論文の内容の要旨

CVD synthesis and characterization of nitrogen-doped SWNTs
（窒素ドープ単層CNTのCVD合成と評価）

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The ability to tune the electrical and optical properties of single-walled carbon nanotubes (SWNTs) is a long-standing goal of SWNT synthesis. The properties of SWNTs are strongly dependent on their structure, and typically become more enhanced as the nanotube diameter decreases. As a result, chirality and diameter control particularly during synthesis offers great potential for tuning the properties of nanotubes. Conventional methods generally provide nanotubes inherently devoid of chirality control. However, their electronic properties may be controlled indirectly by narrowing the diameter range to confine the number of possible chiralities. It is widely accepted that the SWNT diameter is largely determined by the size of the catalyst nanoparticle, and this size relationship has been thoroughly studied. Because of this relationship, there have been many attempts to reduce the SWNT diameter by reducing the catalyst particle size. Supporting materials and templates have been used to influence the diameter of SWNTs via catalyst morphology or cap formation [1–3]. SWNTs with diameters in the range of 0.6–1.1 nm have been synthesized by impregnating SiO_2 particles with Co/Mo [1, 3]. A similar selectivity has been obtained using Co/Fe [2], Fe/MgO [4], and Co incorporated into MCM-411 [5]. These methods, however, require the use of a powder, mesoporous material. Separating the SWNTs from the support requires significant post-processing, which can alter the nanotube properties.

Several methods to alter the SWNT structure during growth have also been demonstrated by changing growth temperature [2, 6], and/or pressure [7, 8]. Changes in diameter along a nanotube axis due to rapidly changing temperature have been previously reported for individual SWNTs [9], DWNTs [10], and other configurations of intramolecular junctions [11, 12]. A potentially non-templated approach to control the SWNT diameter is in addition by the choice of carbon feedstock, such as carbon monoxide [3], ethanol (EtOH) [2], methane [13], acetylene [14], ethylene [15], or other organic chemical sources [16]. There are fewer studies on the influence of the precursor, but SWNT diameters have been found to be sensitive to abrupt changes in feedstock flux [17, 18]. Tian et al. [19] recently demonstrated successful control over the diameter in the range of 1.2 to 1.9 nm by adjusting CO_2 concentration. Selectivity of diameter and chiral angle have also been shown by selective etching [23]. Acetonitrile has also been used to synthesize nitrogen (N)-doped carbon nanotubes [24–26], and some groups have reported a reduction in SWNT diameter due to the presence of nitrogen [26]. However, the role of nitrogen in this diameter change is not yet understood.

Such nanoscale one-dimensional (1D) space inside SWNTs has been additionally attracting many studies relative to the interaction of carbon atoms and encapsulated elements. The nanospace inside SWNTs have been initially realized for high efficiency of hydrogen storage [27]. The confined nanospace has been later on used to the variety of metals oxides by opening nanotube caps after synthesis and re-filling desired metals [28], including zero-dimensional (0D) carbon allotrope as fullerenes (peapods) [29] and nanowires [30]. However, gas molecules can be encapsulated during synthesis, which does not require any cap opening afterward. While carbon nanotubes are being synthesized, the presence of by-product N_2 molecule from decomposition of carbon feedstock has been previously reported [31]. The somewhat encapsulated N_2 molecules are linearly restricted in certain direction by host nanotube-induced interaction inside the confined nanospace of multi-walled carbon nanotubes (MWNTs) or hollow carbon nitride nanofibers [32, 33]. Still, sufficient alignment of 1D N_2 molecules is remained unclear.

In this PhD study, pure and mixed ethanol and/or acetonitrile feedstocks were employed to grow vertically aligned (VA-) SWNTs by no-flow chemical vapor deposition (CVD) from Co/Mo binary catalyst. The mean diameters of the VA-SWNTs synthesized from identically prepared catalyst particles are as different as 2.1 nm for pure ethanol feedstock and 0.7 nm for pure acetonitrile feedstock without changing the vertical alignment [34, 35]. Upon adding marginal amount of acetonitrile into ethanol feedstock, the atomic nitrogen concentration saturates at 1.2 at.%. This saturation correlates with the decrease in mean diameter. The alignment of by-product encapsulated N_2 molecules are studied on nitrogen doping of small-diameter SWNTs during synthesis process by employing high resolution near-edge X-ray absorption (NEXAFS) along with molecular dynamics simulations (MD). The finger-print of co-axially aligned N_2 molecules observed from NEXAFS is observed with polarization dependence that is in agreement with the MD simulation results in which the movement of N_2 is clearly minimized as diameter of host VA-SWNTs reduces [36]. Furthermore, I also demonstrate reversible diameter modulation of vertically aligned SWNTs (VA-SWNTs) by adding acetonitrile to the feedstock during synthesis by alcohol catalytic chemical vapor deposition (CVD). This change was observed regardless of the sequence in which the carbon feedstocks were introduced. Based on this reversibility, investigation of the layer interface, and our previous findings we put forward an explanation of nitrogen's role in reducing the diameter of SWNTs [37].

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