

# Efficient CVD Growth of Single-Walled Carbon Nanotubes on Surfaces Using Carbon Monoxide Precursor

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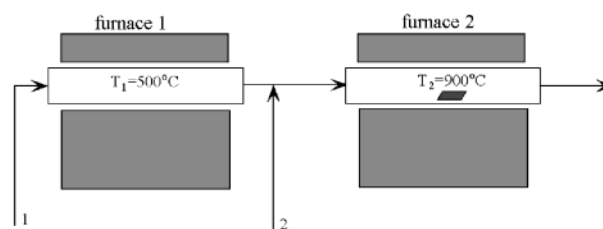
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## ABSTRACT

Single Walled carbon nanotubes (SWNTs) were grown directly on flat substrates using chemical vapor deposition (CVD) method with carbon monoxide and hydrogen mixture as feeding gas. Comparing with other CVD methods, this new approach yields higher efficiency and more reproducible results in obtaining high quality SWNTs separated as individual nanotubes on substrates. Such samples can be used to fabricate nanodevices directly with no further purification or dispersion. Important factors that affect the nanotube growth and possible mechanisms are also discussed.

Since their discovery, single-walled carbon nanotubes (SWNTs) have been heavily studied owing to their outstanding physical and chemical properties.<sup>1</sup> They are widely considered as ideal candidates for interconnections and active components in nanoscale electronic devices. Recent research has demonstrated SWNT-based nanodevices, such as quantum wires,<sup>2</sup> field-effect transistors,<sup>3–5</sup> field emitters,<sup>6</sup> etc. Until recently, most of the SWNT-based devices used materials synthesized by either the laser ablation method<sup>7</sup> or the arc method,<sup>8</sup> where the as-grown samples have to be purified and suspended in solvent before deposition on surfaces for device fabrication. The processes of purification and suspending nanotubes in solvent involve the use of highly oxidative chemicals and ultrasonication that are known to create defects on nanotubes and alter their electronic properties. For nanoscale electronics, defect-free SWNTs on surfaces are especially desirable. An alternative and successful way to fabricate nanotube devices is to use nanotubes grown directly on surfaces to avoid the undesired purification steps. However, up to now, surface growth of SWNTs has been limited to chemical vapor decomposition (CVD) of methane on metal nanoparticles supported on surfaces.<sup>9–12</sup> The growth conditions are critical for the preparation of nanotubes with high purity and efficiency. Here we report an improved CVD method for the growth of SWNTs on surfaces using monodispersed Fe/Mo nanoparticles as the catalyst and a mixture of carbon monoxide (CO) and



**Figure 1.** Schematic setup of the two-furnace CVD system.

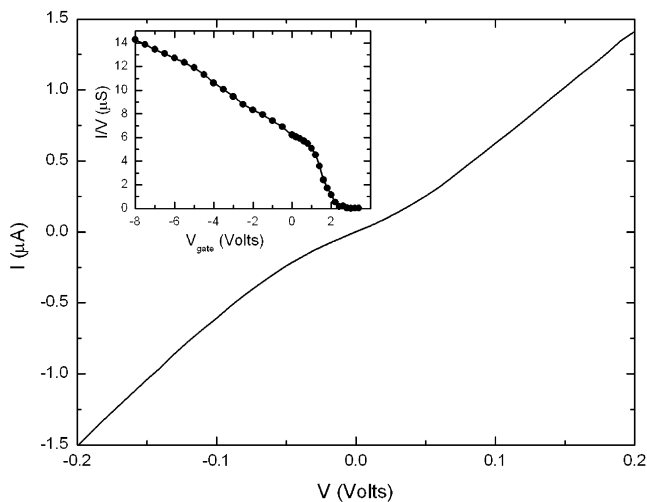
hydrogen (H<sub>2</sub>) as feed gas. In contrast to CVD of methane,<sup>9–12</sup> this method allows higher efficiency for nanotube growth and easier control of the growth conditions, thus offering more reproducible results.

In our experiments, the catalysts are monodispersed Fe/Mo nanoparticles (4.2 nm) prepared according to reference 13. The nanoparticles can be dissolved in nonpolar solvents such as hexane. They were deposited on the substrate by slow evaporation of the solution. The substrate was then annealed in air at 700 °C for 10 min to remove the organic coating on the particles formed during their preparation steps.<sup>13</sup> Si/SiO<sub>2</sub> substrates were purchased from MEMC Electronic Materials with 500 nm SiO<sub>2</sub> layer. Alumina (sapphire A plane) and magnesium oxide substrates (Superconductive Components, Inc.) were also used. To grow nanotubes, we used a two-furnace setup (Figure 1). The substrates were loaded into the second furnace. Before the growth, H<sub>2</sub> was introduced from both inlets at 400 sccm (standard cubic centimeter per minute) while the furnaces were heated to the required temperature ( $T_1 = 500$  °C,  $T_2 =$

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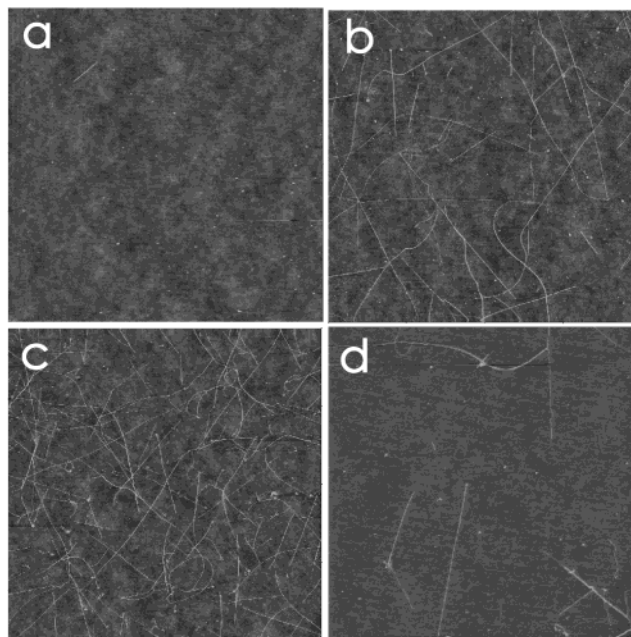
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**Figure 2.** I–V characterization of an individual nanotube connected between two Au electrodes at liquid nitrogen temperature. Inset: Gate dependence of conductance as 100 mV bias voltage.

900 °C). The H<sub>2</sub> from inlet 1 was then switched to CO while flow rate of the H<sub>2</sub> from inlet 2 was adjusted accordingly. In all experiments discussed here, the total flow rate is fixed at 1200 sccm and the reaction time is 15 min. After growth, CO was replaced by H<sub>2</sub> and the system was cooled to room temperature. The same procedure was followed for SWNTs growth on Al<sub>2</sub>O<sub>3</sub> and MgO substrates. The samples were characterized by AFM (Digital Instruments Nanoscope IIIa) and SEM (FEI Company XL-FEG/SFEG), showing the characteristics of SWNTs as observed by our group and other groups.<sup>9–11</sup> In addition, individual nanotubes grown on surfaces were connected to Au electrodes using standard e-beam lithography. To prepare the sample for electrical characterization of individual nanotubes, substrates with well-separated nanotubes were first coated with PMMA. Standard e-beam lithography was used to create parallel electrode patterns on surfaces. After removing exposed PMMA, Au metal was evaporated on exposed surfaces to connect nanotubes. AFM was used to ensure only one nanotube was connecting the electrodes before measurements. Figure 2 shows a typical result of the electrical measurements on an individual nanotube performed with the sample immersed in liquid nitrogen. The I–V curve at zero gate voltage demonstrates resistance in the 100 kOhm range, which drops by about 50% at higher source-drain voltages. The inset shows the nanotube conductance measured at a 100 mV bias, as a function of the gate voltage. The conductance drops by several orders of magnitude at the pinch-off voltage of about +2V ( $dI/dV$  measurements performed by a lock-in amplifier at a 10 mV excitation level demonstrate a very similar behavior). These observations are consistent with a p-type semiconducting nanotube doped by adsorbed molecules.<sup>4,5</sup> As an added proof that the nanotubes grown here are SWNTs, samples grown on powdered catalysts under similar conditions were proven to be high quality SWNTs using TEM and Raman spectroscopy.<sup>14</sup>

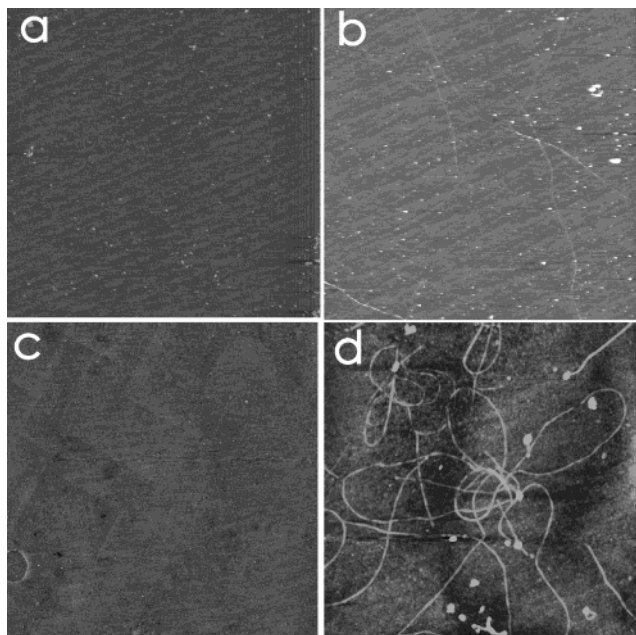
We have found that the thermal pretreatment of CO at 500 °C in a separated furnace was crucial to obtain clean



**Figure 3.** AFM images of SWNTs grown on Si/SiO<sub>2</sub> surfaces at different hydrogen concentrations. (a) pure CO, (b) 20% H<sub>2</sub> in CO, (c) 50% H<sub>2</sub> in CO, and (d) 80% H<sub>2</sub> in CO. All images are 10 × 10 μm.

SWNT samples. Without the pretreatment, the entire substrate surface was covered by nanosized particles, making the sample unusable. We believe these particles are caused by the decomposition and catalytic effect of an iron pentacarbonyl (Fe(CO)<sub>5</sub>) impurity presented in commercial CO. A strong evidence to support our conclusion is that the quartz tube in the first furnace turns gray/black after each experiment due to deposition of iron and carbon, while the quartz tube in the second furnace is clean. This observation may explain why there is no previous report of the surface growth of SWNTs using CO as feed gas, although growth of SWNTs in bulk using CO CVD has been well studied.

The second important factor we have found is the effect of hydrogen. Figure 3 shows typical results with different H<sub>2</sub> concentration in the feed gas. All substrates were prepared to have same density of Fe/Mo nanoparticles before SWNT growth. Using pure CO as feed gas, the yield of SWNT was extremely low: there were almost no nanotubes on the substrates (Figure 3A). When 20% H<sub>2</sub> was added, the amount of SWNTs was greatly increased (Figure 3B). The highest yield of SWNTs was achieved when the concentration of H<sub>2</sub> was between 35% and 65% (Figure 3C). As the concentration was increased above this range, SWNT growth was gradually suppressed (Figure 3D). The Si/SiO<sub>2</sub> surface was very clean with no amorphous carbon deposition under all H<sub>2</sub> concentrations. Unlike methane CVD, which requires precise control of experimental conditions such as the growth temperature, composition of feed gas, and type of promoter used in the experiment<sup>11</sup> to grow clean SWNTs on surfaces, the growth conditions using the new method can be satisfied over a broad range of temperature and feed gas compositions. Satisfactory growth yield can be achieved when the reaction temperature is between 800 and 900 °C and for hydrogen



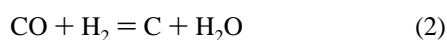
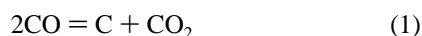
**Figure 4.** AFM images of SWNTs grown on  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  surfaces at different hydrogen concentrations. (a) pure CO on  $\text{Al}_2\text{O}_3$  substrate, (b) 40%  $\text{H}_2$  in CO on  $\text{Al}_2\text{O}_3$  substrate, (c) pure CO on  $\text{MgO}$  substrate, and (d) 40%  $\text{H}_2$  in CO on  $\text{MgO}$  substrate. All images are  $5 \times 5 \mu\text{m}$ .

concentration ranging from 20% to 80%. To focus the effect on feed gas, we have fixed all our growth temperatures at  $900^\circ\text{C}$ .

In addition, this new method has much higher growth efficiency in terms of the ratio of the number of SWNTs grown to the number of the Fe/Mo nanoparticles on the surface. Under the optimal conditions, the ratio is about 1:10 to 1:15, which is much higher than the result from the similar procedure using methane as feeding gas.<sup>13</sup>

Such  $\text{H}_2$  effect was also present when other substrates were used. As shown in Figure 4, on alumina and magnesium oxide substrates, when pure CO was used, the yield of SWNTs is extremely low. With addition of hydrogen, the yield is improved significantly. However, substrate still plays an important role in determining the relative yield of nanotubes. Among the three substrates, Si/SiO<sub>2</sub> shows the highest yield of SWNTs and alumina the lowest. More work is being done to understand the substrate effect.

To understand the effect of hydrogen, we have to focus on the chemical reactions that happen in our system. On the surface of the catalyst nanoparticles, two chemical reactions are responsible for carbon deposition:



When pure CO is used, the Boudouard reaction 1 is the only reaction for the production of carbon. Previous studies for bulk growth on both supported catalyst<sup>15</sup> and catalysts formed in gas phase<sup>16</sup> have shown that CO disproportionation is the rate-limiting step in the synthesis process. After hydrogen

is introduced into the system, the reaction rate for the formation of carbon is increased. Previous studies on the impact of addition of  $\text{H}_2$  on the SWNTs yield in gas-phase synthesis of SWNTs<sup>16</sup> have shown an optimal concentration of 25%  $\text{H}_2$  for the highest yield. In addition, several groups have reported enhanced yield of solid carbon product with addition of  $\text{H}_2$  to CO.<sup>17–20</sup> Such an enhancement in carbon production can be interpreted in two ways. First carbon deposition can be accelerated directly through hydrogenation of CO (reaction 2). Second, it is also reported that adsorbed  $\text{H}_2$  on the catalyst surfaces catalyzes the disproportionation of CO (reaction 1).<sup>18</sup> Our observation does not allow us to rule out any one of the mechanisms. It is possible that both mechanisms are in effect. Taking such acceleration in carbon deposition into account, it is feasible to explain the observed higher yield of nanotubes with CO and  $\text{H}_2$  mixture as caused by the increased carbon deposition rate on the surface of the catalysts.

In conclusion, we present a new CVD method to grow SWNTs on surfaces with high efficiency using CO and hydrogen mixture as feed gas. The formation of SWNTs is greatly enhanced by addition of hydrogen. The highest yield can be achieved within a large window of  $\text{H}_2$  concentration and temperature, so the results are easily reproducible. The SWNTs grown by this method have the advantage that they contain fewer defects than the samples prepared by deposition of bulk synthesized SWNTs since there is no ultrasonic agitation or purification involved. For researchers who are interested in exploiting the unique electronic properties of SWNTs, this new method represents a more reproducible and efficient way to prepare well separated individual SWNTs on substrates directly.

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