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Well graphitised nanocarbons including onion-like fullerenes and single- and multi-walled carbon nanotubes (CNTs) were synthesised in high yield by automatic arc-discharge method in solution. This technique is considered a low-cost method since it does not require any expensive equipment. Herein, an arc discharge full automatic set-up was used for fabrication of CNTs which enables controlling of the gap between the two electrodes and the voltage as well. Carbon nanostructures under a controlled amount of voltage (from 10 to 30 V) were synthesised where Ni : Mo as a catalyst and LiCl 0.25 M as a solution were used. Subsequently, a modified acid treatment method was applied as purification stage of the products. The production rate of CNTs was as high as 7.7 mg min^{-1} while the voltage was set at 30 V. Scanning electron microscopy and transmission electron microscopy as well as Raman spectroscopy were employed to study the morphology of these carbon nanostructures. The results indicated that CNTs synthesised at a voltage of 30 V had the best quality and elongated straight structures. The mechanism of the voltage conditions for preparing nanocarbons as well as their characterisation are discussed.

Keywords: carbon nanotube; arc discharge; catalyst; synthesis; voltage

1. Introduction

Carbon nanotube, a new structure of carbon element, is composed of graphene sheets rolled into closed concentric cylinders with a diameter of the order of nanometres and have length about 1 μm [1]. Various structures of carbon nanomaterial have attracted a great deal of attention from the research community since they exhibit excellent physical properties and potential technological applications. Both onion-like fullerenes and carbon nanotubes (CNTs) have become the subject of intensive research since they were discovered [1,2]. In addition to CNTs, spherical carbon onions are interesting because they are expected to have superior lubrication properties [3]. Carbon plasma, generated by laser ablation [4] or arc discharge has been used routinely in the production of fullerenes and CNTs [5].

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Within these conventional methods, the submerged arc discharge in liquid has been recently proposed and is being investigated for the fabrication of nanomaterials. The arc discharge in liquid nitrogen was utilised in the production of CNTs for the first time in the 2000s [6]. Lange et al. [7] generated onions, nanotubes and encapsulates by arc discharge in water. Guo et al. [8] reported that nanocarbons including onion-like fullerenes and multi-walled CNTs were synthesised in high yield by arc discharge in water between the two electrodes.

High yield, large scale and cost efficient approaches to such nanostructures should be considered. The arc in liquid method has recently been developed to synthesise many kinds of nano carbon structures such as carbon onions, carbon nanohorns and CNTs [9]. This technique is considered as a low-cost method because it does not require any expensive equipment.

In this study, preparation of nanocarbons by automatic arc-discharge technique in solution and their purification with the modified acid treatment method are investigated. It is noteworthy that the discharge in water is erratic, thus it is critical to control precisely the arc gap in order to run the arc continuously [7]. In this research work, the voltage effects on the production of the nanostructures by applying a variety of voltage values in different experiments are examined while voltage and the gap between two electrodes are mechanically kept constant in each experiment.

2. Experimental

2.1. *Materials*

All chemicals were of analytical grade and aqueous solutions were prepared with doubly distilled water. LiCl (Fulka®, Sweden), garfit powder (Merk®, Germany), Mo 99% (Sigma®, UK) and Ni 99.5% (Merk®, Germany) were purchased as salt and catalyst, respectively. A direct current (DC) arc discharge was generated in deionised water herein between two electrodes submerged in 3000 cm^3 of solution in a Pyrex beaker ($15 \times 20 \times 20\,cm^3$) as a container. The arc discharge was initiated by contacting the 99.9% pure grounded anode (8 mm diameter, Germany) with a cathode (12 mm diameter, Germany) of similar purity submerged to a depth of 3 cm in solution. A 2 mm diameter hole was drilled in the anode and filled with a mixture of catalyst powder.

2.2. *Synthesis*

The most important aspect in this article is the synthesis of CNTs by controlled voltage while the other experimental conditions are constant. The other experimental conditions we have used in this article are based on the reference [10] (belongs to the authors) which optimised the other conditions in CNTs synthesis.

A schematic representation of automatic arc-discharge apparatus is shown in Figure 1; a digital image of the arc discharge in water is also shown. The bright area between the electrodes indicates the arc-plasma region. A high-purity graphite rod aligned horizontally was used as the fixed anode and the cathode which was free to move horizontally. Both electrodes were connected with a digital controllable DC power supply and submerged in LiCl with concentration 0.25 M in a Pyrex beaker. Arc discharge in deionised water and liquid nitrogen are erratic due to their electrical insulation [7]. The electrical conductivity

of LiCl solution is also better than deionised water and liquid nitrogen [11]. Therefore, LiCl was used as the aqueous solution. However, evaporation of the solution during the arc discharge was considered to be negligible.

The arc discharge and consequent consumption of the anode increase the distance between the two electrodes and decrease the voltage between them as well. In order to keep the voltage and the gap between the two electrodes constant the program automatically compares the initial voltage with the voltage of two electrodes with an accuracy of 0.1 V. Based on the calculated difference the program calculates the proportional coefficient for the proportional controller. This determines the forward movement of the anode electrode for the step motor which is designed to control the motion of the anode electrode.

The voltages used in this study varied from 10 to 30 V. The arc discharge in water was found to be stable and could be run for several minutes as long as a cathode–anode gap of 1 mm was maintained [12]. Ni : Mo with ratio 1 : 2 was selected as the catalyst in this experiment [10]. The water turned dark gray gradually during the continuous arc discharge. Then a Millipore filter was used to separate the floating materials on the surface of the water and the deposits on the bottom of the container. In addition, the deposits on the cathode were disregarded. The amount of this deposit in arc discharge in solution is negligible due to collision of the medium in high temperature which will cause the deposits to separate from the cathode. The products were separated by Millipore filter paper and subsequently dried in an oven at 80–100°C for 5 h.

2.3. *Purification*

The as-prepared deposit was purified using different combinations of the following purification steps for all tests. First 0.5 g of as-prepared deposit were sonicated in 12 N HCl for 20 min and the resulting solution was left to stand overnight. Then it was refluxed in 6 N HCl for 6 h. After treating the deposit with acid, the resulting solution was diluted with distilled water and centrifuged. Subsequently, the supernatant solution was decanted

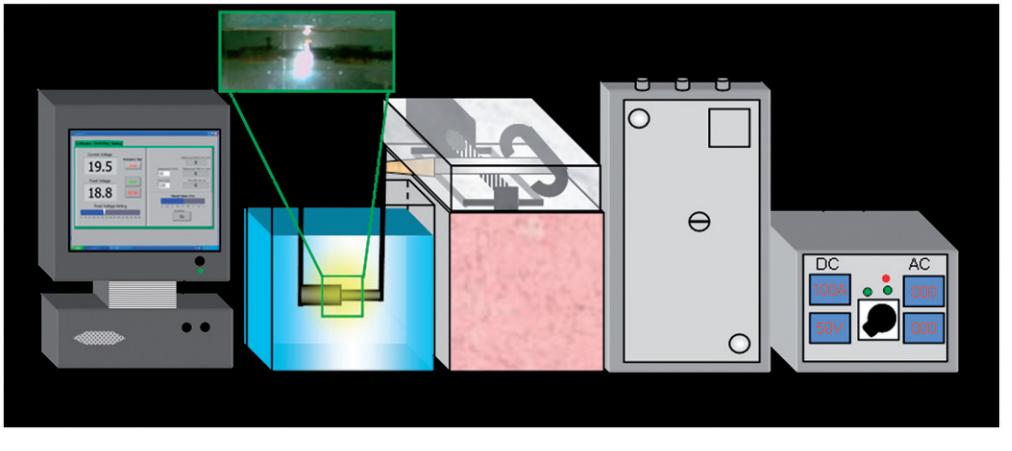

Figure 1. Schematic representation of the apparatus used for arc discharge in water with a digital image of the discharge.

and the residue was transferred onto a Millipore filter paper. The residue on the filter paper was washed with distilled water (4–5 times) to remove the acid. The residue was dried in an oven at 80°C–100°C for 5 h. After that, the nanocarbons were weighted and kept in desiccators [13]. The products were observed by using scanning electron microscopy (SEM) to analyse the samples. As for SEM (Philips, XL30) observation, a layer of gold was deposed on the samples by physical vapour deposition method utilising a Sputter Coater machine (BAL-TEC, Poland, SCDOOS). However, transmission electron microscopy (TEM: Philips, EM 208) and Raman spectroscopy have been used.

3. Result and discussion

3.1. *Voltage effect upon produced nanocarbons*

For an investigation into the effects of any changes in voltage on the nanocarbon productions, three experimental cases with different voltages (10, 20 and 30 V) were carried out. Figure 2 illustrates the SEM images of these samples. Figure 2(a) shows the sample synthesised by an arc-discharge method in the coloured lithium 0.25 M and Ni : Mo with ratio 1 : 2 as a catalyst with 10 V voltage value.

As Figure 2(a) illustrates, no CNTs were fabricated at a voltage of 10 V. But the fullerenes are observed in the sample. Figure 2(b) illustrates another sample which has the same condition of the previous experiment while the voltage was kept at 20 V. Both CNTs and fullerenes are observed in this sample, but the fullerenes are cleaved to the CNTs and in some places the fullerenes are encapsulated in the CNTs.

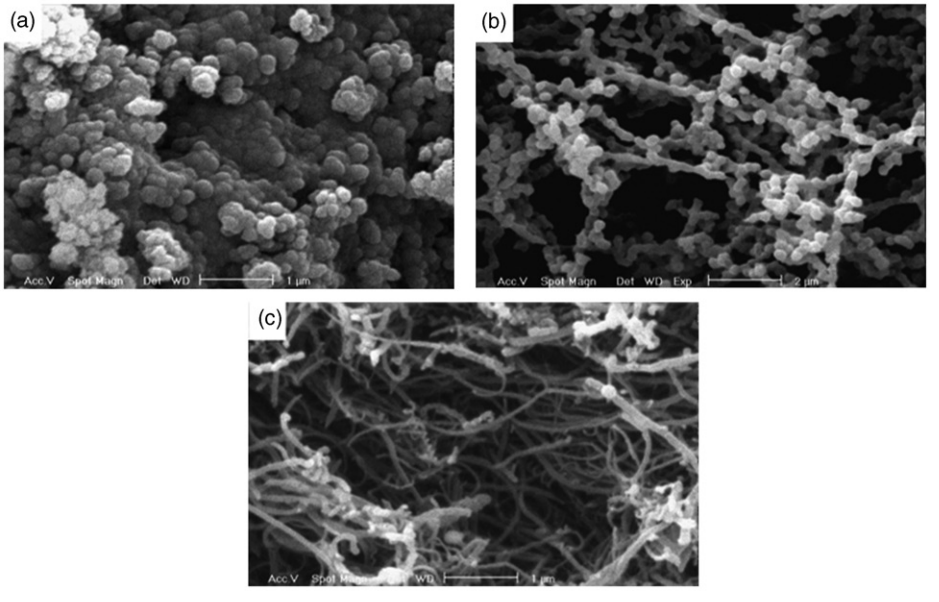

Figure 2. (a) SEM images of the produced sample by arc discharge at a voltage of 10 V. (b) SEM images of the produced sample by arc discharge at a voltage of 20 V. (c) SEM images of the produced sample by arc discharge at a voltage of 30 V.

Figure 2(c) illustrates a different sample in the same condition with a voltage of 30 V. It shows CNTs which have elongated straight structures. At the higher voltages the arc was not continuous and the plasma was not stable due to the high turbulence which occurred in the solution. In order to analyse produced nanocarbons in more detail, the samples were sonicated in ethanol for 5 min to prepare them for the TEM observation. Figure 3 shows a TEM micrograph of the CNTs after the purification step. It is observed that the CNTs have narrow distribution diameters. The CNTs are of high quality with straight parallel walls with quite a clean surface. In this TEM, single-walled nanotubes (SWNTs) with a diameter of 1–2 nm and multi-walled nanotubes (MWNTs) with a diameter of 3–5 nm and with lengths around a micrometre can be observed.

It is obvious that the anode electrode consumes because of the spark between the two electrodes and its elements transform to the nanostructure. Table 1 shows the consumption rates of the anode at different voltages and the production rate after the purification step. Moreover Figure 4 represents the weight loss of the anode and the

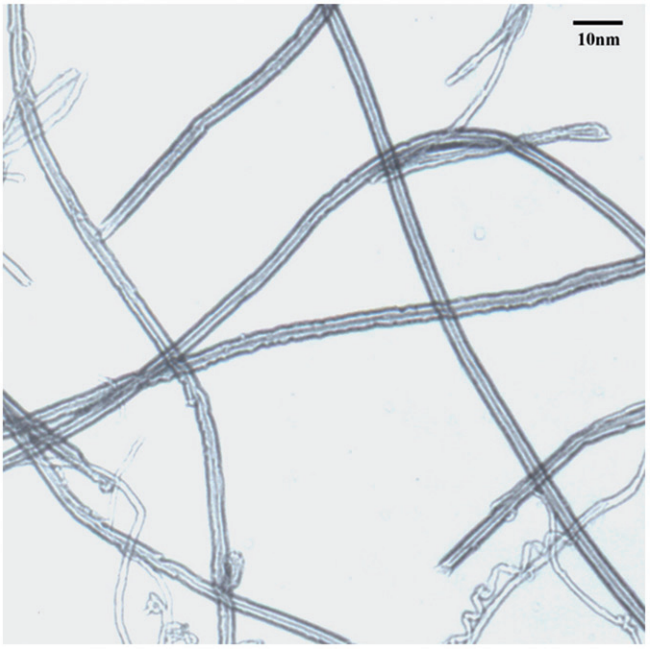

Figure 3. TEM micrograph of the CNTs after purification step.

Table 1. Anode consumption rate in different experiments.

Voltage value (V)	Anode consumption rate (mg min^{-1})	Production rate (mg min^{-1})
10	93	2.4
20	211.8	5.8
30	231.6	7.7

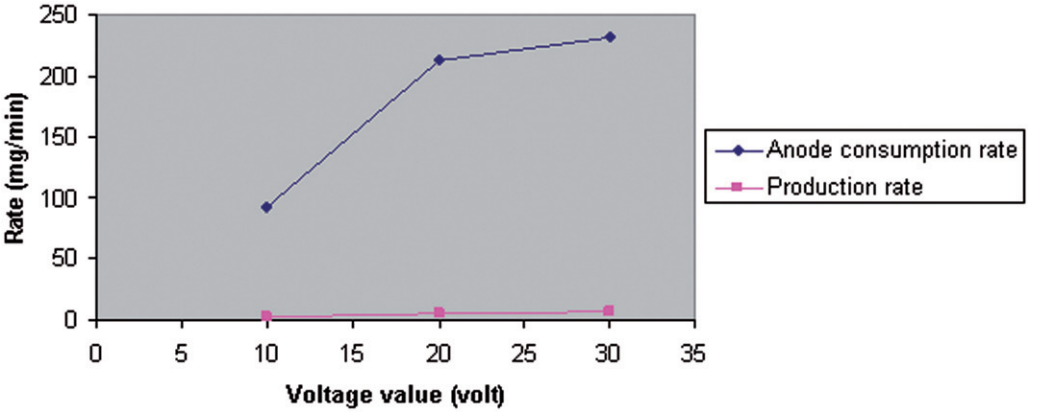

Figure 4. Plot of anode consumption rate and production rate *vs.* voltage during arc discharge in liquid.

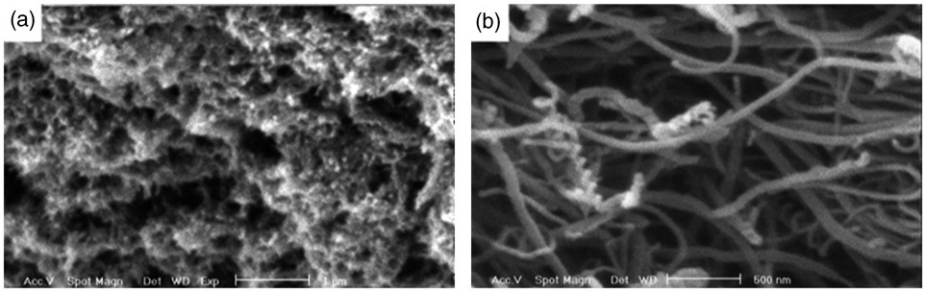

Figure 5. (a) The SEM images of CNTs before purification stage. (b) The SEM images of CNTs after purification stage.

production rate *versus* voltage. As expected, the consumption rate of the anode and the production rate increase with the increased voltage. It can be seen from Table 1 that a high production rate of CNTs is achieved at a voltage of 30 V. This is a good result in comparison with the results of the other studies in this field [10,14].

3.2. *Analysis of the produced CNTs*

Figure 5 illustrates the SEM images of CNTs before and after purification. Figure 5(b) shows the SEM image of purified CNTs in which some impurities have been removed by the described method. By all appearances it is cleaner than that in Figure 5(a), which is the SEM image of as-grown CNTs. Contrasting the two images we can conclude that the carbon and catalyst impurities were relatively removed in this process.

A Raman spectrum of the purified sample (after applying the purification procedure) is shown in Figure 6. The peaks at 1236 and 1579 cm^{-1} correspond to disorder (D-band) and

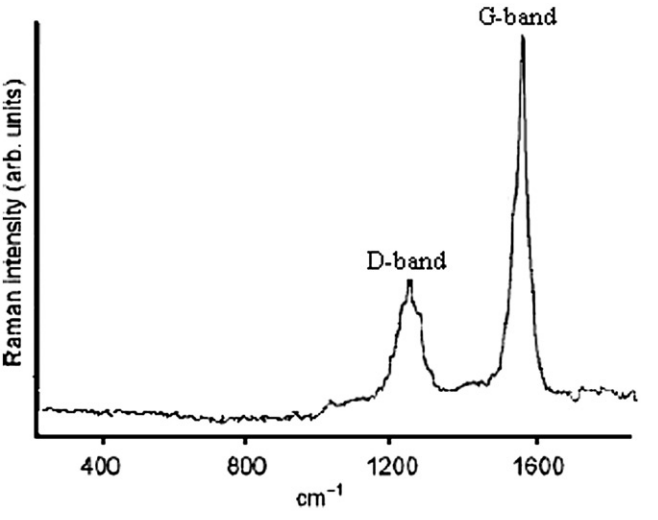

Figure 6. Raman spectra of CNTs, after purification by acid treatment.

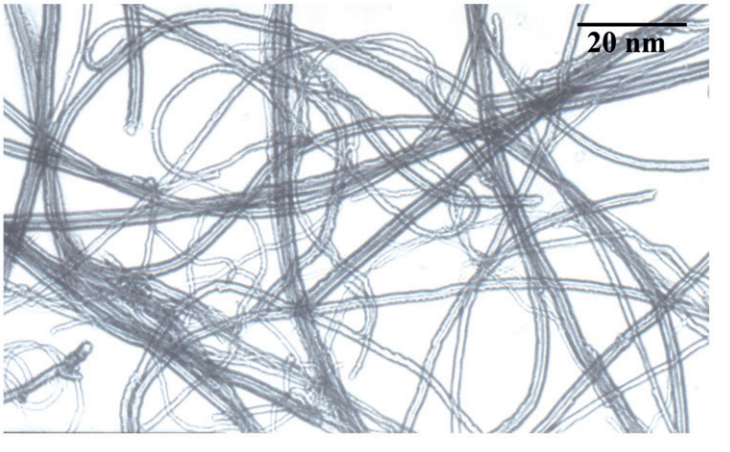

Figure 7. The TEM image of CNTs after purification stage from a bigger area.

graphite (G-band) bands, respectively. The former is an indication of the presence of defective and the latter one refers to the well-ordered graphite. The decrease in D peak intensity indicates a reduction in the relative amount of disordered carbon of the samples. As can be seen, it is an acceptable spectrum. The ratio of G : D is about 2.65 which shows that impurities such as carbon amorphous, graphite and catalyst particles were removed. The G : D ratio is a measure of the 'purity' of the CNTs [15]. Therefore, the purification step was effective in removing impurities from CNTs. Figure 7, which is an image of a purified sample, clearly indicates that almost all impurities which existed before purification have been successfully removed after the purification step.

4. Conclusion

In this study nanocarbons were successfully synthesised in large quantities by a DC automatic arc discharge in solution. Arc discharge occurred between two graphite electrodes and voltage varied in the range of 10–30 V. In order to remove the impurities, acid treatment was carried out. The TEMs and SEMs of the synthesised materials showed the formation of fullerene at a voltage of 10 V, while both CNTs and fullerenes were fabricated at a voltage of 20 V. In contrast, the elongated CNTs were synthesised with high quality at a voltage of 30 V. By the results of the experiments, the rate of production efficiency and anode consumption was increased by increasing the voltage amount. The rate of production of CNTs was as high as 7.7 mg min^{-1} at 30 V, which was more proper than what was already reported in literatures. To the best of our knowledge, the current study is the first one that has demonstrated optimised fabrication of nanocarbons based on an automatic arc-discharge set-up in solution and this area deserves further investigation [16].

Acknowledgements

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