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Synthesis of carbon nanotubes and nanoballs by swirled floating catalyst chemical vapour deposition method

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The ferrocene catalysed decomposition of acetylene by swirled floating chemical vapour deposition method was studied in this work. Analyses of the products formed confirm the presence of carbon nanotubes and carbon nanoballs. These materials were synthesized at different production conditions; high flow rates of carbon source and carrier gases as well as low decomposition temperature were found to be responsible for the formation of CNBs. TEM images also show that both CNTs and CNBs contain low contents of iron impurities and amorphous carbons.

Keywords: SFCCVD; CNTs; CNBs; Synthesis; Purity

1. Introduction

Carbon nanotubes (CNTs) will continue to attract attention of researchers because of their increasing versatility in many applications [1–5]. Methods such as arc-discharge [6], laser ablation [7] and chemical vapour deposition (CVD) [8–9] are being employed to produce CNTs. It has been reported that CVD is highly favoured for mass production of these materials to meet their rising demand for several technological developments [10–13].

In an attempt to scale-up the production of these materials and increase their purity, many other techniques of CVD have been developed [9,14–16]. These methods employ different catalysts and carbon sources to synthesize CNTs. As a result of this, various other nanoparticles such as nanofibres and nanoballs are being produced alongside CNTs.

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Hence, many types of CNTs and their allied nanoparticles are now widely available in the market.

Purification processes have always been taken into consideration in the synthesis of CNTs. This is due to impurities that are usually associated with these products as a result of either the catalyst used [17–22], or various parameters such as temperature employed in the decomposition process. A lot of purification steps are always adopted depending on the level of impurities in the materials. However, these steps could damage the structure of CNTs, hence efforts are being intensified to reduce these steps and minimize or completely eliminate the impurity content during synthesis of these materials [23–26].

This work describes an improved technique of synthesizing CNTs and carbon nanoballs (CNBs) using ferrocene catalyst and acetylene carbon source. This new CVD technique is termed swirled floating catalyst chemical vapour deposition (SFCCVD) method. The materials synthesized were obtained at different operating parameters of temperatures, flow rates of carbon source and carrier gases, and without employing any purification method, their TEM images show that they are of high purity.

2. Experimental

The apparatus used for the production of CNTs and CNBs is the one developed by Iyuke [27], termed swirled floating catalyst chemical vapour deposition reactor (SFCCVD). This equipment has been fully discussed in our previous works [28–31]. Briefly, it consists of a vertical quartz reactor immersed in a tubular furnace with sensitive temperature regulator. Gases (argon, nitrogen, hydrogen and acetylene) flow into the reactor with the aid of system of valves and rotameters through a swirled coiled passage which leads from catalyst vaporizer. The upper end of the reactor is connected to a condenser which leads to two delivery cyclones where the products are collected. The ferrocene catalyst used was poured into a silica vaporizer placed on a mantel heater with a sensitive temperature regulator. This catalyst vaporizer is connected to the swirled mixer which in turn leads into the reactor.

Nitrogen was first turned on to purge the system of any impurity. The reactor and ferrocene heater were switched on while the nitrogen was running. At reactor temperature of about 300°C, nitrogen was turned off to prevent it from reacting with oxygen. Argon was then turned on at a flow rate of 181 ml/min to continue purging and act as a carrier gas. At reactor temperatures of 900, 950, 1000 and 1050°C and catalyst heater set at 150°C, 5 grams of ferrocene was charged into the heater while hydrogen was turned on at flow rates of 181 and 248 ml/min and acetylene was turned on at flow rates in the range of 181–370 ml/min. The system was allowed to run for 10 minutes after which the ferrocene had been exhausted. The smoky products or carbon vapour evolved from the reactor was cooled at the condenser and collected in the cyclones. The wall of the reactor was also scrapped clean of the materials therein. These raw products were analysed with transmission electron microscope (TEM), and X-ray diffraction (XRD).

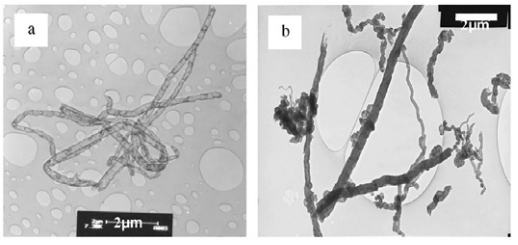

Figure 1. TEM images of pure CNTs produced at (a) 1000°C and (b) 1050°C.

Table 1. Production conditions of CNTs and CNBs.

Flow rate of gases (ml/min)		Carbon products composition at various temperatures (°C)			
Hydrogen	Acetylene	900	950	1000	1050
118	181	CNBs + CNTs	CNBs + CNTs	CNTs	CNTs
118	248	CNBs + CNTs	CNTs	CNTs	CNTs
118	308	CNBs + CNTs	CNTs	CNTs	CNTs
118	370	CNBs	CNTs	CNTs	CNTs
181	370	CNBs	CNTs	CNTs	CNTs
248	370	CNBs	CNTs	CNTs	CNTs

3. Results and discussion

Figures 1(a–b) show the TEM images of the products obtained at various production conditions specified in table 1. These images reveal that each of these structures is hollow with inner diameter and length of several nanometres which confirm the presence of CNTs. The diameter distribution of the CNTs based on the measurement from the TEM images is shown in figure 2. This result reveals that the diameter of the CNTs increases with increase in temperature. This could be attributed to the fact that at high temperature the decomposition of acetylene was enhanced which led to graphite generation and consequently increase in formation of the walls of CNTs [32].

The X-ray diffraction (XRD) pattern of the sample (figure 3) reveals the characteristic pattern of graphitized carbon which is similar to the ones reported by Zhang *et al*. [33] and Kong and Zhang [34]. The graphitic line (002) of this sample was observed at diffraction peak of 25.8° corresponding to inter-planner spacing of about 0.343 nm which is usually attributed to CNTs. This pattern also indicates high degree of crystalinity which suggest low content of amorphous carbon and impurities from the catalyst which are usually iron particles [35]. This observation is a marked difference from the results of many other CVD processes where impurities from catalyst employed in the pyrolysis process are always associated with the CNTs and various purification processes are usually adopted to remove them [26, 32, 36]. It could be suggested that effective utilization of the ferrocene catalyst during the decomposition process could have been responsible for the low content of iron impurities in the CNTs. Traces of amorphous carbon impurities which are known to form as a result of insufficient catalyst used in the decomposition of the carbon sources, were not present in these structures. Also, argon/hydrogen and not nitrogen/hydrogen [37] were used as carrier

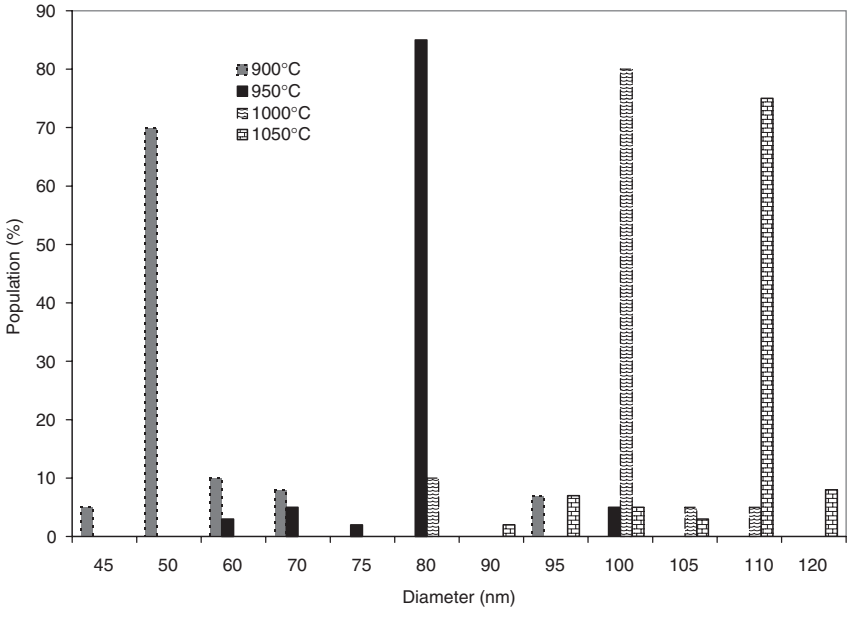

Figure 2. Size distribution of CNT sample at various decomposition temperatures.

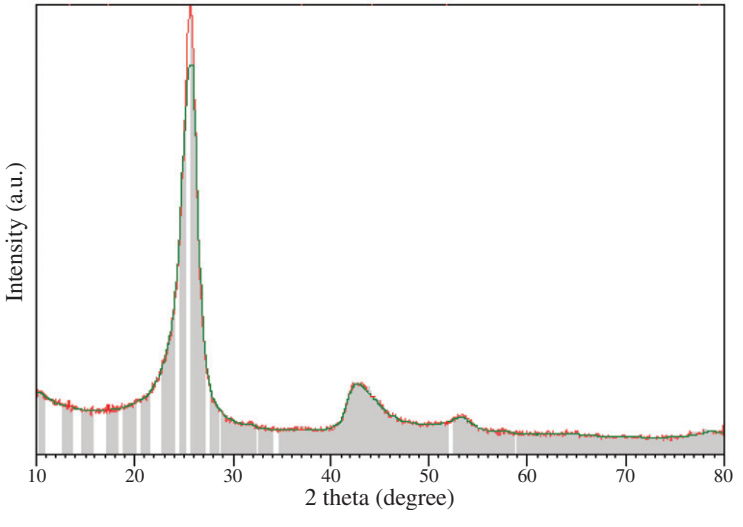

Figure 3. XRD pattern of raw CNTs sample.

gases to eliminate the possibility of high temperature oxidation of nitrogen which may introduce impurities in the products, while argon created neutrality in the system during production and cools the system after production hence its flow rate was kept constant at 181 ml/min. Hydrogen on the other hand has been found to play an intermediate role in the formation of CNTs [31].

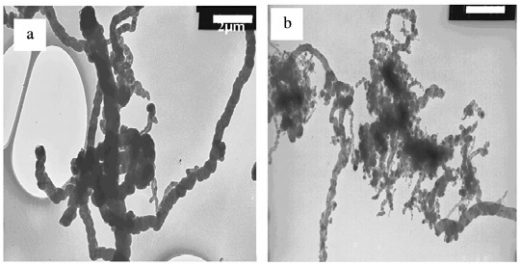

Figure 4. TEM images of combination of CNTs and CNBs produced at (a) 950°C, $C_2H_2 = H_2 = 181$ ml/min, (b) 900°C, $C_2H_2 = H_2 = 181$ ml/min.

Table 2. Products distribution of samples at hydrogen flow rate of 118ml/min and acetylene flow rate of 308 ml/min.

	Products distribution (%)		
Temperature (°C)	CNTs	CNBs	Fe
900	7	92	1
950	94	4.5	1.5
1000	98.5	–	1.5
1050	99.5	–	1

Table 3. Products distribution of samples at hydrogen flow rate of 118ml/min and acetylene flow rate of 370 ml/min.

	Products distribution (%)		
Temperature (°C)	CNTs	CNBs	Fe
900	9	89.5	1.5
950	96.5	1.5	2
1000	98.5	–	1.5
1050	99	–	1

Figures 4(a–b) show the TEM images of products obtained at conditions specified in table 1. These images contain a mixture of both CNTs and CNBs and the quantity of each product is dependent on the flow rates of carbon source and carrier gas as well as the decomposition temperature. The products distribution of these nanoparticles as observed from the TEM images at various temperatures, acetylene flow rate and constant hydrogen flow rate of 118 ml/min are presented in tables 2 and 3. The iron content obtained in the product distribution was based on the percentage composition of ferrocene catalyst used in the synthesis of these nanoparticles.

Figures 5(a–b) show the products obtained at hydrogen flow rate in the range of 181–248 ml/min and constant acetylene flow rate of 370 ml/min at the decomposition temperature of 900°C as shown in table 1. These products contain agglomerate CNTs which are similar to the carbon nanoballs reported by Liu *et al.* [38]. The formation of these products could be attributed to decomposition temperature, flow rates of acetylene (carbon source) and hydrogen employed during the production of these materials.

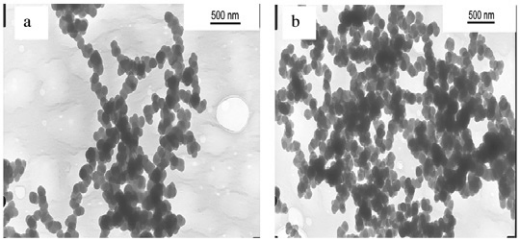

Figure 5. TEM images of pure CNBs produced at (a) 900°C, $C_2H_2 = 370$ ml/min, $H_2 = 181$ ml/min (b) 900°C, $C_2H_2 = 370$ ml/min, $H_2 = 248$ ml/min.

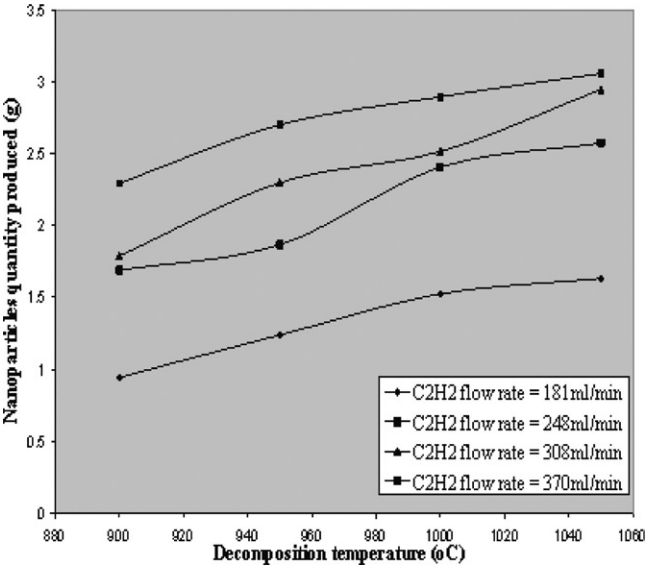

Figure 6. Decomposition temperature Vs quantity of nanoparticles produced at different flow rates of acetylene and constant flow rate of hydrogen.

It was observed that these materials were produced at low decomposition temperatures and high flow rates of acetylene and hydrogen. High flow rates of these gases resulted to low residence time within the reactor and the scattered catalyst particles within the carbon matrix formed different CNTs formation sites. These sites could not grow at low residence time and temperature; hence they culminated into CNBs. These CNBs have uniform diameter ranges between 90 and 300 nm with population distribution of about 95%. This is also a sharp contrast from the findings of Liu *et al.* [38] where insufficient catalyst was attributed to the production of CNBs when horizontal reactor, $Fe(CO)_5$ catalyst and pentane carbon source were used.

It can also be observed that these nanoballs contain negligible traces of iron impurities and amorphous carbon, the reason for this has been explained earlier. Figure 6 shows the effect of decomposition temperature and acetylene flow rate on the quantity of nanoparticles produced. The figure reveals that the quantity of nanoparticles produced increased with temperature and the flow rate of acetylene at

constant flow rate of hydrogen carrier gas of 181 ml/min. Thus the highest quantity of nanoparticles produced was obtained at temperature of 1050°C and acetylene flow rate of 370 ml/min. Comparing this result with table 1, it is observed that a mixture of carbon nanotubes and nanoballs was produced at low reaction temperature and high flow rate of acetylene.

4. Conclusion

This work focused on the synthesis of CNTs and CNBs from pyrolysis of acetylene in a swirled floating chemical vapour deposition reactor using ferrocene as the catalyst. Results obtained revealed that CNBs were produced at 900°C, mixture of CNTs and CNBs was produced at 950°C, while CNTs were produced between 1000–1050°C at different flow rates of acetylene and hydrogen, and highest quantity of these products was obtained at 1050°C when the flow rate of acetylene was 370 ml/min at hydrogen flow rate of 118 ml/min. TEM images of the products revealed that they contain little amount of iron particles and amorphous carbon.

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