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ORIGINAL RESEARCH PAPER

Functionalized Carbon Nanotubes Produced by APCVD using Camphor

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Abstract

A simple chemical vapor deposition technique at atmospheric pressure (APCVD) is adopted to synthesize the aligned arrays of functionalized multi-walled carbon nanotubes (AMWCNTs) without using any carrier gas, at 230°C, 750°C and 850 °C. Camphor ($C_{10}H_{16}O$) is used as carbon source because this botanical hydrocarbon is chip and abundant which convert the CVD technique to a green method for production of carbon nanotubes (CNTs). The oxygen atoms in camphor oxidize the amorphous carbons and create hydroxyl functional groups in AMWCNTs. The molecular structure of camphor lead to form hexagonal and pentagonal carbon rings which increase the growth rate and alignment of MWCNTs. In this work, AMWCNTs are grown on silicon substrate, copper, and quartz. The synthesized AMWCNTs are characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and transmission electron microscopy (TEM). The SEM results show that the deposited CNTs are formed in vertical aligned arrays and each has a functional OH group which is seen in FTIR spectroscopy results.

1. Introduction

Carbon nanotubes (CNTs) are one of the allotropic forms of carbon that were extensively studied due to their exceptional mechanical, electrical [1] and optical properties [2]. Individual CNTs are believed to be better conductors than copper and stronger than steel, while having a density about four times smaller than these materials [1]. This kind of material has a nanoscale tubular structure consisting of several layers of grapheme sheets and are known as multi-walled carbon nanotubes (MWCNTs) [3].

Although this structure had been synthesized, studied and reported by several researchers during 1952–1989 [4-5], Iijima's detailed analysis of helical arrangement of carbon atoms on seamless coaxial cylinders in 1991 has been believed as the first discovery report [3]. Despite the remarkable properties, CNTs have some major drawbacks being difficult to handle due to their small dimensions, expensive and being incompatible with industrial orders.

Aligned arrays of multi-wall carbon nanotubes (AMWCNTs) are one of the important architectures of CNTs because they can directly be used as field emitter in flat panel displays or as reinforcing agent in composite materials [6-7]. However, there are ongoing

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challenges within the biomedical and healthcare sector, for the ability to measure and detect specific biomarkers at molecular levels [8]. In this regards, there is a need for smaller, faster and cheaper biosensors. Recent developments in the field of nanotechnology using AMWCNTs provide a solution for construction of biomedical devices. For example, biosensors, that are modified using CNTs and AMWCNTs, are used to detect the total cholesterol values in human blood [9].

Lot of works has been carried out in developing new and efficient synthesis routes for the production of CNTs and AMWCNTs in high quantities and in ordered layouts. The three most widely used techniques are electric arc-discharge [10], laser ablation [11] and chemical vapour deposition (CVD) [12]. CVD is performed in different conditions; one of these methods is catalytic thermal decomposition of hydrocarbons at atmospheric pressure chemical vapor deposition (APCVD). APCVD technique is relatively simple, low-cost and scalable technique for producing CNTs [13] which is employed in this paper to produce functionalized AMWCNT using only a solid source.

2. Materials and Experiments

2.1. Materials

Camphor (Merck95%), ferrocene (Merck98%) without special purification, wafer silicon (100), copper plates (99%), quartz substrates, hydrofluoric acid (38% Merck), ammonia (25% Merck), nitric acid (dr.Mogalleli (65%)), deionized water, acetone (dr.Mogalleli 99%) and sulphuric acid (95% -98%) were used as starting material. Ferrocene was chosen among the many catalysts that have previously been used in the CVD techniques and camphor was used as the carbon source. Camphor is the crystallized latex of cinnamomum camphor tree of lauraceae family. Camphor is very cheap, and also simple to pyrolysis due to its volatile and non-toxic nature. It sublimates at room temperature. At the first experiment, camphor and ferrocene are placed in a quartz tube, separately. The quartz substrates are placed in the tube at a measured distance to lie in the centre of the two furnace zones. In subsequent experiments, camphor–ferrocene mixture is placed in the tube as the source.

2.2. Experiments

The applied technique uses two simple experimental setups include two furnaces with the three thermal zones. Synthesis of CNT has been carried out using a single step pyrolysis technique which consists of a triplet hot zone in regular CVD and pyrolysis methods. A photograph of the simple CVD set-up used for the synthesis of AMWCNTs is shown in figure 2b. Calibrated temperature profile across the furnace is shown in figure 2a.

In the first step, 10 mg of catalyst material and 1 g of carbon source material, separately, were put in a large quartz tube with the diameter of 7 cm and the length of 100 cm, which is shown in figure 1.

In the second step, a small quartz tube is place into the latest furnace to limit the gas precursor concentration in a smaller place and so increase the deposition rate.

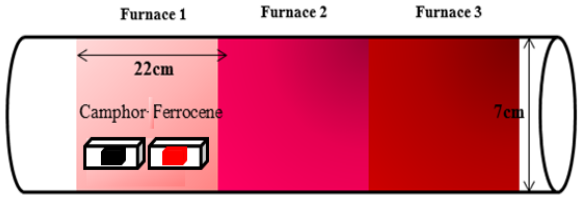


Fig. 1. Schematic of APCVD reactor and the location of camphor, ferrocene

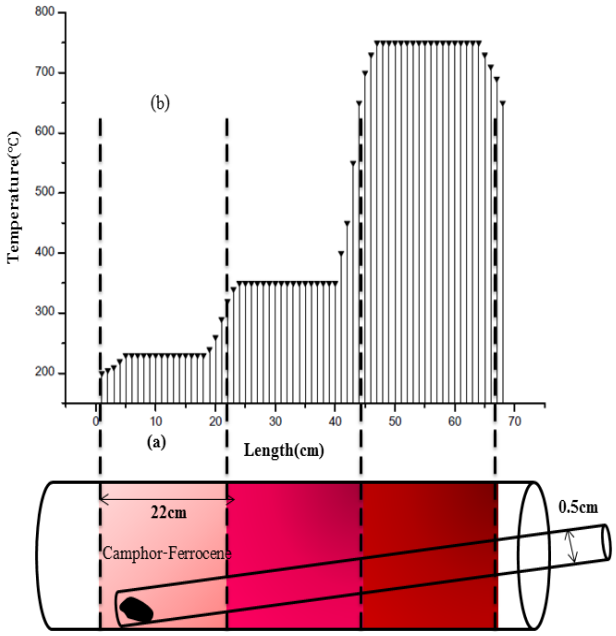


Fig.2. (a) Schematic diagram of the single-stage pyrolysis set-up. (b) Calibrated temperature profile across the furnace.

A mixture of 10 mg of catalyst source material and 1 g of carbon source material is taken in a smaller

quartz tube with the diameter of 0.5 cm and the length of 100 cm, that is shown in figure 2 (a).

The entrance of the smaller tube is kept in the first thermal zone of the bigger tube, while its exit is open. As a result, the pressure inside is maintain equal to the atmospheric pressure. A mixture of camphor and ferrocene is placed in the first zone and the substrate is kept in the third thermal zone where the deposition is happened. The furnace is heated up to the desired pyrolysis temperature (750 ◦C) at a heating rate of 20 ◦C min^{-1}. The deposition was done on three different substrates, silicon, copper and quartz, according to the conditions which are mentioned in table1.

Table 1
Temperature zones of the furnace for different substrates.

Substrate	Weight ratio camphor / ferrocene	First temperature zone	Second zone temperature	third zone temperature
Silicon	100	230	350	850
Quartz	100	230	350	750
Copper	100	230	350	750

Camphor and ferrocene are vaporized, simultaneously, at 230 ^{o}C, in the first zone, and paralyzed at 750-850 ^{o}C, in the third zone. The reaction is continued for 20 min and then cooled down to room temperature. Then the smaller quartz tube is taken out of the furnace. In this technique, neither predeposited metal catalyst nor carrier gas is used. The degree of amorphous carbon and catalyst particles present in the as-synthesized materials depends on preparation conditions. The purification of the as-synthesized sample was done using the standard oxidation and acid bath treatment method [14]. Different techniques are used to obtain information concerning the type and structure of the synthesized CNTs.

3. Results and discussion

The scanning electron microscopic (SEM) is used to determine the alignment of the CNT arrays, while the transmission electron microscopic (TEM) is done to determine the walls numbers and the diameter of the CNTs.

Also, Fourier transform infrared (FTIR) spectroscopy is used to study the quality of the functional groups attached to the carbon nanotubes.

3.1. SEM analysis

Figure 3(a,b) shows SEM images of the samples which were deposited in the big quartz tube. These figures suggest that there is no CNT deposition on quartz and silicon substrates. Carbon produced by this method further is conical shape because the catalyst particles on substrate for the production carbon nanotubes are less than the amount required.

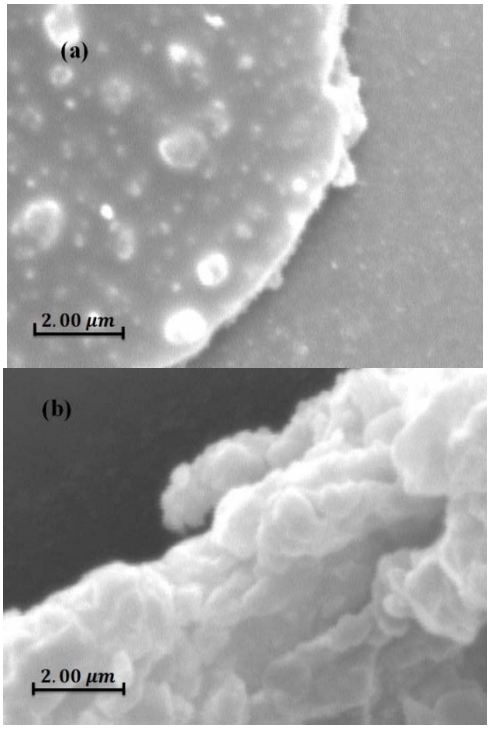


Fig 3. (a) SEM images of carbon deposition on silicon substrates. (b) Carbon images separated from quartz substrate

SEM devices that do not imaging along the axis of Z need the deposited carbon to be scraped from the surface of silicon and copper and then covered with a thin layer of gold. This work is performed to show if there exist any array of deposited CNTs. Figure 4 (a, b) shows SEM images of deposited carbon on silicon substrates, after removing them from the substrates. As it is seen, there are no carbon nanotubes among the black carbon obtained by this method.

The SEM results of prepared samples in the small quartz tube are shown in figure 5. Figure 5 (a, b) shows SEM images of AMWCNTs grown from camphor on a flat copper substrate. The respective SEM images of aligned arrays of CNTs synthesized from camphor, using ferrocene on a wafer silicon substrate are shown in figures 5 (b, d). In these images

there is a high ordered array of CNTs that could be suitable for fabrication of high sensitive sensors.

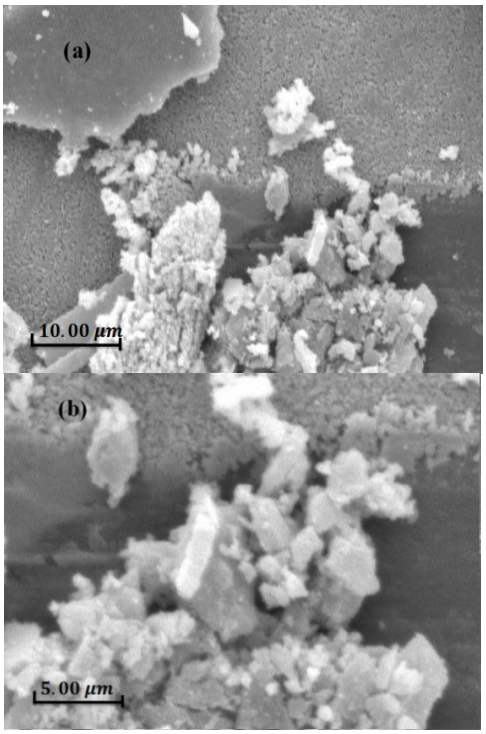
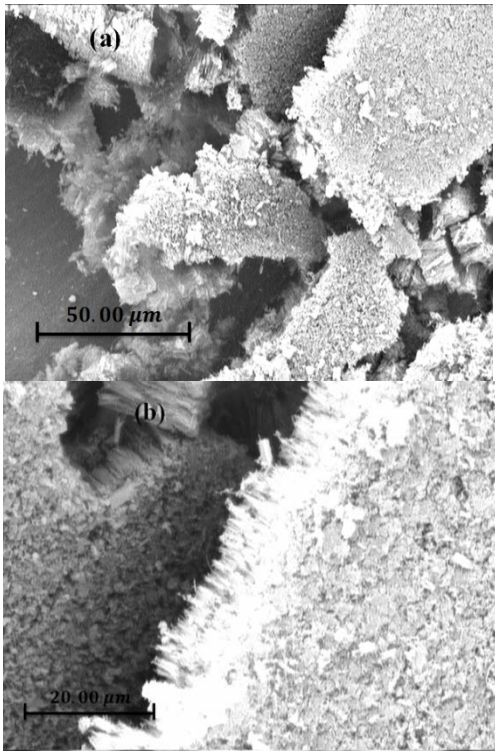


Fig. 4. (a),(b) SEM images of carbon deposited on silicon substrate after removing from its substrate



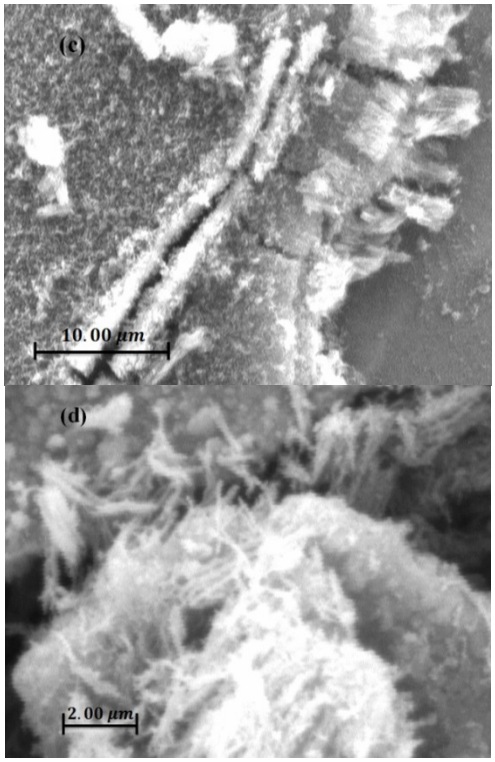


Fig. 5. (a), (b) SEM image of deposited carbon on copper substrate, after removing them from its substrate. (c), (d) SEM image of deposited carbon on silicon substrate, after removing them from its substrate

3.2. TEM analysis

The respective TEM images, figures 6 (a, b), show that the tubes are multi-wall in nature. The CNT with open lumens is seen in TEM image (a) while the CNT with close lumens is seen in TEM image (b), these two images suggest that the growth mechanism of CNTs includes both tip growth mechanism and base growth mechanism [15].

In addition, AMWCNTs show a diameter of about 30 nm. Remarkable difference in molecular structure of camphor from conventional CNT precursors, methane, acetylene, benzene, etc is shown in Figure 7(a) [16]. Camphor molecule has ten carbon atoms: seven of these atoms form a strong three-dimensional structure consisting of hexagonal and pentagonal rings. The hexagonal and pentagonal rings are as essential constituents of fullerene and tube-like structures which are determine growth rate and the growth mechanism of the CNTs.

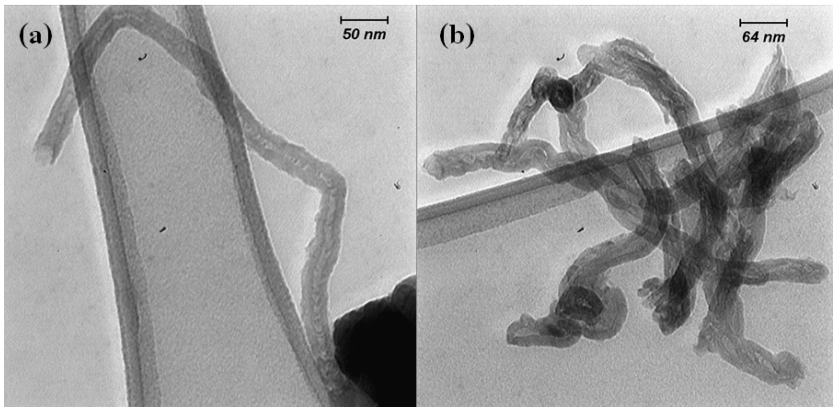


Fig. 6. TEM images of CNTs. (a) CNTs have base growth mechanism. (b) CNTs have tip growth mechanism

During pyrolysis, methyl carbons are easily detached from the molecule but breaking of the three dimensional carbon skeleton of camphor is less probable than planar (benzene-like) rings. Hence, we think that at the third zone of furnace and higher than700℃ might be sufficient energy to detach the top carbon atoms as a result created the hexagonal and pentagonal rings. Using of this hexagonal and pentagonal rings in addition to increasing rate of growth, producing aligned arrays of carbon nanotubes.

3.3. FTIR analysis

Infrared spectroscopy is a crucial tool to characterize the structure of matter at the molecular scale. Based on the singular resonant vibrational modes of different branches or body parts of a molecule [17], pristine CNTs show very weak resonant frequencies in the infrared spectrum in the 400–4000 cm^{-1} range. These structures are symmetric so do not have specific absorption in this spectral region. Presence of functional groups on CNTs cause that this structure have absorption in this region.

FTIR spectroscopies of CNTs represent this hydroxyl functional group by absorption peaks belonging to hydroxyl functional group in wave numbers 1061 cm^{-1} and 3400 cm^{-1}. To achieve an absorption diagram fitting Used of carbon nanotubes has been made by arc discharge with a length of 30 μm and functionalized by acid bath treatment method. These structures have been hydroxyl functional group as a result absorption peaks belonging to hydroxyl functional group in wave numbers 1040 cm^{-1} and 3400 cm^{-1}. Absorption peak belonging to wave numbers 1040 cm^{-1} dependant on chemical bonding C-H and3400 cm^{-1} dependant on chemical bonding C-O thus carbon nanotube sample have a hydroxyl functional group that is shown in Figure 8(a). Camphor contains one oxygen atom per molecule so during pyrolysis, this oxygen helps in oxidizing amorphous carbon and production of hydroxyl functional group in carbon nanotubes. Camphor decomposition process has been done at temperatures of 750 °C and 850 °C, during increasing decomposition temperature will provide enough energy to break the double bonds as a result is produced less amorphous carbon by free oxygen atoms. Absorption peaks belonging to the AMWCNTs are shown in figure 8(b, c).

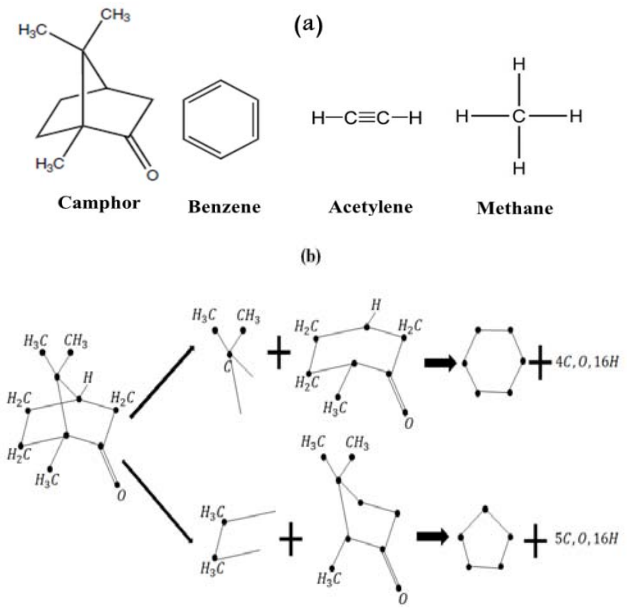


Fig7. (a) Difference in molecular structures of camphor from conventional CNT precursors, methane, acetylene, benzene.(b),(c) the hexagonal and pentagonal rings produced after easy removal of groups carbons [16]

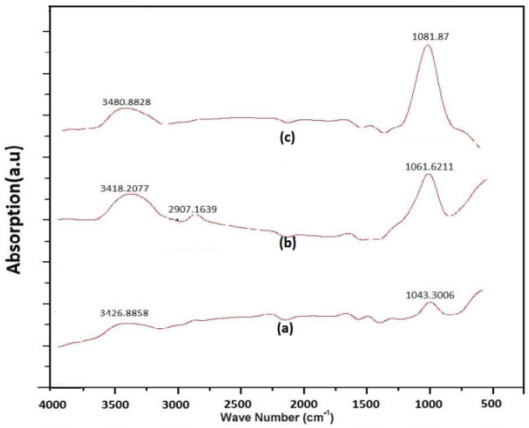


Fig. 8. (a) FTIR of purchased CNTs containing hydroxyl functional group. (b) AMWCNTs produced in 750 ^{o}C . (c) AMWCNTs produced in 850 ^{o}C

4. Conclusions

AMWCNTs were synthesized by APCVD method in two size of quartz tube. Experimental results in big quartz tube show that formation of amorphous carbon is extremely high and AMWCNTs is prepared in low yield by catalytic decomposition of camphor at atmospheric pressure. The experimental results in small quartz tube show that amorphous carbon is lower than previous results and AMWCNTs have been prepared in high yield. The results of characterization are shown the hydroxyl functional group, length 10 μm, diameter 30 nm and aligned arrays of MWCNTs. The employed process is extremely simple and easy to scale up for mass production. This green, regenerative and cheap material makes an alternative and competent nanotube producer of the future.

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