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High quality SWCNT synthesis in the presence of NH_3 using a vertical flow aerosol reactor

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High quality single-walled carbon nanotubes (SWCNTs) were synthesized in the presence of ammonia (NH_3) using a vertical flow aerosol reactor and collected directly from the gas phase in a simple continuous process. The morphology of the carbon network and the quality of the SWCNTs was investigated combining local and overall probes such as TEM, electron diffraction, STM, Raman and optical absorption.

Representative STM image of a single-walled carbon nanotube synthesized by aerosol CVD (8 x 2 nm, measured at a bias of 1V and a tunneling current of 0.2 nA).

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1 Introduction Among the various methods to synthesize carbon nanotubes (CNTs), chemical vapour deposition (CVD) has been found to be efficient and selective for either single-walled (SWCNT [1-4]) or multiwalled [5] carbon nanotube growth. In particular, floating catalyst, i.e. aerosol CVD [6-8], has potential for large-scale SWCNT production, since it is a continuous process involving both catalyst particle formation and SWCNT nucleation and growth. The product can be directly collected from the gas phase in room temperature at the reactor outlet without disturbing the synthesis.

Furthermore, methods from aerosol science can be adapted to provide on-line information on the reactor process conditions [9]. This helps to partially eliminate the need for time and resource consuming *collect samples - characterize properties - alter parameters - iterate* -cycles. Such methods include the measuring of particle mobility size distributions at reactor outlet by condensation particle counter / differential mobility analyzer (CPC/DMA [10]), and gas-phase composition measurements by Fourier trans-

form infrared spectroscopy (FT-IR), yielding information about the chemical composition of the reactor atmosphere.

In this contribution, we study the effect of ammonia (NH_3) in producing high quality SWCNTs from CO using vertical flow aerosol CVD with Fe catalyst [11, 12]. The produced SWCNT material has been characterized by optical (Raman, optical absorption) and microscopic (TEM, SEM, STM) methods.

2 Experimental methods

2.1 Synthesis The vertical flow aerosol synthesis method used has been modified from [11]. Briefly, catalyst particles were grown *in situ* by ferrocene vapour decomposition [9, 11]. The precursor was vaporized by passing ambient temperature CO (with a flow rate of 300 cm³/min) through a cartridge filled with ferrocene powder. The flow containing ferrocene vapour was then introduced into the high temperature zone of a ceramic tube furnace through a water-cooled probe and mixed with a CO side flow (100 cm³/min). The partial vapour pressure of ferrocene in the reactor was maintained at 0.7 Pa. The reactor set tempera-

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ture was either 825 or 1000 °C, with the maximum wall temperature being about 60 °C higher.

In addition to CO, small amounts of NH₃ (0 to 5000 ppm) and CO₂ (0 to 5000 ppm) were added with the CO side flow, controlled by mass flow controllers (MFCs).

Samples were collected directly from the gas phase at reactor outlet either by an electrostatic precipitator (ESP [13]) on carbon coated copper grids, or by filtering on Millipore filter papers.

2.2 Characterization The aerosol mobility number size distributions (NSDs) in the size range of 15–300 nm were measured by a differential electrical mobility particle sizer system, consisting of a differential mobility analyser (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3022). The DMA system allowed the measurement of the electrical mobility of aerosol particles and to distinguish catalyst particle aggregates from naturally charged bundles of CNTs [9], which have a larger mobility diameter which depends on bundle size.

The morphology and structure of the product was investigated by scanning electron microscopy (SEM, Leo Gemini 982), transmission electron microscopy and electron diffraction (Philips CM200-FEG TEM at 80 kV, with Gatan 794 multiscan CCD camera). Also, low temperature scanning tunnelling microscopy (STM, Omicron Nanotechnology, operating under UHV conditions at 5K) was conducted for samples collected directly on gold substrates by ESP [14].

Raman spectra for samples collected on Millipore filters were measured at ambient conditions using a 632.81 nm HeNe laser (Jobin Yvon Labram 300, Stigmatic 300 spectrograph). Optical absorption spectra were measured using a double line UV-Vis-NIR spectrophotometer (Perkin Elmer lambda 900) after transferring the films from the filters onto glass plates [15].

The gaseous components of the reactor outlet gases were studied by Fourier-transform infrared spectroscopy (FT-IR, GASMET DX4000).

3 Results

3.1 Gas measurements FT-IR measurements of the reactor outlet gases investigated the chemistry taking place inside the reactor. Introducing 625 ppm of NH₃ increased the measured amount of CO₂ from 290 to 410 ppm. Note that some CO₂ is always produced on the reactor walls, and is vital to the synthesis of good quality SWCNTs in the ferrocene system [16]. Furthermore, 220 ppm of hydrogen isocyanide, HCN, was detected when NH₃ was introduced into the reactor. At 825 °C the effect of NH₃ was less pronounced due to the lower temperature and the amount of added CO₂, but the analyzable compounds remained the same. Note, however, the limitation of the method in not being able to detect symmetric molecules (e.g. N₂ and H₂).

Table 1 Descriptive statistics of the NSDs measured by DMA/CPC at 1000 °C and 825 °C with different amounts of in-

troduced CO₂ and NH₃. The columns show: synthesis temperature, introduced CO₂ and NH₃ flows in ppm of the inlet flow, geometric mean mobility diameter of the NSD, total concentration of nanotube bundles measured in 10⁶ particles/cm³, and a normalised figure of merit estimate of the yield in percent of the maximum at each temperature calculated as the product of geometric mean and total concentration.

Temp (°C)	Intr. NH ₃ (ppm)	Intr. CO ₂ (ppm)	Geo. mean (nm)	Total conc. (10 ⁶ /cm ³)	Yield est. (%)
1000	0	0	115.1	3.30	100
1000	250	0	65.3	0.76	13.1
1000	625	0	39.1	0.80	8.2
825	0	5000	98.2	3.08	100
825	500	5000	91.4	1.39	42.0
825	500	2500	99.1	1.00	32.8
825	1000	5000	58.9	0.17	3.3
825	1000	2500	76.2	0.11	2.8

3.2 Aerosol measurements With the help of CPC/DMA measurements of the NSDs at reactor outlet [9], we determined that the maximum amount of NH₃ allowed without severely disrupting CNT growth is very low, less than 0.05% (500 ppm) in terms of atomic N/C ratio in the inlet gases. Even this small amounts of NH₃ limit the yield at 1000 °C, which normally is higher than at 825 °C (see Table 1).

At 825 °C, CO₂ is introduced into the reactor for the optimal production of SWCNTs [16]. When 500 ppm of NH₃ was also introduced, there was a decrease in synthesis yield, illustrated by the descriptive statistics of the nanotube bundle mobility NSDs shown in Table 1. With 1000 ppm of NH₃ the yield was quite low, and changing the amount of introduced CO₂ did not affect it. Note that the normalised figure of merit estimate for the yield is included merely to facilitate comparison.

3.3 Sample morphology and structure SEM measurements of the product material deposited on TEM grids by ESP show a typical random network of nanotubes. Increasing the amount of introduced NH₃ beyond 500 ppm decreases both the number and the lengths of the tubes dramatically. With 250 ppm of NH₃ at 1000 °C and 500 ppm at 825 °C the network is somewhat sparser, but there is still a significant amount of product.

TEM observations show that the tubes produced without NH₃ were typical for the ferrocene system, with small bundles of SWCNTs about 300 nm in length at 1000 °C and few µm at 825 °C. See Fig. 1 for TEM images of a sample synthesized with 5000 ppm CO₂ and 500 ppm NH₃. Imaging and electron diffraction were conducted on 152 individual nanotubes or small nanotube bundles on a single TEM grid collected from those synthesis conditions, and only SWCNTs were found.

Figure 1 A representative TEM micrograph showing individual SWCNTs crossing a holey TEM carbon grid. The tubes appear straight and long (over 2 μm). Both high-resolution TEM image (b) and electron diffraction patterns (c and d) indicate the high quality wall structure of the nanotubes. Using intrinsic layer line distance analysis [27], the diffraction patterns (c and d) were indexed as (15, 13) for (c) and (15, 11) for (d), with tube diameters of 1.90 nm and 1.77 nm, respectively.

Atomic-scale resolution images from STM measurements of several tubes synthesized at 825 $^{\circ}\text{C}$ with 5000 ppm of CO_2 and 500 ppm of NH_3 with no post-synthesis annealing whatsoever reveal the fine crystalline structure of the SWCNTs, without any defect observed among the tubes investigated (see Figure in the abstract).

3.4 Optical measurements The properties of the produced SWCNTs were assessed by Raman measurements of samples collected on Millipore filters, and optical absorption measurements of samples transferred onto glass plates. Table 2 shows the G/D ratios from the measured Raman spectra. The G/D ratio in Raman has been used as a

Table 2 Optical measurements for selected samples collected on Millipore filters. The columns show: synthesis temperature, introduced CO_2 and NH_3 flows in ppm by volume of the inlet gas flow, G/D ratios determined from Raman spectra measured using a 632.81 nm excitation, and nanotube mean diameters estimated from the optical absorption spectra.

Temp. ($^{\circ}\text{C}$)	Intr. NH_3 (ppm)	Intr. CO_2 (ppm)	G/D ratio	Mean diam. (nm)
1000	0	0	9.6	1.7
1000	250	0	14.4	1.6
1000	625	0	4.2	1.4
825	0	5000	15.6	1.3
825	500	5000	46.6	1.8
825	500	2500	14.0	1.4

Figure 2 Optical absorption measurements of samples synthesized at 825 $^{\circ}\text{C}$ measured after transferring onto a glass plate. A is measured from a sample synthesized with 5000 ppm of CO_2 and no NH_3 ; B with 2500 ppm CO_2 and 500 ppm of NH_3 ; and C with 5000 ppm CO_2 and 500 ppm NH_3 . The peaks indicated by the letters correspond to the E_{22} transition.

characteristic of high-quality SWCNTs synthesized by many methods, such as HiPco [17], alcohol-assisted CVD [18, 19], CoMoCat [20], and water-assisted CVD [1, 21]. At 1000 $^{\circ}\text{C}$, there is a slight increase of the ratio with 250 ppm of NH_3 ; note however that synthesis yield is much lower than without added ammonia. At 825 $^{\circ}\text{C}$, although the yield of synthesis is lower with 500 ppm of NH_3 , the quality of the produced tubes is higher, as shown by the increased G/D ratio with 5000 ppm of CO_2 . Note also that the combination of good yield and highest G/D ratio is obtained with added NH_3 ; even though the yield with just 5000 ppm of CO_2 is higher (Table 1), the quality of the product is significantly lower.

The optical absorption measurements for three samples synthesized at 825 $^{\circ}\text{C}$ with slightly different amounts of introduced CO_2 and NH_3 are shown in Fig. 2. From the optical absorption spectra the diameter distributions of the produced tubes can be estimated based on the extended tight binding model [22]. Similar absorption measurements were also conducted for samples synthesized at 1000 $^{\circ}\text{C}$, and the estimated diameters of the nanotubes are shown in Table 2.

4 Discussion

The introduction of NH_3 into the reactor offers a possibility to shift the diameter distribution of the produced SWCNTs, as evidenced by the optical absorption measurements shown in Fig. 2 and Table 2. As the diameters of SWCNTs synthesized by CVD are determined at nucleation [23–25], and depend on the catalyst particle sizes [20, 26], the shift in the diameter distribution to larger diameters may be due to the catalyst particle sizes at nucleation being correspondingly larger. The reactive NH_3 species might delay the nucleation until the catalyst particles have grown slightly larger than they would have without it. Another possibility that cannot be ruled out with the present

experimental setup is the selective etching of small diameter SWCNTs, whose carbon network is more reactive. Increased yield of DWCNTs was ruled out by TEM observations (Fig. 1).

Furthermore, considering the data in Tables 1 and 2 we conclude that very small amounts of ammonia can be beneficial for producing high quality SWCNTs in the ferrocene aerosol system, particularly at lower temperatures. Even though there is a decrease in yield, at 825 °C the three-fold gain in the G/D ratio and the increase in the quality of the produced SWCNTs is considerable. The effect appears similar to the role played by CO₂ in etching the produced tubes of amorphous carbon and defects [16]. At 1000 °C ammonia is too reactive, which can be understood to be due to the thermodynamics of the CO disproportionation reaction. The lower the temperature, the more oxidisers (etching agents) can be added.

5 Conclusions High quality SWCNTs were synthesized in the presence of ammonia in a vertical flow aerosol reactor. At synthesis temperatures of 1000 °C, added ammonia decreases the yield considerably, while at 825 °C the decrease is much smaller with 500 ppm NH₃. At this temperature, NH₃ also induced an increase in the quality of the produced SWCNTs and increased their mean diameter. Thus added ammonia played a double role of enhancing the quality of the produced SWCNTs while allowing the diameter distribution to be controlled.

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