

Research Article

Nitrogen-Doped Carbon Nanotubes Synthesised by Pyrolysis of 4-[[(Pyridine-4-yl)methylidene]amino]phenyl)ferrocene

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Received 3 June 2013; Accepted 13 August 2013

Academic Editor: Myoung-Woon Moon

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Nitrogen-doped carbon nanotubes (N-CNTs) were synthesized by pyrolysis of 4-[[(pyridine-4-yl)methylidene]amino]phenyl) ferrocene in a solution of either acetonitrile or toluene as carbon source. This was achieved by testing three different growth temperatures (800, 850, and 900°C), and the 850°C was found to be the most favourable condition for N-CNT growth. At the lower temperature of 800°C, amorphous carbon was mainly formed while at the higher temperature of 900°C, the yield of carbon spheres (CSs) increased. Apart from the variation in temperature, the formation of other shaped carbon nanomaterials (SCNMs) was found to be carbon source dependent. Acetonitrile was found to produce mainly N-CNTs with “bamboo” morphology while toluene formed a mixture of pristine CNTs and N-CNTs in the ratio of 1 : 1. N-CNTs, and other SCNMs synthesized were characterized by means of TEM, SEM, Raman spectroscopy, TGA, and elemental analysis.

1. Introduction

The introduction of heteroatoms into the backbone of carbon nanotubes (CNTs) changes their structural, chemical, and electrical properties [1]. Doping CNTs with nitrogen creates superficial defects that alters the chemical properties of CNTs and creates a path to reactivity and applications [2]. Some of the potential applications of N-CNTs include lithium storage [3, 4], biosensors [5, 6], fuel cells [7, 8], drug delivery [9], catalytic support [10], field emission [4, 11], and electronic devices [12], among others.

Heteroatom doping was first reported by Stephan et al. [13]. They doped CNTs with nitrogen and boron by means of the arc discharge method. Currently, nitrogen doping is accomplished by either *in situ* or *ex situ* [14] methods whereby in the latter the walls of CNTs are functionalized with nitrogen-containing groups by use of molecules such as NH₃ [15] subsequent to CNT synthesis. Another useful example of *ex situ* technique which does not involve a simple molecule but a complex has been illustrated by Schilling and Bron [16], where they functionalised multi-walled CNTs with the aid of a nitrogen-containing complex, iron tetramethoxyphenylporphyrin chloride (FeTMMP-Cl).

On the other hand, nitrogen doping using *in situ* synthesis has been reported by means of arc discharge [17], laser ablation [18], and chemical vapour deposition (CVD) [19] techniques. In general, the CVD method is preferred since it is more economical, relatively easier to produce and scale up the synthesis of N-CNTs. In this approach, the carbon source also provides the nitrogen source [2, 20]; however, the catalyst can also act as a source of nitrogen [9, 21]. Additional examples include the use of nitrogen source that is completely separate from the carbon source and the catalyst [22].

N-CNTs can be identified by the characteristic “bamboo” morphology that arises due to the presence of nitrogen, which introduces defects and pentagon rings in the graphene network that results in a positive curvature of the tubular layer [1]. The distance between each bamboo compartment has been found to be directly proportional to the amount of nitrogen doping with a smaller size compartment signifying a higher nitrogen doping level [23]. Organometallic complexes, especially ferrocene and its derivatives, have been used as both catalysts and as carbon sources for the synthesis of CNTs and other shaped carbon nanomaterials (SCNMs) [24]. The use of ferrocene and acetonitrile has also been investigated [25]; however, in this

paper we report on the use of an organometallic complex, (4-[(pyridine-4-yl)methylidene]amino)phenyl)ferrocene, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_{17}\text{H}_{13}\text{N}_2)]$, which is a novel ferrocenyl derivative as a catalyst for the synthesis of N-CNTs. It does not only act as the source of active metal iron nanoparticle but also as nitrogen and carbon source in a solution of acetonitrile or toluene. This paper also explores the variation of growth temperature and how it affects the yield, type of SCNMs formed and level of nitrogen doping.

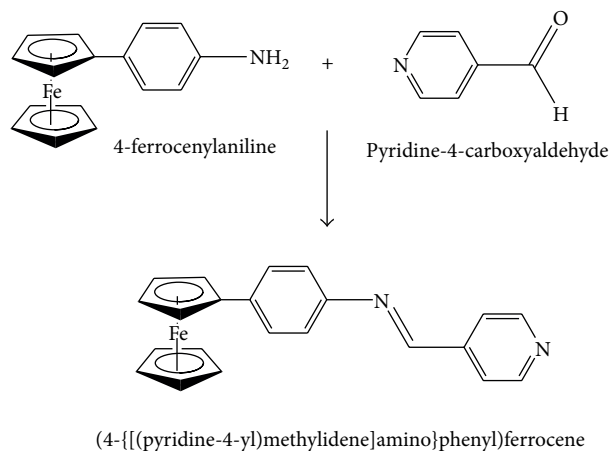
2. Experimental

All the chemicals used were of analytical grade and were used as received unless stated otherwise. The catalyst precursors were synthesized as previously reported: 4-nitrophenyl ferrocene [26] and 4-ferrocenylaniline by catalytic reduction of 4-nitrophenyl ferrocene as reported by Altaf et al. [27]. In brief, 2 g of 4-nitrophenyl ferrocene was dissolved in 100 mL of methanol, and 2.62 g of zinc powder was slowly added to the mixture while stirring. Then 4 mL of formic acid was added drop wise, and thereafter the mixture was heated to 70°C. The reaction was monitored by TLC, and the reaction product was isolated with a yield of 85%. (4-[(Pyridine-4-yl)methylidene]amino)phenyl)ferrocene was prepared as reported earlier by our group [28] under solvent-free conditions. Briefly, this involved mixing 4-ferrocenylaniline (130 mg, 0.47 mmol) and pyridine-4-carboxyaldehyde (76 mg, 0.71 mmol) in a Pyrex tube fitted with a ground glass joint (Scheme 1). The solid mixture was thoroughly ground leading to a melt, which solidified once it was left to stand under vacuum. The red solid was then subjected to column chromatography using a solvent mixture of hexane:dichloromethane in the ratio of 8:2. The pure product was isolated and obtained as red crystals.

An amount of 2.5 wt.% of (4-[(pyridine-4-yl)methylidene]amino)phenyl)ferrocene was used as a catalyst in the CVD floating catalyst method to synthesize N-CNTs. The setup of the reactor used was based on a previously reported design [29]. A quartz tube (inner diameter 27 mm and length 850 mm), used as the reactor vessel, was placed inside a muffle/tube furnace (model no. TSH12/50/610, Elite Thermal Systems Ltd) fitted with a main zone temperature controller (Eurotherm 2416). The temperature was controlled and set to the desired maximum reaction temperature (T_{max}), that is, 800, 850, or 900°C. The purging and reducing gas was 10% H_2 in argon (v/v) set at a flow rate of 100 mL/min. When the desired temperature (T_{max}) was attained, a solution of 2.5 wt.% catalyst and the carbon source was injected at a rate of 0.8 mL/min with the aid of a New Era Inc., syringe pump (model no. NE 300). The carbonaceous materials obtained from the uniform hot zone were collected and weighed. The products were characterized by means of transmission electron microscopy (TEM), scanning electron microscopy (SEM), Raman spectroscopy, thermogravimetric analysis, and elemental analysis.

3. Results and Discussion

The catalyst, (4-[(pyridine-4-yl)methylidene]amino)phenyl)ferrocene was easily synthesized under solvent-free



SCHEME 1: Solvent-free synthesis of (4-[(pyridine-4-yl)methylidene]amino)phenyl)ferrocene.

conditions to obtain an excellent yield (162 mg, 94%) and characterized as before [28]. The catalyst was further utilized in a solution of either toluene or acetonitrile as the carbon source to synthesize shaped carbon nanomaterials (SCNMs) by means of the floating catalyst CVD method. Apart from the catalyst, acetonitrile was also used as an additional nitrogen source, and the results obtained are shown in Table 1.

From the results, three types of SCNMs were formed, that is, CNTs, amorphous carbon (Ac), and carbon spheres (CSs). These results are in agreement with the findings of Nxumalo et al. [30] who reported formation of similar products by pyrolysis of ferrocenylaniline or a mixture of ferrocene and aniline in different proportions by using toluene as the carbon source at 900°C. However, in their case they also obtained carbon fibres. It is evident that the resultant products and their distribution are dependent not only on the catalyst and carbon source used, but also on the choice of reaction conditions such as reaction temperature (T_{max}), reaction time, gas flow rate, and pressure [31]. Figure 1 shows the TEM images of a representative samples of the SCNMs obtained.

The TEM images in Figure 1 show that the CNTs formed have “bamboo” shaped compartments which usually signifies nitrogen doping. Bamboo compartments arise due to formation of pentagonal rings in the graphene network, which induces positive curvature in the graphene layer [1]. Inclusion of nitrogen or oxygen in the carbon graphene network is relatively easy. This is more so due to similarities in their hybridisation and bond length, that is, $\text{C}=\text{C}$, $\text{C}=\text{O}$, and $\text{C}=\text{N}$ being 1.38 Å, 1.36 Å, and 1.34 Å, respectively. However, the $\text{C}=\text{N}$ bond length is shorter than that of $\text{C}=\text{C}$, and hence it distorts the order in the graphene matrix by introducing pentagons which cause strain in the structure [32]. These distortions created by the nitrogen atoms cause defects and are seen to be more concentrated in the inner layer than other layers, and hence the bamboo morphology is more pronounced inside the tube [33].

3.1. Effect of Carbon Source. The effect of the carbon source on the size of individual bamboo compartments, wall thickness

TABLE 1: Products obtained by pyrolysis of 4-[(pyridine-4-yl)methylidene]amino}phenyl}ferrocene (2.5 wt.%) in a solution of toluene or acetonitrile.

Temperature (°C)	Carbon source	Yield (mg)	Composition of the product*	Avg. ID (nm)	Avg. OD (nm)
800	Toluene	176	40% T; 60% Ac	10.19	60.19
	Acetonitrile	100	60% T; 40% Ac	31.309	50.64
850	Toluene	300	50% T; 45% CS; 5% Ac	15.62	68.31
	Acetonitrile	178	85% T; 15% Ac	54.248	60.709
900	Toluene	570	2% T; 98% CS	25.36	73.76
	Acetonitrile	240	20% T; 80% CS	65.69	76.47

*The composition of the products is based on acceptable counting procedures using electron micrographs; at least 50 images were used in each case and over 200 SCNMs were counted per sample.

T: carbon nanotubes; Ac: amorphous carbon; CS: carbon spheres; Avg. ID: average inner diameter; Avg. OD: average outer diameter.

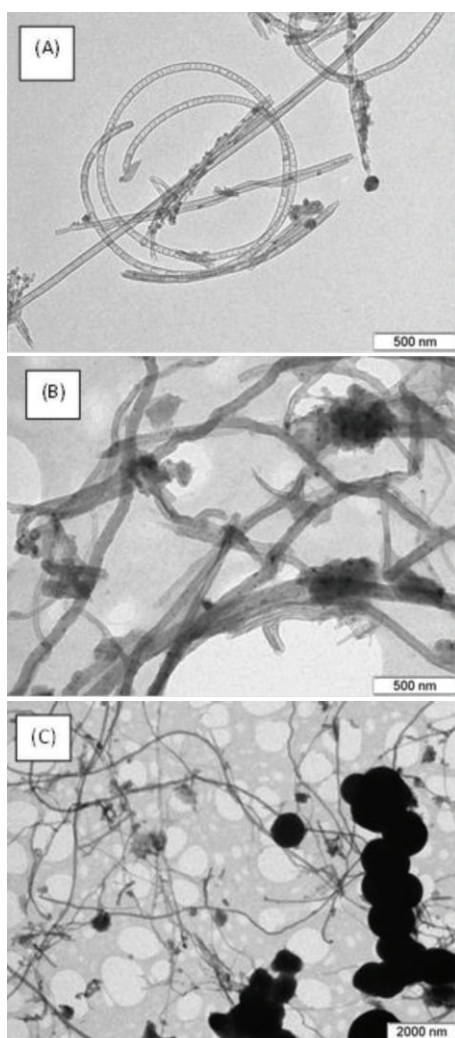


FIGURE 1: TEM images of SCNMs synthesized from a solution of (A) acetonitrile at 850°C, (B) acetonitrile at 800°C, and (C) toluene at 850°C.

and general morphology of CNTs was investigated. This was accomplished by comparing the type of CNTs formed when a solution of acetonitrile or toluene was used as the carbon source. Figure 2 shows some TEM images of N-CNTs grown from a solution of either acetonitrile or toluene.

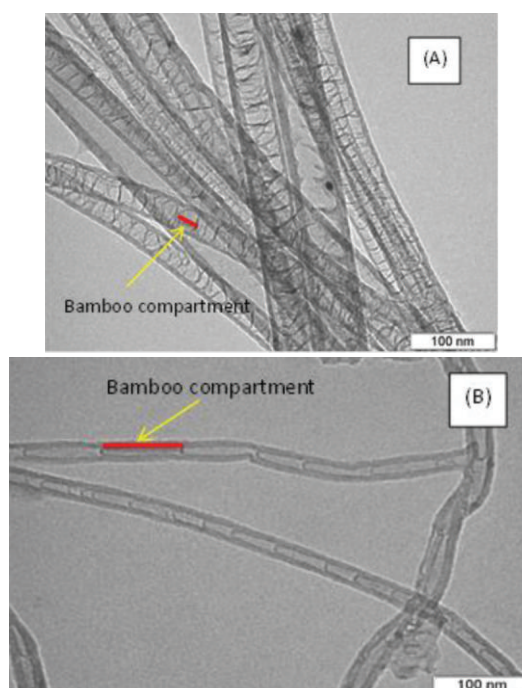


FIGURE 2: TEM images of N-CNTs synthesized at 850°C from a solution of (A) acetonitrile and (B) toluene. The red lines and arrows on the images indicate the individual bamboo compartments.

The sizes of each bamboo compartment were different and this has a direct relationship with the amount of nitrogen from the nitrogen source. N-CNTs synthesized from a solution of acetonitrile formed shorter bamboo compartments compared with the ones formed from a solution of toluene. A possible explanation could be that more nitrogen atoms are incorporated into the structure since apart from the ferrocenyl derivative which contains nitrogen, the acetonitrile solvent also introduces additional nitrogen which would also be involved in the doping process. These findings concur with those of Nxumalo et al. [30], who observed a decrease in bamboo compartment size and more individual compartments in each tube, which was an indication of the increased extent of nitrogen doping. Chen et al. [8] also reported a positive correlation between higher nitrogen content in the carbon source and higher nitrogen doping in the N-CNTs.

In addition to the bamboo compartment size, the use of acetonitrile formed N-CNTs with bigger internal diameters and smaller wall thicknesses. The increased internal diameter and reduced wall thickness could be due to the level of nitrogen doping. Our findings concur with those of Ionescu et al. [34] who reported an increase in internal N-CNT diameter and decrease in wall thickness with increased nitrogen doping.

Some of the CNTs synthesised in a solution of toluene lacked bamboo structures, indicating that effective nitrogen doping did not readily take place in the graphene network. The number of N-CNTs (with bamboo structures) and pristine CNTs was in the ratio 1:1. This was determined by counting tubes in at least 50 images. Koós and coworkers [31] made a similar observation when they synthesized N-CNTs in a solution of toluene in 5% benzylamine. This suggests that nitrogen doping significantly depends on both choice of carbon source and catalyst [35]. It was noted that N-CNTs synthesised from a solution of acetonitrile were well aligned (Figure 3(a)). On the other hand, the pristine CNTs (as determined by lack of bamboo structures) synthesised from a solution of toluene were observed to have kinks, were wavy, and not aligned (Figure 3(b)). A possible reason could be that products derived from the latter approach were not only less ordered, but also intermingled with a mixture of pristine CNTs and N-CNTs, and hence distorting the alignment of the tubes [31].

3.2. Effect of Growth Temperature. Varying the growth temperature was found to have an effect on the level of nitrogen doping, yield, and the graphitic nature or crystallinity of N-CNTs.

3.2.1. The Nitrogen-Doping Percentage. Elemental analysis (CHNS) was used to study the relationship between growth temperature and nitrogen-doping. It was observed that the nitrogen-doping percentage increased from zero to 2.21% in N-CNTs synthesised in a solution of toluene as the growth temperature increased from 800 to 850°C. When a solution of acetonitrile was used, a similar, but more effective, doping trend was observed; that is, the nitrogen-doping percentage increased from 3.96% to 17.57% in the same temperature range. However, a different trend was observed when the growth temperature was increased to 900°C when acetonitrile was used as a carbon source. The doping percentage decreased to 3.47%. A possible explanation of this reduction could be that as the growth temperature was raised to 900°C, elemental nitrogen that is usually incorporated into the graphene structure did not react but escaped through the exhaust system, and this was evident from the water trap showing more vigorous bubbling. Our findings concur with Tang et al. [35], who reported that the level of nitrogen-doping decreased by half when the temperature was increased from 800 to 900°C. The highest nitrogen doping was noted at 850°C in a solution of acetonitrile indicating a direct relationship between nitrogen doping, growth temperature and amount of nitrogen in the carbon sources. Furthermore,

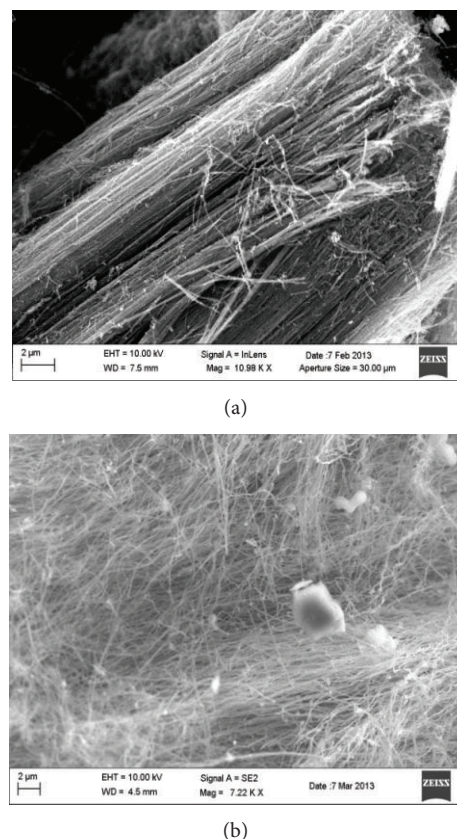


FIGURE 3: SEM images of CNTs synthesized at 850°C from a solution of (a) acetonitrile and (b) toluene showing the former to be well aligned and the latter to be wavy.

in terms of the extent of nitrogen doping, the elemental analysis at 850°C strongly correlates with the TEM observations (Figure 2) and results discussed above.

3.2.2. N-CNT Yield and General Morphology. Generally the yield of N-CNTs increased with growth temperature for both acetonitrile and toluene. A solution of toluene gave a higher yield (176, 300, and 570 mg) compared with acetonitrile (100, 178, and 240 mg) at 800, 850, and 900°C, respectively (Table 1). It was also evident that the type of SCNMs formed changed with growth temperature. At 800°C, a lot of Ac formed but the amount decreased as the growth temperature increased to 900°C. However, the percentage of CS increased with growth temperature. A possible reason could be due to agglomeration of catalyst nanoparticles into bigger particles at higher temperatures (note that catalyst concentration was kept constant) and hence favouring the growth of other nanomaterials other than CNTs [36]. Seah et al. [37] also observed a similar trend at high temperature, and attributed this to higher catalyst/carbon ratio would also lead to catalyst particles agglomerating at a higher rate, hence, becoming too large and thus resulting in unfavourable conditions for 2 CNT growth.

The morphology of the N-CNTs such as the outer diameter (OD) was observed to change with growth temperature.

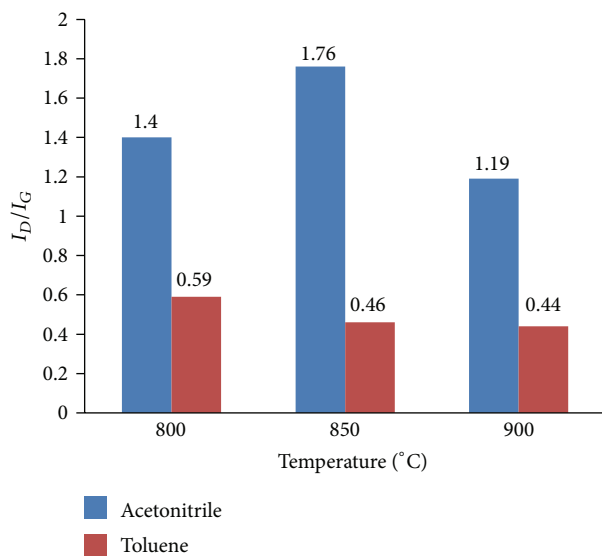


FIGURE 4: Raman chart comparing I_D/I_G ratio at the different growth temperatures.

The OD of the tubes was observed to increase with increase in growth temperature for acetonitrile (Table 1). However, when using a solution of toluene, it was only possible to compare samples at temperatures of 800 and 850 °C, and the trend was similar. A possible explanation for the increase in outer diameter with increase in temperature could be due to agglomeration and increase in catalysts particle sizes which favour formation of CNTs with large outer diameters. N-CNTs synthesised with a solution of acetonitrile at 850 °C had larger outer diameters (60.79 nm) compared with those grown from a solution of toluene (55.3 nm). In contrast, at 800 °C N-CNTs from toluene had bigger outer diameters than those from acetonitrile (60.19 nm compared with 50.64 nm, resp.). As for the internal diameter (I.D.), N-CNTs synthesised from acetonitrile were larger compared with ones grown from toluene. The opposite was observed for the wall thickness of N-CNTs synthesised from toluene that showed thicker walls compared with those grown from acetonitrile as the carbon source.

3.2.3. Graphitic Nature/Crystallinity. Raman spectroscopy was used to study the effect of growth temperature on the graphitic nature of N-CNTs. Two major peaks were observed: the G-band (between 1560 and 1599 cm^{-1}) which originates from the Raman E_{2g} mode and the D-band (between 1347 and 1363 cm^{-1}) which is the disorder-induced band. The intensities of the G-band and D-band were observed to differ, and evidence can be seen from the I_D/I_G ratio (Figure 4).

This ratio is an indicator of the graphitic nature of the N-CNTs or degree of disorder, and it was observed to increase from 800 to 850 °C for tubes synthesised with acetonitrile. Nitrogen doping in N-CNTs increased as the growth temperature rose from 800 to 850 °C which implies a higher level of disorder, and this agrees with the results from elemental analysis and the TEM observations. In contrast, the I_D/I_G ratio of tubes synthesised from toluene decreased between

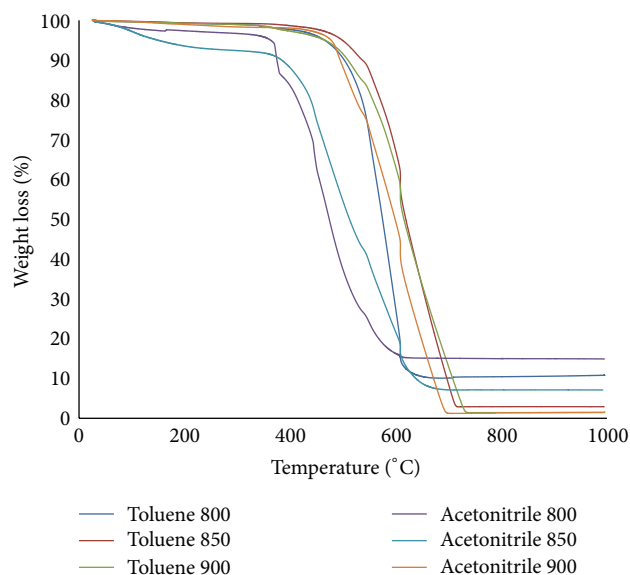


FIGURE 5: Thermogravimetric analysis of SCNMs at different growth temperatures (°C) in a solution of either toluene or acetonitrile.

800 and 850 °C, which is an indication of the formation of more graphitic tubes. However, Table 1 shows a reduction of Ac product as the growth temperature increases, and this could also be a possible reason for the increase in the graphitic nature of the product at higher temperature. Generally, the N-CNTs synthesised in a solution of acetonitrile were found to be more disorderly at all growth temperatures, and this is possibly due to the level of nitrogen doping.

Thermogravimetric analysis was used to investigate the thermal stability of SCNMs synthesised at different growth temperatures in a solution of acetonitrile or toluene. Figure 5 shows the thermograms.

SCNMs synthesised from a solution of toluene were thermally more stable compared with those grown from acetonitrile as confirmed by observing the initial decomposition temperature. A possible explanation is that toluene provided more pristine CNTs, which are more structured with fewer defects, while acetonitrile mainly formed N-CNTs, which is inline with our elemental analysis results, TEM observations, and Raman analysis. N-CNTs, synthesised at a temperature of 850 °C which had the highest level of nitrogen-doping, showed the least thermal stability. The decomposition temperature increased from 481 °C to 600 °C for N-CNTs synthesised from acetonitrile at growth temperatures of 850 and 900 °C, respectively. This shows that the thermal stability increased as the growth temperature increased from 850 to 900 °C which supports the decrease in the level of nitrogen doping.

4. Conclusion

N-CNTs were synthesised by pyrolysis of (4-[(pyridine-4-yl)methylidene]amino)phenyl)ferrocene in a solution of either toluene or acetonitrile. Acetonitrile formed N-CNTs

with mainly bamboo morphology indicative of nitrogen doping. The N-CNTs were found to be generally less thermally stable and less graphitic. Also the thermal stability decreases as the level of nitrogen doping increases. A solution of toluene formed a mixture of nitrogen-doped and pristine CNTs. In general, the growth temperature was found to affect the yield, type of SCNMs formed, and level of nitrogen doping. Hence, this study has shown that the SCNMs synthesised depend on the conditions of synthesis and the precursors used.

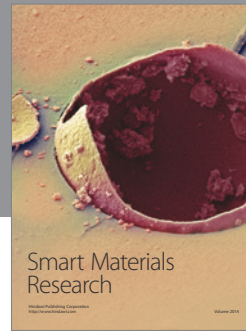
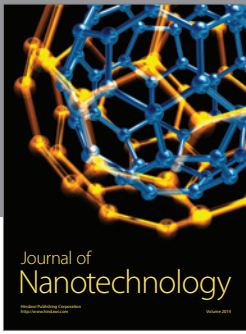
Acknowledgments

The authors wish to thank the University of KwaZulu-Natal, the National Research Foundation (NRF) and the India, Brazil, and South Africa (IBSA) energy project for financial assistance.

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