The Use of NH₃ to Promote the Production of Large-Diameter Single-Walled Carbon Nanotubes with a Narrow (n,m) Distribution

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ABSTRACT: We demonstrate here a simple and effective (n,m)-selective growth of single-walled carbon nanotubes (SWCNTs) in an aerosol floating catalyst chemical vapor deposition (CVD) process by introducing a certain amount of ammonia (NH₃). Chiralities of carbon nanotubes produced in the presence of 500 ppm NH₃ at 880 °C are narrowly distributed around the major semiconducting (13,12) nanotube with over 90% of SWCNTs having large chiral angles in the range 20°–30°, and nearly 50% in the range 27°–29°. The developed synthesis process enables chiral-selective growth at high temperature for structurally stable carbon nanotubes with large diameters. With optical responses can be detected. Quantitative evaluation of the nanotube population is another issue since there is a lack of knowledge of the optical efficiency as a function of (n,m), not to mention the environmental effects.

In this communication, we report on the development of a new approach based on an aerosol floating-catalyst CVD process in order to promote the growth of SWCNTs with controlled chiral structure. By introducing a small amount of ammonia (NH₃) as an additive into the reaction, we succeeded in producing high-quality SWCNTs at a relatively high temperature, whose chiralities are largely clustered into a group around the (13,12) nanotube. The average tube diameter is 1.67 nm. Over 90% of SWCNTs were distributed in the high chiral angle region close to the armchair structure. Instead of optical measurements, structural characterization was carried out using electron diffraction technique which allows direct (n,m) measurements on individual SWCNTs. Electron diffraction analysis of SWCNT bundles endows us with further chiral angle distribution information. The measurements are free of nanotube environment effects.

SWCNTs were synthesized in a gas-phase floating catalyst CVD reactor where iron nanoparticles derived from ferrocene vapor decomposition act as catalyst in a 400 cm³/min flow of carbon monoxide (CO) and 2 cm³/min of carbon dioxide (CO₂) at 880 °C. As an etching agent, small amounts of NH₃ were introduced into the reaction to amend the nanotube structure. Three samples were obtained by regulating the amounts of NH₃ at 0 ppm, 500 ppm, and 1000 ppm, respectively, with all other parameters unchanged. All samples have been investigated by transmission electron microscopy (TEM) using a Philips CM200 FEG microscope and a JEOL-2200FS double aberration-corrected microscope, both being operated at 80 kV, which is well below the electron knock-on damage threshold for carbon. The (n,m) determination from electron diffraction patterns (EDPs) of individual SWCNTs was based on a calibration-free intrinsic layer-spacing method. In addition, EDPs of SWCNT bundles provided supplementary knowledge on the chiral angle distributions in the samples.

Electron microscopy observation showed that SWCNTs have been produced in the samples with NH₃ at 0 ppm as well as 500 ppm. Compared with that in the 0 ppm NH₃ sample, the yield of nanotubes is lower and the nanotubes are less bundled in the 500 ppm NH₃ sample. It is remarked that there are no carbon nanotubes observed in the sample synthesized with 1000 ppm NH₃. A representative TEM overview image of SWCNTs in the

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500 ppm NH₃ sample is presented in Figure 1a, where an individual nanotube is framed. Shown in Figure 1b and 1c are its high-resolution TEM image and the corresponding electron diffraction pattern (EDP), from which the chiral indices of the tube have been indexed as (13,12). More images and EDPs for the three investigated samples are available in the Supporting Information (Figures S1−S3). In general, the structure of the floating catalyst CVD nanotubes is well crystallized due to the high growth temperature. On the basis of electron diffraction analysis of 108 individual SWCNTs in the 500 ppm NH₃ sample, and 95 nanotubes in the 0 ppm NH₃ sample, we obtained (n,m) maps for both samples as shown in Figure 2. In the 500 ppm NH₃ sample, in total 37 different chiral structures were identified, of which the three main chiralities (13,12), (12,11), and (13,11) with abundances of 13, 8, and 8, respectively, constitute nearly 30% of the investigated nanotubes. In addition, the chiralities of the SWCNTs are seen intensively clustered into a narrow region around the major semiconducting (13,12) nanotube. In contrast, in the 0 ppm NH₃ sample, the chiralities are more broadly distributed. Out of 95 investigated nanotubes, a total number of 52 different ones are recognized in a different chiral configuration with (12,10) showing only a slightly higher abundance. We note that the fractions of semiconducting tubes in the above two samples, 65% for the non-NH₃ sample and 74% for the NH₃-enhanced sample, do not show substantial differences from each other nor from their inherent population of around 67%.

The prominence of the chirality distribution in the NH₃-enhanced sample is more effectively displayed in Figure 3 (red bars), which illustrates the ratio $R_x/R_2$ as a function of chiral angle. Here, $R_x$ ($x = 1−3$) indicates the percentage of nanotubes with chiral angles in the ranges $0°−10°$, $10°−20°$, and $20°−30°$, respectively. Our statistical data show that the 500 ppm NH₃ sample has more than 90% SWCNTs with large chiral angles in the range $20°−30°$, and about 50% in the range $27°−29°$. For the purpose of comparison, Figure 3 includes also the $R_x/R_2$ ratio for the 0 ppm NH₃ sample (blue bars), a CoMoCAT sample⁵ (brown bars), and a hypothetical ratio calculated on the basis of the theoretical model proposed by Ding et al.¹⁸ (green bars). It is apparent that the NH₃-enhanced sample stands out, giving an extremely high ratio of $R_x/R_2$, which demonstrates the high selectivity for growing SWCNTs with a narrow chirality distribution by introducing a certain amount of NH₃ into the CVD reaction. It is worth remarking that electron diffraction evaluation of SWCNT bundles leads to the same conclusion (Supporting Information, Figure S4).

Statistical analysis of the nanotube diameter distributions in the above two carbon nanotube samples are presented by the histograms in Figure 4 where red represents the 500 ppm NH₃ sample, and blue represents the 0 ppm NH₃ sample. In general, the nanotube diameters in both samples are similar, and close to those of conventional floating-catalyst-produced carbon nanotubes.¹⁹ The average diameter is 1.60 nm for the 0 ppm NH₃ tubes and 1.67 nm, slightly increasing, for the 500 ppm NH₃ tubes. This implies that a small amount of NH₃ (up to 500 ppm) has little influence on the catalyst particle sizes, which are known to determine the nanotube diameters.²⁰ However, carbon nanotube growth was found to be terminated when 1000 ppm NH₃ was added into the reactor (Supporting Information, Figure S3).

It is an open question to discuss the role of NH₃ in growing SWCNTs with a narrow chirality distribution. On the basis of the existing experimental data, one reasonable explanation can be proposed that, as a strong etchant, NH₃ selectively etches off SWCNTs with small chiral angles, which are more reactive and less stable compared to high chiral angle tubes.²¹ The same applies to nanotubes of smaller diameters due to their higher curvature,²² which would explain the slightly enlarged average nanotube diameter as NH₃ is introduced. The NH₃ etching

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Figure 1. (a) Typical TEM overview image of SWCNTs produced in the presence of 500 ppm NH₃, (b) high-resolution TEM image of an individual SWCNT and (c) its corresponding EDP.

Figure 2. (n,m) maps for samples produced with (a) 0 ppm NH₃ and (b) 500 ppm NH₃.
action may take effect on the catalyst clusters already during nucleation, suppressing the growth of smaller chiral angle tubes that have a relatively larger number of dangling bonds on the growing edge of the hexagonal network. Those etching effects could explain the decreased yield and the reduced bundling of nanotubes observed with added NH$_3$. Apparently, such etching behavior would hardly lead to considerable electrical selectivity in the NH$_3$-enhanced sample.

Without doubt, the amount of NH$_3$ used in the reaction is a crucial factor. An excessive amount of NH$_3$ leads to a termination of the growth of carbon nanotubes. On the other hand, fine-tuning the NH$_3$ concentration could conceivably enhance chiral angle selectivity. Furthermore, recently it was reported that the etching effects as its selectivity is not certainly known at the moment, although we have preliminarily considered NH$_3$ etching effects as its origin. Further studies are in progress to address this issue. The developed synthesis process enables chiral-selective growth at high temperature for structurally stable carbon nanotubes with large diameters. This research opens up potential routes toward tunable $(n,m)$selective growth of single-walled carbon nanotubes.

**ASSOCIATED CONTENT**

*Supporting Information.* Figures S1–S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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