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Linking growth mode to lengths of single-walled carbon nanotubes

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ABSTRACT

Elucidating the key factors that determine the lengths of single-walled carbon nanotubes (SWCNTs) is of great importance for understanding the origin of chiral selectivity. We use transmission electron microscopy to thoroughly investigate as-grown SWCNTs. The lengths and growth modes of SWCNTs were decided by bright-field imaging. Their respective chiral angles were calculated on the basis of nanobeam diffraction patterns. Systematic investigations reveal that there is no correlation between the SWCNT length and its chiral angle. Instead, it shows that SWCNT lengths depend more on their growth mode, i.e. the link between SWCNT and its seeding catalyst particle. Atomistic computer simulations demonstrate that low carbon fractions in the catalyst lead to so-called tangential growth, with a partial wetting of the metal in the tube, where metal catalyst tends to be deactivated by graphite layer encapsulation and results in short SWCNTs. In contrast, a high carbon concentration inside metal particle favors perpendicular growth modes, where only the tube lip is in contact with the catalyst. Catalysts adopting perpendicular mode could have a longer lifetime, thus catalyze the growth of long SWCNTs. Finally, the carbon concentration related growth mode was applied to interpret diverse SWCNT growth results.
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1. Introduction

Searching for chiral selectivity during the chemical vapor deposition (CVD) growth of single-walled carbon nanotubes (SWCNTs) is a much coveted goal that has been partially reached in a number of experiments [1–6]. However, the rationale behind these successful achievements has never been fully understood, precluding coherent synthesis strategies. So far, two theories have been proposed to interpret the chirality selectivity: one is nucleation control, where SWCNTs with specific chirality nucleate on the catalyst nanoparticles [2,3,5], accounting for the controlled growth. The other is SWCNT growth kinetic control [7–9], where SWCNTs with certain structure grow faster and longer than others, leading to their selective growth characterization results. In this context, SWCNTs' length, diameter and chirality together with the sizes of the nanoparticles from which they grow appear as important quantities to investigate, in order to gain a better understanding of SWCNT growth mechanisms.

In order to clarify possible factors that affect SWCNT lengths, a prominent screw-dislocation model has been proposed [7], with the main result that the nanotube growth rate should be proportional to its chiral angle. This model was extended by further taking the nanotube/catalyst interface thermodynamics into account [8]. Based on this approach, SWCNT growth rate and possibly length should be correlated with its chiral angle. However, the finding of a link between SWCNT growth rate/length and chiral angle is at odds with the overall conclusions of some studies [10,11]. Using *in situ* Raman spectroscopy, Rao et al. [10] measured the growth rates of nine individual tubes and found them proportional to their chiral angles, in agreement with the above model [7]. However, recent Raman mapping on SWCNTs with five kinds of chiralities showed no length dependence on tube chiral angle [11].

The discrepancy in experimental findings is likely due to the limited amount of data acquired in the above experiments [10,11].

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In both cases, Raman spectroscopy is used to follow isolated SWCNTs grown on surfaces. As the resonance window of Raman scattering for a bare-isolated SWCNT is very narrow (~10 meV) [12,13], for a given laser wavelength, the probability to satisfy the resonant condition for observing an individual SWCNT is less than 1%. Moreover, the relatively low spatial resolution of Raman spectroscopy, which is limited by diffraction to about half the wavelength of the excitation light, challenges researchers to measure tubes which are not very long [11]. Consequently, in order to precisely measure tube lengths and explore the factors that could affect them, we should resort to other more reliable techniques.

In this work, we combine high-resolution transmission electron microscopy (TEM) and nanobeam electron diffraction (ED) to thoroughly characterize SWCNTs synthesized on porous SiO_2 membrane. We stress that the strength of our approach is first, to measure, on a given tube, its chiral angle, length and the nature of its link to seed particle from which it has grown and second, to perform these measurements in a statistical way, independently of the nature and morphology of the tubes inspected. First of all, the tube length and chiral angle were determined, with the result that we found no correlation between the SWCNT length and its chiral angle. Secondly, we demonstrated the SWCNT length could be related with the tube growth mode, depending on links between tubes and their seeding particles. Finally, computer simulation was applied to show that catalyst particles growing SWCNTs by a tangential mode, tend to be deactivated by fully wetting the inner part of the tube, accounting for the shorter SWCNTs obtained in these CVD conditions.

2. Materials and methods

2.1. Preparation of Fe catalyst

Iron hydroxide nanoparticles were prepared by hydrolysis of $FeCl_3$ [14]. In brief, $FeCl_3$ with a mass of 0.08 g was first dissolved in 5.0 mL H_2O. The solution was added dropwise to 180 mL boiling water under stirring. The prepared Fe-containing colloid was diluted in ethanol and then dispersed onto TEM grid coated by porous silicon oxide layer. The dispersed Fe catalyst was calcined in air to remove possible contaminations.

2.2. Growth of carbon nanotubes by CVD

Growth of carbon nanotube was carried out in a horizontal CVD system equipped with a quartz tube (inner diameter: 40 mm). The TEM grid with Fe nanoparticles was heated to 900 °C with a flow of He (200 sccm). After reaching the desired temperature, CH_4 with a flow rate of 200 sccm was introduced into the reactor to replace He. After reaction for 2 min, CH_4 was switched off and the system was cooled down under the protection of He.

2.3. Characterizations of carbon nanotubes and catalyst particles by TEM

The morphology and structure of both catalyst and carbon nanotubes were characterized by a JEOL-2200FS FEG TEM/STEM and JEOL aberration-corrected ARM 200 Cold-FEG microscope operated at 80 kV. The TEM micrographs were used to measure the lengths of SWCNTs. Structural assignments of the SWCNTs are done by analyzing their nanobeam electron diffraction patterns [15].

2.4. Calculations of interactions between SWCNTs and metal nanoparticles

To study the interaction of carbon with nickel at the atomic level, we have developed a tight-binding model based on a description of the local electronic density of states of each atom at the fourth moment level. This provides an efficient tool to calculate the energies of systems containing a few hundreds of Ni and C atoms [16,17]. The energetic model is then implemented in a Monte Carlo code using either a canonical or grand canonical algorithm with fixed volume, temperature, number of Ni atoms, and carbon chemical potential [18].

3. Results and discussion

Fig. 1a presents photograph of a 2.1 μm-long SWCNT measured by superimposing 5 TEM images taken along the tube. Both ends are marked with yellow arrows. A high resolution image was taken from the SWCNT across a hole (Fig. 1b), with a measured diameter of 3.6 nm. Nanobeam ED was performed on the suspended section of the SWCNT, the pattern of which is shown in Fig. 1c (a magnification is presented in ESI Fig. S1a). ED pattern of an SWCNT is consisted of many separated layer-lines parallel to each other. Based on the strategy of “intrinsic layer-line spacing” [15], the chirality indices of the SWCNT are assigned to (45, 1), with a chiral angle of 1.1°. Such an assignment is also confirmed by the simulated ED pattern of one (45, 1) SWCNT (ESI Fig. S1b). Fig. 2 depicts TEM micrograph of a short SWCNT (Fig. 2a) and its corresponding ED pattern (Fig. 2b). The tube has a length of only 40 nm. Analyzing its ED pattern gives chiral indices of (25, 23), a tube with diameter of 3.3 nm and chiral angle of 28.6°. Such an assignment is also verified by the simulated ED pattern of a (25, 23) tube (Supporting Information Fig. S2) and the diameter of tube measured from Fig. 2a.

In contrast with Raman spectroscopy which can only detect SWCNTs that are in resonance with the laser wavelength, characterizations adopted here not only permit precise determination of SWCNT lengths by TEM, but facilitate unambiguous assignment of SWCNT chirality using nanobeam ED. Therefore, it allows investigating a number of randomly distributed SWCNTs with different chiralities, and very importantly without any preference. The diameter and chirality measurements were performed on 92 SWCNTs, grown in one experiment using CH_4 as a feedstock. Fig. 3a depicts the plot of SWCNT lengths as a function of chiral angles. Obviously, no correlation could be identified between the length of the SWCNT and its chiral angle. For example, a (25, 13) SWCNT (ESI Fig. S3) with a chiral angle of 19.7° has a length of only 140 nm, while a (27, 14) one with similar chiral angle (19.6°) exhibits a length of more than 3200 nm (ESI Fig. S4). Similarly, the SWCNT length does not depend on the diameter of tube (ESI Fig. S5a) or the size of catalyst particle (ESI Fig. S5b).

The conclusion is in agreement with the work of Inoue et al. [11], who reported that tube lengths show no clear dependence on chiral angles based on resonance Raman characterizations. However, due to the limitations of Raman spectroscopy, only 5 types of SWCNTs in the $2n + m = 29$ family were presented in their work [11]. Our work includes more SWCNTs, we can thus more safely conclude that the SWCNT lengths do not correlate with their chiral angles, which affects confidence in the general relevance of the proposed screw dislocation growth model [7], as far as the tube length reflects the growth rate.

Neglecting the role of the catalyst is clearly a rough simplification in the screw dislocation model and the role of the catalyst nanoparticle should be taken into account in more realistic models. Thus, further searching for correlations, we rely on previous work showing that the diameter ratio between SWCNT and its linked catalyst particle ($R_d = D_{SWCNT}/D_{NP}$), was a relevant quantity to consider. It enabled classifying the SWCNT/nanoparticle contact into so-called “tangential”, and “perpendicular” growth modes [19]. The stability of these different configurations could be related to

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