

# MICROWAVE PLASMA-ENHANCED CHEMICAL VAPOUR DEPOSITION GROWTH OF CARBON NANOSTRUCTURES

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**Keywords:**

amorphous carbon  
reduction; carbon  
nanotubes; hydrogen-  
to-carbon ratio;  
microwave plasma-  
enhanced chemical  
vapour deposition;  
nanostructures

**Dates:**

Received: 17 June 2009  
Accepted: 08 Mar. 2010  
Published: 20 May 2010

**How to cite this article:**

Singh SR, Jarvis ALL.  
Microwave plasma-  
enhanced chemical  
vapour deposition growth  
of carbon nanostructures.  
*S Afr J Sci.* 2010;106(5/6),  
Art. #183, 4 pages. DOI:  
10.4102/sajs.v106i5/6.183

**This article is available  
at:**

<http://www.sajs.co.za>

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**ABSTRACT**

The effect of various input parameters on the production of carbon nanostructures using a simple microwave plasma-enhanced chemical vapour deposition technique has been investigated. The technique utilises a conventional microwave oven as the microwave energy source. The developed apparatus is inexpensive and easy to install and is suitable for use as a carbon nanostructure source for potential laboratory-based research of the bulk properties of carbon nanostructures. A result of this investigation is the reproducibility of specific nanostructures with the variation of input parameters, such as carbon-containing precursor and support gas flow rate. It was shown that the yield and quality of the carbon products is directly controlled by input parameters. Transmission electron microscopy and scanning electron microscopy were used to analyse the carbon products; these were found to be amorphous, nanotubes and onion-like nanostructures.

**INTRODUCTION**

Carbon nanotubes (CNTs), since their discovery almost two decades ago, have proved to be interesting structures; exhibiting field-emission, superconductivity, capillarity and high stiffness.<sup>1,2,3,4,5</sup> These properties have allowed for the development of numerous experimental devices, such as field effect transistors with a CNT channel, probe tips for microscopy and chemical sensors.<sup>6,7,8</sup> Other carbon nanostructures, such as nanonecklaces and onion-like nanostructures (ONs),<sup>9</sup> have also been grown from similar processes to those used to produce CNTs.<sup>9,10</sup> Various methodologies have produced CNTs; the more popular methods being laser ablation, arc discharge and chemical vapour deposition (CVD).<sup>11,12,13,14,15,16,17,18</sup> In a CVD process, a gas comprising carbon, such as carbon monoxide or an evaporated hydrocarbon, is dissociated into its constituent elements in the presence of a metallic catalyst. The metal catalyst provides nucleation points for the growth of the carbon nanostructures, with the diameters of any CNTs grown depending on the size of the metal particle on which it nucleates.<sup>19</sup> A support gas (usually argon or hydrogen) may be introduced into the system in order to reduce the quantity of amorphous carbon formed and increase CNT yield.<sup>20,21,22,23</sup>

The described system is a variant of the CVD process and utilises plasma to provide additional energy to the system to decompose the carbon-carrying precursor; this form of CVD process is known as plasma-enhanced chemical vapour deposition (PECVD). A few of the advantages of this method are the flexibility of the carbon precursor and process parameters such as reaction temperature and pressure. There is, subsequently, more freedom in controlling the method and manner of nanostructure growth, making PECVD an attractive option for researchers.

In order to research various carbon nanostructure properties, such as bulk conductivity, one needs a simple, reliable method to produce such structures. To this end, we developed a plasma-enhanced chemical vapour deposition method which, with minor adjustments, such as a change of hydrocarbon precursor and/or the variation of support gas flow rate, results in the formation of different nanostructures.

**EXPERIMENTAL SETUP**

The experimental setup utilised a microwave PECVD technique to atomise a hydrocarbon precursor. The entire process occurred within a plasma chamber that was placed inside a 1000 W microwave oven and is shown schematically in Figure 1. The only modification made to the oven was the replacement of the standard door with an aluminium sheet; the magnetron, waveguide and cavity remained intact. The plasma chamber was made from borosilicate glass; comprising a modified standard 1000-mL flask with two glass inlet tubes attached tangentially to the sides. The hydrocarbon precursor and support gases were injected into the plasma chamber through each of these inlets. A third outlet tube was inserted into the 'neck' of the flask, leading to a rotary pump. The uppermost part of the third tube also formed a stand for an aerial and substrate.

The presence of hydrogen is an important component in the production of CNTs in a CVD process.<sup>20</sup> Hydrogen was therefore selected as the support gas, at a flow rate that varied between 0 L/min and 10 L/min. Three base hydrocarbons were selected as a carbon source based on their hydrogen-to-carbon ratio. These were ethanol (3:1), xylene (10:8) and toluene (8:7). The growth of CNTs utilising these three hydrocarbons as the precursor has been previously demonstrated.<sup>19,24,25,26,27</sup> It has been established that thiophene acts as a promoter in the formation of CNTs.<sup>28,29</sup> For the ethanol experiments, varying concentrations (by weight) of thiophene were added. The hydrocarbons were introduced into the plasma chamber by pumping in the liquid form.

An 'aerial', comprising a stainless steel base and a 2 mm diameter Nilo K<sup>®</sup> (Ni 29%, Fe 53%, Co 17%; Goodfellow Cambridge Ltd, Huntingdon, United Kingdom) tip was located on the borosilicate stand within the plasma chamber. Nilo K<sup>®</sup> was selected as its constituent elements have been previously utilised as catalysts in CVD processes.<sup>28,30,31,32,33,34</sup> The aerial served three purposes: confining the plasma to the immediate proximity of the aerial tip, functioning as a catalytic source for CNT growth and providing a

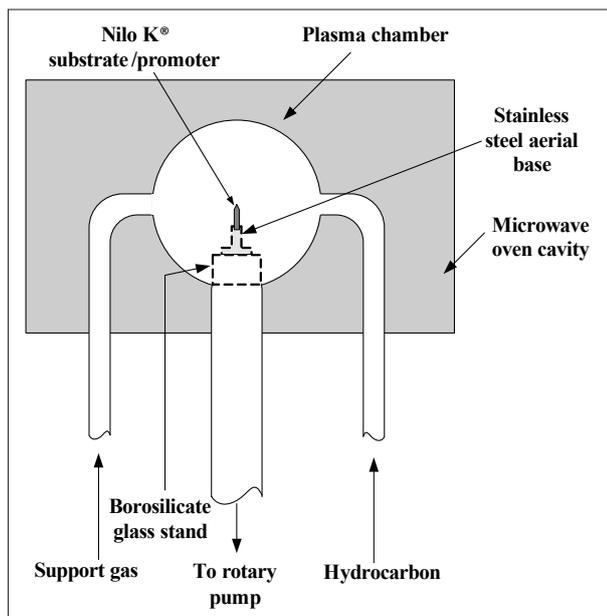


FIGURE 1

Schematic of the microwave plasma-enhanced chemical vapour deposition system

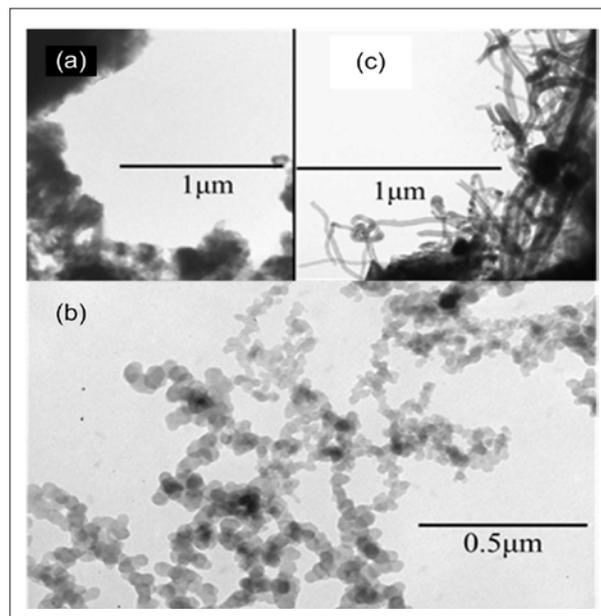


FIGURE 3

Transmission electron micrographs of the ethanol (without a promoter) experiment

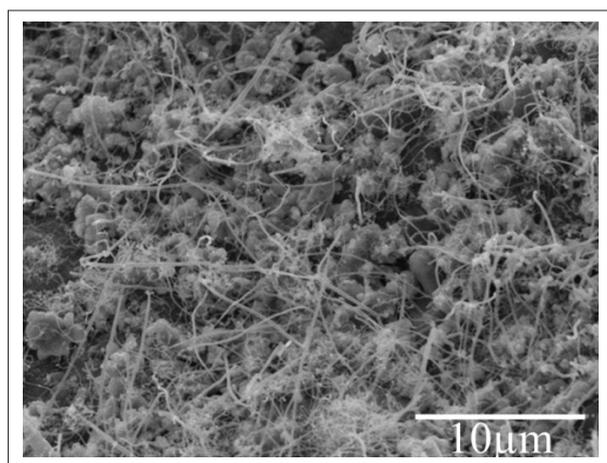


FIGURE 2

Scanning electron micrograph of carbon nanotubes formed at a non-optimal point for the outlined process, where carbon nanotubes are shown in the presence of amorphous carbon

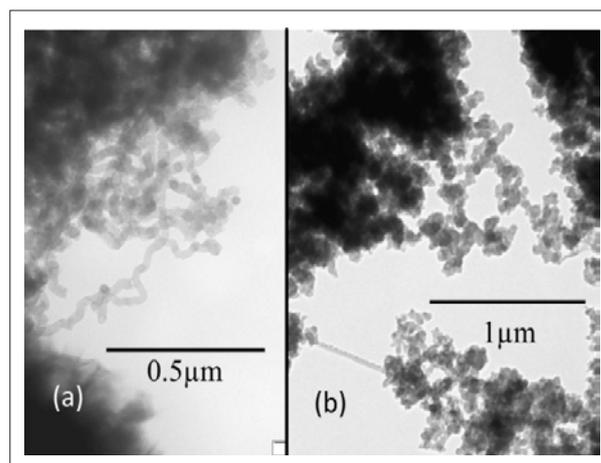


FIGURE 4

Transmission electron micrograph showing the product formed when 0.5% thiophene (by weight) is added to ethanol

substrate on which the CNTs could form. Plasma confinement is vital in order to prevent the melting of the plasma chamber. The operating temperature was estimated to be between 800 K and 1100 K, by observing the effect of the plasma on the borosilicate chamber and the Nilo K<sup>®</sup> aerial.

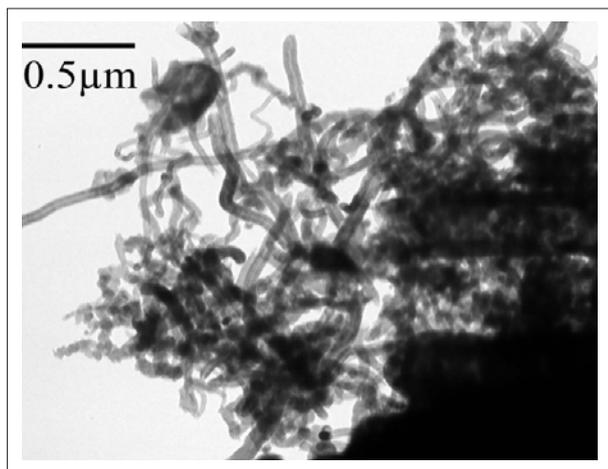
For all of the ethanol experiments (thiophene quantity notwithstanding), deposition occurred only on the aerial tip; the xylene and toluene experiments, however, resulted in the sides of the plasma chamber being coated with a carbon film. The quality of the nanoprodukt formed was assessed via microscopy and analysis of samples was conducted using a JEOL JEM 1010 transmission electron microscope (JEOL Ltd, Tokyo, Japan) and a LEO 1450 scanning electron microscope (Carl Zeiss SMT Ltd, Cambridge, UK).

## RESULTS

Scanning electron microscopy (SEM) analysis indicated that the technique reliably produced various carbon nanostructures, including ONNs and CNTs. Figure 2 shows CNTs formed amidst amorphous carbon.

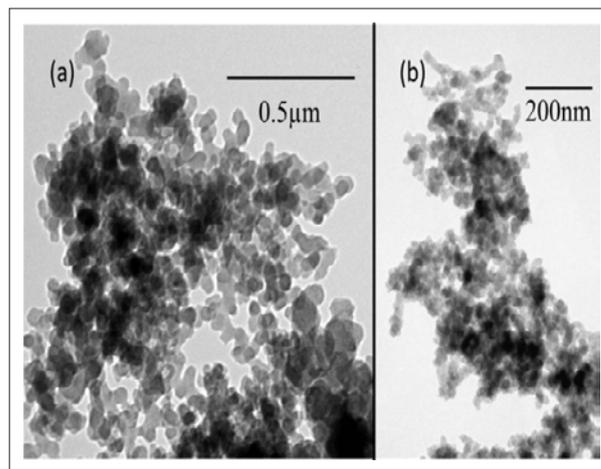
Transmission electron microscopy (TEM) analysis revealed that the described technique yielded various nanostructures, including the conventional CNTs, Y-junction tubes<sup>34</sup> and ONNs. Figure 3 shows the nanostructures formed in the experiments conducted with ethanol (excluding a promoter) as the carbon source. At low or no hydrogen flow, the product was dominated by amorphous carbon; Figure 3a shows amorphous carbon formed at a hydrogen flow rate of 1 L/min. As the hydrogen flow rate was increased, the quantity of amorphous carbon was reduced and ONNs were formed; Figure 3b shows the ONNs formed at a hydrogen flow of 5 L/min. As the hydrogen flow rate was increased even further, CNTs were formed, rather than ONNs; Figure 3c shows the CNTs that formed at 10 L/min. However, the CNTs formed in the ethanol-only experiments were characterised by uneven tube walls and had variable diameters. This was a result of the variable growth site sizes on the Nilo K<sup>®</sup> aerial tip.

Figure 4 shows the product formed when 0.5% thiophene (by weight) was added to ethanol. It was immediately apparent that the addition of thiophene resulted in an increase in the number of CNTs produced. Figure 4a shows uneven-walled



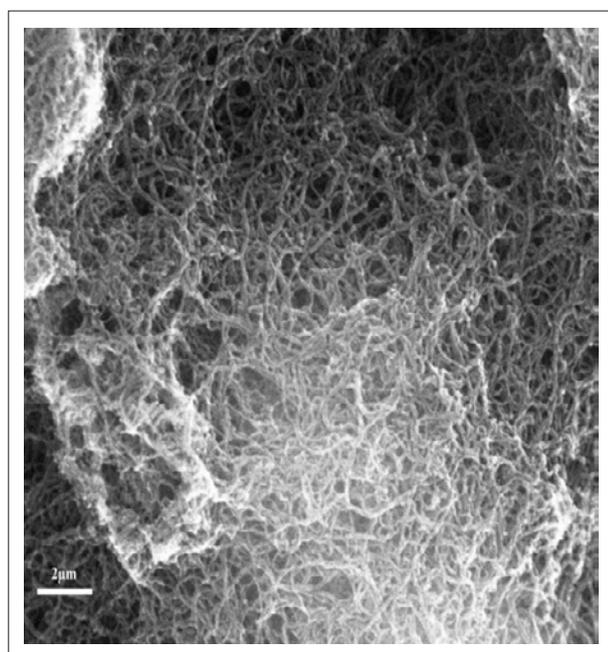
**FIGURE 5**

Bundles of smooth-walled carbon nanotubes formed with 1.5% thiophene and a hydrogen flow rate of 1 L/min; the CNTs grown here vary in individual tube diameters and reduced quantities of amorphous carbon can be observed



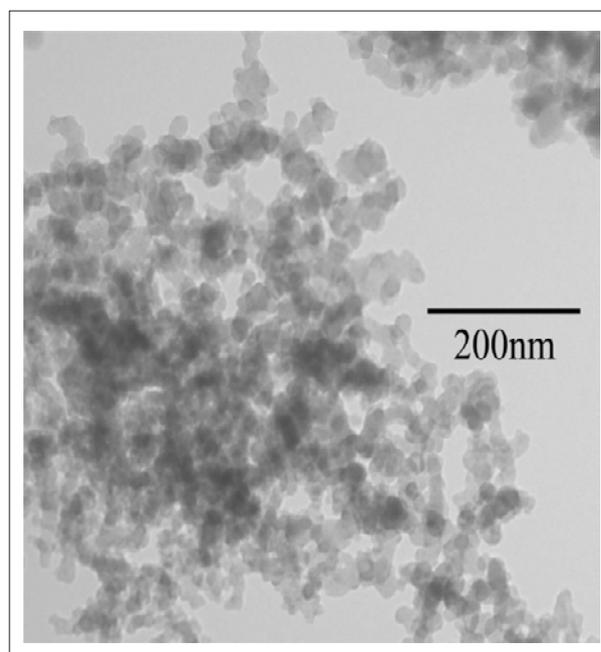
**FIGURE 8**

Transmission electron micrograph of onion-like nanostructures grown with toluene as the base hydrocarbon



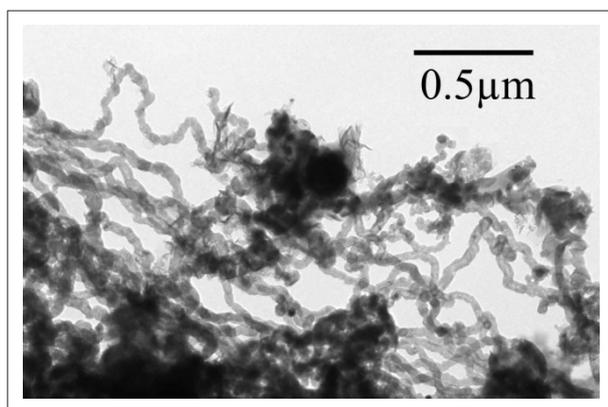
**FIGURE 6**

A plethora of carbon nanotubes grown with an ethanol-thiophene solution as the hydrocarbon source and hydrogen as the support gas; this sample was sonicated in ethanol before scanning electron microscopy analysis



**FIGURE 9**

Transmission electron micrograph of onion-like nanostructures formed with xylene as the precursor and no support gas



**FIGURE 7**

Poorly formed carbon nanotubes formed at a hydrogen flow rate of 10 L/min; while the tubes have uneven walls, diameters appear to be consistent from tube to tube

CNTs formed with variable diameters without the addition of hydrogen, while Figure 4b shows ONSs formed at a hydrogen flow rate of 7.5 L/min. It was observed that, when compared to the ethanol-only experiments, the production of the ONSs was delayed (in terms of hydrogen flow rate). In the ethanol-only experiments, the ONSs were found to grow when the hydrogen flow was between 5 L/min and 7.5 L/min, whereas when 0.5% thiophene was added to ethanol, the ONSs only began to form at 7.5 L/min. It was also observed that as the hydrogen flow rate increased, there was a decrease in the formation of amorphous carbon.

No ONSs, and a considerably reduced amount of amorphous carbon, were produced when 1.5% thiophene (by weight) was added to ethanol. Without hydrogen, CNTs were formed in abundance, but were characterised by uneven tube walls and other deformations such as branching. As the hydrogen flow rate was increased to 1 L/min, the quantity and quality of CNTs improved, as shown in Figure 5. CNTs grown here had

smooth walls, but exhibited slight variations in individual tube diameters, with reduced quantities of amorphous carbon in the sample. A SEM micrograph of these tubes, with the sample sonicated in ethanol, is shown in Figure 6.

As the hydrogen flow rate was increased even further, it was observed that amorphous carbon was removed. It appears, however, that there was an optimal hydrogen flow rate for this process, beyond which the quality of the CNTs produced decreased, as shown in Figure 7.

Changing the hydrocarbon precursor to toluene (without a promoter) yielded very different results. The only nanostructures found at all hydrogen flow rates tested were ONSs. Figure 8 shows the product formed at, (a) the lower (0 L/min) and (b) upper limits (10 L/min) of hydrogen flow. In both cases, the entire plasma chamber was coated with the product, compared to just the Nilo K<sup>®</sup> aerial tip in the ethanol-based experiments. There appeared to be no amorphous carbon formed at any hydrogen flow rate when toluene was introduced as the hydrocarbon precursor.

Utilising xylene as the hydrocarbon precursor yielded similar results to those from the toluene experiment. This result was not unexpected, due to the similar hydrogen-to-carbon ratios of the two hydrocarbons. Amorphous carbon was absent from any of the samples and, once again, ONSs were the only structures observed at all tested hydrogen flow rates. The plasma chamber, including the aerial, was coated in the product. Figure 9 shows the ONSs formed without hydrogen.

## CONCLUSION

This work has demonstrated that, under different input parameters (i.e. the variation of the hydrocarbon precursor or the flow rate of hydrogen) our apparatus could selectively produce CNTs or ONSs. For the production of CNTs, one would use an ethanol-based solution as the hydrocarbon source. The addition of thiophene to the ethanol promoted the growth of smoother CNTs and also increased the yield of CNTs at a constant hydrogen flow rate. For the growth of ONSs, either toluene or xylene could be used. It was observed that an increase in hydrogen flow reduced the formation of amorphous carbon. Variations in the CNT diameters were attributed to the non-uniform growth sites on the Nilo K<sup>®</sup> aerial tip. As our apparatus utilised a minimally modified, conventional microwave oven for the production of carbon nanostructures, we consider this method simpler and cheaper than other equivalent microwave PECVD techniques that incorporate waveguide components such as matchers, directional couplers and tuners.

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