Nitrogen-doped SWCNT synthesis using ammonia and carbon monoxide

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Great effort has been directed into modifying the electrical properties of produced carbon nanotubes by chemical doping and – in parallel – into controlling their chirality. We present a new approach to synthesizing nitrogen-doped single-walled carbon nanotubes (SWCNTs), based on gas phase floating catalyst CVD. The nitrogen content in the tubes was verified by transmission electron microscopy/electron-energy loss spectroscopy (TEM/EELS), and their chiral angle distribution found by electron diffraction (ED) to be skewed toward armchair tubes. Additionally, the optical properties of the material were probed by multi-frequency Raman spectroscopy and optical absorption.

1 Introduction Despite intense research effort, the realization of the full potential of carbon nanotubes has been hindered by the persistent difficulty in controlling the electronic properties of an ensemble of synthesized nanotubes. Advances in nanotube separation [1–3] have finally provided metallicity-selected [2, 4] samples for fundamental studies. However, extensive processing is always required, introducing defects and limiting the amount of material available. A lot of effort has been directed to controlling the chirality of produced nanotubes during synthesis, to some extent successfully [5–7].

An alternative route toward controlling the electronic properties of nanotubes – inspired by semiconductor technology – is via doping with foreign chemical elements. The two obvious alternatives are the nearest neighbors to carbon in the periodic table, boron and nitrogen [8–11]. Nitrogen in particular has attracted much attention due to its suitable atomic size. Furthermore, the potential applicability for N-doped nanotubes looks very promising [12]. The synthesis of nitrogen-doped multiwalled carbon nanotubes (N-MWCNTs) is nowadays an easy task using a variety of methods [13]. However, the synthesis of single-walled nitrogen-doped nanotubes (N-SWCNTs) has proven much more challenging [14, 15], particularly using different variations of the chemical vapor deposition (CVD) technique [16–19].

Here, we present a new approach to synthesize N-SWCNTs using a gas phase floating catalyst CVD method where carbon monoxide (CO) acts as carbon source, ammonia (NH3) as the nitrogen source (and etching agent [20]), and iron particles derived from ferrocene as the catalyst [21]. The nitrogen content in the tubes has been verified by transmission electron microscopy/electron-energy loss spectroscopy (TEM/EELS), and their chiral angle distribution found by electron diffraction (ED) to be skewed toward armchair tubes. Additionally, the optical properties of the material were probed by multi-frequency Raman spectroscopy and optical absorption.

2 Experimental methods

2.1 Synthesis The synthesis method has been described in detail previously [20, 21]. Briefly, catalyst
particles are grown in situ by ferrocene vapor decomposition in a CO flow of 400 cm³/min. The reactor set temperature chosen for study was 1000 °C, with the maximum wall temperature being about 60 °C higher. In addition to CO, small amounts of NH₃ (0–650 ppm) were added. The role of NH₃ is dual, as it acts as the nitrogen doping source as well as an etching agent. Samples were collected directly at the reactor outlet either by an electrostatic precipitator (ESP [22]) onto carbon coated copper TEM grids, or by filtering onto Millipore filter papers.

2.2 Characterization Electron energy-loss spectra were recorded using a VG-HB501 dedicated scanning transmission electron microscope (STEM) instrument equipped with a cold field emission gun (FEG), operated at 100 keV with an energy resolution close to 0.7–0.8 eV in the core-loss region. Convergence angle on the sample and collection angle of the spectrometer were 15 and 24 mrad, respectively. This spectroscopic information was obtained using the spectrum-imaging (SPIM) acquisition mode [23]. For the spectra acquisition, a slightly defocused electron probe was scanned in a small area of a few nm².

The morphology and structure of the samples on TEM grids was also investigated by TEM and ED (Philips CM200-FEG TEM at 80 kV, with Gatan 794 multiscan CCD camera). The chiral angles were determined by ED using intrinsic layer line distance analysis [24].

In addition, a multi-frequency Raman study was performed by recording spectra with a Dilor xy triple monochromator spectrometer for the 488, 514, 568, and 632 nm excitation wavelengths. Additionally, a Bruker Fourier transform (FT)-Raman spectrometer operating in ambient conditions with a 1064 nm excitation was used.

3 Results Figure 1 displays an EEL spectrum (C- and N-K edges), which is a sum of 5 EEL spectra with an acquisition time of 20 s each, recorded on the marked area shown in the bright field micrograph of a bundle of N-SWCNTs synthesized at 1000 °C with 625 ppm NH₃. The energy loss near-edge feature (ELNES) of the C-K edge consists of a π^* peak at ~285 eV and a well-defined σ^* band starting at ~292 eV. These signatures are typical for the sp² hybridization of the C atoms in a graphitic network, and indicate that the SWCNTs are well crystallized. Concerning the N-K edge shown as inset of Fig. 1, we observe a peak at ~398 eV that could be assigned to pyridine-like configuration, and in some cases, also a peak at ~401 eV, which is assigned to a graphitic environment [13, 14, 23, 25, 26]. Furthermore, the incorporation of nitrogen into the carbon network was found to be inhomogeneous, ranging from 0 to ~3 at.%. The mean nitrogen content is estimated to lie around ~1.7 at.%. This value is close to the one found on N-SWCNTs synthesized via the laser vaporization technique [25].

ED was conducted on 46 individual nanotubes on a TEM grid sample synthesized with 250 ppm NH₃ at 1000 °C, and their chiral angles determined [24]. It was found that the chiral angle distribution was skewed toward armchair tubes (Fig. 2). This is in contrast to samples produced in the same conditions without ammonia, where the chiral distribution is typical and more random.

Raman spectra were recorded for samples synthesized at 1000 °C with 0, 250, and 650 ppm NH₃. Figure 3 contains the most representative features that serve as a fingerprint of SWCNTs [27]. Figure 3a shows the disorder-induced Raman peak (D) and the G band, which correspond to SWCNTs. It is clear, that regardless the excitation wavelength, the I_D/I_G ratio increases with the increase of ammonia used during the synthesis process. The intermediate frequency modes also showed noticeable differences, which we do not discuss in further detail. The radial breathing modes (RBMs) have been thoroughly recorded with various laser lines (c and d), and in addition, we used optical absorption spectra (not shown here) to approximate – based on an extended Kataura plot – the mean diameters of the nanotubes in the 0, 250, and 650 ppm NH₃ samples as 1.5 ± 0.2, 1.6 ± 0.3, and 1.4 ± 0.2 nm, respectively. The G’ band recorded with the 488 nm excitation is shown in Fig. 3b. Maciel et al. reported on the use of this Raman feature as a signature of doping in...
SWCNTs [28]. We observe in Fig. 3b a downshift of 1.4 cm$^{-1}$ at the center of the maximum of the G from the first sample synthesized with ammonia with respect to the pristine material. The additional shift of $\sim$2 cm$^{-1}$ in the upper spectrum could be related to a higher doping level. However, given the slightly different morphology of the nanotube material, at this point we cannot attribute the additional G shift nor the differences in the RBMs [16] of the samples to an increasing doping level.

4 Discussion The introduction of NH$_3$ into the reactor enabled the synthesis of nitrogen-doped SWCNTs in a simple process. Ammonia is a volatile gas and likely breaks down catalytically on the iron clusters along with CO [29], providing free atomic nitrogen, which is incorporated into the growing nanotube structure. The uniformity and level of nitrogen doping seems to be somewhat variable according to EELS, which is likely due to the very low flow rate of NH$_3$ needed for successful synthesis, which is the minimum possible for the mass flow controller. Using a dilution system for NH$_3$, which would allow accurate control of the introduced amount in the few hundred ppm level, should improve the uniformity. Nonetheless, successful synthesis of N-doped SWCNTs with separated carbon and nitrogen sources offers the prospect of a controllable doping level once the process is optimized.

Moreover, it seems that the introduced NH$_3$ shifts not only the diameter distribution of the produced nanotubes (as previously reported [20]), but also the chiral angle distribution (Fig. 2). High chiral angle nanotubes are enriched compared to the pristine material. As the yield in our process is also significantly lower when NH$_3$ is used [20], we can speculate that ammonia could act as a powerful etching agent, similar to CO$_2$ [30–32], attacking the weaker C–C bonds of small chiral angle tubes [33, 34]. In the literature, armchair-enriched synthesis has been reported to be related to the shape of supported bimetallic catalyst particles [7, 35]. It is doubtful the same mechanism would apply to floating iron particles. It is worth noting, that the opposite trend has been observed in single-walled boron nitride nanotubes (SW-BNNTs), where zigzag and near to zigzag configurations are preponderant. In this case, it has been proposed that this fact could be related to the presence of nanoparticles (of B in this case) playing the role of catalyst [36].

Of course, it is possible that the nitrogen doping itself is the cause of the changes in both the diameter and chiral angle distributions. We must note that theoretical calculations of N-SWCNTs have implied that nitrogen could destabilize armchair tubes [37] (see, however, also Ref. [26]). Furthermore, it has been predicted that substitutional nitrogen should favor zigzag configurations [38], perhaps supporting the observation of pyridinic N dopants in our samples. For N-MWCNTs, diameter reduction [39] and ordering between shells [40] have also been reported.

5 Conclusions Nitrogen-doped single-walled carbon nanotubes with a high proportion of high chiral angle tubes have been successfully synthesized using a gas phase floating catalyst CVD method with separated gaseous carbon and nitrogen precursors. The content of nitrogen in the tubes varied from 0 to $\sim$3 at.%, with a mean around 1.7%.
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