Aerosol Catalyst Particles for Substrate CVD Synthesis of Single-Walled Carbon Nanotubes**

By Paula Queipo, Albert G. Nasibulin, Hua Jiang, David Gonzalez, and Esko I. Kauppinen*

Individual single-walled carbon nanotubes (SWCNTs) were grown by a CVD method on thin SiO₂ films using iron and carbon monoxide as the catalyst material and the carbon source, respectively. Catalyst particles were produced via physical vapor deposition (PVD) as an aerosol using a hot-wire particle generator and then deposited by two different approaches. Particles collected onto the substrates by diffusion inside the reactor led to the production of large diameter SWCNTs (∼3–6 nm) with lengths up to 30 μm. An outside deposition, via electrostatic precipitator, resulted in the synthesis of longer SWCNTs (≥50 μm) with smaller diameters (<2 nm).

Keywords: Aerosol, Carbon nanotubes, Catalyst particle size, Hot-wire particle generator, Transmission electron microscopy

1. Introduction

SWCNTs have unique properties that have prompted their use in many different fields.[1–3] Many devices such as field-emission displays, field-effect transistors (FETs), or scanning probe microscope tips have already been built using CNTs.[2,4] Success in many applications strongly depends on the ability to synthesize CNTs with controlled properties. For instance, semiconducting SWCNTs are needed for FETs,[5] controlled diameter CNTs are necessary for the preparation of hybrid materials,[6] or gas storage,[7] and vertically aligned CNTs are important for field-emission applications.[8] There are three main methods of producing SWCNTs:[9] arc-discharge, laser ablation, and CVD. Arc-discharge and laser ablation are based on the vaporization of solid carbon targets including transition metals at high temperatures. Generally, a complex mixture including CNTs, graphic and amorphous carbon, and catalyst particles is obtained by these methods, making purification an unavoidable step.[10] CVD has been described as a versatile technique for the production of CNTs at low temperature and under ambient pressure,[9] and nanotubes with varying structures, controlled diameters, and chiralities have already been grown by this method.[11–14] Recent results[13–16] suggest that the diameter of CNTs is correlated to the size of the catalyst particles. For that reason, the synthesis of size-controlled nanoparticles represents a promising way to control the diameters of the CNTs. In most of the CVD methods, catalyst particles are prepared by wet chemical methods and deposited on the substrate by impregnation or other coating techniques.[11,14–17] Such approaches involve various intermediate time-consuming stages such as preparation of particle precursor solutions, deposition onto the substrate, and calcination. Furthermore, the control of the particle size normally implies the use of surfactants that can cause particle contamination.[14–16] Another common way of producing nanoparticles is to deposit a thin metal film on substrates by sputtering[18] or evaporation.[18] The film thickness and/or the preheating temperature have been used to control the size of the nanoparticles, and so the resultant CNT diameters. However, the formation of nanoparticles when heating the film is a random process and a wide distribution of diameters is still generated. Thus, it is very desirable to develop straightforward methods for the production and deposition of catalyst nanoparticles with controlled sizes. Aerosol techniques represent a simple and promising alternative. For instance, the laser ablation method was used to generate various kinds of nanoparticles for the synthesis of both single- and multiwalled CNTs.[19–21] In that case, a differential mobility analyzer (DMA) was used for the particle size selection. Recently, our group has reported on the effective production of size-controlled Fe and Ni aerosol catalyst particles based on evaporation-condensation, i.e., PVD, using a hot-wire generator (HWG).[22–24] This metho-
od allows the synthesis of metal particles under ambient pressure with sizes in the range 1–15 nm and a geometric standard deviation as small as 1.2. These nanoparticles were subsequently used for the growth of SWCNTs in the gas phase.\cite{22,23}

In the present study, we have combined the synthesis of aerosol particles with their further utilization as catalysts for substrate CVD production of CNTs. Two different methods were used. In the continuous route, catalyst particles generated by a HWG were introduced into a laminar flow reactor and deposited directly in the reactor onto perforated SiO2 films by diffusion. The non-continuous approach was developed in order to increase particle collection efficiency. In this case, particles were predeposited on substrates outside the reactor via electrostatic forces. CO and Fe were used as the carbon source and catalyst particles, respectively.

2. Results and Discussion

2.1. Synthesis of CNTs in a Continuous Process

In an attempt to avoid the common intermediate stages for catalyst preparation, a continuous CVD method for CNT synthesis was developed. In this approach, catalyst particle formation, deposition, and the synthesis of CNTs took place inside the reactor in subsequent steps. Catalyst particles were introduced at reactor set temperatures of 400, 500, and 600 °C. In order to prevent sintering of the particles, resulting in their excessive growth, CO was introduced into the reactor. The carbon prevented any additional growth of the particles, making them suitable for the synthesis of SWCNTs, and also facilitated control of the particle size and thus, the diameter of the nanotubes. In order to check the conditions of the particle synthesis, aerosol measurements using a differential mobility analyzer (DMA) were carried out. The number size distributions (NSDs) of the particles coming from the reactor at various temperatures are shown in Figure 1. The mean mobility diameter of iron particles covered by carbon was typically around 4.5 and 5.5 nm at 400 and 500 °C, respectively. When increasing the collection temperature to 600 °C, a bimodal distribution was obtained with a shift to larger particle sizes. In this case, the peaks were observed at 4.5 and 8 nm and related to catalyst particles covered by carbon and gas-phase grown CNTs, respectively.\cite{22,23,25}

The produced nanoparticles were deposited on the substrate downstream of the reactor by diffusion\cite{29} at a temperature ca. 120 °C (point C1, Fig. 2). After the collection and the nanotube growth at 880 °C, the products obtained were directly analyzed by transmission electron microscopy (TEM). It was found that CNTs were formed from the particles collected at these three temperatures, however, their morphologies differed. Figure 3 shows a typical example of the as-grown nanotubes. The CNTs synthesized from particles collected at 400 and 500 °C were single-walled with lengths varying from approximately 3 to 30 μm (Fig. 3a and b, respectively). They were clean, i.e., almost no carbon deposits in their walls, and individual, i.e., not in bundles. High resolution TEM images showed that some of the SWCNTs had a catalyst particle attached to one end. As an example, Figure 4a shows an Fe particle of 4.9 nm in a ca. 5.5 nm diameter SWCNT. Inactive particles were also found in these samples. In order to avoid overestimated diameters due to flattening of CNTs caused by the van der
Waals interactions with the substrate,[27] these diameters were measured in the perforated area of the SiO₂ films. SWCNTs diameters estimated from TEM images had a distribution in the range 2.8–6.0 nm. Our results indicate that the nanotubes synthesized from the catalytic disproportionation of CO under these conditions are among the largest diameter SWCNTs produced by CVD methods.[28,29] As an example, Gu et al.[28] observed SWCNTs with diameters up to 7.6 nm grown using CH₄ as the feedstock. Large diameter tubes are particularly interesting for studying diameter-dependant properties,[7] for developing new materials,[6] or for applications such as field-effect transistors[30] or gas-storage media.[7]

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Waals interactions with the substrate,[27] these diameters were measured in the perforated area of the SiO₂ films. SWCNTs diameters estimated from TEM images had a distribution in the range 2.8–6.0 nm. Our results indicate that the nanotubes synthesized from the catalytic disproportionation of CO under these conditions are among the largest diameter SWCNTs produced by CVD methods.[28,29] As an example, Gu et al.[28] observed SWCNTs with diameters up to 7.6 nm grown using CH₄ as the feedstock. Large diameter tubes are particularly interesting for studying diameter-dependant properties,[7] for developing new materials,[6] or for applications such as field-effect transistors[30] or gas-storage media.[7]

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

Electron diffraction patterns were taken from some of the isolated SWCNTs in order to determine their chiralities and to more accurately measure their diameters. An example is shown in Figure 5. This tube is indexed as (25,24) with a diameter of 3.3 nm and a helical angle of 29.3°.

CO₂ concentrations up to 2000 ppm were measured by Fourier transform infrared (FTIR) spectroscopy in the effluent gas coming from the reactor. Thus, for the further development of our CVD method, the formation of CNTs in the gas phase should be avoided and, in consequence, collection temperatures should be < 600 °C.

In order to improve control of the catalyst particle size and to avoid possible losses due to diffusion on the reactor walls, Fe particles were also collected upstream near the HWG at ca. 400 °C (point C2, Fig. 2). This also avoided the gas-phase growth of CNTs, since nanotubes in the aerosol have been found to grow only in a limited space (growth window) in the high-temperature zone of the reactor.[51] The deposition onto the substrate was carried out under an outer flow of N₂ or CO. In this case particle sintering was prevented by reducing the distance between the substrate and the particle formation zone (from ca. 40 cm in the downstream configuration to ca. 4 cm in the upstream approach). The SWCNTs produced had a narrower diameter range (3.7–5.6 nm).
2.2. Synthesis of Carbon Nanotubes in a Non-continuous Process

The above-mentioned continuous approach for the growth of CNTs allowed us to produce size-controlled SWCNTs in a one-step process. However, the main disadvantages of the described process were the low efficiency and poor control of the catalyst particle deposition onto substrates. In order to improve these, the catalyst particle synthesis and their collection at ambient temperature were performed outside the reactor using a bulb HWG and an electrostatic precipitator (ESP) (Fig. 6). The application of an electrical field enabled us to significantly increase the particle collection efficiency with respect to that obtained by diffusion forces alone.[26] In this case, Fe particles were produced by a bulb HWG and had a mean diameter around 3 nm as measured by high-resolution DMA.[24] The hot wire and the substrate were also closely placed (as in the upstream collection in the reactor) to avoid losses and excessive particle growth.

Due to the improved control of the deposition process, more nanotubes were synthesized. Scanning electron microscopy (SEM) and TEM studies revealed a significant change in the diameters and lengths compared to the CNTs synthesized by the continuous approach. An example of the CNTs produced is depicted in Figure 7. They were also single-walled, however, with diameters from 1.2 to 1.8 nm and longer than 50 μm. Normally they were entangled as can be seen in Figure 7b. A few ~4 nm diameter SWCNTs were also found. As particle collection took place outside the reactor, the grid is exposed to the ambient atmosphere during transportation from the ESP to the reactor. Thus, deposited particles can be oxidized and become inactive for growth. Moisala et al.[3] showed that metal oxide particles should be reduced in order to behave as catalysts in CNT formation. For that reason, a higher H₂ concentration was added to the flow before and during the growth step. Nevertheless, H₂ can also play another role in the system, providing additional carbon for the synthesis of the CNTs, due to the CO hydrogenation reaction, as shown in Reaction 2.

\[
H_2(g) + CO(g) \leftrightarrow C(s) + H_2O(g), \quad \Delta H = -136 \text{ kJ mol}^{-1} \quad (2)
\]

It was previously found in the aerosol method that the replacement of an H₂/N₂ mixture by pure H₂ led to an increase in CNT length from 60 to 300 nm.[31] Thus, the production of longer SWCNTs by CVD can also be explained by the use of a higher H₂ concentration.

2.3. Synthesis of CNTs Directly from the Ni Grid: Control Experiments

Commonly used carbon-coated copper TEM grids were not suitable as substrates in our process due to their low resistance to high temperatures. Therefore, Ni grids with perforated thin SiO₂ films were chosen. However, it is known that Ni can be used as a catalyst for the growth of CNTs.[8,19,32] Furthermore, Du and Pan[32] grew multiwalled CNTs by directly using Ni grids as catalytic active substrates. When analyzing the samples obtained with both approaches, it was observed that many of the SWCNTs had one of their ends on the Ni metal grid (Fig. 8a). It can be speculated that CNTs start to grow from Ni. Therefore, a blank experiment was carried out, in which the Ni grid, without deposited Fe particles, was heated in the reactor under suitable conditions for CNT growth.

Very few CNTs were found, indicating a low catalytic activity of the Ni metal grid. CNTs produced in this case were
mainly double-walled (Fig. 8b). They also had large diameters (~7–8 nm), but they were covered with carbon deposits along their length.

In order to further examine the possible influence of Ni, energy dispersive X-ray (EDX) spectroscopy of the samples obtained by the outside and inside approaches, was carried out. Particles attached at one end of the tubes were specially analyzed to determine their origin. Using this technique, no Ni was found in any particle suggesting that the SWCNTs are formed from Fe catalyst nanoparticles and not from Ni or Fe–Ni alloys.

3. Conclusions

Aerosol catalyst particles were produced by a physical vapor nucleation method and deposited onto thin, perforated, SiO2-coated Ni TEM grids for their further use in CNT growth using CVD. Two different approaches were developed: the continuous and noncontinuous. In the continuous method, particles collected onto the substrates by diffusion inside the reactor led to the synthesis of large diameter (3–6 nm) SWCNTs with lengths up to 30 nm. These nanotubes are among the largest diameter SWCNTs produced by CVD. When the particle collection was carried out at temperatures ≥ 600 °C, CNTs were formed in the gas phase. In the noncontinuous approach, an outside particle deposition via electrostatic forces resulted in the formation of longer (more than 50 μm) SWCNTs with smaller diameters (below 2 nm). The increase in the H2 concentration in the system contributed to the increase in the length of SWCNTs. Ni particles coming from the grid were found to act as a catalyst for the growth of large-diameter double-walled CNTs.

4. Experimental

In order to control the catalyst particle synthesis, aerosol measurements were performed downstream of the reactor. The number size distributions of the aerosol product in the range 2–100 nm were measured by a DMA system consisting of a charger, classifier, and an ultratine condensation particle counter (UCPC 3027, TSI Inc. USA).

Perforated SiO2 film supported on Ni TEM grids (Structure Probe, Inc. USA) were used as the substrates. The morphology of the as-grown CNTs was examined by field emission SEM (Leo Gemini DSM982) and field emission TEM (Philips CM200 FEG). EDX (Noran Voyager M305) analysis was performed to characterize the elemental composition of the substrate and the deposited particles. The gas phase composition after the reactor was analyzed on-line by a Gasmet FTIR spectroscope.

Production and Deposition of Catalyst Particles in the Continuous Method: Fe catalyst particles were produced under ambient pressure by metal vaporization, subsequent vapor cooling resulting in particle formation due to supersaturated vapor nucleation, and particle growth by vapor condensation and cluster coagulation using a HWG [22,23]. The HWG consists of a resistively heated thin (0.25 mm diameter) iron wire in a flow. It was located inside a 25 cm long ceramic tube (external and internal diameters of 12.5 and 9 mm, respectively) that was inserted inside a vertical laminar flow reactor. The device consisted of a stainless-steel tube with an inner diameter of 2.2 cm inside a 44 cm long furnace (Fig. 2). The stainless steel tube used in the experiments was composed of Fe(53), Ni(20), Cr(25), Mn(16), Si(0.5), and C (0.05 wt.-%). The end of the HWG tube was placed at a reactor temperature of about 400 °C. The produced Fe catalyst particles were carried into the reactor under a mixture of H2/N2 (mole component ratio of 7:93) with a flow rate of 360 cm3 min−1. In the reactor, the flow containing the nanoparticles was mixed with an outer flow of CO or N2 (380 cm3 min−1).

A stainless-steel rod of 6 mm in diameter with a holder was designed for inserting the substrate into the furnace. Due to the temperature profile along the reactor, the substrate temperature was controlled using a thermocouple inserted inside the rod. The grids were placed in two different positions inside the reactor: downstream and upstream (positions C1 and C2, respectively in Fig. 2). The reactor set temperatures were 400, 500, and 600 °C when collecting downstream, while the temperature was maintained at 850 °C for the upstream approach. Measured temperatures in positions C1 and C2 were ~120 and 400 °C, respectively. Particle collection was carried out for 40 min.

Production and Deposition of Catalyst Particles in the Non-continuous Method: Fe catalyst particles were produced by the HWG located inside a glass bulb. An ESP (InTox Products, USA) was placed at the outlet of the bulb as shown in Figure 6. The perforated SiO2-coated Ni TEM grids used as substrates were located inside the ESP. A N2/H2 gas mixture (mole component ratio 93:7) was passed through the HWG at a flow rate of 890 cm3 min−1. The grid was then attached to the rod.

CNT Growth: For the growth of CNTs, the substrate was located in the high temperature zone of the reactor (Fig. 2, position G). After the particle collection inside the reactor, the rod was lifted up or down to this position. The reactor was operated under ambient pressure and at a set temperature of 850 °C. The substrate temperature was controlled by a thermocouple and maintained at 880 °C for 30 min. After the reaction, in order to cool the substrates, the rod was lifted up to the cooling zone (porous tube dilutor with a 2 L min−1 N2 flow rate) and the CO flow in the reactor was replaced by N2.

In the case of iron deposited using the ESP, the substrates were placed directly in position G. Before the CO introduction into the system, catalyst particles were reduced at 880 °C for 5 min under a flow of H2 and N2 (340/380 cm3 min−1). Afterwards, the N2 flow was replaced with CO (380 cm3 min−1) while the H2 flow rate was lowered to 240 cm3 min−1.

Received: November 2, 2005
Final version: February 22, 2006