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Control of the single-wall carbon nanotube mean diameter in sulphur promoted aerosol-assisted chemical vapour deposition

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Abstract

The influence of gas flow on nanotube diameter during the synthesis of high-purity, very long single-wall carbon nanotubes (SWCNT) via aerosol-assisted chemical vapour deposition is reported. The sample morphology, nanotube yield, defect concentration and amount of carbonaceous impurities, as well as the mean diameter and the diameter distribution of the SWCNTs were analysed by combined scanning- and transmission electron microscopy, Fourier Transform Raman spectroscopy and optical absorption spectroscopy. The results show that by using a solution of ferrocene and sulphur in *m*-xylene the addition of sulphur as a promoter was found to enhance the SWCNT growth and to increase the yield. A reduction of the mean diameter and a change in the diameter distribution are observed when the total gas flow is increased.

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1. Introduction

Since their discovery in 1991 [1] carbon nanotubes (CNTs) have attracted wide-spread attention. Several methods can be used for nanotube production, the most popular being arc-discharge [2], laser-ablation [3] and chemical vapour deposition (CVD) [4], such as the HiPco process [5]. The unique electrical and mechanical properties of these sp²-hybridised molecular nanostructures make them one of the most promising building blocks for nanoscale science and nanotechnology. Their small size, large aspect ratio, large current carrying density, ballistic transport properties, and exceptional mechanical properties [6]

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make CNTs a suitable material for nanoelectronics and nanomechanics, as well as for composite materials [7], field emission displays [8], ultrastrong yarns [9], interconnects [10] and batteries [11]. So far a lot of different nanoscale devices based on CNTs as active elements such as single molecule transistors [12], nanobalances [13], and nanosensors [14] have been successfully produced. Many applications such as reinforced polymer composite materials, field emission displays, ultrastrong yarns, interconnects and batteries need very pure, well defined and cheap CNTs on a bulk scale. For this purpose, CVD is a very promising technique because of its upward scalability, low cost and rather low production temperatures as compared to standard laser ablation and arc-discharge techniques. The low production temperatures offered by CVD make it suitable for applications requiring low temperatures, since it can be more easily integrated in currently used technological processes [15]. Among the available CVD processes, the

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injection CVD and the aerosol-assisted (AA) CVD method are exceptionally cheap and well suited for scaling up for mass production of CNT with a defined nanotube diameter distribution. These processes have already been widely used for the growth of multi wall CNTs (MWCNT) [16–21] and have been recently successfully applied for the synthesis of SWCNT and double wall CNTs (DWCNT) [22-24]. Recently, this CVD process has also been applied for the direct spinning of carbon nanotube fibers in a continuous manner [25]. Moreover, the addition of a sulphur-containing compound such as thiophene or of pure sulphur to ferrocene was found to be effective in promoting the growth of SWCNTs and in increasing the yield of SWCNTs under different growth conditions [23,26,27]. Others reported the growth of DWCNTs upon the addition of thiophene [24] or of pure sulphur [22,28,29] under similar conditions. Hence, the addition of these compounds is effective as a promoter for SWCNT or DWCNT growth in a rather broad range such as 0.5-5 wt.% of thiophene [27] or within 512:1 to 2:1 the molar ratio of ferrocene to sulphur [28]. However, it was found when sulphur is eliminated from the catalyst, there is a striking difference in the nanotube products, in terms of the quality and yield [28]. Without hydrogen flow, the yield of CNT growth was found to rapidly decrease [23]. Experimental results at different temperatures indicate that the sulphur tends to be more effective for the CNT growth at a higher temperature >1000 °C. These results are in good agreement with Zhou et al. who reported an increase of the nanotube production rate for increasing temperatures [28].

In this contribution, we present new results on high yield AA-CVD growth of SWCNT by using a solution of ferrocene and sulphur in *m*-xylene. We show that the total gas flow is one of the key parameters in the high yield production of SWCNT and has a peculiar influence on the nanotube diameter and diameter distribution. An increase of the gas flow yields to a decrease of the SWCNT mean diameter and an altered diameter distribution.

2. Experimental

Our experiments were carried out in an equipment which we used before to prepare well-aligned MWCNT arrays and which is described in detail in Ref. [16]. In contrast with the parameters of preparing aligned MWCNT arrays, we increased the reaction temperature to 1050 °C, the maximum available temperature, and introduced sulphur as a promoter. Ferrocene and a small amount of sulphur (Fe:S = 10:1, atomic ratio) were mixed and ground using a mortar and pestle and then were dissolved in *m*-xylene, forming a solution of 40 mg/ml. Ultrasonicating the solution of ferrocene and sulphur in *m*-xylene with an excitation frequency of 850 kHz produces an aerosol. The aerosol droplets produced by ultrasonication are transported by a 100 sccm Ar carrier gas flow. They are then accelerated to the reaction furnace by a 100 sccm argon dilution gas. An additional gas inlet was attached to introduce a reaction gas consisting of controlled amounts of Ar and H₂ into the hot zone of the reaction tube, which has a diameter of 3.5 cm. The total gas flow was increased stepwise from 300 sccm to 1500 sccm while keeping the Ar:H₂ ratio constant at 2:1. In the hot zone the solvent evaporates and ferrocene decomposes to provide the iron catalyst required to nucleate nanotube growth with m-xylene acting as the carbon source. In all the experiments the reaction time was kept constant at 20 min. Because the mixture of ferrocene and sulphur flows through the reaction region continuously, SWCNTs are grown continuously in keeping with a large amount of produced material, thus making full use of the advantages of the floating catalyst method. All our experiments were performed at atmospheric pressure.

The reaction product is blown out from the reaction zone (with a temperature profile ranging from 800 °C to 1050 °C) and deposit on the end of the quartz tube as films, where the temperature is below 400 °C. After the precipitated films are peeled off the reaction tube and get transformed into long fibers. This is quite different from the preparation of aligned MWCNT arrays, where the carbon nanotubes stay in the reaction zone during the whole reaction. As will be shown in detail below, this fact points towards a high yield of SWCNT with a low amount of other carbonaceous material.

The reaction products were characterised using scanning electron microscopy (SEM) (Philips XL30), transmission electron microscopy (TEM) (Tecnai F30 (FEI)), Fourier Transform Raman spectroscopy (FTRS) with a Bruker FT RFS 100/s Raman spectrometer and optical absorption spectroscopy (OAS) with a Bruker IFS 113 V/88 spectrometer.

3. Results and discussion

We first turn to a local scale analysis of the sample morphology and structure using both SEM and TEM. In Fig. 1 the morphology of a typical as-grown sample is shown for the two limiting gas flows used in our experiments at different magnifications. As can be seen, by varying the total gas flow, the SEM micrographs of all samples are very similar regarding the diameter and length of the fibers of SWCNT bundles but the overall density of the film changes with the gas flow. The density of the film is bigger for smaller flow rates since with a higher gas flow more SWCNTs are carried out through the gas outlet due to the SWCNT growth occurring in the gas phase. On the other hand, both SEM and TEM images clearly show that for our optimized growth conditions very long carbon nanotubes with a very low amount of amorphous carbon impurities are synthesized.

Direct evidence for the growth of SWCNT is given by transmission electron microscopy (TEM) as depicted in Fig. 2. In the overview images of the samples produced at 300 sccm (Fig. 2a) and at 1500 sccm (Fig. 2b) as the total gas flow again it can be observed that the as produced unpurified material contains very little carbonaceous impurities and the nanotubes are very long. The overall amount of catalyst particles encapsulated by carbon shells is covering about 20% of the produced carbon nanotubes. This is less than is observed for SWCNT raw material produced by the laser ablation process under optimal conditions. These samples contain an overall SWCNT yield compared to catalyst impurities of 31 wt.% as determined by atomic adsorption spectroscopy [30]. Therefore, our analysis of the TEM overviews shows that the purity of produced CNTs is very high and this high purity is independent of the total gas flow. We now turn to the analysis of the type of the produced CNTs using high resolution TEM micrographs. Typical results for the samples produced at 300 sccm and at 1500 sccm gas flows are depicted in the lower panels (c) and (d) of Fig. 2, respectively. Independent of the gas flow we observe some separate SWCNT but



Fig. 1. Typical SEM micrographs of the as-produced SWCNTs. Upper panels: Overview of the material produced at 300 sccm (a) and at 1500 sccm (b) as a total gas flow. Lower panels: High resolution SEM micrographs of the material produced at 300 sccm (c) and at 1500 sccm (d) as a total gas flow.

most of the material forms bundled SWCNTs, what is expected for high purity SWCNT samples. The diameters of the SWCNTs typically range between 1 and 3 nm. The walls of the SWCNTs are very straight and there is nearly no amorphous carbon coating on the SWCNT walls. This is again quite comparable to laser ablated SWCNT material produced under optimized conditions [30]. From an analysis of several TEM micrographs, we observe that the samples hardly contain any DWCNTs (<3% after extensive search in the sample) and no MWCNTs. This is in contrast to previous results using similar process parameters and a total gas flow ranging from 3000 to 3500 sccm using a quartz tube with a diameter of 45 mm, in which a very high yield of DWCNTs was claimed [22]. The differences in the results are an open question and need to be further investigated. Some possible explanations from our detailed analyses will be given below. In summary, our TEM analyses suggest that within the used gas flow range, very high quality SWCNTs are produced with only a negligible amount of other CNTs (DWCNT and MWCNT) and other carbonaceous species.

However, TEM is only a local scale analysis, and is thus selective. In addition, radiation damage can influence the analysis of the defect concentration and it is also very time consuming. Moreover, accurate diameter analysis requires the microscope to be highly calibrated and clear identification of matching SWCNT walls is more complicated when the SWCNT are in bundles. Thus, the analysis of the mean diameter and diameter distribution has to be treated with some caution. Therefore, we further characterized our samples optically with bulk scale measurements in order to estimate the relative defect concentration, mean diameter and the diameter distribution.

In particular, Raman spectroscopy, in this case FTRS, is a powerful tool to analyse SWCNT. The technique allows the diameters of the nanotubes to be evaluated from resonantly enhanced nanotubes by the inverse diameter dependence of the radial breathing mode (RBM) [31]. A value of $\delta v = 234 \text{ cm}^{-1}/d + 14 \text{ cm}^{-1}$ is a well established relation [32]. This also enables SWCNT and DWCNT to be distinguished. For DWCNT, two RBM regions, corresponding to the inner and outer nanotubes, separated in a first approximation by the van der Waals (vdW) distance exist. Differences in the inter tube spacing lead to a fine splitting of the RBM of the inner tubes components [33]. The upper spectrum in the figure corresponds to a total gas flow of 300 sccm and the next four spectra below have a total gas flow ascending by 300 sccm. In addition, the lowest



Fig. 2. Typical TEM images of the as-produced SWCNT containing fibers. Upper panels: Overview of the material produced at 300 sccm (a) and at 1500 sccm (b) as a total gas flow. Lower panels: High resolution TEM micrographs of the material produced at 300 sccm (c) and at 1500 sccm (d) as a total gas flow.

spectrum in Fig. 3(a) corresponds to a DWCNT sample obtained by annealing peapods for 15 min [34]. When increasing the total gas flow stepwise from 300 sccm to 1500 sccm, while keeping all the reaction parameters constant, we find a stepwise shift of the main constituent of the RBM to bigger wave numbers, corresponding to a shift in the diameter distribution towards greater numbers of narrow diameter tubes. The corresponding evaluated diameters in resonance with the 1064 nm laser excitation lie between 0.9 and 1.75 nm. The existence of two RBM regions, corresponding to inner and outer nanotube separated by the van der Waals (vdW) distance is observed for annealed peapods [33]. The four upper spectra show only one RBM region, clearly demonstrating that there are nearly no DWCNTs present in those samples. The main component in resonance shifts from 1.6 nm to 1.3 nm. Only, for the spectrum from SWCNT synthesized with a 1500 sccm total gas flow, there are two RBM regions observed corresponding to diameters between 1.75–1.5 nm and 0.95-0.9 nm. However, there are only a few pairs of corresponding RBM frequencies suggesting the formation

of a few DWCNT. Hence, the sample still contains as a major constituent SWCNT with a broad diameter distribution but with a mean diameter shifted to lower values as compared to the upper four samples with lower gas flow. In addition, this sample contains only a minor DWCNT contribution relative to the reference sample or to literature results on high yield hot wall CVD synthesis of DWCNT [35]. These results of a broad diameter distribution of SWCNT are also in good agreement with the TEM results. Moreover, as mentioned above, our results are in disagreement with some previous Refs. [22,28,29] claiming to have synthesized primarily DWCNTs but presenting only a very broad distribution of diameters between 1.8 and 0.9 nm with a vanishingly small amount of couples of corresponding RBM frequencies corresponding to the inner and outer tubes of DWCNT.

Additional information about the sample quality and the presence of SWCNT and DWCNT can be extracted from the region of the strong tangential modes or graphitic G-lines at around 1600 cm^{-1} , which consist of six components [6]. There are longitudinal optic (LO) and transversal



Fig. 3. Five typical spectra for samples synthesized with the same reaction conditions but different gas flows: 300 sccm, 600 sccm, 900 sccm, 1200 sccm and 1500 sccm from top to bottom and one reference spectra below. (a) Raman results for the spectral ranges from 120 cm^{-1} to 450 cm⁻¹ and from 1200 cm⁻¹ to 1900 cm⁻¹. The arrow points towards the D line in the samples with exceptionally low D/G ratios of less than 0.03. The lowest curve depicts a reference sample of DWCNT produced by the transformation from C_{60} peapods [34]. (b) OAS results for the range of the first two absorption peaks of the semiconducting SWCNTs for the different gas flows of 300 sccm, 600 sccm, 900 sccm, 1200 sccm and 1500 sccm from top to bottom. The lowest curve depicts a reference sample of purified laser ablation material with a diameter distribution of 1.37 ± 0.07 nm [30]. For clarity and a better comparison the relative peak intensity is divided by three for this curve. The dotted lines point to groups of SWCNT with preferred diameters as indicated by the numbers. The inset shows the OAS spectrum before subtracting the background of the sample with 1500 sccm gas flow.

optic (TO) phonons with A_1 , E_1 and E_2 symmetry. Because of the so-called depolarization effect, the resonance with light polarized perpendicular to the nanotube axis is suppressed [36]. Thus for SWCNTs in random orientation the G band mainly consists of A_1 LO and TO phonons and E_1 and E_2 phonons are much weaker. If metallic nanotubes are resonant, the lower frequency component of the G band becomes a Breit-Wigner-Fano line shape. In the case of DWCNTs the shape of the G band is changed due to the existence of an inner nanotube with a diameter less than 1 nm. It has been observed that the G band becomes broader and has an additional fine structure as compared to SWCNTs. This is due to the strong dispersion of the TO components of the G band with decreasing nanotube diameter [37] and due to metallic constituents in the DWCNT [38]. For DWCNT this leads to a bimodal distribution of nanotube diameters, which can be clearly monitored by Raman spectroscopy and can be seen as a fingerprint for the presence of DWCNT in the sample [35]. As can be seen in Fig. 3(a) there is basically no change in the width, position of the main component (1590 cm^{-1}) and shape of the G-line between the five different AA-CVD samples. This is again in contrast to the DWCNT reference sample, which either has a strongly increased width or a clearly pronounced double peak structure from the corresponding bimodal contribution of inner and outer tubes being in resonance with the main components at 1581 cm^{-1} and 1590 cm^{-1} , respectively (see also lowest curve and Ref. 35).

Furthermore, the relative defect concentration in the samples can be analysed in a non-destructive way from the ratio between the G-line and the defect induced D-line at around 1250 cm^{-1} . This line is due to a second order Raman process only possible via the scattering on a defect in the SWCNT [39,40]. As can be seen in Fig. 3(a) the D/G ratio in all our samples is below 0.03. This points towards the high quality of the SWCNT samples as compared to, e.g., MWCNT produced by the same method, which have a D/G ratio of at best 0.5 [16]. Compared to the laser ablation material and optimized SWCNT samples from other CVD processes [41] the size of this D line is also in the same range. The remaining very low amount of defects are most likely related to the reminiscent contribution of amorphous carbon species and can be easily removed by a heat treatment in air. Such a method has been already applied successfully in the purification of DWCNT [42].

We now turn to the bulk scale analysis of the mean diameter and diameter distribution and relative yield of the produced SWCNT. OAS has been proven to be a powerful tool to evaluate these properties [43,44]. In principle OAS probes the joint density of electronic states weighted with the matrix elements for the optically allowed transitions [45] and probes all nanotubes at once since white light is used as a light source [43]. Thus OAS can be used for reliable diameter analyses with appropriate corrections for excitonic effects [46,47]. For the determination of the mean diameter using the E_{11}^{S} peak a relation of $E_{11}^{S} = 2\gamma_0 a_0/d - \Delta$ is well established, where $\gamma_0 = 2.9 \text{ eV}$ is the tight binding overlap integral, a_0 the C–C distance of 0.142 nm and Δ is an excitonic correction factor which is dependent on the nanotube diameter and chirality as well as on the tube-tube and tube environment interactions and is of the order of 70 meV for bundled SWCNT. Using $E_{22}^{\rm S} = 4\gamma_0 a_0/d$ the effect of the excitonic corrections are negligible and the mean diameter and diameter distribution can be accurately determined [36,43]. Since OAS is sensitive to carbonaceous impurities, it can be used to determine the nanotube yield by the area under the E_{11}^{S} [30,43,44] and E_{22}^{S} peak [48], respectively. Since the OAS from graphite is expected to show a linear increase with energy, the linear part in the OAS was attributed to the impurities and the ratio between the peaks due to van Hove Singularities from nanotubes versus the linear background was taken as a measure of purity. The results are depicted in Fig. 3(b). The inset shows a typical OAS spectrum before strapping the background after normalizing at the minimum between the E_{11}^{s} and E_{22}^{s} peaks at about 0.9 eV. The lowest curve shows the OAS spectrum of the purified laser ablation material (divided by three for clarity) with a mean diameter of 1.37 nm for comparison. Taking the ratio to a purified laser ablation sample as reference the relative purity of the as produced optimised laser ablation material 50% [30,44], we find that for our samples produced at

different gas flows the relative nanotube yield is between 25% and 50%. The mean diameter and diameter distribution in the AA-CVD samples is also strongly dependent on the gas flow. Most of the produced SWCNT have diameters between 1 and 2 nm. The dotted lines in the figure correspond to the fine structure in the first OAS peak pointing to a preferential growth of SWCNT with diameters of 1.05, 1.15, 1.28, 1.36, 1.48, 1.66 and 1.86 nm, respectively. From a root mean square fit the mean diameter of the SWCNT changes from 1.5 nm (300 sccm gas flow) to 1.45 nm (600 sccm), 1.4 nm (900 sccm) to 1.3 nm (1200 sccm) and 1.25 nm (1500 sccm). Compared to the reference sample of purified laser ablation material with a Gaussian diameter distribution of 1.37 ± 0.07 nm [30], the variance in the diameter distribution also changes with the gas flow. The sample with 600 sccm has the highest relative nanotube yield of 50% and also a Gaussian distribution with a variance which is 0.35 nm and therefore roughly five times bigger than the purified laser ablation sample. Interestingly, for all other samples the diameter distribution does not follow a Gaussian which might be due to a non stochiometric distribution of the catalyst precursors. This points out that the SWCNT can be produced in a high yield by the AA-CVD process and have, compared to other CVD processes, a rather narrow diameter distribution, with a mean diameter between 1.25 and 1.55 nm that can be controlled by the gas flow. Two inter-related thermal effects could explain the decrease in mean diameter of the SWCNT with increasing gas flow. An increased gas flow will lead to a reduced residence time of catalysts clusters in the hot zone of the reaction chamber and will also cool the clusters more rapidly due to the faster flowing gas being cooler. These effects essentially lead to reduced catalyst particle sizes and narrower catalyst particle size distributions. It is generally accepted that SWCNT diameter is strongly dependent on the catalyst cluster size and this type CVD technique used here bears some similarities to laser evaporation. Thus, the growth and nucleation of the SWCNT may occur through a similar mechanism as described in [49].

4. Conclusions

In summary, using AA-CVD with sulphur as a promoter and within a range of total gas flows between 300 and 1500 sccm very high quality and very long SWCNTs with a low defect concentration are produced with a low amount of other CNTs (DWCNT and MWCNT) and other carbonaceous species. A decrease of the mean diameter of the SWCNT diameter distribution can be obtained by increasing the total gas flow in keeping with a constant high yield of SWCNT. This points out that AA-CVD is a suitable method for the high yield production of SWCNTs and which provides control over the diameter and diameter distribution of the produced SWCNTs by changing the process parameters.

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