Role of hydrogen in affecting the growth trend of CNT on micron spherical silica gel

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Abstract. Grafting CNTs onto substrates such as fibres and microparticles offers an alternative approach to tackle the issues associated with dispersion in a composite matrix, as well as additional benefits (hybrid effects) provided by these dual-filler systems. One approach to obtain such hybrid systems is the direct growth of nanotubes on the supporting fibre or particles. Previous study has shown that the CNTs would grow on the silica microparticles with the morphology closely related to the operating conditions such as temperature and time. However, the role of hydrogen in affecting the tube's morphology was not explored before. The particles were synthesized via chemical vapour deposition (CVD) method. Spherical silica gel with 40 - 75 μm diameter was used as the substrate. Toluene and ferrocene were used as the hydrocarbon and catalyst source, respectively. The reaction time was kept for four hours while the temperature was maintained at 850°C. The FESEM and TEM investigation proved that the flow hydrogen during reaction caused a tremendous difference in the outer diameter of the synthesized CNTs. Relatively thin CNT was observed under 50 ml/min of hydrogen flow compared to the particles synthesized without hydrogen. Raman spectroscopy of the CNTs revealed three bands; the disorder-induced D mode (~1321 cm^{-1}), the tangential G mode (~1570 cm-1) and second order G' mode (~2642 cm^{-1}). Raman analysis shows that the synthesized CNTs exhibited all these peaks, confirming the existence of CNTs. As G peak is more intense than D peak for all samples synthesized under hydrogen flow, it can be concluded that CNTs synthesized is indeed of high quality. It can be confirmed that hydrogen plays an important role in influencing the morphology of the synthesized tubes.

1. Introduction

Carbon Nanotube (CNT) gained its popularity as material with extraordinary mechanical, electrical, and thermal properties. The applications that utilized the CNTs cover a wide range; which include as filler in composites, in vivo biomedical application, solar thermal applications; just to name a few. As such, the dimensions and morphology of the CNTs need to be precisely controlled. However, CNTs tend to agglomerate, which causes a real problem if they were to be used as filler in composites. Various work reported on tackling the dispersion issues such as applying high shear force [1], intensive tip sonication [2] and/or mixing the CNTs with surfactant [3]. These processes however involve many steps that proven difficult for industrial processing, which may results in the change in the overall composite processing cycle [4].

Growing CNTs on a substrate via chemical vapor deposition method (CVD) offers an alternative in introducing the CNTs into polymer matrix [5]. The examples of the substrates used are carbon fiber [6], silica fiber [7], and alumina oxide [8]. These CNTs were grown directly on the substrates and become strongly attached to them. As the substrate is normally in micron size, the agglomeration and within the polymer matrix is hindered. Ultimately, the viscosity increment of the resulting suspension became minimum [9].

Several reports have mentioned about the CVD parameters involved during producing these hybrid structures [10]. However, no detail report has been focused on the effects of varying hydrogen flow rate on this porous spherical substrate. Previous study reported the growth of CNT on porous substrate [5] but without the hydrogen flow rate. There was also a report on the effects of hydrogen flow rate where it was reported that hydrogen affects the CNT morphology and crystalline structure [11]. Hydrogen was also reported to etch pyrolytic carbon from the catalyst which eventually delaying the catalyst poisoning [12]. This study investigates the effects of co-flowing hydrogen into CVD on the morphology and crystallinity of the CNTs obtained as well as the amount of CNTs obtained.

2. Experimental

In this work, the CNT was produced under atmospheric pressure in a horizontal CVD. The set up of the CVD system is similar to the one published previously [5], which consists of an electrical furnace, quartz tube, liquid feeding system, and pre heater. Prior to that, the temperature profile along the furnace was performed to identify the area, which constitutes the temperature closest to the set temperature. The zone was located within 10 – 20 cm from the entrance. As such, the substrate and subsequently the CNT product will be collected from this zone.

The synthesis of CNT on spherical silica gel was performed in this CVD system by introducing catalyst via non-floating method. Silica gel was purchased from Sigma Aldrich, which is of high purity grade. According to the safety date sheet, the pore diameter of the porous silica was reported to be 6 nm and the size of the gels in the range between 40 to 75 μm. Toluene and Ferrocene (both purchased from Sigma Aldrich) were used as hydrocarbon source and catalyst, respectively. First, the quartz boat containing silica and catalyst (1:1 wt. %) was placed within the heating zone. Then, the temperature was increased to 850°C while flowing the Argon gas at 300 ml/min. The furnace was left for 10 minutes after the temperature reached 850°C, to allow thermal equilibrium. At the same time, the preheater was also set to 180°C. Then, the toluene was injected into the system at a flow rate of 0.04 ml/min for 4 hours. Once the reaction is over, the toluene flow was stopped, the furnace was set to room temperature, and the Argon flow was set to 100 ml/min. The product was collected once the furnace was cooled.

The experiment was also repeated to assess the effects of hydrogen in influencing the CNT growth. The hydrogen was introduced only during the time when toluene was injected. Two flow rates of hydrogen were used which are 50 ml/min and 100 ml/min. For such cased the flow rate of Argon was reduced to 250 ml/min and 200 ml/min, respectively to ensure that the residence time within the furnaces remains constant for all cases.

All samples including the spherical silica gel substrate were viewed under Zeiss Gemini Scanning Electron Microscope 500 (FESEM). A small amount of sample was placed on a conductive and adhesive carbon tape, which was placed on an aluminum stub. The image was viewed under high vacuum, without undergo coating. Besides FESEM, the sample was also subjected for High Resolution Transmission Electron Microscopy (HRTEM), which was also performed to view the tube's inner diameter (ID) and the outer diameter (OD) as well as wall formation. The samples were viewed under bright field mode by using LIBRA 200FE. Thermo Gravimetric Analysis (TGA) was also used to determine the amount of the CNTs produced as well as the oxidation temperature, which indicates the thermal stability of the sample. Simultaneous thermal analyzer (STA) 8000 by Perkin Elmer was used in this work. Approximately 10 ± 0.5 mg particle was placed in the pan sample holder before heating it (from 30°C to 1000 °C at 5°C/min) in oxygen atmosphere at a flow rate of 20 ml/min. Raman Spectrometry (inVia Contor Raman microscope by Renishaw) was also used to confirm the

crystallinity of the samples produced. The laser wavelength was set to 532 nm with 10s of exposure time and 10% laser power.

3. Results and Discussion

Figure 1 below show the FESEM images captured for all samples viewed at relatively low (left) and high (right) magnification. Without H_2, the CNT density seems higher (Fig 1a) and the tubes appear thicker (Fig 1b). Increasing the H_2 flow rate to 50 ml/min and 100 ml/min resulted in the formation of thinner tubes (Fig 1d and 1f). However, it should be mentioned that the CNT density seems to reduce slightly for samples produced with H_2 atmosphere (Fig 1c and 1e).
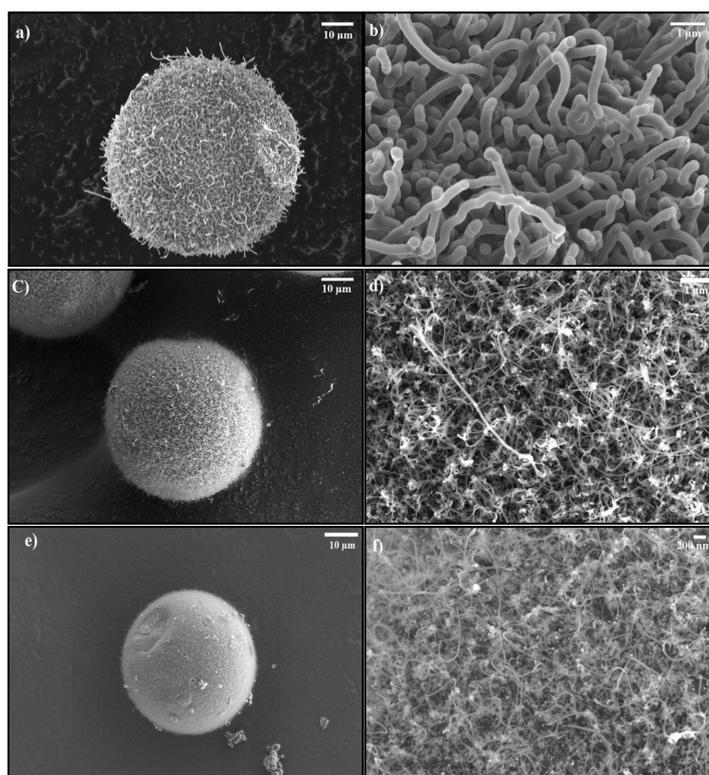

Figure 1. Typical FESEM images of CNT synthesized on spherical silica substrate under 0 ml/min H_2 (a and b), 50 ml/min H_2 (c and d), and 100 ml/min H_2 (e and f).

It can be seen immediately that the tubes synthesized without H_2 flow appear thicker (Fig 1b), compared to the those synthesized under 50 ml/min H_2 flow rate (Fig 1d) and under 100 ml/min H_2 flow rate (Fig 1f). It could also be seen that the density of the CNTs seemed to be higher when no H_2 was introduced. It is also obvious that the OD of the tubes synthesized under H_2 atmosphere is smaller, especially at 100 ml/min H_2 flow rate.

Typical images obtained from HRTEM analysis are as shown in Figure 2. It becomes apparent that the tubes synthesized in the absence of H_2 flow are very thick due to the deposition of amorphous carbon coating the wall (Fig 2a and 2b). This indicates excessive deposition of pyrolitic amorphous carbon during these 4 hours of growth time. However, it can be seen that the outer diameter (OD) of the tubes synthesized under hydrogen flow is smaller (Fig 2c and 2d). A well graphitic wall was also observed in the samples synthesized in the presence of hydrogen at both flow rates. The outer walls also appear to be free from amorphous coating, demonstrating the role of H_2 in etching the unwanted amorphous carbon deposition on the outer walls, causing a formation of thin OD of the synthesized CNTs.
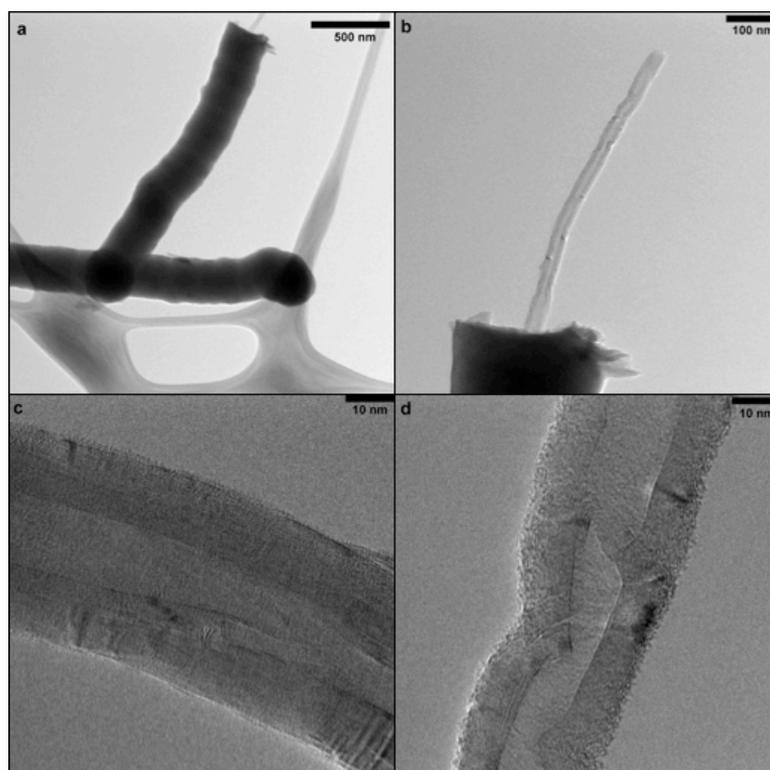
Figure 2. Typical TEM images of the CNTs produced without hydrogen flow (a and b), 50 ml/min H_2 (c), and 100 ml/min H_2 (d).

Further investigation on the inner diameter (ID) size shows that values do not change drastically regardless whether the H_2h is introduced or not (Fig 3). The mean ID values recorded are 27.46 ± 1.80 nm (no H_2), 10.44 ± 2.93 nm (50 ml/min H_2), and 9.29 ± 2.35 nm (100 ml/min H_2); which indicates that H_2 flow does not exert any effects on the ID size of the tubes. FESEM images of the uncoated porous substrate revealed that there exist pores with sizes within the range of the mean ID of the tubes. In the CNT growth via CVD, the catalyst that was already placed within the heating zone first decomposed into iron and deposited over the porous substrates. Then, the toluene decomposed on the catalyst to yield carbon and hydrogen atoms. These carbon atoms underwent surface diffusion along the catalyst surface before forming a tubular structure [13]. It can be concluded in this study that the pore size restricts the catalyst size, which eventually restricts the ID of the tubes.
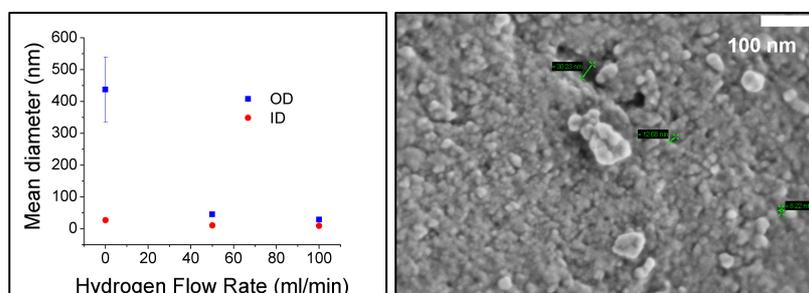
Figure 3. The mean OD and ID of the tubes synthesized (left) and FESEM image of the uncoated substrate showing the size of the pores which are 30.23 nm, 12.68 nm, and 8.22 nm from top to bottom, respectively (right).

In TGA analysis, the particles were heated at a fixed heating rate from room temperature to 1000°C in oxygen environment. The CNTs would start to decompose between 450 – 550°C. As such the weight loss shown in Figure 4 represent the amount of CNT grafted on the substrate. Presence of H_2 decreased the CNT amount, with the sample produced at 100 ml/min H_2 resulting in the lowest CNT amount. Although the CNT amount is the highest when no H_2 is present, the quality is the poorest as evidenced from FESEM and TEM analysis.
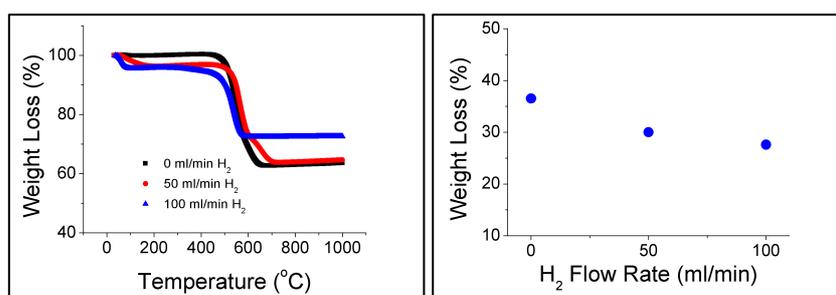

Figure 4. TG curves for samples produced (left) and the corresponding carbon content (right).

Raman analysis provides a quick, nondestructive technique in assessing the crystallinity of the CNT. The G band is the characteristic peak for the stretching vibration of carbon sp2 bonds in a hexagonal lattice, and the D band corresponds to the disordered sp2 phase plus possible contributions of the scattering of sp3-bonded carbon. It can be seen that all specimens display peaks near 1336 and 1590 cm^{-1}, assigned to the D- and G-bands, respectively (Fig 5 (left)). The D peak is very weak in the case for samples produced under 100 ml/min H_2 flow, indicating CNTs produced is of low defects. The peak intensity ratio of the G band to the D band (I_G/I_D) is also shown that indicates the CNT crystallinity (Fig 5(right)). In the presence of hydrogen flow, the ratio is more than 2, indicating high crystallinity of the CNTs produced. The value is highest in the case of 100 ml/min H_2. H_2 etched the amorphous materials, minimizing the defects on CNT walls and hence increasing the I_G/I_D ratio.
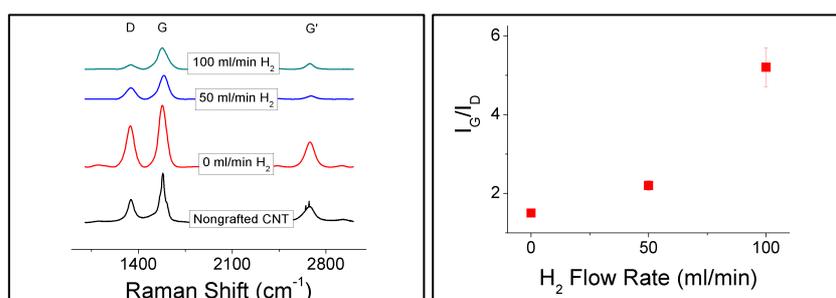

Figure 5. Raman Spectra for sample of different hydrogen concentrations where the spectra for nongrafted CNT (purchased) is shown for comparison (left) and the corresponding I_G/I_D ratio (right).

4. Conclusions

In this work, CNTs were successfully synthesized on porous spherical silica substrate via CVD method. The mean ID follows the pore size of the substrate, regardless of the H_2. The mean OD shows an obvious difference; where higher H_2 flow rate causes thinner OD formation, demonstrating role of H_2 in etching the outer wall of the tubes. Raman results confirm high crystallinity of the samples produced at high H_2 flow rate.

Acknowledgement

References

[1] Sandler JKW, Kirk JE, Kinloch IA, Shaffer MSP, and Windle AH, 2001 *Polymer* **44** 5893

[2] Ryan KP, Cadek M, Nicolosi V, Blond D, Ruether M, and Armstrong G, 2007 *Compos. Sci. Technol.* **67** 1640

[3] Islam MF, Rojas E, Bergey DM, Johnson AT, and Yodh AG, 2003 *Nano Lett.* **2** 269

[4] Godara A and Vaugien T, *JEC Composites*, 2009 64

[5] Othman RN, Kinloch IA, and Wilkinson AN, 2013 *Carbon* **60** 461

[6] Qian H, Bismarck A, Greenhalgh ES, Kalinka G, and Shaffer MSP 2008 *Chem Mat.* **20** 1862

[7] Qian H, Bismarck A, Greenhalgh ES, and Shaffer MSP 2010 *Carbon* **48** 277

[8] He DL, Bozlar M, Genestoux M, and Bai JB 2010 *Carbon* **48** 1159

[9] Wilkinson AN, Kinloch IA, and Othman RN 2016 *Polymer* **98** 32

[10] Huang SM 2003 *Carbon* **41** 2347

[11] Zhang H, Cao G, Wang Y, Yang Y, Shi Z, and Gu Z 2008 *J. Phys. Chem. C* **112** 12706

[12] Wasel W, Kuwana K, Reilly PTA, and Saito K 2007 *Carbon* **45** 833

[13] Oberlin A, Endo M, and Koyama T 1976 *J Cryst Growth* **32** 335