin film of depositing Ni on the surface of the CNTs is expected to break up and agglomerate into nanoparticles to minimize surface energies.[19] Further, since we observe an onset of branching formation with an increase in the applied field used to form the dc glow discharge (the field strength roughly parallels the energy of the ions in the plasma), we have additional support for the proposed mechanism of CNT-end Ni particle sputtering for formation of the new smaller Ni catalyst particles. Keeping the other experimental conditions fixed, if during the second growth stage we use an applied voltage of under 525 V to form the dc glow discharge, then no branching occurs. If we apply over 550 V, then branching is observed. From this we conclude that somewhere between 525 and 550 V, the plasma power becomes such that sputtering of the Ni catalyst particles are possible. If sputtering is occurring from the original Ni catalyst particle, we might also expect to see a reduction in size when this main particle continues to grow in the second growth stage. We do not see very clear evidence of this, but due to the size differences between the original CNTs and the branches, it is estimated that only a 1 nm reduction in the diameter of the initial Ni catalyst particles would provide more than enough Ni to seed all of the observed branches. A schematic illustration summarizing the sequence of events in our proposed grown model is shown in Figure 3.

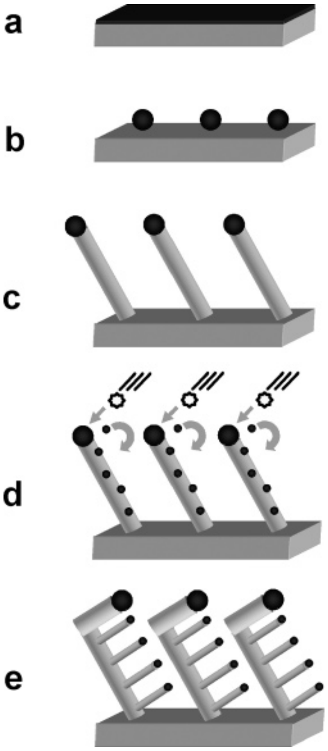

Figure 3. Schematic illustration of the sequence of events leading to the formation of a multibranched CNT structure. A thin film of Ni catalyst is initially deposited onto a Si substrate (a). After heating, the thin film breaks up and agglomerates into nanoparticles (b). Each of the Ni particles serves as a catalyst for the growth of a CNT (c). The CNTs are grown aligned to each other and at some acute angle with respect to the substrate. After the initial CNT growth stage, the processing conditions are altered to cause the initial Ni catalyst particle to be sputtered by the ion bombardment from the dc plasma (d). The sputtered Ni deposits on the surfaces of the initially grown CNTs and eventually agglomerates into new smaller catalyst particles and nucleate new CNTs which grow as branches on the original CNTs. Due to changes in the cathode geometry, the initial CNTs to continue to grow aligned with the newly formed CNT branches along a different direction than the original growth step (e).

The self-seeding processing that results in the CNT branchings has some inherent randomness. It is not possible for us to precisely control the size and location of each CNT branch using the method we demonstrate here, but we do have some control. We can increase the degree of sputtering that occurs from the initial Ni catalyst particle by increasing the plasma power. This allows us to control the density of the branches. The positions of the branches might also be controlled if we added in an additional step of patterning a mask over parts of the initial CNT surfaces or directly patterning the catalyst particles for each branch using electron beam lithography.

In addition to the great potential for new forms of electronic devices, one of the possible applications of nanotubes which may have major industrial impact much sooner is as high-surface-area electrodes in fuel cells. Due largely to the rising costs of energy and to many environmental concerns for present energy sources, an interest in fuel cell research is rapidly growing. For hydrogen as well as direct methanol fuel cells, electrocatalysts based on Pt are often used.

The size, shape, and distribution of catalyst particles plays a key role in their catalytic activitites.[20] A number of ways are being investigated to manufacture an effective structure with Pt catalyst particles of the appropriate size and distribution, some of which include using CNTs as the support scaffold for the catalyst particles.[21−25] While in some of these works Pt particles of 2−4 nm have been synthesized, they all have other drawbacks. Most require deposition of the Pt nanoparticles onto the CNTs by means of an aqueous solution. After such an aqueous processing, the CNTs tend to form severely agglomerated bundles greatly reducing the available surface area. For an improved Pt catalyst particle supporting structure, it is desirable to have an as-grown CNT array with smaller diameter and higher density CNTs containing all of the Pt catalyst particles exposed on the surfaces of the CNTs.

To demonstrate a use for our new multibranching CNT structure, we used it as a scaffold for the support of Pt nanoparticles (Figure 4). This application enables us to have a high concentration of Pt particles that are separated from each other within the three-dimensional CNT branches while not requiring control over individual branch locations. Although the most common methods of attaching Pt nanoparticles to CNTs involve aqueous solutions, we sought to avoid the problems associated with that since we wanted to maintain the unique multibranching CNT structure. We simply sputtered a thin film of Pt on our multibranched CNT structure while rapidly rotating the sample and followed this deposition by annealing under an inert atmosphere. The Pt formed into isolated nanoparticles which covered the surfaces of the CNTs, and as predicted,[19] the smaller diameter CNT branches lead to smaller diameter Pt particles forming on their surfaces. This composite structure could potentially serve as the catalyst support for future fuel cells and other electrochemical catalytic reactions.

In summary, a novel multibranching CNT structure is synthesized using field-guided bidirectional growth. The mechanism of branching is explained in terms of self-seeding of Ni catalyst sputtered from the original catalyst particles in the backbone CNTs. Such an array of Y-junction nanostructure can be useful for fabrication of high-density array of nanoelectronics switches and transistors. It is also shown that the branching induced a large increase in surface area that can be beneficial in supporting very fine Pt nanoparticles for fuel cell and other catalytic applications.

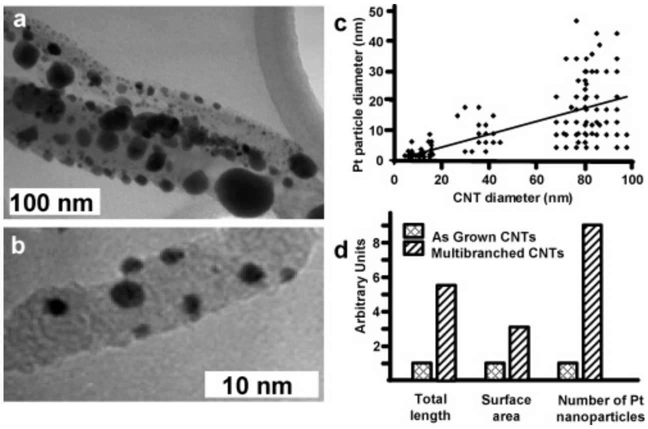

Figure 4. (a) A TEM image of a few CNTs of various diameters. The largest dark contrast particles in the lower right are Ni catalyst particles that led to the growth of the CNTs. The majority of the other particles lining their surface are Pt. (b) A higher magnification TEM image showing a small diameter CNT with many ∼2 nm Pt particles. The data bars are 100 nm in (a) and 10 nm in (b). (c) A plot illustrating the trend of Pt particle size verses the diameter of the CNT they were formed on. It is clear that on the smaller diameter CNTs, only small Pt particles form. (d) Three histograms comparing the total length, surface area, and number of Pt nanoparticles formed on each original CNT for both the as initially grown CNT array and the multibranched structure. As expected, all of these values are significantly higher for the multibranched CNT structure.

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