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Carbon nanotubes produced from hexane and ethanol

D. Mendoza[a,*], P. Santiago[b], and E. Reyes Pérez[a]

[a]*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,*
Apartado postal 70-360, 04510 México D.F. México.
[b]*Instituto de Física, Universidad Nacional Autónoma de México,*
Apartado postal 20-364, 01000 México D.F. México.

The synthesis of multi-wall carbon nanotubes using hexane or ethanol as the carbon source, hydrogen as the carrier gas, and iron as the catalyst with a thermal chemical vapor deposition method, is reported. It was found that the use of ethanol as the carbon source under low temperature (700°C) gives better results than other liquid precursors in obtaining long and clean carbon nanotubes on quartz substrates.

Keywords: Carbon nanotubes; chemical vapor deposition.

En este trabajo se reporta la síntesis de nanotubos de carbono de paredes múltiples empleando la técnica de descomposición térmica de vapores. Se emplean hexano y etanol como precursores líquidos para el carbono, se utiliza hidrógeno como gas de arrastre y hierro como catalizador. Se encuentra que la descomposición de etanol a 700°C sobre sustratos de cuarzo da lugar a nanotubos largos con pocas impurezas.

Descriptores: Nanotubos de carbono; descomposición térmica de vapores.

PACS: 61.46.fw; 81.16.Be; 81.16.Hc

1. Introduction

Carbon nanotubes have proven to be a very interesting material due to their unique physical properties. They are considered to be a quasi one-dimensional system which can behave as a metal or as a semiconductor depending on structural factors. Due to their electronic and mechanical properties, and because of their hollow structure, many potential applications have been proposed such as nanometer-sized electronic devices, composites with other materials and also for hydrogen storage [1]. The methods for the synthesis of carbon nanotubes are of great importance, some applications require great amounts of this material, other cases high purity is the more important property, or for some applications the growth with special morphology or in specific substrates following particular patterns are the important characteristic. Many techniques have been developed for these purposes, for example: arc-discharge, laser ablation and thermal chemical vapor deposition technique (CVD) [2]. CVD has proven a useful method to grow carbon nanotubes due to its versatility in the use of a great variety of carbon precursors and catalysts. Another advantage of CVD over the other two methods is that it is possible to grow carbon nanotubes on different substrates by covering them with a suitable catalyst. Moreover, if the catalyst is deposited following some specific pattern, then the carbon nanotubes can grow on the substrate with the same morphology as that of the catalyst pattern. For example, highly patterned vertically organized nanotube structures up to 2.5 millimeters height have been obtained [3], and also hexagonal [4,5] and triangular [6] lattices of carbon nanotube arrays have been fabricated that can be considered a two-dimensional photonic crystal with interesting optical properties in the visible region of the spectrum.

In this work we report experimental results on the synthesis of carbon nanotubes using two distinct liquids as the carbon source and iron as the catalyst in a simple CVD system. We have obtained the optimal conditions for growing carbon nanotubes on substrates for future experiments on optical and transport properties.

We have chosen the use of liquids and not gases as the carbon source because the use of large containers and valves is avoided; instead a small bubbler with small liquid volume (around 20 ml) is sufficient for several experiments. Furthermore, the system is very versatile for working with many liquids and also with liquid mixtures. For the present purpose we have selected two liquids as the carbon source: hexane and ethanol. It has been reported in the past that by using these liquids and with some variants of the CVD method, very long carbon nanotubes have been obtained. In fact, by using an enhanced vertical floating technique, long strands (up to 20 cm) of single wall carbon nanotubes (SWNT) have been produced [7]. Alternatively, with the same method, but with ethanol as the carbon source, a continuous production of SWNT and multiwall carbon nanotube (MWNT) fibers has been reported [8]. Recently, a very long (up to 4 cm long) isolated SWNT has been synthesized by the CVD method using ethanol as the carbon source [9].

In the next few paragraphs we shall describe the experimental method and the results for the production of carbon nanotubes. This method is similar to that reported in Ref. 9, with some differences such as: the carrier gas and the technique for depositing the precursor of the catalyst. Because in this reference very long carbon nanotubes synthesized at 900°C were reported, we primarily chose the same temperature in our process, but for purposes of comparison we also arbitrarily selected a lower temperature for the synthesis (700°C).

2. Experimental details

Our system consists of a horizontal furnace with a quartz tube (with a 2.2 cm internal diameter, and 2.5 cm external diame-
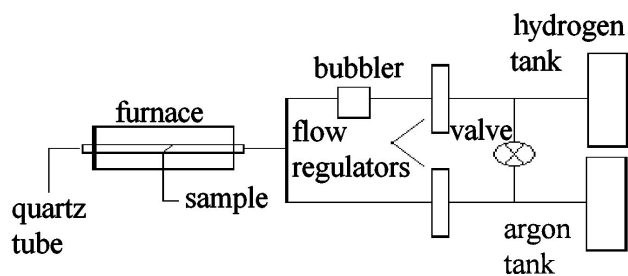
FIGURE 1. Schematic diagram of the CVD system.

ter) as the reaction chamber in which controlled flows of argon and hydrogen can be introduced directly or via a bubbler with the desired liquid as the carbon source (Fig. 1).

We used iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) as the precursor of iron which acts as the catalyst [10], preparing a 120 mM solution of iron nitrate in ethanol and spin-coated on clean fused quartz substrates. These substrates are loaded at the center of the furnace where the temperature in the interior of the quartz tube has been previously calibrated. At the beginning of the process, pure argon (126 sccm) is directly introduced into the tube furnace for several minutes to displace the air, then the temperature is raised to the desired value (700°C and 900°C in approximately 30 and 40 minutes respectively). When the target temperature is reached, the argon flow is switched off and pure hydrogen (450 sccm) is directly introduced for a period of 5 minutes to displace the remaining argon. Then a flow of hydrogen (88 sccm) is now passed through the bubbler with 20 ml of hexane or ethanol for 60 minutes. In Ref. 9, a lower flow of the carrier gas is used, but due to technical limitations of the flow controller used in our experiments, flows lower than 80 sccm are difficult to control, so we decided to use a flow of 88 sccm for the carrier gas in all the experiments. Note that at this stage, hydrogen, which is the carrier gas through the bubbler, and the vapor of the liquid are the only gases that are introduced into the tube furnace. At the end of this process, the flow of hydrogen through the bubbler is switched off and is replaced with pure argon directly into the tube furnace (126 sccm, for 15 minutes) to displace the remaining mixture of hydrogen and liquid vapor and therefore, to avoid any deposition of undesired carbonaceous material during the cooling of the furnace. Finally, the furnace is switched off and cooled to room temperature under the argon flow.

The synthesized material was scratched off the quartz substrates and sonicated with ethanol for 10 minutes; a few drops of this suspension were deposited on copper grids for transmission electron microscopy (TEM) observation, using a JEOL JEM-1200 and JEOL 2010 FasTem microscopes.

3. Results

Figure 2 shows low resolution TEM images of the obtained carbon nanotubes. In the case of hexane, at 700°C many nanotubes with different diameters and other carbonaceous particles are observed (Fig. 2a). The growth at 900°C produces

large nanotubes and fewer carbonaceous particles (Fig. 2b). In the case of ethanol, longer nanotubes and clean material are obtained at 700 °C (Fig. 2c) compared to the case of 900°C (Fig. 2d). The main conclusion of these results is that the longest and cleanest nanotubes are obtained using ethanol as the carbon source and a low temperature for the growth (700°C). The other important fact is that all the observed nanotubes are of multi-wall nature, such as is shown in Fig. 3, where a lateral view of a carbon nanotube produced with hexane (a), and a closed tip of a nanotube produced with ethanol (b) are observed in high resolution TEM images.

On the other hand, the role of oxygen and hydrogen in the growth process of carbon nanotubes is not clear, but it was proposed that these may inhibit the production of other kinds of carbonaceous material and enhance the growth of the nanotubes. In the case of oxygen, it is believed that the alcohol molecule is decomposed on the catalyst surface forming OH radicals, these then react with neighbouring carbon atoms with dangling bonds to form CO and in this way the amorphous carbon is removed at the very early stage [11]. With this process, the catalytic particle can always have a clean surface that allows for a longer time of activity thus leading to longer carbon nanotubes [9]. Although there are no models to explain the role of hydrogen in the growth process, it would be probable that similar reactions on the catalyst surface may occur where volatile species are formed, preferentially with carbon dangling bonds. Other mechanisms have been also proposed when hydrogenation of hydrocarbons occurs; in this case the reactions may be exothermic and then the local temperature on the catalytic particle is raised, thus promoting the growth of nanotubes instead of other carbonaceous particles [12]. In other reported experiments, the importance of the use of hydrogen has been confirmed because without the use of hydrogen as the carrier gas, and its replacement by argon for example, the yield of nanotube growth decreases and no long strands are produced [7,8]. It should be noted that when we use argon as the carrier gas in our experiments, the deposition of carbonaceous material on the interior wall of the quartz tube in the hot zone is evident, and a clean quartz tube is observed after the growth process when hydrogen is used, obtaining a carbon deposit only on the substrates. These facts demonstrate the etching characteristic of hydrogen and the importance of the catalyst on the substrate for growing carbon nanotubes.

Returning to our results, we believe that the effectiveness of hydrogen in the case of hexane (Figs. 2a and 2b) is better at higher temperatures, because at lower temperatures more carbonaceous particles are obtained, such as that observed in Fig. 4a where the catalyst particle is entirely covered with carbonaceous material. An EDS analysis on the particle (Fig. 4b) shows that pure iron is located in its interior and no oxygen is detected, indicating that even when the nanoparticle has been exposed to the ambient, the carbon works as a very effective protecting layer. It is also interesting to note that, when hexane is used as the carbon source, long iron
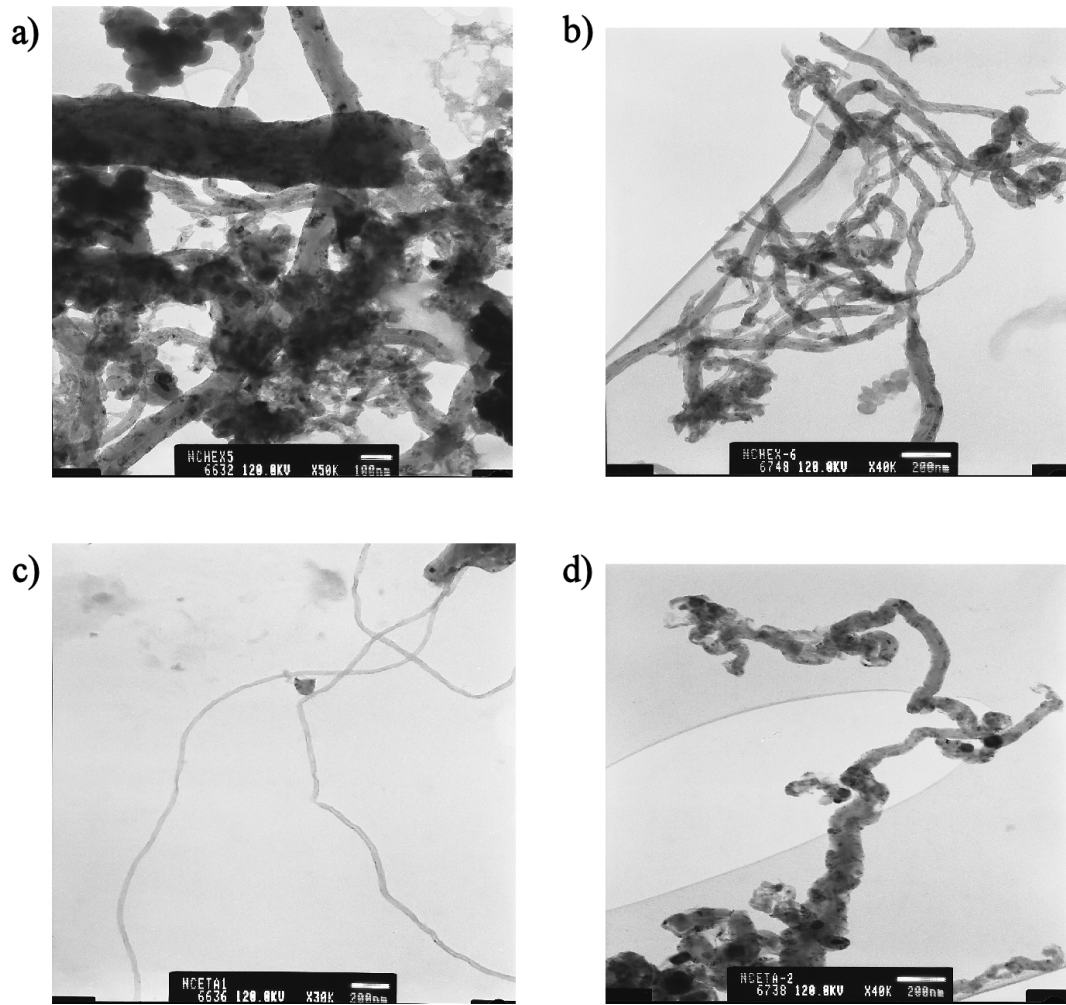
FIGURE 2. Low magnification TEM images of carbon nanotubes obtained using hexane as the carbon source at the synthesis temperature of (a) 700°C, (b) 900°C, and ethanol as the carbon source at (c) 700°C, (d) 900°C.
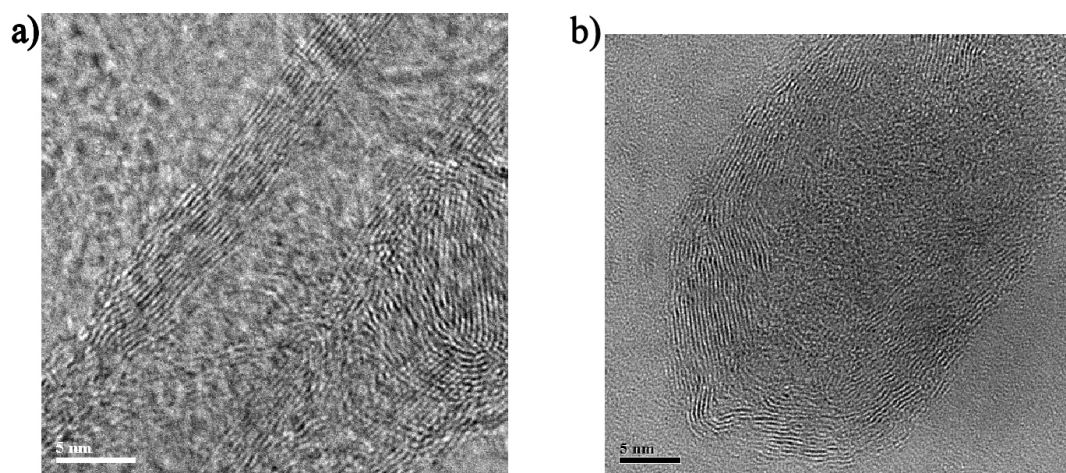

FIGURE 3. High resolution images of the multiwall carbon nanotubes obtained at 700°C, (a) from hexane and (b) from ethanol carbon sources.
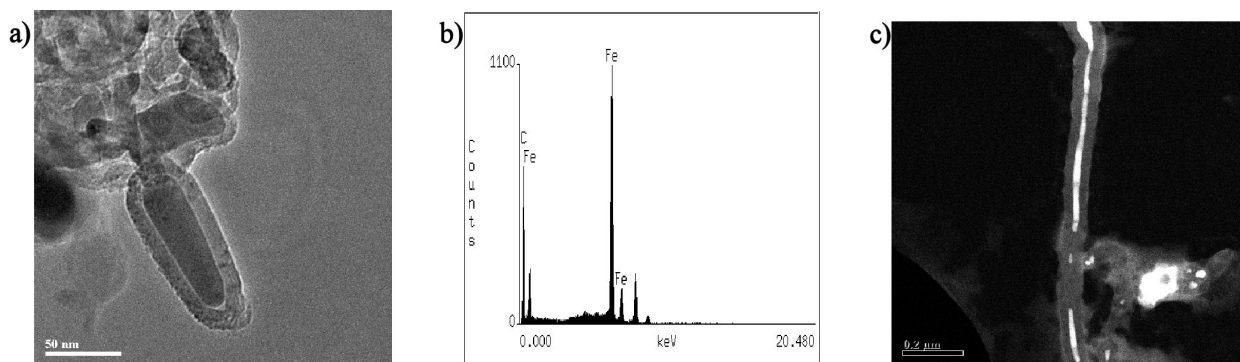
FIGURE 4. (a) Carbonaceous particle obtained with hexane at 700 °C and (b) EDS analysis showing that no oxygen is present in the core (b), the un marked peaks correspond to the copper grid of the sample holder. (c) Z-contrast image of a carbon nanotube filled with iron synthesized under the same conditions as (a).

nanowires inside carbon nanotubes are frequently observed (Fig. 4c). Why this filling process occurs at low temperature (700°C) is not clear to date (the melting temperature of bulk iron is around 1535°C) and it deserves further investigation. It should be noted that carbon nanotubes have been filled with high melting temperature compounds, such as FeCo alloys, using synthesis temperatures as low as 650°C [13], but the filling mechanism is not clear. On the other hand, it is known that the melting temperature of nanoparticles can be considerably lower than the corresponding value in bulk. For example, in the case of nanoparticles of iron with sizes around 3 nm, their melting temperature can be lower than 700°C [14]. In recent experiments the eutectic temperature of iron-carbon alloy has been found to be in the order of 700°C [15]. With this information we may speculate that in our case some catalyst nanoparticles may be in the liquid state, promoting the nanotube growth and filling them with iron by means of a capillary effect. The fact that only some nanotubes are filled with iron may be related to the specific growth conditions and by non-homogeneous zones of the catalyst on the substrate, where in some regions the size of the catalyst nanoparticles meet the conditions for being in a liquid state.

In the case of ethanol as the carbon source, a low temperature appears to be better than higher temperatures for obtaining long carbon nanotubes. We believe that in the case of higher temperatures, two processes that inhibit the growth of long nanotubes may occur. In one case, the combined etching characteristic of OH radicals and hydrogen may be strong enough that not only the amorphous carbon is eliminated, but also the growing nanotubes suffer the attack of the etchants. In the second possibility, the OH radicals may react with hydrogen to form water, making the elimination of the amorphous carbon on the catalyst less effective and so depressing the growth of nanotubes (see discussion above).

4. Conclusions

In conclusion, we have presented here the experimental results using a simple thermal chemical vapor deposition system for obtaining carbon nanotubes. The main advantage of the method is the great variety of liquids that can be used as carbon source. Hexane and ethanol were used as the source of carbon and under our synthesis conditions, multiwall carbon nanotubes were obtained using iron as the catalyst. Our experimental results indicate that longer nanotubes can be obtained with the use of ethanol at 700°C, probably due to the effect of OH radicals which inhibit the production of amorphous carbon, activating the catalytic property of the iron particle and enhancing the growth of longer nanotubes.

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∗ Corresponding author, doroteo@servidor.unam.mx

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