Metal-Filled and Hollow Carbon Nanotubes Obtained by the Decomposition of Metal-Containing Free Precursor Molecules

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Vapor-phase pyrolysis of $Fe(CO)_5$ in the presence of another carbon source such as CO or C_6H_6 yields iron-filled or hollow nanotubes depending on the relative concentration of the carbon source. Essentially single-walled nanotubes are obtained when the $C_6H_6/Fe(CO)_5$ ratio is high. Pyrolysis of metallocenes yields metal-filled nanotubes and hollow nanotubes are obtained when metallocenes are pyrolyzed along with benzene. Metal-decorated nanotubes are also obtained by this method.

Introduction

A few of the recent investigations on carbon nanotubes have been directed toward understanding the mechanism of their growth in the presence of metal particles.[1−4] It seems to be generally accepted that metallic particles act as catalysts for the graphitization of carbon present in the vapor phase.[4] To study the role of metal particles in the formation of the nanotubes, metal powders or metals dispersed on oxide supports have been employed as catalysts. A recent study of Dai et al.[4] has shown that nanosized Mo particles supported on fumed Al_2O_3 catalyze the growth of single-walled carbon nanotubes through the disproportionation of CO at 1200 °C. These authors propose that carbon forms a hemispherical graphene cap on the metal particle and that the nanotubes grow from such a graphene cap. Zhang et al.[5] have recently investigated carbon nanotubes filled with iron by incorporating $Fe(CO)_5$ along with helium during the arc evaporation of graphite. On the basis of these studies, Zhang et al. conclude that the growth of iron-filled tubes proceeds by the deposition and surface diffusion of carbon on the liquidlike metal, while the hollow tubes grow spontaneously. We have investigated the formation of carbon nanotubes by the pyrolysis of precursor molecules containing iron and carbon, not only to find ways of making iron-filled nanotubes, but also to understand how the nanotubes grow around the iron particles formed from the agglomerates of metal atoms produced by the decomposition of the precursor. For this purpose, we have employed $Fe(CO)_5$ as the precursor and carried out its pyrolysis in the gas phase in a Ar/H_2 atmosphere at high temperatures. We have then examined the pyrolysis of $Fe(CO)_5$ in the presence of CO or C_6H_6 which acts as an additional carbon source. To corroborate the results of these studies with $Fe(CO)_5$, we have investigated carbon nanotubes formed by the pyrolysis of ferrocene, $Fe(C_5H_5)_2$, and other metallocenes, which not only contain metal but also have a good percentage of carbon.

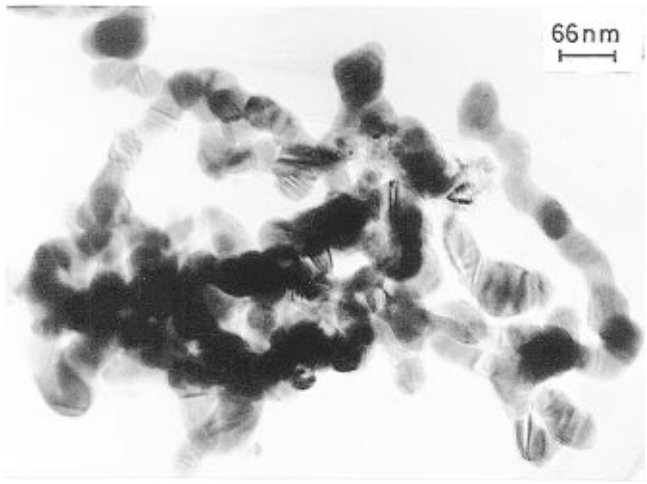

Figure 1. TEM image of amorphous carbon fibers obtained by the pyrolysis of $Fe(CO)_5$ at 900 °C in a 75% Ar−25% H_2 mixture at a flow rate of 50 sccm. Iron particles are seen along the stretches of the fibers.

Experimental Section

Pyrolysis of Precursors. Pyrolysis of $Fe(CO)_5$ was carried out in a quartz tube located in a horizontal tubular furnace. A measured quantity of $Fe(CO)_5$ was placed in the quartz tube near the inlet of the furnace and the desired mixture of gases (e.g., $Ar + H_2$, CO or $Ar + H_2 + C_6H_6$) was passed through the tube to carry the $Fe(CO)_5$ vapors. The flow rate of the gases was monitored with UNIT mass flow controllers. $Fe(CO)_5$ was pyrolyzed at 900 °C in a 75% Ar−25% H_2 mixture at a flow rate of 50 sccm. $Fe(CO)_5$ was also pyrolyzed in a stream of CO (flow rate = 715 sccm) at 1150 °C. $Fe(CO)_5$ was pyrolyzed along with benzene at 900 °C in an 85% Ar−15% H_2 mixture at a flow rate of 1000 sccm. Metallocenes were similarly

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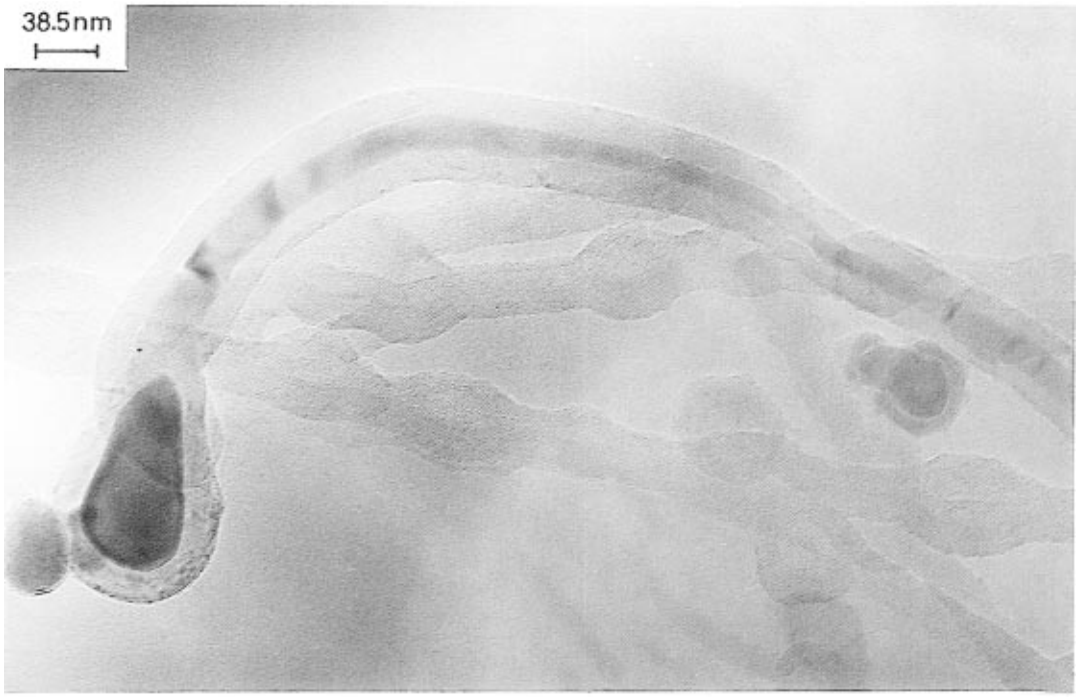

Figure 2. TEM image of an iron-filled nanotube obtained by the pyrolysis of $Fe(CO)_5$ at 1150 °C in a stream of CO (flow rate = 715 sccm).

introduced into the furnace, except that they were preheated to 200 °C in order to sublime them before pyrolysis. Ferrocene was pyrolyzed at 900 °C in a 75% Ar−25% H_2 mixture at a flow rate of 50 sccm. Ferrocene was also pyrolyzed along with benzene at 900 °C in an 85% Ar−15% H_2 mixture at a flow rate of 1000 sccm. Nickelocene was pyrolyzed along with benzene at 900 °C in an 85% Ar−15% H_2 mixture flowing at a rate of 1000 sccm. Cobaltocene was pyrolyzed along with benzene in an 75% Ar−25% H_2 mixture at a total gas flow rate of 50 sccm.

Electron Microscope Studies. The carbon product obtained from the pyrolysis experiments was sonicated in acetone and loaded onto holey carbon grids. Transmission electron microscopy (TEM) was performed using a JEOL JEM-3010 instrument operating at 300 kV. The microscope was equipped with a Gatan fiber optically coupled TV system, Model 622SC, for viewing high-resolution images. Scanning electron microscopy (SEM) was performed on as-prepared samples using a LEICA S440i instrument working at an accelerating voltage of 20 kV and a working distance of about 10 mm.

Results and Discussion

When $Fe(CO)_5$ was decomposed in a reducing atmosphere of 75% Ar−25% H_2 (gas flow rate = 50 sccm) at 900 °C, we obtained amorphous carbon fibers formed around iron particles. A typical TEM image of such fibers is shown in Figure 1. We did not find carbon nanotubes by the pyrolysis of $Fe(CO)_5$ alone. We could however obtain nanotubes by carrying out the pyrolysis of $Fe(CO)_5$ mixed with CO. Clearly CO acts as a carbon source and facilitates the formation of nanotubes. Pyrolysis of $Fe(CO)_5$ at 1150 °C in a stream of CO (flow rate = 715 sccm) gave iron-filled nanotubes. In Figure 2 we show the TEM image of a typical iron-filled nanotube. It is noteworthy that the nanotube is filled completely with iron all along the tube. We also notice the presence of onion-like structures, with the hollows at the center filled with iron. From the image of the nanotube shown in Figure 2, it appears that graphite-like sheaths grow around liquidlike iron metal formed by the decomposition of $Fe(CO)_5$.

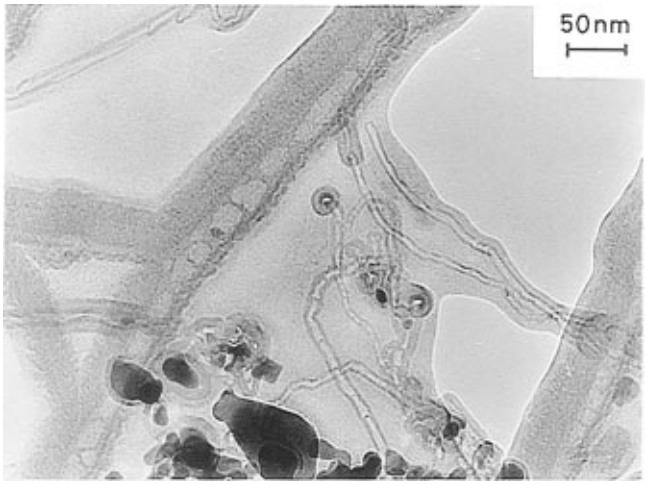

Figure 3. TEM image of thin hollow nanotubes obtained by the pyrolysis of $Fe(CO)_5$ with benzene at 900 °C in an 85% Ar−15% H_2 mixture at a flow rate of 1000 sccm.

To essentially grow hollow nanotubes without much metal inside, it seems necessary to have a better source of carbon along with $Fe(CO)_5$. We could do this by carrying out the decomposition of benzene in the presence of $Fe(CO)_5$. In Figure 3 we show a typical TEM image of nanotubes obtained by the decomposition of benzene and $Fe(CO)_5$ at 900 °C in a stream of 85% Ar−15% H_2 (gas flow rate = 1000 sccm). We obtain extended stretches of fine hollow nanotubes which are essentially single-walled, the iron metal being present at the tips of some of the nanotubes. The nanotubes are initially formed around the iron metal center from where they grow further, but the growth does not require the presence of the metal. To obtain a high yield of hollow nanotubes with negligible quantity of the metal, we have to employ a small percentage of $Fe(CO)_5$ and an excess of C_6H_6. This observation finds further justification from our work on the pyrolysis of ferrocene.

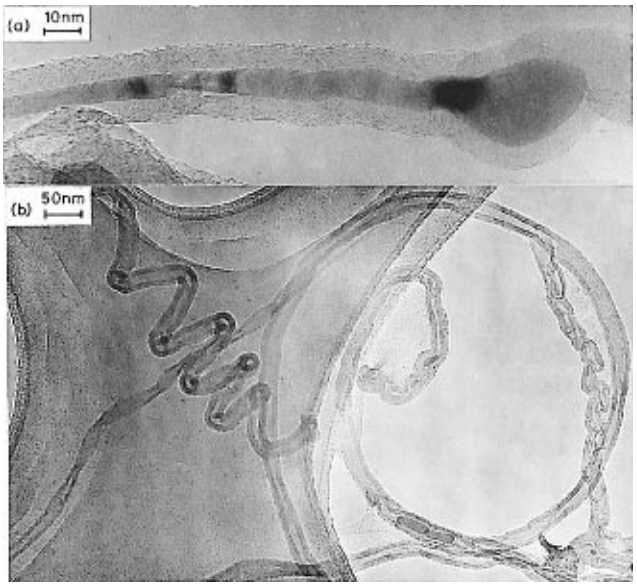

Figure 4. TEM image of nanotubes obtained (a) by the pyrolysis of ferrocene at 900 °C in a 75% Ar−25% H_2 mixture at a flow rate of 50 sccm and (b) by the pyrolysis of a mixture of ferrocene and benzene at 900 °C in an 85% Ar−15% H_2 mixture at a gas flow rate of 1000 sccm. In (a) the nanotube is filled with iron, while in (b) the nanotubes are hollow.

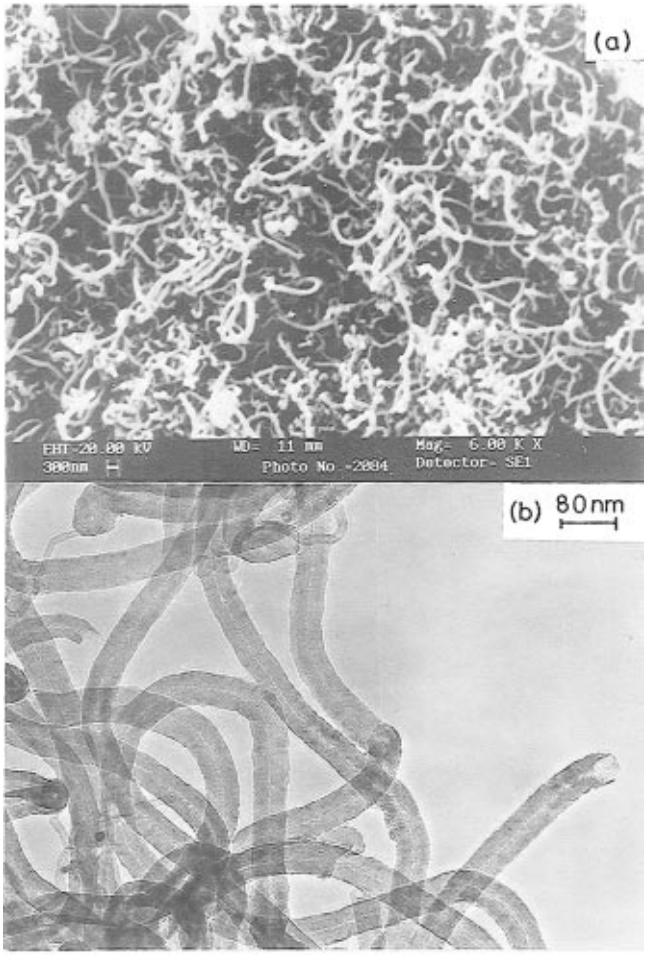

Figure 5. (a) SEM and (b) TEM images of nanotubes obtained by the pyrolysis of nickelocene and benzene at 900 °C in a mixture of 85% Ar−15% H_2 at a gas flow rate of 1000 sccm.

Pyrolysis of ferrocene at 900 °C in a reducing atmosphere of 75% Ar−25% H_2 (gas flow rate = 50 sccm) yields iron-filled nanotubes just as in the case of Fe-

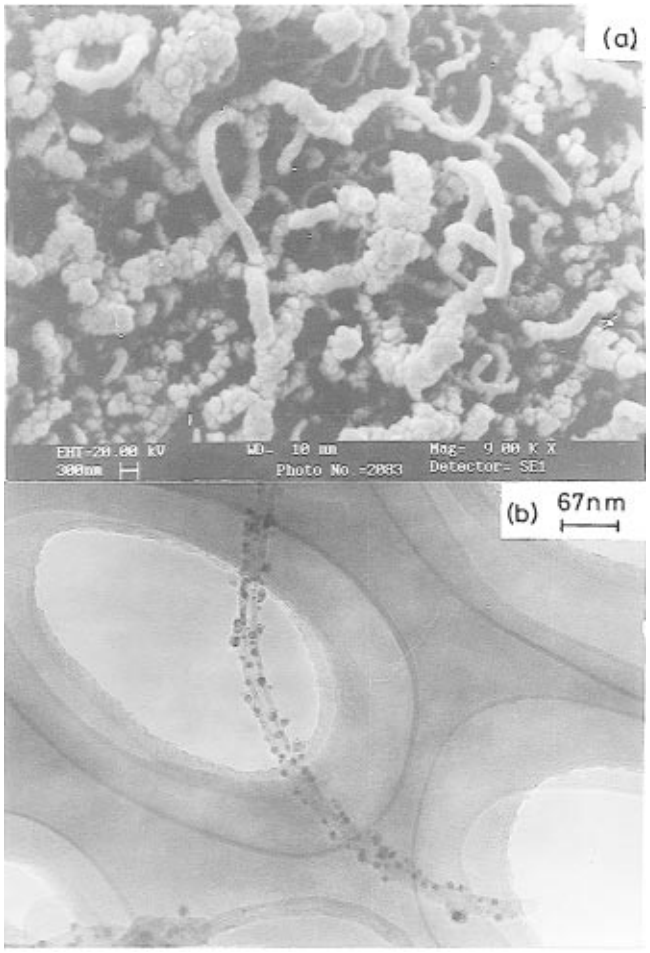

Figure 6. (a) SEM and (b) TEM images of metal decorated nanotubes obtained by the pyrolysis of cobaltocene along with benzene at 900 °C in a mixture of 75% Ar−25% H_2 at a flow rate of 50 sccm.

$(CO)_5$ in the presence of CO. Figure 4a shows a TEM image of a nanotube fully filled with metal obtained by the pyrolysis of ferrocene at 900 °C in an Ar/H_2 atmosphere. However, by carrying out the pyrolysis of C_6H_6 and ferrocene in the presence of another carbon source such as benzene, we obtain nanotubes filled with the metal at the tip or in isolated spots, along with extended stretches of nanotubes. In Figure 4b we show a TEM image of nanotubes obtained by the pyrolysis of a mixture of benzene and ferrocene at 900 °C in an 85% Ar−15% H_2 mixture at a gas flow rate of 1000 sccm to illustrate these features.

Pyrolysis of nickelocene along with benzene at 900 °C in a 85% Ar−15% H_2 mixture at a flow rate of 1000 sccm gave an excellent yield of nanotubes as can be seen from SEM image in Figure 5a. We show a TEM image of these nanotubes in Figure 5b. Nickel metal is found at isolated tips of the nanotubes, but extended stretches of nanotubes occur free of any metal. Pyrolysis of cobaltocene along with benzene at 900 °C in a 75% Ar−25% H_2 mixture at a flow rate of 50 sccm also yielded nanotubes. Employing the same procedure, we have obtained nanotubes that are decorated with nanoparticles of cobalt metal on the outside. SEM and TEM images of such nanotubes are shown in Figure 6a,b, respectively.

The present study demonstrates that carbon nanotubes can be prepared from free precursor molecules

containing iron and carbon. The formation of iron-filled nanotubes by the pyrolysis of such molecules provides a novel means of making metal-filled nanotubes, which are otherwise made by solution methods involving chemical reduction.[6,7] What is more interesting is that extended stretches of hollow carbon nanotubes can be prepared by the vapor phase pyrolysis of iron-containing precursors along with a carbon source such as CO or C_6H_6 wherein the wall thickness is controlled by the relative proportion of the carbon source and the iron-containing precursor. Essentially single-walled nanotubes are obtained when the proportion of the latter is small.

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