One-step path to highly crystalline multi-walled carbon nanotubes with large inner diameters

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Abstract. High crystalline multi-walled carbon nanotubes with large inner diameters have been produced by a one-step synthesis method from ferrocene pyrolysis in a sealed pre-vacuumed quartz tube. Ferrocene serves as both catalyst and carbon source. The diameters of the as-produced carbon nanotubes have been observed by transmission electron microscope to be 40-60 nm with inner diameters of 20-40 t shells for the encapsulation experiments. The high crystallinity of the as-produced carbon nanotubes has also been characterized by Raman scattering and X-ray diffraction (XRD) measurements.

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention due to their unique mechanical and electronic properties since its discovery in 1991[1]. Due to the broad application prospects of carbon nanotubes, such as flat panel display [2, 3], reinforcing phases of composite materials [4], filter membranes [5], nano-package unstable substance, special physical and chemical nanoreactors [6, 7], etc., many countries have increased their research efforts on carbon nanotubes. As far as we know, various methods can be utilized to synthesize carbon nanotubes, such as chemical vapor deposition (CVD) [8], laser vaporization [9], arc discharge [10, 11] and pyrolysis [12]. The carbon nanotubes with large inner cavity, high crystallinity, and no blockage are promising nanoreactors for encapsulation experiments and multiple applications. Different structures of metal-carbon materials, such as different valence state metal-carbide, metal nanowires and different hybridized carbon structures, will be produced inside carbon nanotubes by controlling the reaction conditions. The produced metal carbides will be further applied as contrast agents for MRI. However, the multi-walled carbon nanotubes (MWCNTs) produced from CVD with Co/Fe–Al2O3 as catalysts and ethylene as carbon source proved to have relatively small inner diameters (~5nm) [13], limiting its further applications. Many blockages were also observed from the commercial available MWCNTs. The carbon nanotubes prepared by arc discharge have higher crystallinity, but it was difficult for them to disperse and they have relatively small inner diameters.

As widely reported, the growth of CNTs is a catalytic reaction. Thus, the selection of carbon sources and catalysts are crucial to produce carbon nanotubes with different properties. Ferrocene was widely used as catalyst with carbon sources of anthracene, ethylene, acetylene, benzene, thiophene, propylene and xylene [14] to produce carbon nanotubes. Herein, we proposed a one-step path to produce MWCNTs with inner diameter of 20-40 nm. The inner cavities of the as-produced MWCNTs were found to be clean with very few blockages. Ferrocene was adopted as sole ingredient due to its
low cost and elemental component, where both catalyst and carbon source were included. The experimental parameters, such as temperature, heating rate, reagent amount, quartz tube size, and vacuum have been optimized to produce desired MWCNTs. The as-produced MWCNTs were characterized by transmission electron microscopy (TEM), Raman scattering and X-ray diffraction (XRD) analysis.

2. Experimental
Ferrocene (SCR, ≥ 98%, 500 g) was firstly put into the quartz tube after drying in the oven overnight at 60 °C. The quartz tube (inner diameter 20 mm, outer diameter 24 mm, and height 140 mm) was sealed in the presence of ferrocene under a pressure of 10⁻⁵ Pa. This sealed quartz tube was then heated to 700 °C with a heating rate of 1 °C/min, keeping the temperature for 18 h and then cooling down to room temperature in a Muffle furnace (10*10*10 cm).

TEM images were obtained by JEOL JEM-2100 transmission electron microscope, with an acceleration voltage of 200 kV. Raman spectroscopy were obtained from a single monochromator (Reinshaw inVia) equipped with a CCD array detector (1024×256 pixels), excited by a 633 nm argon ion laser. XRD diffraction (D2PHASER, Bruker) patterns were obtained from a Rigaku SmartLab using Cu/Kα radiation (λ=1.5418 Å) at 40 kV and 30 mA.

![Figure 1](image-url) (a) Schematic diagram of the synthesis of MWCNTs from ferrocene; (b) optical image of the as-produced MWCNTs after pyrolysis.

3. Results and discussion
MWCNTs were synthesized from ferrocene pyrolysis in a sealed quartz tube at 700°C under a vacuum of 10⁻⁵ Pa. A schematic diagram of the vacuum-pumping procedure is shown in Figure 1a. Ferrocene decomposed at high temperature in the sealed space to form a high pressure environment, which contributes to the formation of highly crystallinity CNTs (Figure 1b). The inner diameters of MWCNTs were observed to be uniformly distributed in a range of 30±10 nm, as shown in the TEM images of Figure2. The tube walls of MWCNTs grown at 700 °C are straightly aligned and the number of the walls varies from 30 to 40 (Figure 2c, d) observed by high-resolution transmission electron microscope (HRTEM), suggesting a high crystallinity (Figure 2d, inset).

Raman spectra was also taken to compare the crystallinity of MWCNTs synthesized from our methods (named mCNT) with commercial available ones (Xianfeng Nanomaterials Tech., > 95%), from CVD methods. Two types of MWCNTs were adopted for comparison. The inner diameters of one commercial available MWCNTs are around 20-40 nm, named pCNT-1. The other commercial
available one was measured to have inner diameters of 40-60 nm, named pCNT-2. The Raman spectra of pCNT-1 (Figure 3, red), pCNT-2 (Figure 3, blue), and mCNT (Figure 3, yellow) are shown in Figure 3. A much lower I_D/I_G ratio (0.81) was measured for mCNT, while 1.16 and 1.44 for pCNT-1 and pCNT-2 (Figure 3b), respectively. Less defects and edges were suggested for mCNT, indicating a higher crystallinity. Additionally, a narrow and sharp G band (~1570 cm^-1) with apparent shoulder at the left of D’ band (~1600cm^-1) was found for mCNT. As for pCNT-1 and pCNT-2 samples, the G band and D’ band were broader and harder to distinguish from each other (Figure 3b), which further confirmed a higher crystallinity of mCNT. The much weaker D+D’ band of mCNT than those of pCNT-1 and pCNT-2 further confirmed less defects and higher crystallinity for mCNT [15].

Figure 2. TEM images of (a) and (b) for MWCNTs; HRTEM images of (c) and (d) for MWCNTs.

Figure 3. (a) Overall raman spectra for three MWCNTs. (b) details for D and G bands.
XRD patterns were also taken for all three types of MWCNTs (Figure 4). The sharp peak at 26° is assigned to <0 0 2> planes of graphite, which refers to the graphitic degree of materials. Through Gaussian calculation, the corresponding full width at half maximum (FWHM) for pCNT-1, pCNT-2, and mCNT are 1.76 (Figure 4, red), 1.57 (Figure 4, blue) and 0.88 (Figure 4, yellow), respectively. This also suggests higher crystallinity of mCNT. The XRD peak corresponding to <0 0 2> planes of graphite was also observed to shift to higher angle for mCNT (Figure 4, inset), indicating a slightly narrower interplanar distances. The narrower interplanar distances of <0 0 2> planes confirmed a higher crystallinity of mCNT.

![XRD patterns of three MWCNTs](image)

**Figure 4.** XRD patterns of three MWCNTs (red—pCNT-1, blue—pCNT-2, yellow—mCNT). Inset: details of the main peaks around 26°.

### 4. Conclusions

In summary, a one-step path was developed to synthesize MWCNTs with larger inner diameters, higher crystallinity, and fewer blockages. It was realized by thermally decomposing ferrocene in a sealed quartz tube at 700 °C under a vacuum of 10⁻⁵ Pa without additional carbon sources and catalysts. The inner diameters of the as-produced MWCNTs were observed to be about 20-40 nm and the inner spaces of the carbon nanotubes have been observed to be clean by TEM, providing a broader applications for encapsulation experiments. Meanwhile, the tube walls of MWCNTs are straightly aligned and the number of the walls varies from 30 to 40 observed by HRTEM. Also, Raman and XRD were taken for characterization to compare our mCNT with ones purchased from market. Less defects and higher crystallinity of the as-produced carbon nanotubes have also been characterized by Raman and XRD measurements.

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