Controlled Growth of Single- and Multi-Wall Carbon Nanotube Arrays

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Motivation—Carbon nanotubes (CNTs), perhaps the prototypical nano-material, demonstrate intriguing physical properties and promise a plethora of potential applications, ranging from room-temperature cold-cathode electron field-emitters (pulsed-power, µ-mass spectrometers, low-voltage flat-panel displays) to nanoelectrodes for electrochemical sensing to nm-sized hollow tubes for mass separation and filtration to thermal conducting heat pipes for cooling various platforms. Many of these applications require arrays of highly-crystalline CNTs, to minimize electron and phonon scattering, on a substrate surface with uniform diameters and controlled spacings, and grown preferably at the lowest possible temperatures.

Accomplishment—Arrays of single-wall CNTs (metallic or semiconducting) grow at temperatures > 800 ˚C. Multiwall CNTs grow at lower temperatures and are always electrical conductors, advantageous for most of the above listed applications. Previously, using thermal chemical vapor deposition (CVD), we showed independent control of CNT diameters ranging from 7 – 350 nm (via growth temperatures from 630 – 790 ˚C) and the average spacing apart in arrays from nm's to µm's (via the metal catalyst residual stress and the chemical reactivity of the hydrocarbon feed gas). Only CNTs with diameters < 10 nm were found to consist purely of concentric graphene cylinders.

Recently, we explored CNT growth down to 530 ˚C. These CNTs have superb crystallinity and can result in arrays primarily consisting of single and double-wall CNTs. This is the first demonstration of such small diameter CNTs in arrays and at such low growth temperatures. CNTs harvested from substrates into solution were deposited onto holey-carbon grids for analysis by transmission electron microscopy (TEM). Figure 1 shows clusters of single (530˚C) and double-wall (550˚C) CNTs. Since CNTs with pure graphene sheet outer walls cluster together in solution via Van der Waal's forces, individual CNT structures can be discerned in transmission only from the edge of a bundle.

Figure 2(A) shows the analysis of the TEM images and finds that CNT diameters increase linearly with growth temperature from 530 – 610 ˚C. Resolution is sufficient to count the number of concentric graphene cylinders in a given nanotube. Plotted in Fig. 2(B), an additional graphene cylinder grows ~ with every 20˚C of thermal CVD temperature. The average wall layer thickness, measures to be the same for every sample at 0.375 ± 0.10 nm, comparing favorably with the 0.335 nm interplanar spacing of graphite. The hollow inner core of the CNTs over this entire range of growth temperature is 0.7 ± 0.1 nm.

Significance—Carbon nanotube arrays have potential for many nano-electronic, thermal, and chem/bio sensing applications. For the first time, we demonstrate precise control of CNTs within arrays with thicknesses ranging from 1 – 6 concentric graphene cylinders. Further, these small-diameter and high-crystalline nanotubes are all grown at temperatures below previous reports. In principle, such precise nano-structural control should vastly improve electrical and thermal properties. Future work needs to identify structure-property relationships to develop a better fundamental understanding.

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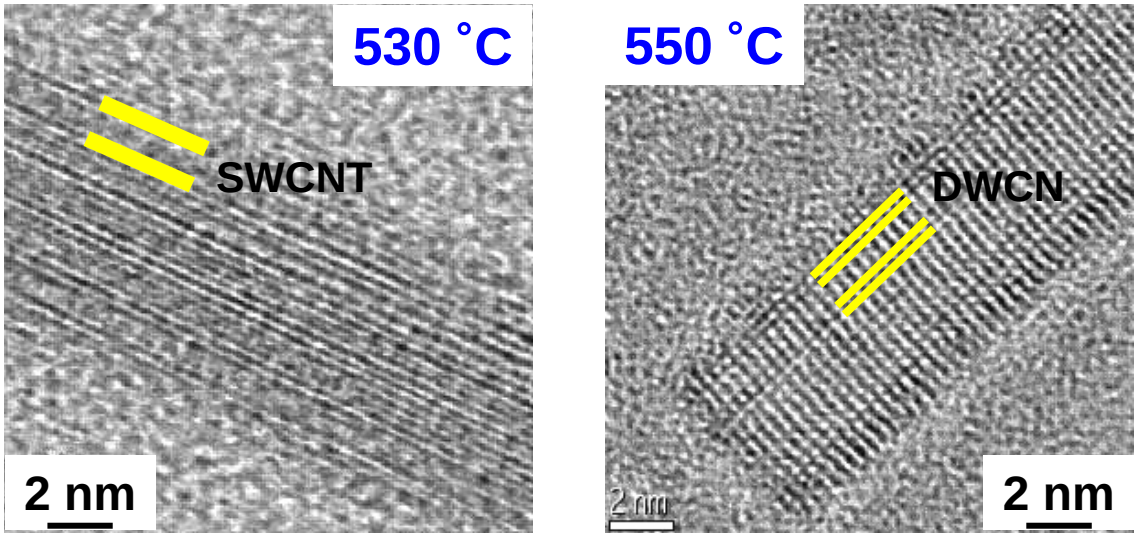

Figure 1. High-resolution TEM images of carbon nanotubes harvested from films grown at 530 ˚C and 550 ˚C. Van der Waal's forces cause the CNTs to agglomerate in bundles; therefore, to discern the structure of individual tubes, attention must be paid to the edge of a bundle where the electrons have the best chance to transmit through only a single nanotube. The 530 ˚C sample yielded single-wall CNTs; the 550 ˚C yielded double-wall CNTs. Examples are highlighted in yellow to guide the eye.

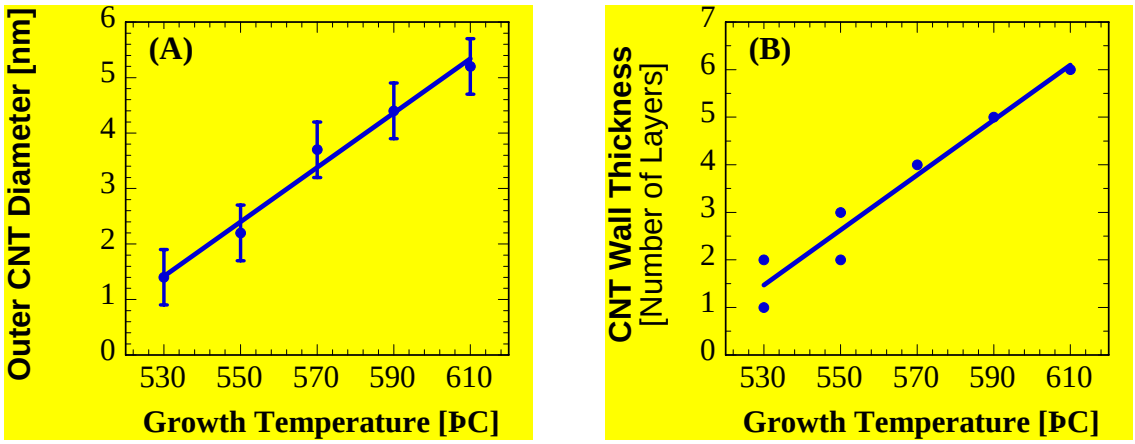

Figure 2. Results from high-resolution TEM images as in Fig. 1. (A) Outer diameters of nanotubes vs. CVD growth temperature. (B) The number of concentric graphene cylindrical sheets per nanotube vs. CVD growth temperature. Note that the wall diameter and number of sheets per wall increase linearly with growth temperature.