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Is molybdenum necessary for the growth of single-wall carbon nanotubes from CO?

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Abstract

Catalytic mixtures of molybdenum and cobalt have been considered essential for the growth of single-wall carbon nanotubes (SWCNT) from carbon monoxide by the chemical vapor deposition method. Here we demonstrated extensive growth of SWCNT with only cobalt as catalyst. The typically subsequent stage of annealing the catalyst in the presence of hydrogen was also eliminated. This process resulted in a near-100% yield of essentially defect-free chiral tubes. Use of electrochemical deposition of the catalyst seed particles may open the door for the production of massive electronic interconnect assemblies of these nanotubes.

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Single-wall carbon nanotubes (SWCNT) have stimulated extensive attention recently [1,2]. Their growth and structure have been a source of numerous studies [3]. One of the growth techniques, which has now established itself as a mainstream method involves the catalytic disproportionation of CO on bimetallic Mo/Co catalysts in a conventional CVD system [4,5]. It was thought that such a method would require a rough surface to support the bimetallic catalyst particles. This led us to synthesize SWCNT within a coherent array of silica sphere matrix [6]. The tubes formed as

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small bundles or, individual strands that were well separated and had an average individual tube diameter of 0.9 nm. The resulting composite films were subsequently used to demonstrate the unique nonlinear optical properties of SWCNT within the three-dimensionally confining environment of opalline, photonic crystal structures [7]. Here we report an extension of this growth method for SWCNT to include untreated flat substrates while using Co only as a catalyst, thus opening the door for a more efficient production of SWCNT.

We used flat substrates of polished silicon wafers and quartz. The nano-size Co particles catalytic seeds were deposited by laser ablation, sputtering and electrochemical techniques. Additional substrates were made of ordered arrays of

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silica spheres with various sphere diameters. These were prepared by hydrolysis of tetraethoxysilane in a mixture of ammonium hydroxide, water and ethanol [6]. The resulting silica spheres were then dispersed in ethanol to form a suspension. The suspension was mixed with methanol solutions of cobalt nitrate and then dispersed on the substrates. Cobalt was also successfully laser ablated on pristine opalline structures.

Cobalt particles were also electrochemically deposited on tungsten-coated substrates. In these experiments the tungsten was used as a cathode. The experiments were conducted in a three-electrode cell with a reference Ag/AgCl electrode and aqueous electrolyte of 0.25 M Na₂SO₄ and 1 mM CoSO₄. The applied potential was controlled between -900 and -1200 mV at potentiostatic transient. The sizes of the catalytic cobalt particles determined from scanning electron microscope images ranged between 20 and 40 nm.

The growth of the SWCNT was conducted in a quartz tube reactor placed in a horizontal tubular furnace. In the case of cobalt nitrate dispersed in the opalline structure, we used the following procedure: following calcination for 30 min in air at 500 °C to decompose the catalyst nitrate to the corresponding oxide, the samples were heated in pure hydrogen at 500 °C to convert the oxides to sub-oxides and metal particles. For the metallic Co particles, which were deposited by physical or electroplating techniques, we followed this recipe: the temperature at the reaction zone was raised to 700 °C, and subsequently pure CO was introduced at 1 atmosphere and a flow rate of 100 cm³/min. and kept under these conditions for 30 min. After completion of the reaction, the reactor was allowed to cool down under flowing argon.

A combination of atomic force microscopy (AFM), scanning electron microscopy (SEM) and Raman spectroscopy was used to characterize the resulting material. The Raman spectra were acquired in a back-scattering geometry using a confocal arrangement. Micro-Raman spectrometers equipped with Peltier stage cooled, charge-coupled device (CCD) detectors were used. The 514.5 nm (2.41 eV) line of an argon ion laser or, the 632.8 nm (1.96 eV) line of a HeNe laser were used to excite the spectra at a power density of approximately

1 kW/cm². The spatial resolution of the imaging system was either 1 or 2 μ m, depending on the objective lens. The acquisition time was typically 10 s averaged over 10 scans.

In Figs. 1a and b, we show SEM images of SWCNT on Si and quartz when using laserablated Co particles. It is evident that bundles with diameters around 20-30 nm were formed between the Co particles. Raman spectroscopy clearly indicated that these bundles are SWCNT. As can be seen from the picture, the growth is directed from one catalytic point to another to form a bridge. Although details of the growth are not yet fully clear, such a process may be essential for a selective growth, which may lead to the fabrication of massive electronic interconnects. Fig. 1c presents AFM images of SWCNT and Co on similar samples and reiterates the fact that the SWCNT bundles bridged the gap between two catalytic points.

Previous reports of carbon nanotube (CNT) produced by CVD methods with Co catalyst resulted in predominantly multi-wall tubes [8]. In contrast, here we show an unexpected selectivity growth of single-wall tubes. Variations in the laser ablation parameters led to different distribution of the catalytic seeds yet; the average diameter of the SWCNT bundles shows little dependence on the seed size (10–20 nm). In addition, systematic experiments were conducted to elucidate the function of H₂ reduction on the Co particles. It turned out that H₂ reduction is not critical to functionalize Co as a catalyst. This further simplifies the synthesis process of SWCNT.

In Fig. 2, we show SEM images of directed growth of SWCNT between islands of the tungsten electrode. Here, the catalytic Co particles were grown by electrode position. The distribution and size of the cobalt particles could be controlled by the deposition parameters, such as, the potential and current density. As can be seen from Fig. 2, domains of aggregated Co particles were formed on the tungsten electrode. The average domain size was about 2 μ m, with 5 μ m spacing between the domains. As noted previously, the average Co particle size was determined to be 30 nm. Both the electrochemically induced particle size and morphology of Co are likely to play important roles in





Fig. 1. SEM images of SWCNTs when using laser-ablated Co particles as catalyst. (a) On a quartz substrate. (b) On a Si substrate. (c) AFM picture of SWCNT on quartz substrate. Left: amplitude mode (bright spots correspond to height of 50 nm). Right: tapping mode. Note the bridging effect in all pictures.

the directed growth of the SWCNT. Electrochemical deposition of the catalyst followed by CVD growth would therefore be expected to make massive electronic interconnects between electrodes for device applications.

Raman spectroscopy was used to further characterize the samples. Fig. 3 shows a typical Raman spectrum taken from samples with laser-ablated Co particles. Raman signals at 520 and 939 cm⁻¹ are due to phonons associated with the Si substrate [9]. The inset shows the low frequency range of the Raman spectrum of SWCNT with a rich structure of bands. These bands correspond to the radial breathing mode (RBM) of single tubes and have been shown to be inversely proportional to the diameter of a single SWCNT, d_t . Since in this frequency range, the Raman-active modes of graphite and graphitic carbons are absent, one can assess the presence of SWCNT in the samples and determine its average diameter and type [10–12].



Fig. 2. SEM images of SWCNTs at two magnifications. The catalyst was electrochemically grown Co particles on tungsten electrodes. Note the connection made by a single tube bundle between two Co particles on islands of the tungsten electrode.

Raman scattering of SWCNT are governed by singularities in the electronic density of states due to its quasi-one-dimensional (1D) nature: the RBM and tangential mode (TM) lines in the first-order Raman spectrum are resonantly enhanced when the laser excitation energy (E_{laser}) is close to an energy separation between singular states, such as occurs for $E_{ii} = E_{11}, E_{22}, \dots$ Resonance in Raman can also occur for the scattered photon, $E_{\text{laser}} = E_{ii} + E_{\text{phonon}}$ for the anti-Stokes processes and $E_{laser} = E_{ii}$ – $E_{\rm phonon}$ for Stokes processes. The energy of these allowed Raman-active transitions depends both on the diameter and on the metallic or, semiconducting character of the tubes. Following the results of [11], semiconducting tubes with diameters around 0.8 and metallic tubes with diameters around 1.1 nm



Fig. 3. Raman spectrum of SWCNTs produced by decomposition of CO at 700 °C on a flat Si substrate with laser-ablated catalytic Co particles. The spectrum obtained was excited at $\lambda = 632.8$ nm (1.96 eV) using a He–Ne laser. The inset shows the low frequency Raman lines. The peaks at 520 and at 939 cm⁻¹ correspond to vibration lines of the Si substrate.

can be resonantly excited with 1.96 eV ($\lambda =$ 0.6328 µm). Similarly, semiconducting tubes with diameter around 0.7 and 1.2 nm, and metallic tubes with diameter around 0.9 nm may be resonantly excited with 2.54 eV ($\lambda = 0.5145 \mu m$). When excited by 2.54 eV, the Raman spectra in the TM range (1400–1700 cm⁻¹) display a regular symmetric shape characteristic of semiconducting tubes rather than the asymmetrically broadened Fano lineshape of metallic tubes. A symmetric profile with a dominant peak around $\omega = 1590 \text{ cm}^{-1}$ and two relatively sharp structures around $\omega = 1560 \text{ cm}^{-1}$ and $\omega = 1550 \text{ cm}^{-1}$ were observed (Fig. 3). In this spectral region, metallic tubes with a diameter around 0.9 nm would display an intense, broad and asymmetric band around $\omega = 1540 \text{ cm}^{-1}$. The absence of these features indicates that metallic tubes in the 0.9 nm diameter range are not present in our sample and the observed spectrum may be attributed to semiconducting tubes either with 0.7 or 1.2 nm tube diameter. Similar characteristics were observed with excitation at 1.96 eV and suggests once again, that 1.1-1.2 nm diameter metallic tubes Table 1

Possible chirality assignments for both the metallic and semiconducting nanotubes in our samples and their ω_{RBM} (calculated and observed) upon the excitation of 632.8 nm (1.96 eV) laser line

Chiral vector index (n, m)	Diameter of tube d_t (nm)	Radial breathing mode frequency ω_{RBM} (cm ⁻¹)		Optical transition mode	
		Calculated ^a	Experiment	Energy (eV) ^b	Denotation ^c
(18,0)	1.429	168.9	168	1.84	E_{11}^{m}
(9,9)	1.238	193.0	190	2.02	E_{11}^{m}
(12,6)	1.260	189.9	190	1.98	$E_{11}^{\rm m}$
(11,5)	1.126	211.0	216	2.18	E_{11}^{m}
(8,8)	1.100	215.7	216	2.28	$E_{11}^{\rm m}$
(10,3)	0.936	251.1	256	1.96	E_{22}^{s}
(11,1)	0.916	256.4	256	2.03	E_{22}^{s}
(7,5)	0.829	281.9	284	1.93	E_{22}^{s}
(8,3)	0.782	298.1	300	1.87	E_{22}^{s}

^a Using the expression $\omega_{\text{RBM}} = 223.5/(d_t(nm)) + 12.5$ and assuming a C–C bond distance of 0.144 nm.

^b See [11,12].

 $^{c}E_{ii}^{s}$ denote *i*th optical transition of a semiconducting tube while E_{ii}^{m} denotes *i*th optical transition energy of a metallic tube.

are not present in our samples: the Raman spectra raises may be attributed to 0.8 nm diameter semiconducting tubes. Thus, based on these highfrequency considerations our results lead to the conclusion, that our samples contain either 0.7 or 1.2 nm diameter tubes. On the other hand, the presence of RBM lines in the low-frequency range, between 250 and 300 cm⁻¹, indicates the abundance of semiconductor tubes with diameters of 0.9 nm and smaller (see Table 1) in addition to small amount of metallic tubes with diameters of 1.1 and larger. Transmission electron microscopy (TEM) of SWCNT within the voids of opalline structure supports the assignment of average tube size of 0.9 nm and smaller. The overall conclusion is that SWCNT in our samples are predominantly semiconductive and are of a size range of 0.7-0.9 nm.

Presence of a weak Raman line near $\omega = 1320$ cm⁻¹ (with 1.96 eV excitation) in Fig. 3 is often identified as the analogous of the D-band in nanocrystalline graphite, which is assigned to disordered sp³ defects. The relatively weak intensity of this line indicates that defects of this type on the sidewalls of the SWCNTs in our sample are very few.

The low frequency Raman spectral region from $\omega = 168 \text{ cm}^{-1}$ to $\omega = 300 \text{ cm}^{-1}$, corresponds to a large distribution of tube diameter (0.78–1.43 nm) and therefore, many different tube geometries need to be considered. Our notch filter starts to cut-off

at 168 cm⁻¹, which precludes third-resonantly enhanced transitions of the semiconductor tubes when excited by the He-Ne laser line (1.96 eV) such transitions are expected in the Raman frequency range between 130 and 160 cm^{-1} . In the case of metallic tubes we limit our attention to resonantly enhanced transitions between two adjacent states. We limit our attention to transitions between adjacent and next-to-adjacent states for semiconductor tubes. The weak peaks presented at $\omega = 384 \text{ cm}^{-1}$ and $\omega = 428 \text{ cm}^{-1}$ are considered as second-harmonic phonons associated with those of the lines at 190 and 216 cm⁻¹, respectively. The assignment of low frequency peaks is given in Table 1. We based this assignment on two criteria: (i) large Raman intensity values are expected only when the transition energy E_{ii} , is close to the energy of the laser line, E_{laser} and (ii) considering the trigonal warping effect [13], large Raman intensity values are expected for armchair or, chiral nanotubes with a large chiral angle. Judging from Table 1 and Fig. 3, most SWCNT in our samples can be assigned as chiral. Whether our synthesis method can be further developed to control the chirality of SWCNT produced is still an open question and further study along this direction is underway.

In summary, we have demonstrated that very high quality SWCNT can be grown on flat surfaces by use of only Co as a catalyst and pure CO as the carbon precursor. No additional annealing stage with hydrogen was necessary. Such simplifications may help to scale up the growth process. In addition, it seems that SWCNT grown this way have a preferential growth, connecting two catalytic points, thus, may enable the fabrication of large scale electronic devices.

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