Facile floating catalyst chemical vapor deposition synthesis of carbon nanotubes for application in sustainable construction composites

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ABSTRACT

Carbon nanotubes (CNTs) are cylindrical nano-sized carbon allotropes made up of rolled up graphene sheets. They are characterized by high surface area and aspect ratio, high thermal stability and excellent mechanical strength and electrical conductivity. In this study, a floating catalyst chemical vapor deposition (FCCVD) method was adopted to synthesize multiwalled CNTs (MWCNTs). The MWCNTs were of high quality and were further purified and oxidized through acid treatment. Nitrogen gas was used as the precursor carrier gas and to create an inert atmosphere during synthesis at high temperatures (750 – 850 °C). The process used, eliminated the need to use other reducing gases like Ar/H_2 gas mixture, making it more facile. The CNT sizes and cystallinity increased with an increase in temperature but were all thermally stable after heating in air. The CNTs were further used in strong construction composite materials.

Key words: carbon nanotubes, floating catalyst chemical vapor deposition, sustainability,

1 INTRODUCTION

Carbon nanotubes are light-weight cylindrical carbon allotropes with excellent inherent properties [1]. They are made up of rolled graphene sheets which can be single, double or multi sheets, resulting in the production of single walled (SWCNTs), double walled (DWCNTs) and multi-walled (MWCNTs) carbon nanotubes respectively [2].

The various types of CNTs give them unique properties and find application in fields such as electronics, reinforcement composites and energy storage, amongst other applications [3]. To increase the application of CNTs to an industrial scale, synthesis processes that produce high purity and volumes of the CNTs must be considered.

The floating catalyst chemical vapor deposition method (FCCVD) among other CVD methods offers an advantage, in that it can be scalable to produce large volumes, as the process can be continuous [4]. In FCCVD, the hydrocarbon and catalyst precursors are introduced inside the reactor simultaneously [5]. Thus, the possibility of catalyst deactivation is eliminated, which assists in the increased productivity of CNTs. The produced CNTs are of high purity and crystallinity which improves their inherent properties [6]. CNTs due to their high strength, high aspect ratio

and small size, have been used as fillers in construction composites. They facilitate load transfer as a result of the bridging phenomena which in turn reduces the potential micro-cracks in composites and improve the overall strength and durability [7].

In this study, a facile synthesis of MWCNTs using only nitrogen as a carrier gas, without the use of a promoter was employed. The effect of growth temperature was investigated on the quality of the CNTs. The intended application of the MWCNTs was the reinforcement of building and construction composites such as bricks.

2 MATERIALS AND EXPERIMENTAL

Nitrogen gas (99.999%) was supplied by Afrox (South Africa). Ferrocene (98%) and toluene were purchased from Sigma Aldrich (South Africa). The materials were used as received without any purification.

A horizontal FCCVD reactor was employed in the synthesis of the MWCNTs. A quartz tube was inserted horizontally into an electrical furnace with the outlet of the tube connected to a gas bubbler. The temperature inside the quartz tube was set at 750-850°C, under a flow on 120 ml/min N_2 at atmospheric pressure.

Typically, 0.4 g catalyst (ferrocene) was dissolved in 10 ml toluene which was the carbon source and stirred for homogeneous mixing. The solution was placed in a 10 ml syringe and injected into the heated quartz tube inside an electronically controlled furnace by means of a syringe pump at 0.2 ml/min injection rate. When the injection was complete, the electrical furnace temperature was allowed to cool down to room temperature under an inert environment (N_2).

The CNTs formed on the walls of the quartz tubes were collected. The FCCVD method resulted in the formation of flaky sponge-like CNT bundles. The CNTs were purified using HNO_3 under reflux at 90 °C for 4 h. The CNTs were then filtered and washed until pH 7. Lastly, the CNTs were oven dried at 100 °C overnight and taken for characterization.

The CNTs were characterized using the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for morphology and size analysis. Furthermore, Raman spectroscopy was used to study the crystallinity and thermal gravimetric analysis was performed to examine the purity and thermal stability of the CNTs.

3 RESULTS AND DISCUSSION

The synthesis of CNTs was investigated over a temperatrure range 750 °C – 850 °C. At a lower temperature (750 °C), the CNTs produced were tangled and other carbon impurities were present as shown in Figure 1 a). This was because of the low rate of decomposition of toluene which allowed the growth of other less crystalline forms of carbon. As the temperature was increased, the presence of amorphous materials was reduced, exhibiting sufficient heat for the synthesis of crystalline CNTs. The average diameter of the CNTs synthesized at 750, 800 and 850 °C was 43, 77 and 83 nm respectively. An increase in temperature resulted in an increase in the diameter of the CNTs. This was ascribed to the catalyst nanoparticles agglomerating at higher temperatures to form larger particles which resulted in CNTs of larger diameters.

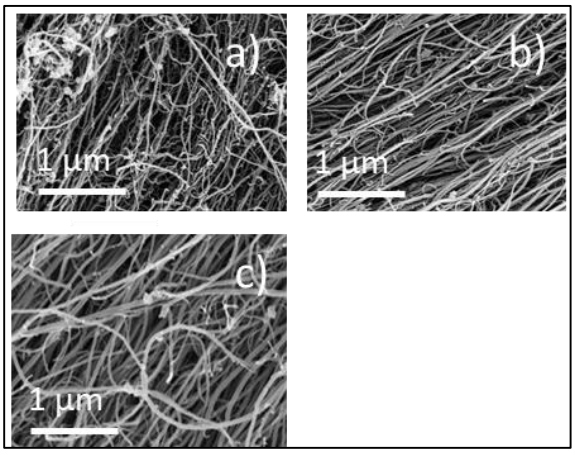

Figure 1: SEM images of CNTs synthesized at a) 750, b) 800 and c) 850 °C

Figure 2 shows that hollow MWCNTs with closed tips were synthesized. The closed-tips signify a base-growth mechanism. Furthermore, the elongated catalyst particles as shown in Figure 2 a) confirms that the catalyst took part in the growth of the MWCNTs. As the growth temperature was increased, the diameter of the MWCNTs increased as also shown in Figure 1. Residual iron particles from the catalyst were observed to be encapsulated within the hollow structure of the CNTs. As the temperature was increased, more crystalline MWCNTs were formed with some structural deformities and impurities. At 850 °C, highly crystalline MWCNTs were produced with minimal impurities.

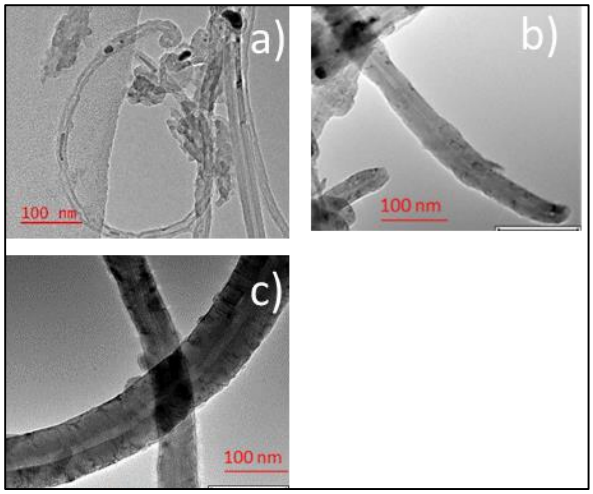

Figure 2: TEM images of CNTs synthesized at a) 750, b) 800 and c) 850 °C

Figure 3 shows the Raman spectra of MWCNTs at varied temperatures. The CNT characteristic bands were present. The D-band was located approximately at 1355 cm^{-1}, the G-band appeared at around 1577 cm^{-1} and the G' band was observed at 2713 cm^{-1}. The G' bands gives an indication of 3D stacking of the material. The G-band is characteristic of ordered graphitic structure. While the D-band is the disorder band which indicates the relative amount of the defective impurities, amorphous carbon or other symmetry-breaking defects [8]. Therefore, the ratio of D to G bands could be used as a direct measure of CNT quality. The I_D/I_G for MWCNTs synthesized at 750, 800 and 850 °C was found to be 0.44, 0.49 and 0.55 respectively. This indicated an increase in crystallinity with an increase in the synthesis temperature which agrees with the other results obtained.

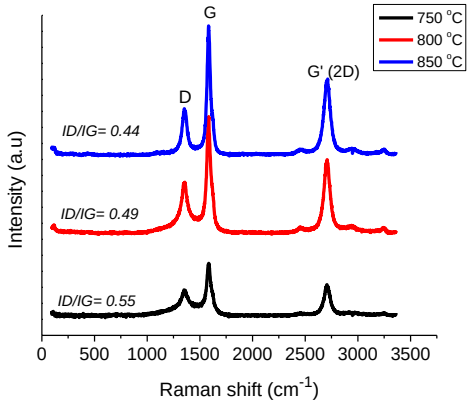

Figure 3: Raman spectra of CNTs synthesized at a) 750, b) 800 and c) 850 °C

In Figure 4, TGA and derivative plots of MWCNTs are represented. At 750 °C, two degradations were observed at 326 and 565 °C. The first degradation was attributed to the decomposition of amorphous carbon, which has been reported to have a low oxidation temperature [9]. At a synthesis temperature of 800 and 850 °C, a major decomposition was observed at 619 and 649 °C respectively, which was attributed to the decomposition of MWCNTs. The oxidation temperature increased with an increase in the synthesis temperature. This suggested that MWCNTs synthesized at higher temperatures were more crystalline as also shown by TEM and Raman results. The residual weight from the iron catalyst was below 7% for all the MWCNTs, which exhibited high purities of above 93%.

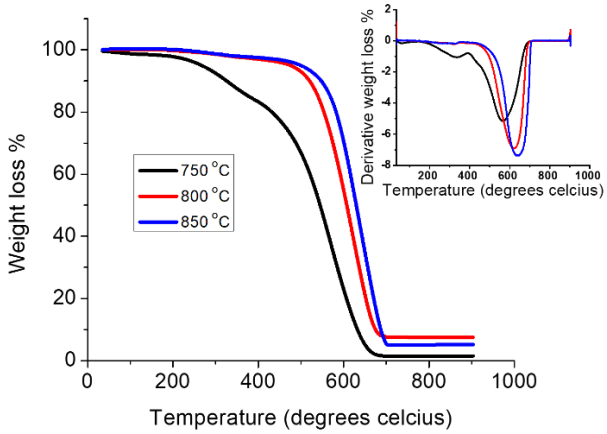

Figure 4: TGA and derivative plots of CNTs synthesized at a) 750, b) 800 and c) 850 °C

4 CONCLUSION

MWCNTs were successfully synthesized using a facile FCCVD method. The study showed that nitrogen only can be used as a carrier gas and also that high quality CNTs can be produced without a support or promoter. An increase in the growth temperature improved the quality of the MWCNTs. Furthermore, the diameter of the MWCNTs was increased at increased growth temperatures. The synthesized MWCNTs have a great potential as reinforcement materials in construction composites.

5 ACKNOWLEDGEMENTS

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