Study of Multi-Walled Carbon Nanotube Synthesis Using Liquid Nitrogen and Post-Process Filtration

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The study deals with the effects of parameters in the synthesis of carbon nanotubes in liquid nitrogen to find the most appropriate conditions such as electrical voltage and time that give carbon nanotubes with large volume and less proportion of impurity, which is a non-nanotubed carbon. The experiment employed the method of arc-discharge between graphite cathode and anode which are immersed in liquid nitrogen. The electrical DC current of 60A and 70A were applied with the time period ranging from 10 seconds to 25 seconds. It was found that the electrical current of 60A and 13 seconds arc-discharge time allowed the largest volume of carbon nanotubes generation. The longer time leads to more impurities around the carbon nanotubes. By the filtration of CNTs-suspended solution using 0.2 micrometers porous paper filter and the characterization using TEM, the carbon nanotubes synthesized in the study were approximately 25 layers multi-walled nanotubes with the average diameter of 18.2 nanometers.

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1. Introduction

New developments in many high technology fields have created the requirement for new manufacturing methods to produce quality nanotechnology materials for various applications. The carbon nanotube (CNT) is one of the materials that has been developed over the years for various mechanical and electrical applications.[1-5] Many uses for CNTs have been proposed, including nanoscale molecular electronics, actuating devices or sensors, and reinforcing fibers in composite materials.[6] The various methods of synthesizing CNTs to obtain the properties appropriate to these applications have been well studied. Those methods include the arc-discharge methods such as a magnetic field synthesis, plasma rotating arc discharge, and arc discharge in liquid nitrogen, as well as synthesis methods using laser ablation and chemical vapor deposition.[7-11] While many of these methods require a large capital investment to establish appropriate facilities, the method involving arc discharge in liquid nitrogen does not, since it can take place in a normal atmosphere with relatively simple apparatus. In Thailand, the manufacture of CNTs is not widespread, and most of those that are produced are used for research purposes.[12-15] We investigated a simple and economic method of synthesizing CNTs for use in future research projects.

2. Experimental apparatus and method

Since our method of producing CNTs relies on using an electrical arc in liquid nitrogen, we designed a stainless tank coated in foamed polystyrene to hold the liquid nitrogen and keep it liquid for as long as possible. We also prepared graphite bars 6 mm and 9 mm in diameter, and 40 mm long. These were held in the liquid nitrogen by mechanical supports. Figure 2 shows the experimental setup of the liquid nitrogen container covered in foamed polystyrene, and the cathode and anode supports, which were connected to the electrical supply of a DC generator. The cathode and anode supports were designed so that the distance between the graphite rods could be adjusted during the experiment to get the arc discharge going between them.

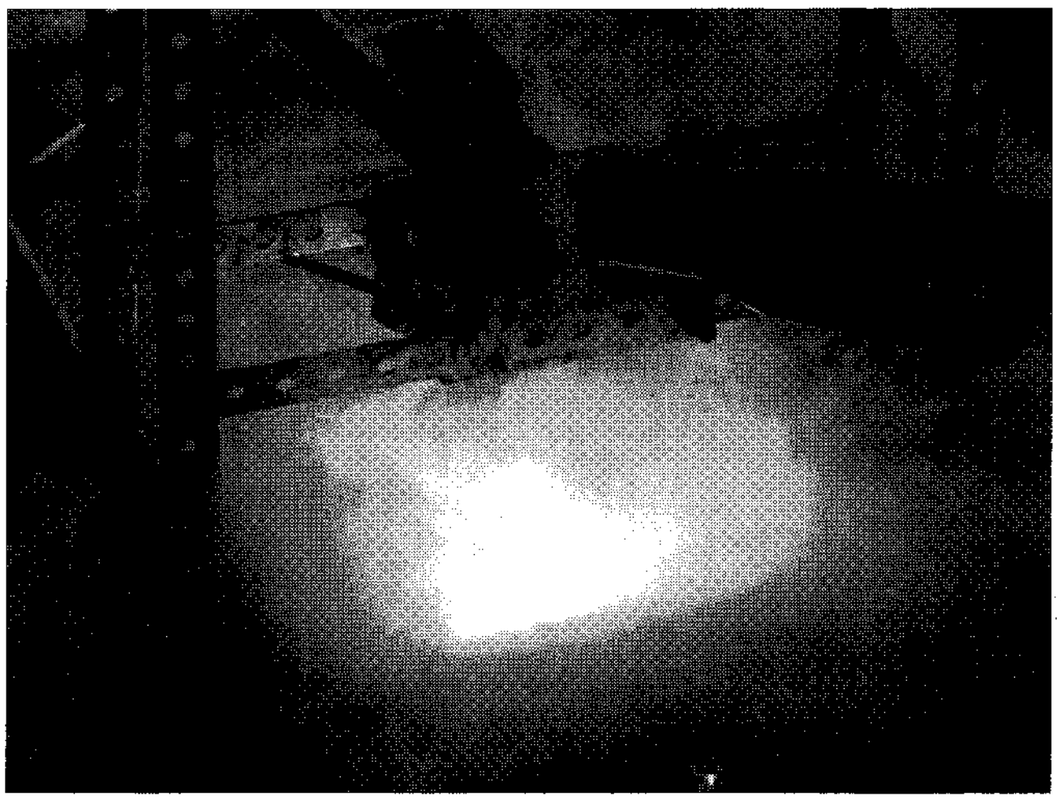

Fig. 1 Graphite cathode and anode arc-discharge in liquid nitrogen in the experiment

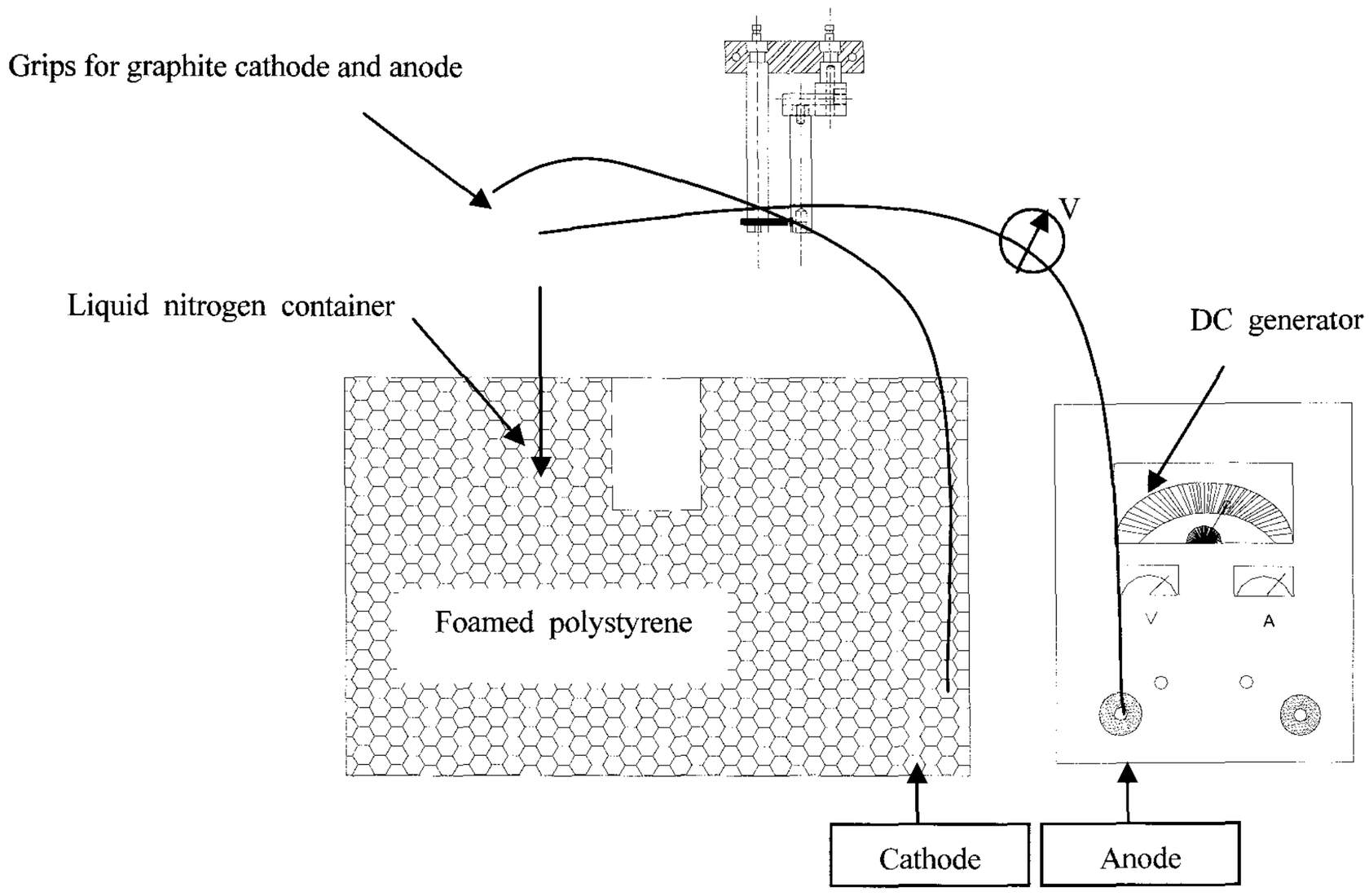

Fig. 2 CNT synthesis apparatus using liquid nitrogen

A portable meter was used to measure the DC current while the arc discharge was in progress. After the graphite cathode and anode were attached to the supports and the liquid nitrogen was poured into the container, the cathode and anode rods were manually adjusted to have a gap of approximately 1 mm between them, and then immersed in the liquid nitrogen. To start the experiment, the DC generator was adjusted to supply a current of 60 to 70 A; the voltage was in the range 26–28 V.

When the gap between the graphite bars is adjusted, the arc discharge starts, and the carbon structure on opposite faces of the graphite bars begins to change at high temperature, cooled immediately to –186°C by the surrounding liquid nitrogen. The arc-discharge time was varied in the range 10–23 s.

When the arc-discharge was completed, CNTs had formed on the surface of anode as shown in Fig. 3. The surface at the center, which seems to be smoother than the outer part, is the area where CNTs were synthesized. This deposit of CNTs on the surface was put into a HNO3 solution and maintained for 3 h at 90°C before being filtered through porous filter paper with holes 0.2 μm in diameter,

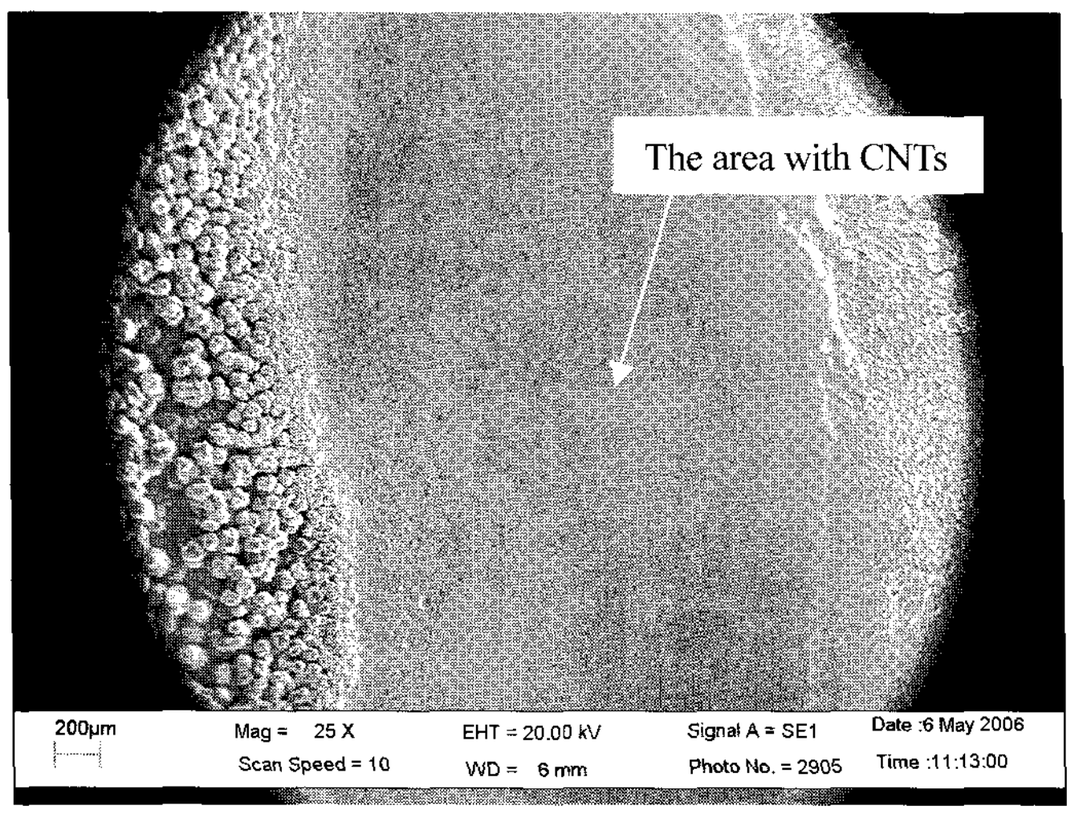

Fig. 3 SEM image of the arc-discharged anode surface with CNTs in the center

assisted by a vacuum pump as shown in Fig. 4. Once they were filtered, rinsed with water, and dried, the CNT properties such as length and diameter could be determined, as well as the number of layers for multi-walled carbon nanotubes (MWNT).

As well as the deposits on the anode, many small pieces of black material collected at the bottom of the liquid nitrogen container. These small particles were part of the deposit on the anode surface that dropped off during the arc discharge. We studied these under a scanning electron microscope (SEM) and determined that they were the same type of CNTs generated on the anode. We used transmission electron microscopy (TEM) at 600,000× to investigate the number of layers in the CNTs.

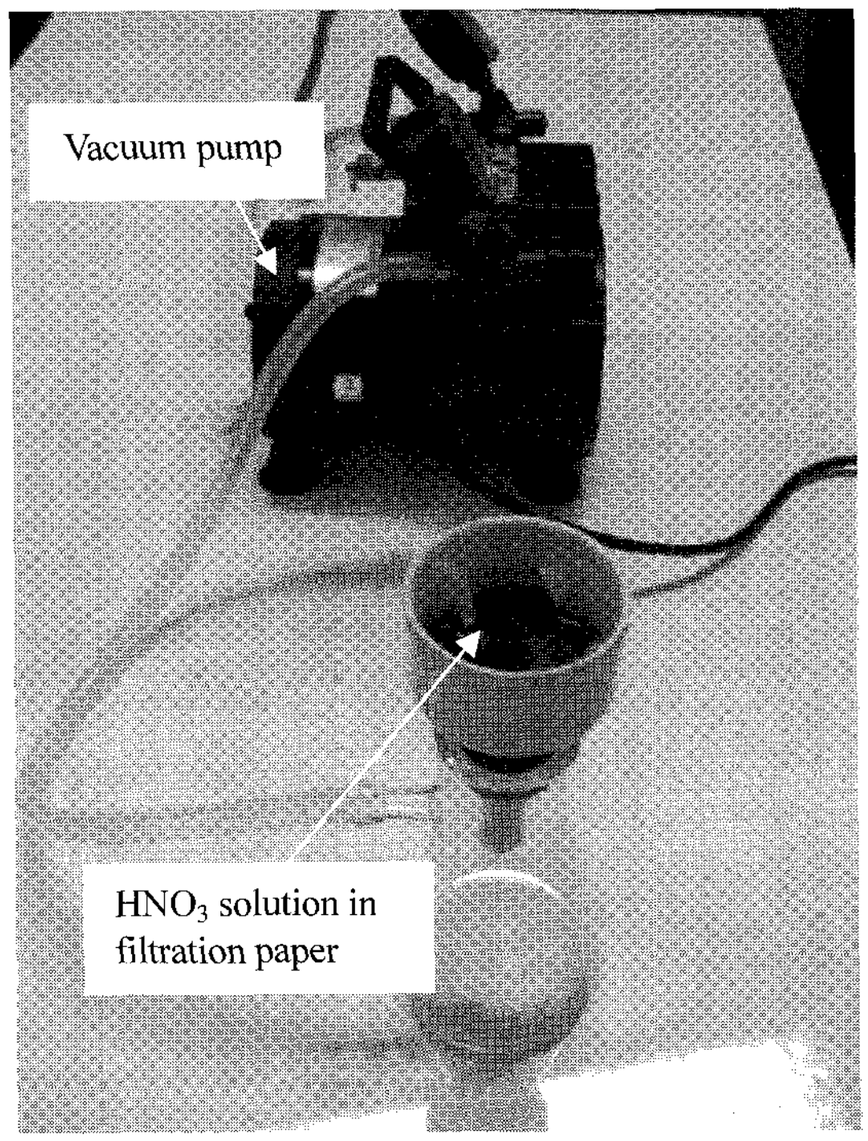

Fig. 4 Filtration of a HNO_3 solution for purification of synthesized CNTs using a vacuum pump

3. Results

Our SEM investigations confirmed that CNTs were produced on the anode surface and found in the black material at the bottom of the liquid nitrogen container.

A current of 60 A for 10 s resulted in a relatively small amount of CNTs compared to other conditions. The CNTs synthesized under these conditions were produced across the whole surface. They were short with many rounded particles, which appeared to be impurities attached to them. For a current of 60 A for 13 s, the CNTs were still produced over the complete surface but were longer and with fewer impurities as shown in Fig. 5 However, when the time increased to 15 s, the impurities also increased.

An arc discharge for 18 s at 60 A resulted in CNTs of various diameters with increased impurities. An arc discharge for 23 s appeared to generate CNTs with unstable diameters along with a large amount of impurities as shown in Fig. 6.

We tried a current of 70 A for discharge times of 10 and 15 s. This produced relatively short CNTs over the whole anode surface with a large proportion of impurities. Figure 7 shows the result for 70 A and 15 s. Table 1 gives a summary of the results for different combinations of current and discharge time. Note that a discharge time of 18 s or longer was not possible at 70 A since at this current, the gap between the anode and cathode steadily widened, and the arc could not be maintained for more than 18 s.

A current of 60 A, a voltage of 26 to 28 V, and a discharge time of 13 s produced the most stable, highest-quality CNTs with the lowest level of impurities. We used CNTs produced under these conditions for further purification using the 90°C HNO3 solution and filtration to remove the impurities.

However, the conditions such as the temperature, the electrical current and voltage, and the gap width between the cathode and anode led to variation in the proportion of CNTs and non-CNT carbon. We confirmed that a condition of 60 A, 26–28 V, and a discharge time of 13 s produced the best CNTs. Although the so-called impurities in this study are made of carbon just like the CNTs, their structural and dimensional differences indicate that they have different properties from the CNTs. One of the aims of this study was to find the conditions that reliably produced the most CNTs and the least impurities.

We used TEM to study the diameter and number of layers of the synthesized CNTs. As shown in Fig. 8, the CNTs synthesized by arc discharge in liquid nitrogen are MWNTs. The TEM image illustrates that they have approximately 25 layers and an average diameter of 18.2 nm. The length ranges from 10 nm to 1 mm. The mechanical and electrical properties of the synthesized CNTs require further study.

4. Conclusions

We studied arc discharge in liquid nitrogen to find a method of generating CNTs with uniform diameters with the least amount of undesirable byproducts. We conducted our tests over the ranges of 60–70 A and 26–28 V with an arc discharge time of 10-23 s.

Table 1 Experiment summary

Current (A)	Discharge time (s)	Diameter (nm)	Results
60	10	20.5	Small amount of CNTs
60	13	18.4	More CNTs
60	15	18.7	Significant amount of impurities
60	18	17.2	More impurities
60	23	17.1	More impurities
70	10	20.3	Shorter CNTs
70	15	N.A.	Shorter CNTs with more impurities

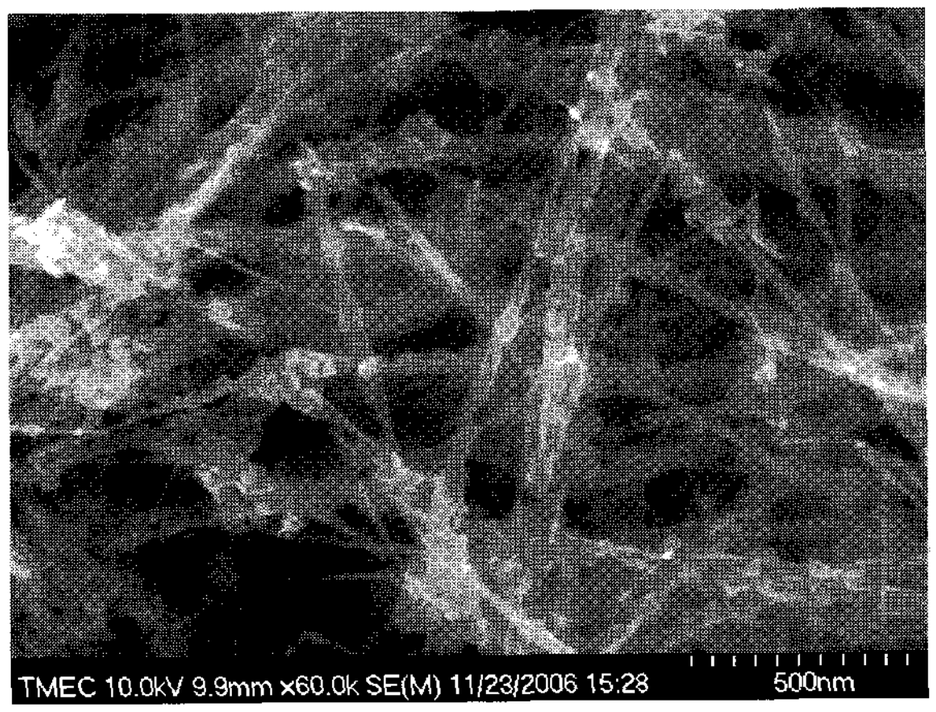

Fig. 5 CNTs synthesized at 60 A, 13 s (SEM, 60,000×)

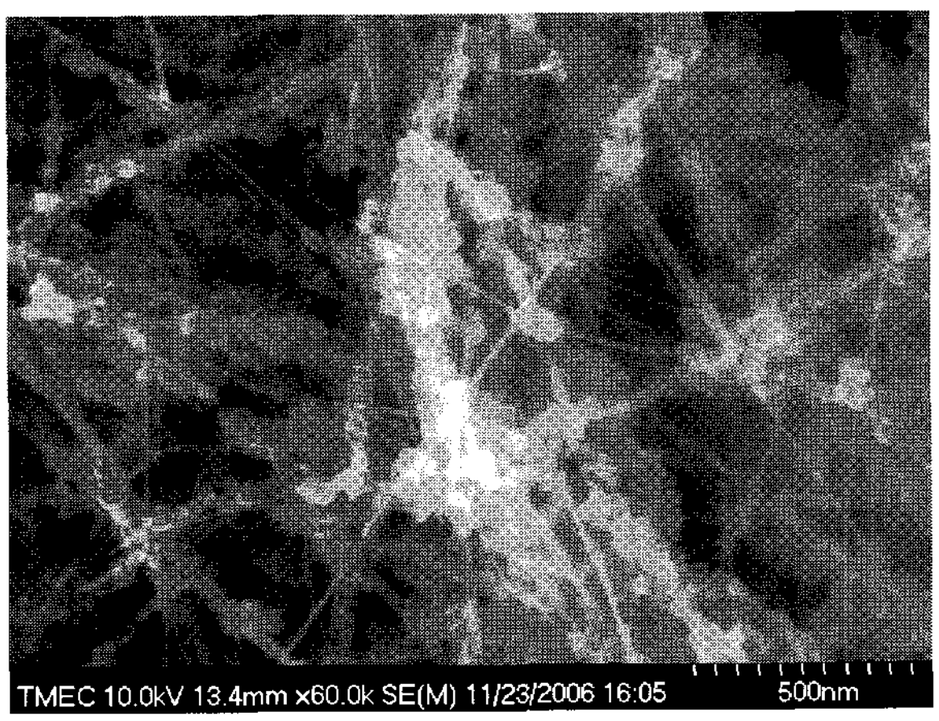

Fig. 6 CNTs synthesized at 60 A, 23 s (SEM, 60,000×)

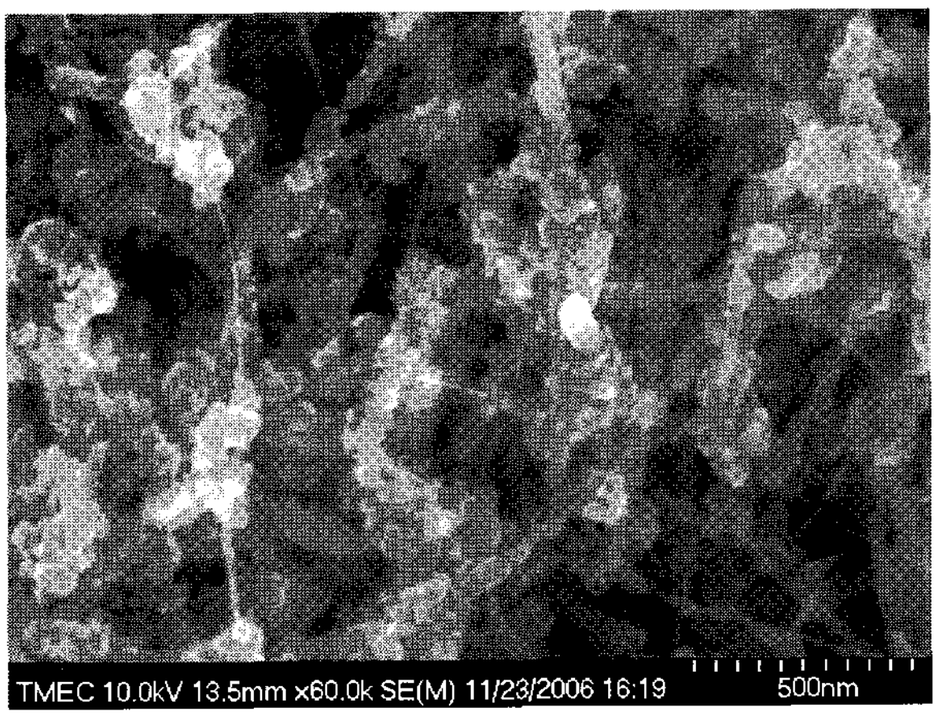

Fig. 7 CNTs synthesized at 70 A, 15 s (SEM, 60,000×)

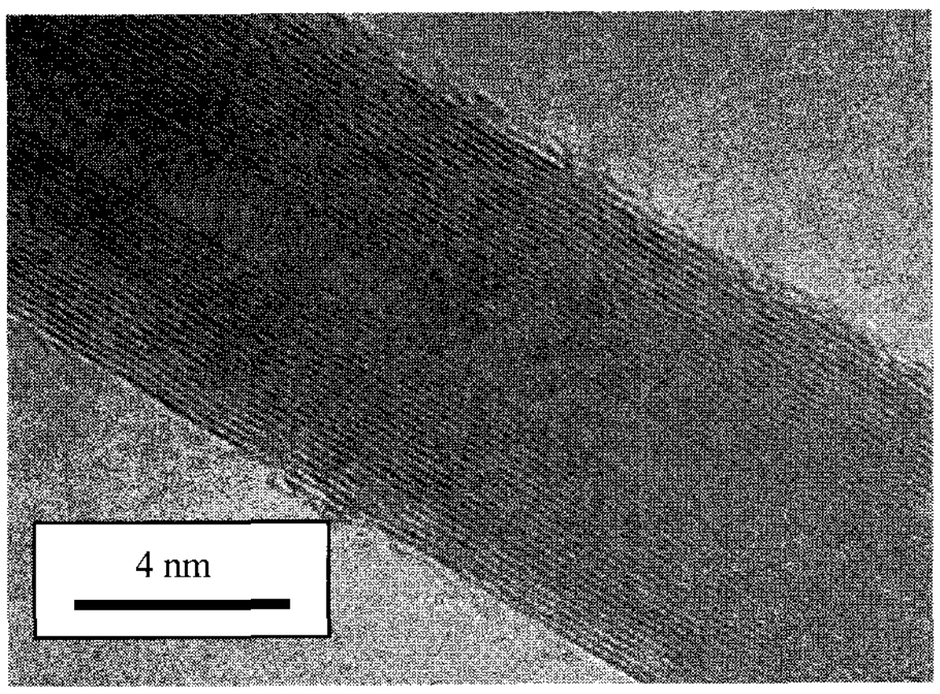

Fig. 8 TEM image of the synthesized MWNTs (600,000×)

After purifying the CNTs by filtering through 0.2-μm filter paper and immersing them in a HNO_3 solution, we concluded that the most appropriate condition was 60 A with a discharge time of 13 s. This produced MWNTs with approximately 25 layers and an average diameter of 18.2 nm.

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