Production of CNT yarns for use as filaments in incandescent bulb: effect of carbon source and state of catalyst on production of CNT

Veronica Bodiba, Ezinne Igokwe, Ndanganeni Mahangani, Oluseyi Aberfa, Michael Olawale Daramola*, Sunny E. Iyuke

School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Wits 2050, Johannesburg, South Africa.

*Corresponding author e-mail address: Michael.Daramola@wits.ac.za

Abstract. Presence of highly aligned carbon nanotubes (CNTs) bundles is a prerequisite to producing good quality CNTs that will retain their original good electrical and mechanical properties when spun into yarn. In this study, effects of carbon source and state of catalyst on the CNT yield and quality during the production of CNTs were investigated. CNTs were produced in a Swirled Continuous CVD reactor using acetylene and methane as carbon sources and ferrocene as a catalyst to investigate the effect of carbon source and the production was carried out with the state of the catalyst altered to investigate effect of state of catalyst on the yield and quality of the CNTs. The quality and purity of the produced CNTs were checked with Raman and Scanning electron microscopy (SEM) provides information on the morphology of the produced CNTs. SEM images of the produced CNTs using acetylene gas reveal the presence of more nanoballs than those produced using methane under the similar conditions. However, amount of CNTs produced using methane is very low compared to the amount obtained when acetylene was used. The CNT yield from methane was enhanced when ferrocene (catalyst) was dissolved in cyclopentane. Results from SEM and Raman Spectroscopy indicates CNT bundles with longer lengths and reduced number of nanoballs when methane was used together with ferrocene dissolved in cyclopentane as compared to using ferrocene in a solid state.

1. Introduction

To maximize the excellent mechanical, electrical and thermal properties possessed by CNTs in the nanoscale in fabrication of components, devices and other applications has increased efforts and interest in production macroscopic assemblies of CNTs. Research aimed at optimizing the production of well aligned, good quality and quantity CNTs to meet the requirements for spinning into yarns are currently on top gear. The catalytic chemical vapor deposition (CCVD) is currently the most viable process for the synthesis of carbon nanotubes. The influence of numerous growth parameters on the resulting nanotubes characteristics, such as diameter, length, number of graphene layers, defect density etc., has been studied [1,2].

Generally, nano-sized transition metal particles, e.g., nickel, iron, cobalt, molybdenum and copper, have been successfully used in CCVD either in oxide or metallic forms or as mixtures [1,2]. The solubility of carbon in catalyst particles determines the ability of metal to catalytically decompose gaseous carbon-containing molecules. As Moisala et al. highlighted in their review, the solubility of carbon in iron and nickel significantly increases for metal particles with a diameter of less than approximately 10 nm [1]. Seidel and co-workers investigated the difference of the carbon nanotubes growth behaviour when Fe, Co, and Ni catalysts were used [3].

The authors observed that the order of the lowest temperature agreements with the order of the bulk melting points of the three transition metals (Ni, 1,450 °C; Co, 1,490 °C; Fe, 1,540 °C). For binary compounds, e.g., cobalt–molybdenum [4], iron–molybdenum [5] and iron–cobalt [6,7], the yield of carbon
nanotubes has been observed to increase significantly. However, the precise catalyst composition has a great influence on the final product. Fe$_{1-x}$Co$_x$ alloys are among the most efficient catalysts for the synthesis of multi-walled carbon nanotubes [6,7]. The resulting yield, as well as the nanotubes characteristics, strongly depends on the parameter x.

Most used carbon precursors in CVD method are methane, carbon monoxide, acetylene, ethylene, benzene and toluene [8]. It has been discovered that the use of unsaturated hydrocarbons as carbon precursors results in high yield deposition rate as compared to the use of saturated hydrocarbons [9]. Saturated hydrocarbons are favoured for the growth of single walled carbon nanotubes (SWCNTs) because they synthesize graphitized filaments with fewer walls than when using unsaturated hydrocarbons. Furthermore, excessive carbon precursor concentration or hydrocarbon self-pyrolysis are some of the causes of catalyst poisoning during high temperature processing. This can be avoided by limiting carbon precursor feed rate to the catalyst particles by controlling partial pressure of carbon precursor and choosing the carbon precursor according to the decomposition rate [10].

Obtaining high quality nanoyarns that will exhibit the same electrical and mechanical properties as the original carbon nanotubes (CNTs) bundles from which they are made has been a great challenge, possibly due to inconsistence in the results reported in literature on the production of high quality CNTs, intermediates for nanoyarn production. Against this background, effects of carbon source and state of catalyst on the CNT yield and quality during the production of CNTs in a Swirled Continuous CVD reactor were investigated in this study.

2. Experimental

CNTs were produced in a swirled continuous CVD reactor using acetylene and methane as carbon sources and ferrocene as a catalyst to investigate the effect of carbon source on the yield and quality of produced CNTs. During the production, 10 g of ferrocene (Fe(CO)$_5$) catalyst was vaporizer at 300°C in the vapourizer attached to the reactor and the vapourized catalyst was carried to the reaction zone, where acetylene or methane and H$_2$ gas were introduced, by argon gas. The flow rate of the carbon source, the argon gas and the H$_2$ gas into the reactor were 150 ml/min, 150 ml/min and 50 ml/min, respectively. The reaction zone (inside the CVD reactor) was maintained at reaction temperature of 850°C and the reaction was run for 12 minutes. The temperature at the reaction zone was measured with a PT-100 thermocouple and controlled with PID controller built with the reactor. To gain insight into the effect of temperature on the yield and quality of produced CNTs, the reaction temperature was varied from 850°C to 950°C at a step change of 50°C.

To investigate the effect of changing the state of catalyst from solid state to liquid state on the quality and yield of CNTs produced in the reactor, 10 g of ferrocene powder was dissolved in 10 ml of cyclopentane. The liquid solution was vaporizer at 300°C in the vapourizer attached to the reactor and the vaporized catalyst was carried to the reaction zone, where acetylene or methane and H$_2$ gas were introduced, by argon gas. The flow rate of the carbon source, the argon gas and the H$_2$ gas into the reactor were 150 ml/min, 150 ml/min and 50 ml/min, respectively. The reaction zone (inside the CVD reactor) was maintained at reaction temperature of 850°C and the reaction was run for 12 minutes. Figure 1 depicts the experimental set-up used in the investigation. The yield of the produced CNTs was calculated by measuring the amount of CNT collected after the production. The quality of the produced CNTs was checked using scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) for morphology and elemental composition; and Raman spectroscopy to check the degree of defect and graphitic formation. The results obtained from the characterization were compared to obtain logical conclusions.
3. Results and discussion

Figure 2 depicts the CNT yield obtained when acetylene and methane were used as the carbon sources. The use of acetylene displayed a higher yield compared to methane at the various temperatures studied. For both the maximum CNT yield was recorded at 900°C, where the CNT yield with acetylene at this temperature is about 14.5 times higher than that of methane. Acetylene gives high yield because it is easier to break carbon chains in unsaturated hydrocarbons than in saturated hydrocarbons \[11\]. The SEM images of CNTs produced are presented in Figure 3. From the images, it is evident that CNTs produced with acetylene contain more of nanoballs than the nanotubes and the length of the nanotubes is short, making production of good quality yarns from these nanotubes a mirage. However, better CNT bundles with fewer nanoballs were obtained when methane was used as a carbon source. The CNTs from methane contain a substantial number of nanotubes with reasonable length and excellent spinnable array required to produce yarns.

EDX could be employed to determine the purity and elemental composition of the produced CNTs from different carbon sources. Elemental compositions of the produced CNTs obtained from EDX are shown in Figure 4. The major component of the products obtained from the CVD using acetylene and methane as carbon sources are carbonaceous in nature (see Figure 4). Acetylene products contain more carbon but the accompanying SEM images indicate the quality of the product. Methane has more impurities from the iron based catalyst but this can be easily purified. The ratio of the intensities of the D and G bands is a suitable identification of the quality of bulk samples. Therefore, from the Raman spectra in Fig 5, it is evident that the use of methane produces CNTs with a fewer structural defects as compared to the CNTs from acetylene. There is also an indication that the methane source produced mostly single-walled carbon nanotubes (SWCNT) and double-walled carbon nanotubes (DWCNT). Both SWCNT and DWCNT show higher differences in intensities of D and G bands \[12\]. The presence of radial breathing mode (RBM) seen in Fig 5b is a strong indication of the presence of SWCNT in CNTs produced from methane carbon source \[13\].
Figure 2: CNT production yield using various carbon sources—(methane and acetylene).

Figure 3: SEM images of CNT produced from (a) Acetylene (b) Methane
Figure 4: Energy Dispersive X-ray spectroscopy (EDX) of CNT produced from (a) Acetylene and (b) Methane

| Element | Weight % | Atomic % |
|---------|----------|-----------|
| C       | 89.08    | 94.37     |
| O       | 5.55     | 4.41      |
| Fe      | 5.37     | 1.22      |
| **Totals** | **100.00** |          |

Figure 5: Raman spectroscopy of a) Acetylene and b) Methane

Fig 6 shows a significant improvement in the yield of CNT produced from ferrocene dissolved in cyclopentane. The maximum yield occurred at 900°C for both the ferrocene in solid state and the ferrocene in liquid state. When ferrocene was dissolved in cyclopentane, the CNT yield was 6.8 times
higher than the CNT yield when ferrocene was in solid state. The higher yield could be attributed to the participation of cyclopentane in the reaction since it is a hydrocarbon, thereby enhancing the carbon concentration in the reaction \[14\]. Comparing the SEM images of the produced CNT bundles when the catalyst was in solid state (Fig 7a) with the SEM image when it was dissolved in cyclopentane (Fig 7b) reveals that there is presence of CNTs together with nanoballs in Fig 7a while Fig 7b shows a better formation of CNTs characterized with long array of spinnable multi-walled and single-walled CNTs with a few number of nanoballs. These types of CNTs formed when ferrocene was dissolved in cyclopentane will result in the formation of high quality CNT yarns would possess the same quality as the original CNTs.

![Figure 6: CNT yield with varying state of catalyst using methane as carbon source.](image)

**Figure 6:** CNT yield with varying state of catalyst using methane as carbon source.

![Figure 7: SEM images for CNT bundles produced at various conditions: (a) Methane used as a carbon source with ferrocene in a solid state and (b) Methane used as a carbon source with ferrocene dissolved in cyclopentane.](image)

**Figure 7:** SEM images for CNT bundles produced at various conditions: (a) Methane used as a carbon source with ferrocene in a solid state and (b) Methane used as a carbon source with ferrocene dissolved in cyclopentane.

**4. Conclusion**

In this study, effect of carbon source and the state of catalyst on the yield and quality of CNTs has been investigated. Results of the investigation reveal that using acetylene as a carbon source yielded higher
amount of CNTs compared to using methane gas. However, the quality of CNTs produced when methane gas is used is far better than when acetylene gas is used. In addition, pre-dissolution of the ferrocene catalyst in cyclopentane prior to vapourization enhances the quality and yield of CNTs produced as compared to non-dissolution of the catalyst prior to vapourization.

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