

Template-Free Directional Growth of Single-Walled Carbon Nanotubes on a- and r-Plane Sapphire

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Single-walled carbon nanotubes (SWNTs) have attracted enormous attention as model systems for nanoscience and nanotechnology.¹ Many applications have been demonstrated, including SWNT transistors and sensors.^{2,3} These devices are typically obtained by locating the nanotubes (via atomic force microscopy (AFM) or patterned catalyst) and then patterning the contacts. To go from discrete devices to scalable and integrable systems, high-throughput synthesis of ordered carbon nanotubes over large areas is of particular interest. This may allow registration-free fabrication and integration of nanotube devices by simply patterning source/drain electrodes at desired locations, as the active material (i.e., nanotubes) is all over the substrate (Figure S1 in the Supporting Information). Aligned nanotubes have been grown with the assistance of an electric field⁴ or the gas flow;⁵ however, it remains difficult to produce planar nanotube arrays over large areas with sufficiently high density and order. Iijima et al. studied the growth of SWNTs using iron-film-coated sapphire substrates, but no orientation control and, hence, no ordered nanotube arrays were observed.⁶ Recently, aligned nanotubes have been shown to grow along the step edges on miscut c-plane sapphire substrates;⁷ however, there is currently a lack of control over the miscut angle, thus resulting in significant variations in the as-grown nanotube orientation and density. We report a surprising discovery of high-throughput growth of highly aligned single-walled carbon nanotube arrays on a-plane and r-plane sapphire substrates with negligible miscut without the apparent involvement of step edges. In contrast, random orientations were observed for nanotubes grown on m-plane and c-plane sapphire with negligible miscut. Our results clearly reveal the importance of the sapphire substrate crystallography and provide a viable way to obtain aligned nanotube arrays.

Our approach employed chemical vapor deposition (CVD) to grow SWNTs on a-plane, r-plane, m-plane, and c-plane sapphire substrates purchased from Marketech International Inc., all with miscut angles $<0.5^\circ$. Ferritin clusters purchased from Aldrich were first dispersed onto the sapphire substrates as catalysts, followed by CVD growth of SWNTs at 900 °C. Gas flows of C₂H₄, CH₄, and H₂ were controlled at 10, 2000, and 800 sccm, respectively. After 10 min growth, the samples were cooled and inspected with scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Figure 1a displays an SEM image of the SWNTs grown on the a-plane sapphire. The nanotubes distributed uniformly over the whole substrate, and their orientations were found to align normal to the [0001] direction of the a-plane sapphire, regardless of the gas flow direction. For instance, the arrow in Figure 1a indicates the gas flow direction used for that specific sample, and one can clearly see that the nanotubes do not grow following the gas flow. These SWNTs are typically tens of micrometers long, with an intertube spacing of ~ 200 nm, as shown in Figure 1b. Higher density (up to 40 SWNTs/ μm) has been achieved by adjusting the

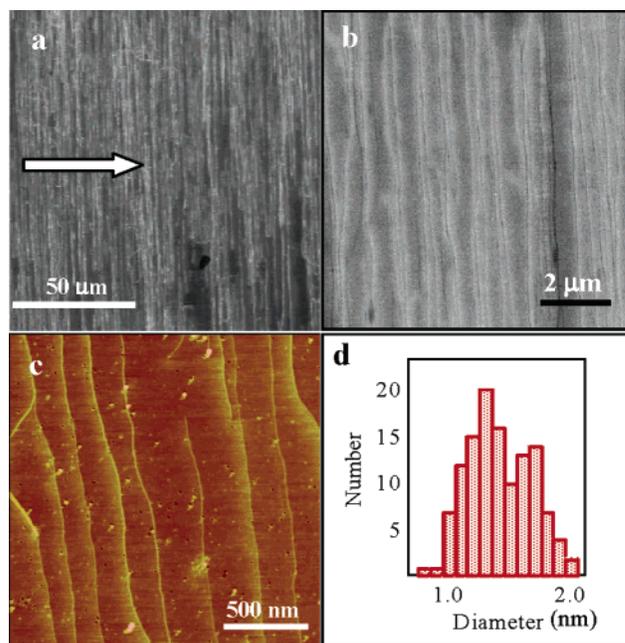


Figure 1. Directional growth of single-walled carbon nanotubes on a-plane sapphire substrates. (a) Low- and (b) high-magnification SEM images of SWNTs. The arrow indicates the gas flow direction. (c) AFM image of the aligned SWNTs. (d) Histogram of the SWNT diameter distribution.

ferritin catalyst density. Figure 1c shows an AFM image of the planar nanotube arrays. The nanotube diameters can be determined from the topographic height, revealing a narrow distribution of 1.34 ± 0.30 nm (Figure 1d). These large-area-ordered nanotube arrays may offer significant advantages for nanotube device fabrication and integration.

Identical growth conditions were used to grow SWNTs on other crystallographic faces of sapphire substrates. We found that the (1102) r-plane sapphire delivered orientation-controlled nanotube growth (Figure 2a) similar to that of a-plane substrates. In contrast, growth on the m-plane sapphire revealed no particular preferential orientation for the nanotubes (Figure 2b), while the c-plane sapphire produced predominantly nanotubes with random orientations with some aligned nanotubes (Figure 2c). We stress that different batches of substrates have been used in our study and that the above-mentioned growth is highly reproducible. We have further compared the nanotube growth using different catalyst preparation methods. Figure 2d shows the result of SWNT growth using 0.3 nm Fe film deposited on the a-plane sapphire substrate as the catalyst. One can clearly see that no aligned growth was found, consistent with the observation in ref 6.

The origin of the orientation-controlled synthesis obtained with the a-plane and r-plane sapphire deserves further study; however, the step-edge-templated growth is likely not the reason. Extensive

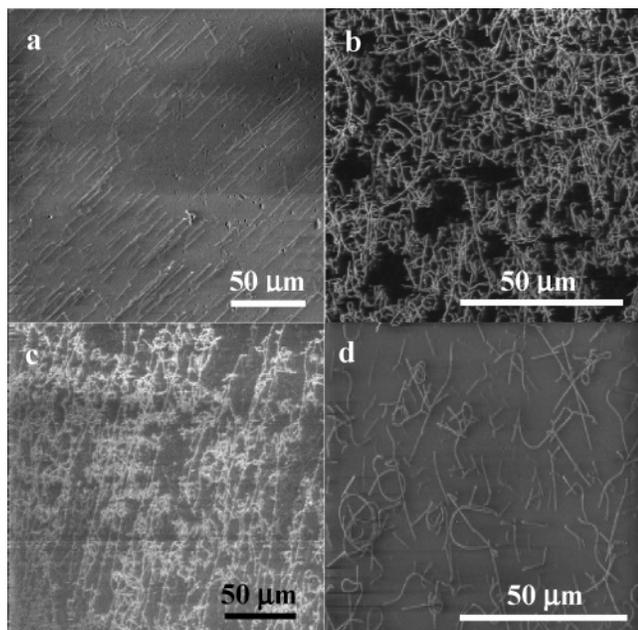


Figure 2. Panels a–c are SEM images of SWNTs grown on r-, m-, and c-plane sapphire substrates, respectively, using ferritin as catalyst. (d) SEM image of SWNTs grown on an a-plane sapphire substrate with a 0.3 nm Fe film as catalyst.

AFM studies have been performed on the sapphire substrates we used, and no correlation between the nanotube orientation and surface morphology has been found for the a-plane and r-plane substrates.⁸ Instead, we suggest that the nanotube/substrate interaction plays an important role for the observed nanotube orientation. Figure 3a shows the schematic diagram of a SWNT on the a-plane sapphire substrate. The high density of atoms lying normal to the [0001] direction of the a-plane sapphire may strongly interact with SWNTs and lead to minimized Lennard-Jones potential.⁹ This mechanism of guided nanotube growth is similar to that of nanotubes grown on single-crystalline silicon substrates.¹⁰ Detailed molecular simulation of the Lennard-Jones potential for nanotubes on various sapphire planes is underway and will be published elsewhere. In contrast, when Fe films were used as the catalyst (Figure 2d), the high-density Fe clusters could prevent direct interaction between the carbon nanotubes and the sapphire substrate, therefore leading to growth with random orientations. We nevertheless stress that the observed orientation control may involve other factors, such as the catalyst–substrate interaction.

To further test the hypothesis, we carried out the nanotube synthesis for the second time using the a-plane sapphire covered with aligned carbon nanotubes. As shown in Figure 3b, ultralong nanotubes (up to millimeters) were found to lie atop the first layer, and their orientation followed the gas flow direction. This is understandable as the second layer of nanotubes was separated from the substrate by the first nanotube layer and, hence, either grew or landed following the gas flow. Such cross-woven nanotubes may eventually render new macroscopic nanotube structures, such as nanotube clothing.

In summary, we have demonstrated directional growth of high-density single-walled carbon nanotubes on a- and r-plane sapphire substrates over large areas. This technique may enable registration-

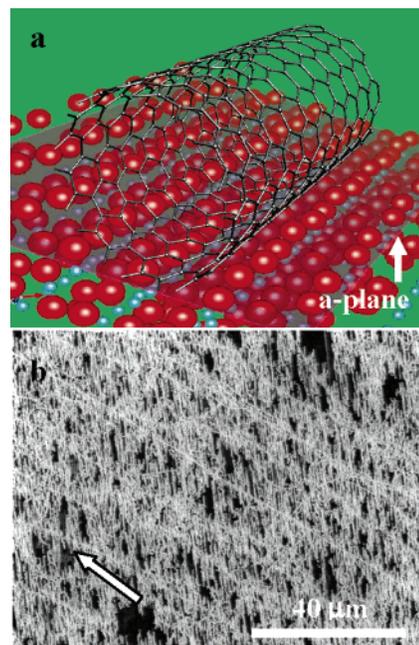


Figure 3. (a) Schematic diagram of SWNT on the a-plane sapphire substrate. The red and blue spheres represent oxygen and aluminum atoms, respectively. The purple plane shows the a-plane orientation. (b) SEM image of SWNTs on the a-plane sapphire substrate after the second nanotube growth. The arrow shows the gas flow direction.

free fabrication of nanotube devices and lead to integrable and scalable nanotube systems. Potential impact includes high-density nanotube-integrated circuits and nanotube sensor arrays/chips.

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Supporting Information Available: Potential applications of aligned nanotube arrays, AFM studies of step edges on the surfaces of sapphire substrates, surface atom layout of sapphire substrates, and size distribution of catalyst particles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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