# Shaping carbon nanostructures by controlling the synthesis process

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The ability to control the nanoscale shape of nanostructures in a large-scale synthesis process is an essential and elusive goal of nanotechnology research. Here, we report significant progress toward that goal. We have developed a technique that enables controlled synthesis of nanoscale carbon structures with conical and cylinder-on-cone shapes and provides the capability to dynamically change the nanostructure shape during the synthesis process. In addition, we present a phenomenological model that explains the formation of these nanostructures and provides insight into methods for precisely engineering their shape. Since the growth process we report is highly deterministic in allowing large-scale synthesis of precisely engineered nanoscale components at defined locations, our approach provides an important tool for a practical nanotechnology. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1395517]

Controlled (deterministic) large-scale growth of nanoscale structures, including carbon nanotubes (CNTs) or nanofibers (CNFs), is an important step in the realization of practical nanoscale devices for applications in scanning microscopy, nanoelectronics, and biological probes, among others. Deterministic growth of a nanoscale structure implies the precise control of its shape, location, and orientation. To date, only cylindrical (tubular) structures such as CNFs have been synthesized in a deterministic way.[1,2] Yet, the ability to precisely engineer the shape of nanostructures in a large-scale synthesis process is a very important aspect of nanofabrication. For example, a conical structure provides substantially higher mechanical and thermal stability than a narrow cylinder, although a cone has lower resolution as a scanning microscopy tip for measuring high-aspect-ratio features (e.g., a deep, narrow trench) and would require higher electric fields when used as a cold cathode in field-emission devices.[3] For applications such as these, the truly ideal tip would have a conical base and a small-diameter, high-aspect-ratio cylinder as a cap. This structure combines the stability of the cone with the advantage of the cylinder for high-resolution measurements and field emission at low applied fields. Indeed, many of the functional nanoscale devices envisioned for nanotechnology require the ability to precisely engineer the nanoscale shape of components during the synthesis process. Progress toward this goal is often stymied by the lack of a fundamental understanding of the synthesis process. In this work, we report the controlled synthesis of carbon nanocones (CNCs) and, from these, carbon nanostructures with cylinder-on-cone shape, along with a model of the synthesis process explaining these results.

In order to initiate growth of a single CNC or CNF, formation of a single catalyst nanoparticle is required.[1] In this work, nickel (Ni) catalyst nanoparticles were formed by first depositing an array of catalyst dots (10 nm Ni/10 nm Ti) of 100 nm in diameter on a Si substrate using conventional electron-beam lithography and electron-gun metal evaporation, followed by dc plasma pre-etching with ammonia and annealing at elevated temperatures ($\sim700\,°C$) in a vacuum chamber with a base pressure of $\sim1\times10^{-5}$ Torr. Plasma-enhanced chemical-vapor deposition (PECVD) was used to produce vertically aligned carbon nanostructures.[1,2,4,5] Briefly, a mixture of a carbonaceous gas and an etchant (40–60 sccm of acetylene and 80 sccm of ammonia) was used. The etchant is needed to etch away graphitic carbon film that continuously forms during the growth from the glow discharge and would prevent the formation of CNFs/CNCs by completely covering the catalyst nanoparticles. The substrates were heated directly by placing them on a heater plate (the cathode of the plasma discharge) and the growth temperature was $\sim700\,°C$. The total gas pressure during the growth was $\sim2$–5 Torr, the dc glow discharge current was maintained at 100 mA, and the discharge voltage was $\sim510$–575 V.

By adjusting the growth parameters such as the ratio of acetylene ($C_2H_2$) to ammonia ($NH_3$), vertically aligned CNCs rather than CNFs, can be formed. Herein the word "nano" refers to the tip diameter of the CNCs; the CNC height and base diameter can be grown to micrometer dimensions, if desired. An example of a vertically aligned CNC array synthesized using PECVD is shown in Fig. 1(a). The remarkable aspect of the growth process is that the tip diameter of the cone does not increase during growth, and is determined by the size of the catalyst droplet. In contrast, the base diameter of the CNC, as well as its height, increases with growth time, i.e., conditions can be selected to permit both lateral and longitudinal growth. Consequently, very tall cones with sharp tips and large robust bases can be formed. Furthermore, by changing the growth parameters (in this case, the relative acetylene content), the cone angle can be controlled. Examples of vertically aligned CNCs with different cone angles are shown in Figs. 1(b) and 1(c). Higher

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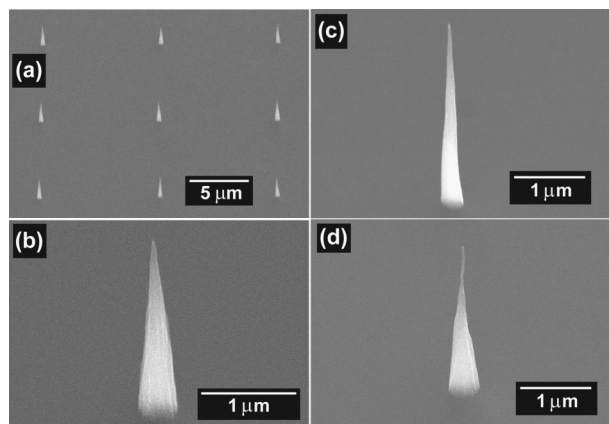[a]Electronic mail: merkulovvi@ornl.gov

FIG. 1. Scanning electron microscopy (SEM) images of (a) an array of carbon nanocones fabricated using plasma-enhanced chemical-vapor deposition with excess of a carbonaceous gas (acetylene); of individual carbon nanocones with (b) larger ($\sim 15°$) and (c) smaller ($\sim 5°$) cone angles grown with gas flows of 60 sccm $C_2H_2$/80 sccm $NH_3$ and 55 sccm $C_2H_2$/80 sccm $NH_3$, correspondingly; and of (d) nanoscale cylinder-on-cone carbon tip synthesized by first growing a carbon nancone (60 sccm $C_2H_2$/80 sccm $NH_3$), followed by growing a carbon nanofiber with the relative acetylene content reduced (50 sccm $C_2H_2$/80 sccm $NH_3$). The growth times for the nanocones in (a), (b), (c), and (d) and for the nanofiber in (d) were 15 and 5 min, respectively. All images were obtained using a Hitachi S4700 high-resolution SEM.
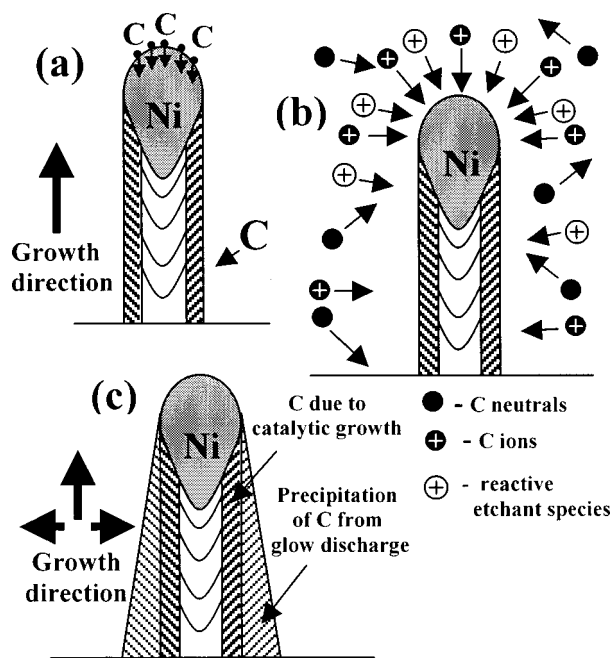


FIG. 2. Schematic representation of the growth of (a) a carbon nanofiber using conventional thermal CVD, (b) a vertically aligned carbon nanostructure using PECVD, and (c) a carbon nanocone formed due to additional precipitation of C at the outer walls during PECVD.

acetylene content yields higher cone angles (increased lateral growth rate), and reducing the acetylene content can bring about a transition between the formation of vertically aligned cones and cylinders.

The formation of the nanocone structure involves the growth of both a central cylindrical CNF and sloped outer walls in essentially separate yet simultaneous processes. Growth of CNFs "from the tip" using conventional *thermal* chemical-vapor deposition (CVD) (Ref. 6) occurs in a three-step process: (i) decomposition of molecules of a carbonaceous gas (e.g., acetylene) at the surface of a catalyst (e.g., Ni) particle; (ii) carbon diffusion through the catalyst particle and subsequent formation of a supersaturated solution of C and Ni (or metastable carbide); and (iii) precipitation of C at the base of the catalyst particle. As a result of this growth mechanism, the catalyst particle moves away from the substrate on the growing tip, and a CNF of approximately constant diameter is formed beneath it [Fig. 2(a)]. The CNF diameter is determined by the catalyst particle size.

In contrast, in PECVD growth of vertically aligned CNFs (VACNFs), for which the gas source consists of a carbonaceous gas (e.g., acetylene) combined with an etchant (e.g., ammonia), the growth process is quite different. In addition to thermal decomposition of acetylene, various species formed in the glow discharge are present as well. These species include C neutrals, C ions, and reactive etchant species ($H^+$, $N^+$, etc.) that are formed from plasma decomposition of acetylene and ammonia [Fig. 2(b)]. The neutrals move in random directions, whereas the electric-field lines govern the direction of travel for the ions. We note that in our case the Debye shielding distance is of the order of 100 $\mu$m.[7] This distance is significantly larger than the CNF height (a few $\mu$m), and therefore, VACNFs are located in the dark space of the glow discharge. If the acetylene content is increased relative to that of ammonia, then in addition to the vertical growth process described above, carbon begins to precipitate

also at the walls of the growing, initially cylindrical VACNF. Precipitation occurs due to an excess of acetylene (or insufficient ammonia etchant), which leads to the carbon deposition rate being higher than its etching rate. Of course, carbon ions and neutrals "consume" reactive etchant species in the gas phase as well. The net result is growth in two directions, rather than one: vertically (catalytic growth via diffusion of C through the Ni particle) and laterally (by precipitation of C from the discharge at the outer walls of the VACNF). Consequently, a conical structure, or a carbon nanocone, can be formed [Fig. 2(c)].

To further investigate and confirm this growth mechanism, high-resolution transmission electron microscopy (HRTEM) studies of these CNCs were performed. The corresponding images are presented in Fig. 3 and clearly show
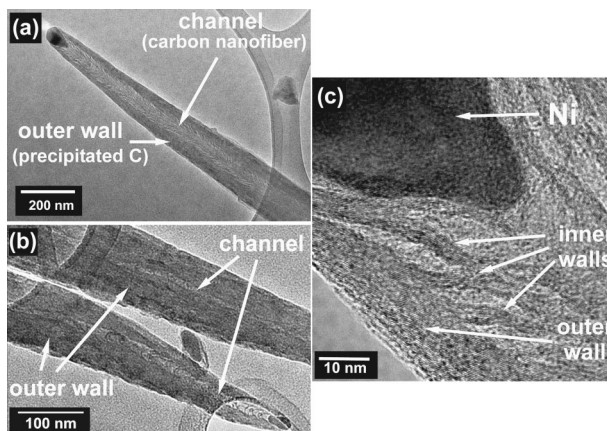


FIG. 3. TEM images of carbon nanocones (CNCs) with (a) smaller and (b) larger cone angles. The central channel of all CNCs is a carbon nanofiber formed due to the catalytic growth process, while the thick outer walls are due to precipitation of excess C from the glow discharge. (c) HRTEM image showing the detailed structure of the CNC channel and outer walls. All images were obtained using a Hitachi HF-2000 TEM.

that CNCs with both small and large cone angles [Figs. 3(a) and 3(b), respectively] have an inner channel of approximately constant diameter that is nearly equal to the Ni catalyst nanoparticle size. As we surmised, this channel is surrounded by solid walls whose thickness is proportional to the cone angle. The more detailed structure in the vicinity of the CNC tip is shown in Fig. 3(c). This image shows the solid, nanocrystalline structure of the outer wall, as well as the separated inner walls that form the channel. The bamboo-like structure of VACNFs (the periodically internally capped channel) was already reported in our previous work.[1] These observations provide strong support for the growth model proposed in this article. The channel is simply the cylindrical carbon nanofiber formed via the catalytic growth, and the solid walls are formed via precipitation of C species from the glow discharge [Fig. 2(c)].

A very interesting and useful consequence of CNC formation is that the shape of vertical carbon nanostructures synthesized by PECVD can be controlled by changing the growth parameters during the growth process. A carbon nanostructure that consists of a nanocylinder (VACNF) grown directly on a nanocone (CNC) can be synthesized as follows. The growth conditions initially are set for the synthesis of a cone. After a CNC of desired length and shape (cone angle) is obtained, the relative acetylene content in the chamber is reduced to suppress growth in the lateral dimension (C precipitation at the outer walls), thus forming a cylindrical VACNF on top of the CNC. Figure 1(a) shows an example of a nanoscale cylinder-on-cone carbon tip fabricated using this technique. Again, the tip diameter of the VACNF is determined by the metal catalyst droplet size and its length is controlled by the growth time. As described earlier, these tips should be useful in applications where both high aspect ratio and mechanical stability are required. Furthermore, the presence of a nanoscale Ni particle at the apex of a cylinder-on-cone nanostructure can be quite useful for scanning microscopy of magnetic materials. The growth method is *completely deterministic* as the tip location, the lengths of the cone and the cylinder, the cone angle, and the diameter of the cylindrical section all can be controlled. Consequently, these tips can be tailored to suit specific applications.

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