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COMMUNICATIONS

Published on Web 10/12/2005

Quasi-Continuous Growth of Ultralong Carbon Nanotube Arrays

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Owing to outstanding mechanical and electrical properties of carbon nanotubes (CNTs), intense research efforts have been made to synthesize aligned long CNTs.[1−3] Chemical vapor deposition (CVD) methods using transition metal nanoparticle catalysts have been widely used to produce long single-walled nanotubes (SWNTs).[4,5] The growth of ultralong CVD SWNTs, whose lengths are up to ∼4 cm, has been reported in the literature.[5] On the other hand, the multi-walled nanotubes (MWNTs) have great potential for nanomechanical and nanoelectrical applications, employing their excellent mechanical properties and hierarchal structures.[6−10] However, the scale and diversity of the MWNT structures have been limited because of short lengths of available isolated MWNTs. In this paper, we present a simple and reliable method to synthesize several centimeters long MWNTs and SWNTs and discuss their structural and electrical characteristics.

Solutions of 0.001−0.1 M $FeCl_3$ in water and ethanol were used as catalytic precursors that are decomposed at high temperatures to produce Fe nanoparticles with different sizes and densities that determine the diameters of CNTs.[5] This simple procedure greatly saves efforts to synthesize nanometer-sized catalyst particles from solution chemistry. The catalyst patterns were created on the substrates using drop-drying or stamping. After calcining the catalysts at 950 °C for 30 min with the H_2 and Ar gas mixture, flowing at the rates of 60 and 200 cm^3/min, respectively, the CH_4 and H_2 gases were flowed at 950 °C for 3 h at the rates of 100 and 60 cm^3/min, respectively.

To grow extremely long CNTs with aligned geometries, a stable laminar gas flow is required to stabilize the catalysts at the tip end of growing CNTs and to travel longer distances. This can be achieved by placing another small quartz tube inside the outer tube (Figure 1). The stability of the gas flow depends on the tube diameter (d) of the small inner growth tube and can be estimated by the Reynolds number $\mathrm{Re} = \rho v d/\gamma$, where ρ is the density, v is the speed, and γ is the coefficient of viscosity.[11] Since catalysts used for the growth of large-diameter MWNTs are less mobile than those used for SWNTs growth, it is essential to have more stable laminar flows with smaller Reynolds numbers. In our case, the Reynolds number is estimated to be 50, which is near the lower limit of conventional laminar flow ranges (below 2000). In the case of the larger-diameter growth tube, which corresponds to a higher Reynolds number, relatively short and disordered MWNTs were produced (Figure 2a), presumably due to nanoscale turbulent flows that disturb the growth of long MWNTs.

The size of catalysts is known to determine the diameters as well as the wall thicknesses of CNTs.[12] In our experiment, usually SWNTs and MWNTs grow together under the same growth conditions, but their ratio changes depending on the concentration

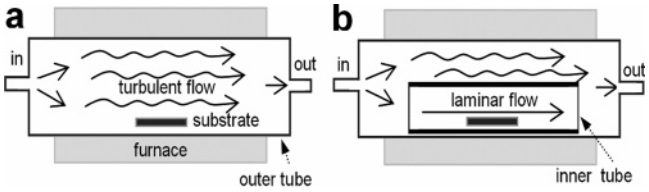

Figure 1. Schematic representation for the diameter-dependent stabilization of reaction gas flows. By inserting the smaller tube inside the outer chamber, microscopic turbulent flows (a) can be stabilized into laminar flows with lower Reynolds numbers (b).

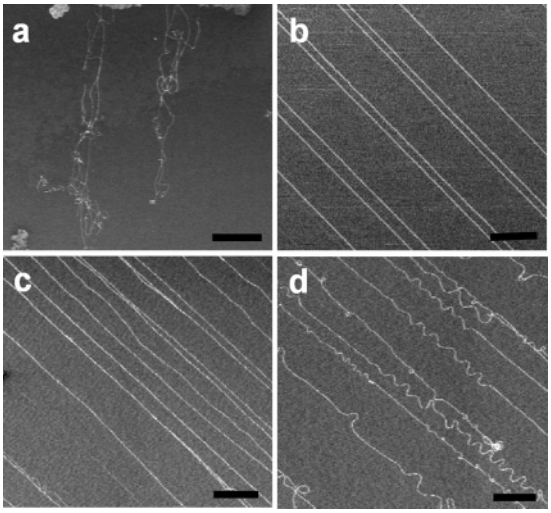

Figure 2. SEM images showing the growth of CNTs depending on Reynolds number (a, b) and the concentration of $FeCl_3$ solutions (b−d). The concentrations of catalysts for b, c, and d are 0.1, 0.01, and 0.001 M, respectively. Note that there are more curvy tubes in d, which indicates the SWNT-dominant growth (because MWNTs are usually straight). Scale bars = 50 μm.

of $FeCl_3$ solutions, which determines the size distribution of catalyst particles (Figure 2b−d). For three different concentrations of $FeCl_3$ solutions (0.001, 0.01, and 0.1 M), the average heights measured by atomic force microscopy were 1.8(0.4), 2.4(0.7), and 3.3(1.0) nm, respectively, where the numbers in parentheses are the standard deviation. This implies that the number of MWNTs increases as the concentration and the size of catalyst particles increase. The growth condition was optimized to synthesize the horizontally aligned ultralong MWNT/SWNTs on the SiO_2 substrates. Typically, well aligned extremely long (up to ∼10 cm) individual CNTs, whose length is limited by the size of silicon wafers or the length of the hot zone of the furnace, were observed (Figure 3a). The growth is likely to continue as long as the reaction gases keep flowing within the laminar range. The CNTs can also grow across 100−500 μm trenches, showing that even large-diameter MWNTs

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10.1021/ja054454d CCC: $30.25

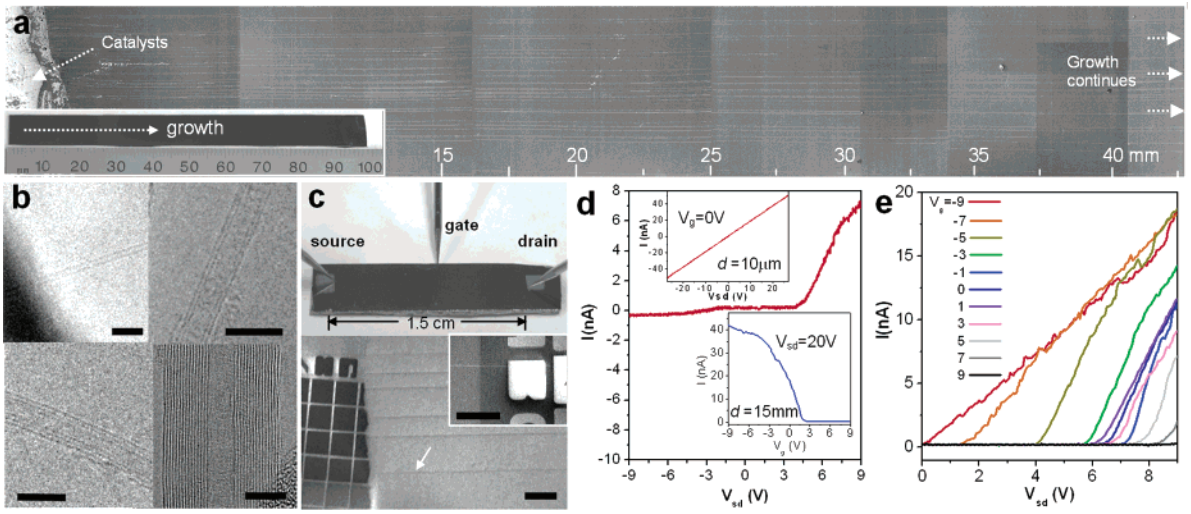

Figure 3. (a) SEM images of centimeter-long CNTs. The inset in (a) shows the optical image of a 10 cm long SiO_2 substrate with ultralong CNT arrays grown from end to end. (b) HRTEM images showing single-, double-, triple-, and multi-walled CNTs. Scale bars = 5 nm. (c) Optical and SEM images of a 1.5 cm long CNT device. The inset image shows the counter electrodes of the CNT marked with the white arrow. Scale bars = 100 μm. (d, e) The $I-V$ curves of a 1.5 cm long CNT. The upper inset in (d) shows the linear $I-V$ curve for the 10 μm long channel. The lower inset shows the gate dependence at V_{sd} = 20 V.

float over the surface due to laminar flows. These suspended ultralong MWNT/SWNTs are useful for high-resolution transmission electron microscopy (HRTEM) investigations. The HRTEM images show that various MWNTs, including double- or triple-walled nanotubes, were synthesized along with SWNTs (Figure 3b).

Since CNTs grown on the substrate are parallel without overlap to each other, we were able to characterize the electron transport properties of extremely long CNTs by contacting individual tubes. Arrays of electrodes were fabricated using TEM grids as stencil masks for thermal evaporation of Au. Within the array, 100 μm^2 Au pads were separated by 20 μm contact individual CNTs (Figure 3c lower panel). By contacting the last and the first electrode pads of the two arrays separated by macroscopic distance (>1 mm), we probed the current (I)−bias voltage (V) characteristics between two terminals as we changed the gate voltage (V_g) at the degenerately doped Si substrate below the 300 nm SiO_2 dielectric layer (Figure 3c). While the $I-V$ characteristic shows a linear ohmic behavior (Figure 3d upper inset), the CNT devices whose channel lengths are longer than ~10 mm often indicate strongly nonlinear characteristics that the current turns on only above certain bias voltages (Figure 3d). Figure 3e shows the $I-V$ characteristics of a 15 mm long individual nanotube. The current increases appreciably for $V > V_{on} = 3$ V. For a large positive bias ($V >$ 10 V), the device behaves like a field-effect transistor, where the current can be modulated by the gate voltage. The rectifying $I-V$ behavior has been observed in SWNTs with intermolecular junctions, where tubes with different chirality join together.[13,14] The turn-on voltages and the nonlinearity of $I-V$ curves can be modulated by gate voltages, implying that the potential barriers of conduction induced by local defects or intramolecular junctions can be controlled by electric field (Figure 3e).

In conclusion, we have developed the method of growing ultralong MWNTs, including SWNTs, by adjusting the diameter-dependent Reynolds number and the concentration of catalytic precursors. These ultralong MWNTs have recently been utilized to extract ultrathin SWNTs.[15] The observed gate-dependent nonlinear $I-V$ characteristics of centimeter-long CNTs would bring about a potential application of these CNTs as multifunctional electronic devices.[16]

Acknowledgment. This research was supported by the NSF Nanoscale Science and Engineering Initiative (CHE-0117752), New York State Office of Science, Technology, and Academic Research, the Korea Science and Engineering Foundation (KOSEF) Creative Research Initiative and postdoctoral fellowship, Brain Korea 21, and the U.S. Department of Energy under Contracts DE-AC02-98CH10886 and FG02 96ER45610.

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JA054454D