

# Inclusion of Crystalline Iron Oxide Nanoparticles in Uniform Carbon Nanotubes Prepared by a Template Carbonization Method

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An attempt was made to encapsulate iron nanoparticles in uniform carbon nanotubes, which were prepared by using an anodic aluminum oxide film as a template. The pyrolytic carbon deposition from propylene was carried out on the uniform channels of the anodic oxide film, and then the MOCVD (metal–organic chemical vapor deposition) technique was applied to incorporate iron into the carbon-coated nanochannels. Ferrocene vapor was used as an iron precursor for the MOCVD under  $H_2$  flow. The iron/carbon nanotube composites were liberated from the anodic oxide film by alkali treatment. It was found that the carbon nanotubes contain crystalline nanoparticles of  $Fe_3O_4$  and their number and size are controllable by changing the MOCVD conditions. Furthermore, no iron oxide particles were found on the outer surface of the nanotubes.

## Introduction

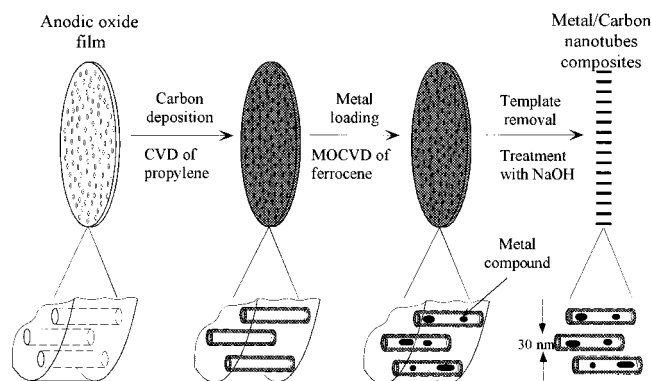
Carbon nanotubes have potential industrial application as well as considerable current fundamental interest. As reviewed by Freemantle<sup>1</sup> and others,<sup>2,3</sup> the metal-filled carbon nanotubes could have a variety of industrial applications as catalysts, electronic devices, an improved magnetic tape, and biosensors. Thus the preparation and application of such metal-filled carbon nanotubes is now becoming a promising and challenging research area. There have been several attempts to insert metal into the tubes prepared by an arc-discharge evaporation technique. These attempts can be classified into the following two methods: one is based on arc-evaporation of a metal-loaded carbon anode and the other one is a two-step method. The former, high-temperature, method can produce mainly metal carbide-filled nanotubes in a single stage,<sup>4–8</sup> but it suffers from a low yield of filled nanotubes, and it produces impurities such as encapsulated carbon clusters and soot. A higher yield of filled nanotubes can be achieved by the latter method, which consists of the opening of nanotube ends and the inclusion of metal into the opened tubes.<sup>9–13</sup>

Early work by Ajayan et al.<sup>12</sup> demonstrated capillary action to fill molten lead into the nanotubes which were uncapped beforehand by oxidation with air. A similar approach has been applied by Ugarte et al.<sup>13</sup> using molten silver nitrate. Green and co-workers<sup>9,11</sup> have developed a wet chemical method, where the nanotubes were treated with  $HNO_3$  in the presence of a soluble metal salt. As a result, the nanotubes got opened by the acid treatment and filled by the salt. Thus, the wet chemical method can be applied to a greater variety of materials than the arc-discharge method. A drawback of this chemical method is that some loading on the outer surface of the nanotubes is unavoidable. For all the methods described here, it is still difficult to control the structure, shape, and size of encapsulated material in the nanotube interior.

Recently, we have prepared carbon nanotubes by a CVD carbon deposition technique using uniform and straight channels of anodic aluminum oxide film as a template.<sup>14,15</sup> The most striking feature of this method is to allow one to produce monodisperse carbon nanotubes with uniform length, diameter, and thickness. The former two parameters are controllable by changing the thickness and the channel diameter of the anodic alumina film, respectively, and the thickness of the nanotubes can be changed by varying the carbon deposition period (the control of the thickness and the channel diameter of the anodic film can be achieved by changing the anodic oxidation period and its voltage, respectively). The resultant tubes are not completely

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**Figure 1.** Schematic diagram of the formation process of metal/carbon tube composites.

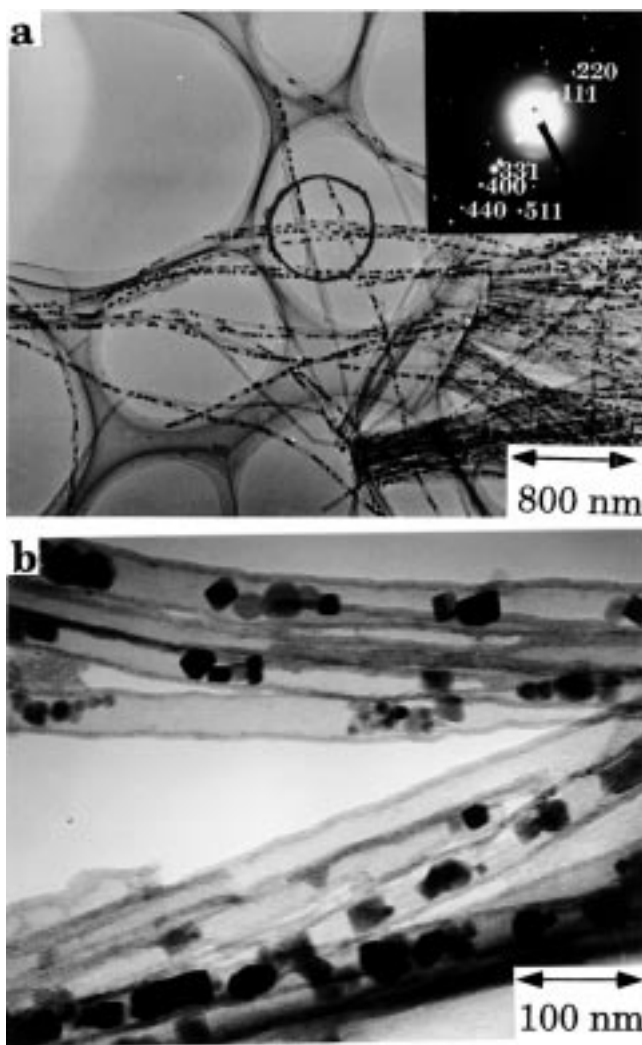
graphitized, but the carbon layers are oriented toward the direction of tube axis. Very recently, Martin and co-workers also have prepared carbon nanotubes by a CVD technique where they found that CVD at a lower temperature with a Ni catalyst and subsequent heat treatment gave highly crystallized nanotubes.<sup>16</sup> The nanotubes prepared by the template method are not capped at both ends. This makes it easy to encapsulate foreign material into the nanotubes. We have prepared Pt metal-filled uniform carbon nanotubes which are completely free from Pt on the outer surface,<sup>17</sup> and we have demonstrated that the shape and size of the Pt metal can be changed by controlling the conditions of Pt loading and the reduction methods. Very recently, Martin et al.<sup>18</sup> also have prepared metal (Pt, Pt/Ru) nanoparticle-loaded carbon nanotubes by the template technique.

Here, we have attempted to prepare iron-filled carbon nanotubes. We have employed the MOCVD (metal-organic chemical vapor deposition) technique for iron loading and investigated the structure of the metal/carbon tube composites with a transmission electron microscope. Furthermore, we would like to emphasize how the metal loading is affected by the MOCVD temperature and its time period.

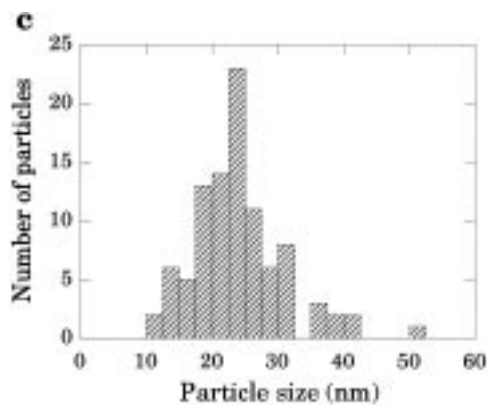
### Experimental Section

An anodic aluminum oxide film was prepared by anodic oxidation of an electropolished aluminum plate at a cell voltage of 20 V in 20 wt % of sulfuric acid at 0–5 °C for 2 h. The details of this method were described elsewhere.<sup>15</sup> The porosity of the anodic films consisted of an array of parallel and straight channels with a diameter of about 30 nm, and the film diameter and its thickness were 20 mm and ~75 μm, respectively. The film was placed in a horizontal quartz reactor (i.d. 40 mm). The temperature of the reactor was increased to 800 °C under N<sub>2</sub> flow and then propylene gas (1.2% in N<sub>2</sub>) was passed through the reactor at a total flow of 1000 cm<sup>3</sup> (STP)/min. The thermal decomposition of propylene in the uniform straight channels of the anodic oxide film results in carbon deposition on the channel wall. After the thermal decomposition for 3 h at 800 °C, the reactor was cooled to room temperature and the film was taken out.

The resultant carbon-deposited film was placed on quartz wool in a vertical quartz reactor (i.d. 20 mm) and subjected to



**Figure 2.** TEM images of the Fe/carbon tube composites prepared at a MOCVD temperature of 400 °C for 3 h with ferrocene vapor pressure of 0.3 kPa: (a) low and (b) high magnification images; the inset picture shows the corresponding SAD pattern for the area indicated by circle in the image a; (c) a histogram of the particle size distribution of the iron oxide nanoparticles in the TEM image a.

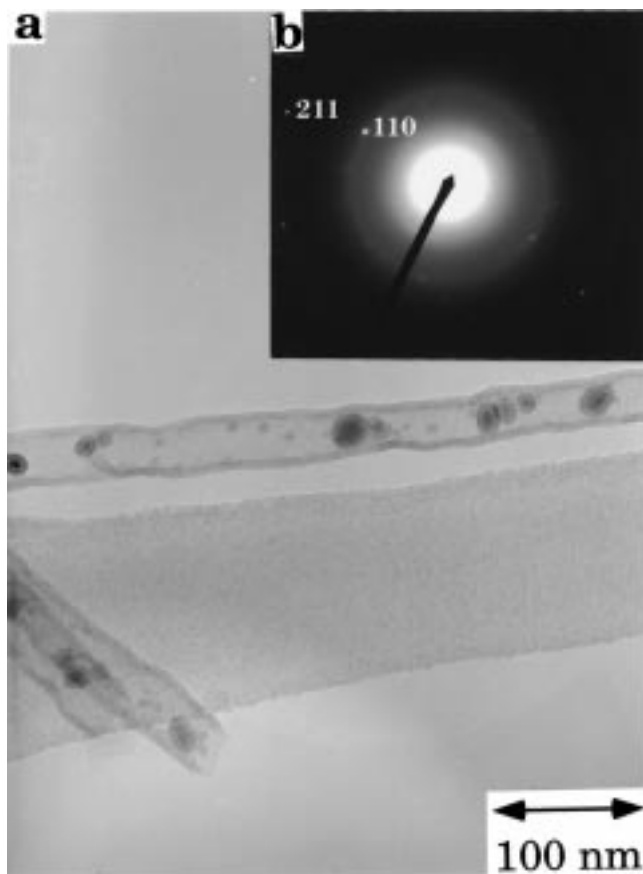


MOCVD of ferrocene (Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>) in the following manner. Ferrocene was vaporized at 90 or 105 °C (corresponding to the vapor pressure of 0.1 and 0.3 kPa, respectively) and then the vapor was introduced into the film in the quartz reactor with H<sub>2</sub> gas (50% in N<sub>2</sub>) at a total flow rate of 100 cm<sup>3</sup>(STP)/min. The feed line was wrapped with heating tapes and maintained at a high temperature to avoid the solidification of ferrocene

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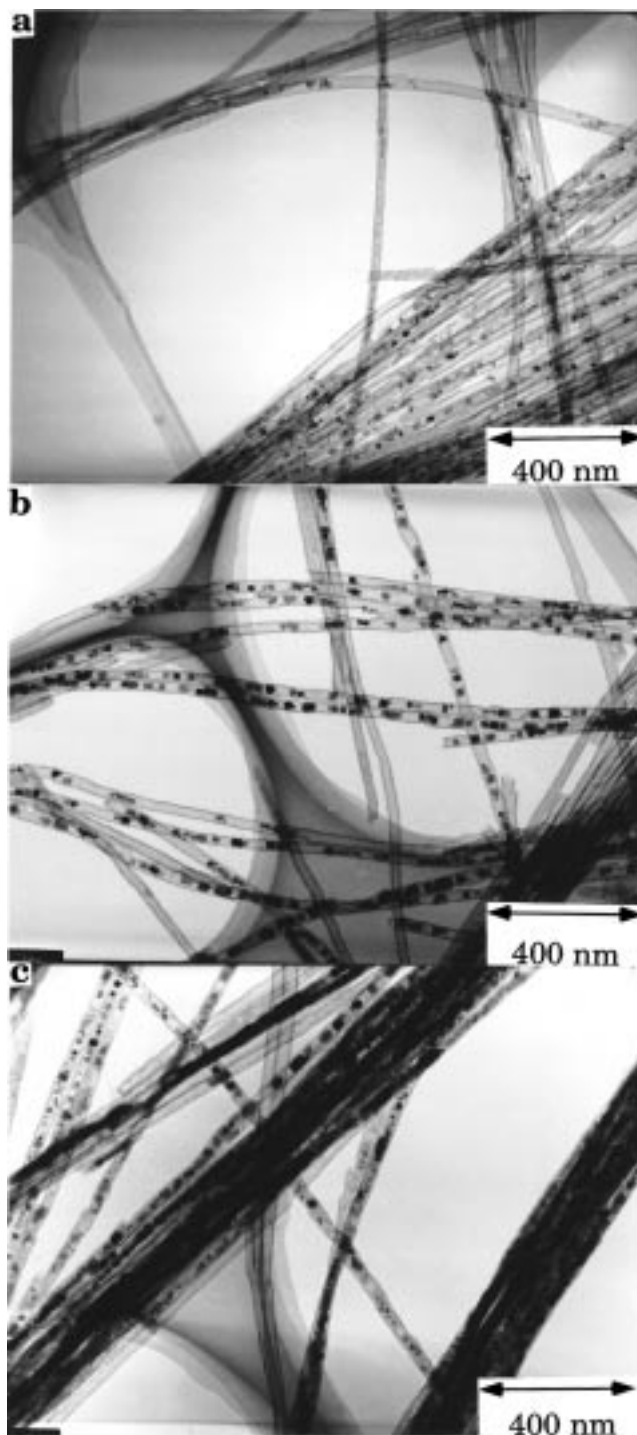
**Figure 3.** TEM images of the composites before the alkali treatment (MOCVD temperature, 400 °C; MOCVD period, 24 h; ferrocene vapor pressure, 0.1 kPa): (a) a bright-field image of an Fe/carbon nanotube composite and (b) SAD pattern of the nanotubes from image a.

vapor. The following two series of MOCVD experiments were performed; one is for 3 h with 0.3 kPa of ferrocene pressure at three different temperatures (350, 400, and 500 °C) and the other one for different time periods (0.5, 1, 3, 6, 12, 24 h) with 0.1 kPa at 400 °C. After the MOCVD, the film was treated with 10 M NaOH solution at 150 °C in an autoclave for 6 h in order to remove the anodic aluminum oxide template. As a result, metal/carbon nanotube composites were obtained as an insoluble fraction. The schematic diagram of the formation process of metal/carbon tube composites is illustrated in Figure 1.

The microscopic features of the resulting composites were observed with a transmission electron microscope (TEM; JEOL, JEM-2010) and their structure was characterized with electron diffraction for selected area (SAD).

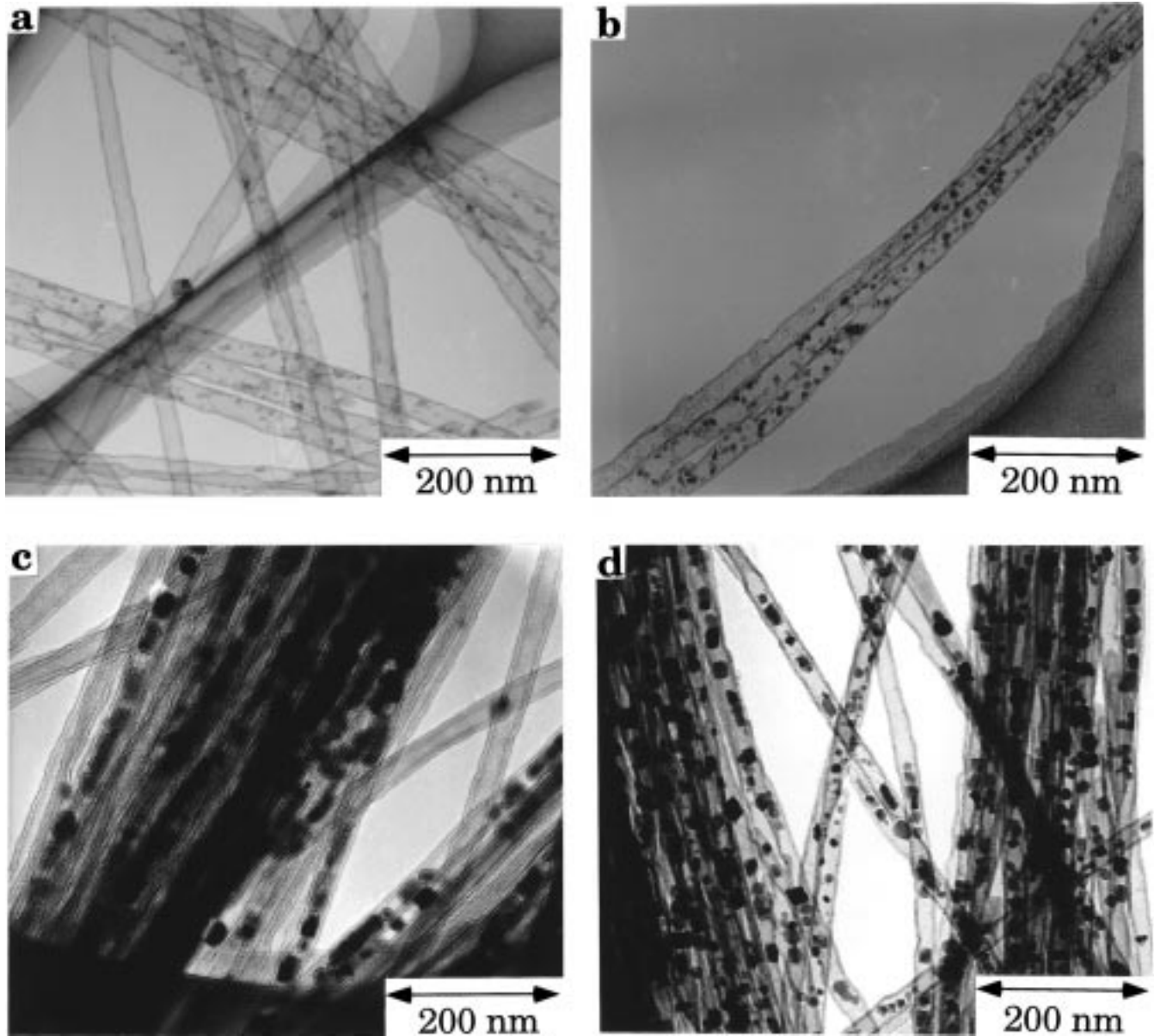
## Results and Discussion

**Characterization of Iron Nanoparticles in a Carbon Nanotube.** Figure 2 shows TEM bright-field images at different magnifications for the Fe/carbon tube composites prepared by MOCVD at 400 °C for 3 h with 0.3 kPa of ferrocene vapor. These images exhibit the presence of uniform carbon nanotubes with an outer diameter of 30 nm and a wall thickness of about 5 nm. Although some of the tubes are empty, the others contain many dark particles. It should be noted that there is no metal deposited outside of the nanotubes. The high-magnification image (Figure 2b) shows that the shape of some particles looks like a cube, implying the high crystallinity of these particles. The inset



**Figure 4.** TEM bright-field images of the composites prepared by the 3-h MOCVD with a ferrocene vapor pressure of 0.3 kPa at different temperatures: (a) 350 °C, (b) 400 °C, and (c) 500 °C.

picture shows the SAD pattern which was taken from the area indicated by a circle in Figure 2a. The pattern presents sharp diffraction spots, which can be indexed to 111, 220, 311, 400, 511, and 440 reflections from cubic magnetite ( $\text{Fe}_3\text{O}_4$ ). In addition to these spots, we could observe arcs and diffused rings from carbon 002, 10, and 11 reflections, which are too weak to recognize from this SAD picture. The appearance of the diffraction for  $\text{Fe}_3\text{O}_4$  as clear spots, not as rings, indicates the high crystallinity of the  $\text{Fe}_3\text{O}_4$  nanoparticles. Some of the particles observed in Figure 2b must be single crystals.



**Figure 5.** TEM bright-field images of the composites prepared at a MOCVD temperature of 400 °C with a ferrocene vapor pressure of 0.1 kPa for different periods: (a) 1 h, (b) 3 h, (c) 6 h, and (d) 12 h.

A maximum caliper diameter of a hundred particles in the image of Figure 2a was measured and the resultant histogram of the particle size distribution is shown in Figure 2c. It was found that their diameters range from 10 to 50 nm with a mean size of 24 nm and a standard deviation of 7 nm. The reason we found particles longer than the tube diameter (20 nm) is that many particles are not spherical and we used the maximum caliper diameter as a measure of size.

The iron oxide was likely formed when the iron-loaded carbon/alumina film was exposed to air and/or when the film was treated with an alkaline solution. To clarify this issue, we tried to characterize the iron-containing carbon nanotubes before the alkali treatment. After the MOCVD experiment, the iron-loaded carbon/ $\text{Al}_2\text{O}_3$  film was taken out into the ambient air and broken into fine pieces. The TEM observation showed that some of the nanotubes project out of broken  $\text{Al}_2\text{O}_3$  pieces and also some of the nanotubes were separate from the film. Figure 3a exhibits the TEM image of

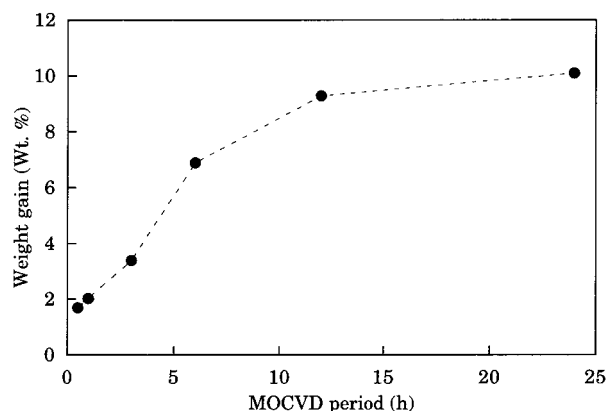
such isolated carbon nanotube containing nanoparticles. Most of these particles comprise a dark core surrounded with another type of substance, whereas such a dual structure was not observed in the case of the very small particles. The corresponding SAD pattern (Figure 3b) presents sharp clear spots which were identified as the reflection from  $\alpha\text{-Fe}$  (the spots can be indexed to 110, 211), and the diffuse rings were from the carbon nanotube, respectively. Together with these clear spots, we could observe several very weak spots, all of which can be assigned to the reflection from  $\text{Fe}_3\text{O}_4$ . Taking the presence of two types of iron species ( $\alpha\text{-Fe}$  and  $\text{Fe}_3\text{O}_4$ ) into consideration, we can explain the formation of a dual structure in the following way. Initially, iron metal particles were deposited in the nanotube hollow by MOCVD under  $\text{H}_2$  flow. When these particles were exposed to air, their surface was oxidized to iron oxide ( $\text{Fe}_3\text{O}_4$ ) to leave the metal ( $\alpha\text{-Fe}$ ) in the particle core, while very small metal particles were completely oxidized by the air exposure. Upon further exposure to

air and/or the subsequent alkali treatment, the remaining metal core was oxidized to  $\text{Fe}_3\text{O}_4$ , as observed in Figure 2.

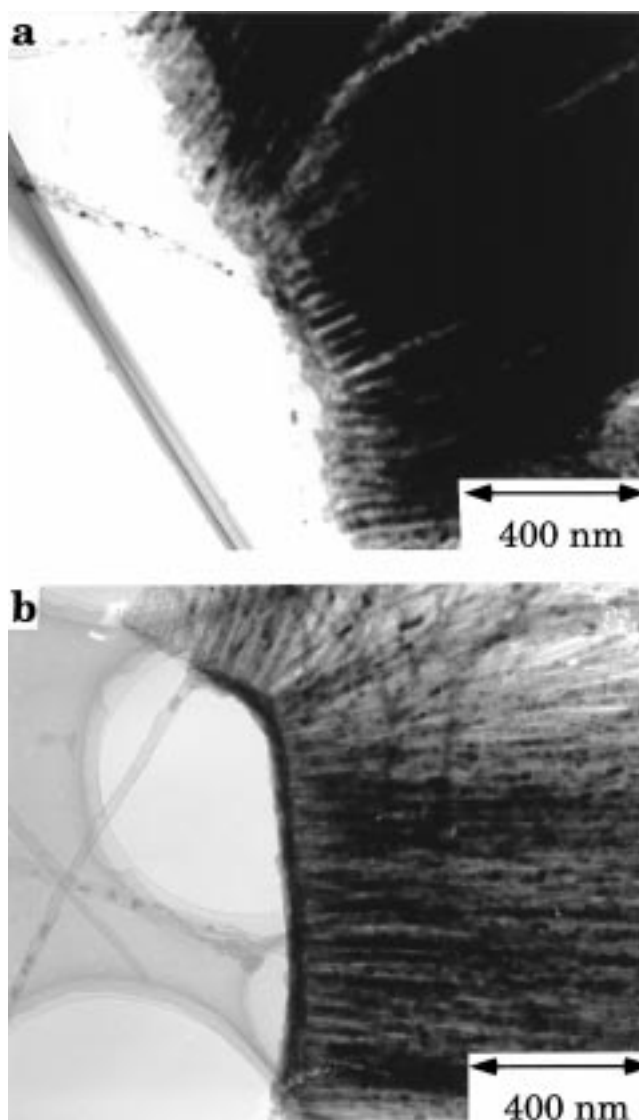
**Effect of MOCVD Temperature.** Figure 4 exhibits the TEM bright-field images for the Fe/carbon tube composites prepared at three different MOCVD temperatures (350, 400, and 500 °C) for the same period (3 h) with the same ferrocene vapor pressure (0.3 kPa). For all the cases, crystalline nanoparticles were observed and their chemical form was identified to be  $\text{Fe}_3\text{O}_4$  by the corresponding SAD patterns (not shown here). The size and number of nanoparticles were, however, greatly influenced by the MOCVD temperature. In the case of the low-temperature MOCVD (350 °C, Figure 4a), the mean size of the particles observed in this figure is 16 nm with a standard deviation of 5 nm. At the MOCVD temperature of 400 °C (Figure 4b), the size of nanoparticles is  $24 \pm 7$  nm (mean  $\pm$  standard deviation). At 500 °C (Figure 4c), although a few nanotubes remain barren, most of the nanotubes are filled and some of them look completely filled with the metal compound. The fraction of empty tubes in this case was quite low in comparison with the former two cases. These findings indicate that the number of nanoparticles and their size increased with the MOCVD temperature. Such increases in number and size are reflected in the weight gain of the carbon-coated film; the gain was 3.4, 4.1, and 8.3 wt % at 350, 400, and 500 °C, respectively. By assuming all the iron compounds to be  $\text{Fe}_3\text{O}_4$ , we can estimate that the iron oxide occupies 8, 10, and 20% of the total volume of the tube interior when the MOCVD was performed for 3 h at 350, 400, and 500 °C, respectively.

As we described above, the MOCVD at 500 °C resulted in greater iron incorporation; the sample prepared at 500 °C contains approximately two times as much iron as the sample prepared at the lower temperatures. This trend may be explained by the thermal stability of ferrocene, which only undergoes significant decomposition at temperatures in excess of 450 °C.<sup>19,20</sup> The MOCVD at this temperature, however, suffered from the formation of large amount of soot outside the film. We chose, therefore, 400 °C as the MOCVD temperature to observe the effect of the MOCVD period on iron encapsulation.

**Effect of MOCVD time period.** Figures 5 and 7 show the bright-field TEM images of the composites prepared for different MOCVD periods (0.5–24 h) at the same temperature (400 °C) with 0.1 kPa of ferrocene vapor. All the SAD patterns from the corresponding TEM images indicated that the inside nanoparticles are magnetite ( $\text{Fe}_3\text{O}_4$ ). When the MOCVD was carried out only for a short period, 0.5 h, most of the nanotubes were found to be empty. Only a few of them contained nanoparticles, whose mean size was 5 nm with a standard deviation of 1 nm. In the case of the 1 h of MOCVD (Figure 5a), many tubes remained empty, but the nanoparticles observed in several tubes have much larger size,  $16 \pm 5$  nm, than the case of 0.5 h. With a further increase in the MOCVD period (Figure 5b,c), the number of empty tubes decreased and the number of



**Figure 6.** Effect of the MOCVD time period on the weight gain of the carbon-coated film.



**Figure 7.** TEM images of the end of the Fe-filled nanotube bundle prepared at a MOCVD temperature of 400 °C with a ferrocene vapor pressure of 0.1 kPa for different periods: (a) 12 h and (b) 24 h.

nanoparticles increased. After 6 h of MOCVD (Figure 5c), we could observe many nanoparticles of the size  $20 \pm 9$  nm, but some of the tubes were still empty. In contrast to these results, when the MOCVD period was

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increased to 12 h (Figures 5d), the iron incorporation in the tubes was appreciably enhanced, and as a result, all the tubes contain nanoparticles with a mean particle size of  $22 \pm 7$  nm. The weight gain of the film due to iron loading was plotted against the MOCVD period in Figure 6, where the weight gain increases with the period, as one can expect from the above TEM images (Figure 5). The weight gain after 12 h of MOCVD was 9.3%, which corresponds to 22% filling of the total volume of the tube interiors. Another set of MOCVD experiments gave the same weight gains, indicating our MOCVD run to be reproducible.

When the carbon/ $\text{Al}_2\text{O}_3$  film was subjected to the MOCVD, one can suppose that iron was deposited not only on the inner surface of the channel but also on the outer surface of the film, i.e., the outside of the channel mouths. This means that a large amount of iron would be found on the ends of the nanotubes. This is, however, not the case in the 12-h MOCVD experiment. The end of an iron-filled nanotube bundle is shown in Figure 7a, where there was almost no iron deposition on the end portion. On the other hand, such iron deposition was clearly observed in the case of the MOCVD carried out for 24 h. This very long MOCVD run did not significantly increase the number and size of incorporated nanoparticles in comparison with the case of the 12-h MOCVD. This can be explained by the iron blockage on the entrance of the carbon-coated channels, which prohibited further inclusion of ferrocene vapor. It is found in Figure 6 that there is a leveling off in the range of 12–24 h. This phenomenon accords with the finding that the size and number of nanoparticles of the 24-h

MOCVD are not considerably higher than those of the 12 h treatment.

### Conclusions

We have demonstrated the encapsulation of iron oxide into uniform carbon nanotubes by the MOCVD technique using ferrocene as an iron precursor. The iron oxide is present in the nanotube hollow as crystalline  $\text{Fe}_3\text{O}_4$  nanoparticles. It was found that the size and number of such nanoparticles can be easily controlled by changing the MOCVD temperature or its period. Under proper MOCVD conditions, all of the nanotubes include  $\text{Fe}_3\text{O}_4$  nanocrystals with an average size 24 nm, and more than 20% of the total volume of the tube hollow is filled with nanoparticles. Furthermore, it should be noted that no iron compound was observed on the outside wall of the tubes. This is due to the preparation technique, viz., iron was loaded into the carbon-coated alumina film before the removal of the alumina template; thus, there was no contact between iron and the outer wall of the tubes.

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