



Research paper

Spontaneous and controlled-diameter synthesis of single-walled and few-walled carbon nanotubes

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ABSTRACT

In this study, we explored the spontaneous and controlled-diameter growth of carbon nanotubes. We evaluated the effects of catalyst density, reduction time, and a number of catalyst coating on the substrate (for multi-walled carbon nanotubes) on the diameter of single-walled carbon nanotubes and the number of layers in few-walled carbon nanotubes. Increasing the catalyst density and reduction time increased the diameters of the carbon nanotubes, with the average diameter increasing from 1.05 nm to 1.86 nm for single-walled carbon nanotubes. Finally, we succeeded in synthesizing a significant double-walled carbon nanotube population of 24%.

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1. Introduction

Carbon nanotubes (CNT) are currently in the limelight in scientific as well as engineering fields owing to their unique characteristics. CNTs possess high thermal conductivity, electrical conductivity, and unique optical properties [1–6], which enable their application in various engineering fields, and for nano-electronic devices [7], hydrogen storage [8], electron field emitters [9], and field effect transistors (FET) [10,11]. Over the years, various methods have been developed to synthesize CNTs, such as arc discharge [12,13], laser ablation [14,15], and catalytic chemical vapor deposition (CVD) [16–18]. The CVD process provides a reliable approach to grow nanotubes on different substrates and is well-suited for the scalable growth of high purity multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs).

The characteristics of CNTs depend on the number of layers and its chirality. In the case of SWCNTs, the characteristics are determined by the chirality, while in MWCNTs, the characteristics depend on the number of walls, with the properties approaching that of amorphous carbon as the number of layers increases. CNTs with “few” layers are usually distinguished from MWCNTs and are termed as double-walled carbon nanotubes (DWCNTs) or triple-walled carbon nanotubes (TWCNTs). In general, the characteristics exhibited by few-walled carbon nanotubes tend to be different

from those of MWCNTs and are often more desirable for engineering applications. DWCNTs and TWCNTs are therefore deemed interesting materials in the scientific and engineering fields. CNTs with a few walls are superior to SWCNTs and MWCNTs in some respects; they are thermally more stable than SWCNTs [19] and mechanically more flexible than MWCNTs [20].

Previous studies have found that the diameter of CNTs depends on the size of the catalyst particle [21,22] and the catalyst chemistry [23]. While many studies have explored the possibility of controlling the diameter of the CNT using photolithography [24–28], and recently some outstanding results were reported using discharge method [29–31] and chemical vapor deposition method for synthesis of vertically aligned DWCNTs [32]. In this study, we focused on controlling the layers carbon nanotube without using the expensive method of photolithography. Instead, we examined changing catalyst density, reduction time, and number of dip-coating immersions on the substrate (for MWCNTs), and observed the effect on the diameter of SWCNTs and the distribution in the number of layers of MWCNTs. Consequently, we found the reduction time to be the most influential parameter, and thereby succeeded in synthesizing DWCNTs with a population of 24%.

2. Experimental

The catalyst was coated onto a quartz glass substrate by employing the dip-coating method. We dispersed cobalt acetate and molybdenum acetate dimers in ethanol and controlled their concentration to be between 0.01 and 0.1 wt%. During the

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dip-coating process, the quartz substrate was immersed in the abovementioned solution 1 to 5 times and the lifting speed was fixed to be 6.0 cm/min. The spurious organic compounds on the substrate were removed by baking at 400 °C for 10 min in atmospheric conditions.

Fig. 1 shows a schematic of the experimental apparatus used for synthesizing CNTs. The electrical furnaces were heated up to 800 °C and the Ar/H₂ flow was maintained at 300 sccm and 40 kPa to reduce the catalyst. This reduction process was also expected to affect the sintering of catalyst particles. Therefore, we varied the sintering time after reduction from 0 to 180 min. After the reduction process, CNTs were synthesized from an ethanol precursor using the CVD method. The reaction pressure, flow rate and reaction time were 1.3 kPa, 450 sccm, and 10 min, respectively.

Transmission electron microscopy (TEM) and Raman spectroscopy analyses were carried out to measure the diameter and number of layers. First, Raman spectroscopy was employed to roughly estimate the effect of dip-coating and calcination times. The excitation wavelengths used were 632, 514, and 488 nm. In the case of the SWCNTs, radial breathing modes (RBM) were employed to estimate the distribution of diameters as a function of wavenumbers as shown below, though this mode is a resonant signal.

$$d = \frac{248}{w}$$

While several candidate-equations have been proposed to express the relationship between the diameter and wavenumber [33–37], we employed the abovementioned equation, where d is the diameter and w is the Raman shift. The RBM peak was verified by a Kataura plot [38].

3. Results and discussion

Referring to a scanning electron microscopy (SEM) image of as-grown CNT, some of samples showed standing CNT forest (shown in the supplemental materials) on the substrate that is so-called vertically aligned CNT film. This is because when catalyst particles are uniformly dispersed on the entire substrate surface, CNTs grow from all the particles to the same extent. Here, if the density of the particles is sufficiently high, the CNTs are unable to grow along the

surface, but grow perpendicular to the substrate. This phenomenon has been reported by Murakami et al. using similar experimental conditions [39].

Fig. 2 shows the representative RBM spectra obtained using an excitation wavelength of 632 nm. For the data shown in Fig. 3, we fixed the number of immersions during dip-coating, as well as the density of the dip coating solution in order to isolate the effect of reduction time, which influences particle sintering. The peak at around 200 cm⁻¹ is found to always dominate for all conditions. However, it is clear that the diameter distribution shifts to become broader as the sintering time becomes longer. Because the RBM mode is a resonant signal, the RBM distribution cannot be used to calculate the exact diameter distribution of SWCNTs. However, we evaluated the qualitative effect of the catalyst density and reduction time on the average diameter of the SWCNTs by roughly estimating the average diameter (\bar{d}) using data from three different excitation wavelengths (488, 514, and 632 nm) in accordance with the equations shown below:

$$\bar{A}_{i,\lambda} = \frac{A_{i,\lambda}}{\sum_i A_{i,\lambda}}$$

$$\bar{d} = \frac{1}{3} \left[\sum_i \bar{A}_{i,632} \cdot d_{i,632} + \sum_i \bar{A}_{i,514} \cdot d_{i,514} + \sum_i \bar{A}_{i,488} \cdot d_{i,488} \right],$$

where $A_{i,\lambda}$ is the spectral area under the peak observed using an excitation wavelength of λ , and $d_{i,\lambda}$ is the corresponding diameter obtained from the first equation.

Fig. 3 shows a contour map, which expresses the relationship between the diameter, the catalyst density in solution, and the reduction time. Although, the calculated average diameter is a rough estimation using three different values of excitation wavelength, the qualitative effect of the catalyst preparation on the diameter is evident in Fig. 3. Since the diameter of the SWCNT is strongly affected by the size of the catalyst particles, we speculate that the catalyst particles grew larger during the reduction process. This increase in diameter with the reduction time was observed even when using a low-density catalyst solution. However, the number density of the particles was not sufficiently large to allow sintering into larger diameter particles. It is difficult to count all of catalyst particles, so that we measured the particle diameter

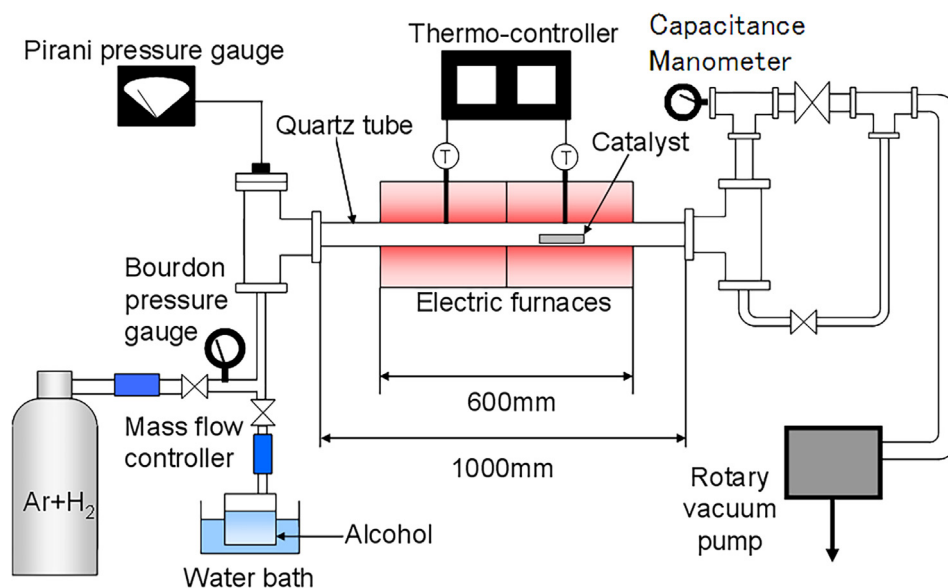


Fig. 1. Schematic of the experimental apparatus.

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