

Chemical Vapor Deposition Based Synthesis of Carbon Nanotubes and Nanofibers Using a Template Method

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We have developed a new approach for preparing graphitic carbon nanofiber and nanotube ensembles. This approach entails chemical vapor deposition (CVD) based synthesis of carbon within the pores of an alumina template membrane with or without a Ni catalyst. Ethylene or pyrene was used in the CVD process with reactor temperatures of 545 °C for Ni-catalyzed CVD and 900 °C for the uncatalyzed process. The resultant carbon nanostructures were uniform hollow tubes with open ends. Increasing the deposition time converted the carbon nanotubes into carbon nanofibers. Transmission electron microscopy and electron diffraction data show the as deposited graphitic carbon nanofibers synthesized with the Ni catalyst were not highly ordered. Heating the carbon-containing membrane at 500 °C for 36 h, however, converts the carbon nanofibers into highly ordered graphite. The electron diffraction data show a spotted diffraction pattern characteristic of single-crystal graphite with the graphitic planes parallel to the long axis of the nanofibers.

Introduction

An enormous interest has recently developed in the area of nanostructured materials.¹ We have been exploring a template synthesis method for preparing micro- and nanostructured materials.^{2–5} This method entails synthesizing the desired material within the pores of a template membrane with cylindrical pores of uniform diameter,^{2–4} and has been used to make tubules and fibrils composed of polymers, metals,⁶ semiconductors,⁷ metal oxides,⁸ carbon,⁹ and composite materials.^{5,10} Methods used to synthesize such materials within the pores of the template membranes include electroless metal deposition, electrochemical synthesis, in situ polymerization, and sol–gel methods.^{4,8} While these methods have proven useful, additional methods of synthesis are needed to produce tubules and fibrils of other types of materials.

Chemical vapor deposition (CVD) is a versatile process in which gas-phase molecules are decomposed to

reactive species, leading to film or particle growth.¹¹ CVD processes can be used to deposit a wide range of conducting, semiconducting, and insulating materials.¹² A recent thrust^{13,14} of CVD techniques has been the controlled fabrication of nanomaterials in porous hosts,^{15,16} including zeolite nanochannels.¹⁷ Two advantages to CVD methods are the ability to controllably create films of widely varying stoichiometry and to uniformly deposit thin films of materials, even onto nonuniform shapes.¹⁸

We have recently used a combination of CVD and template synthesis methods to fabricate TiS₂-coated gold fibers for preparation of battery electrodes.^{5,10} These microtubular TiS₂ electrodes show higher capacities, lower resistance, and lower susceptibility to slow electron-transfer kinetics than thin film TiS₂ electrodes. In the present work, we extend this new method to the production of fibrils and tubules of graphitic carbon. Interest in new carbon structures arises primarily from the numerous potential applications in a variety of areas,¹⁹ including electrochemistry.²⁰ The use of metal catalysts such as Ni, Fe, Fe–Cu, and Pt has been

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explored in an effort to control the size and morphology of carbon nanostructures formed through the decomposition of hydrocarbons.^{21,22} Our primary interest is in the production of a material that could be used as the anode in a rechargeable lithium nanobattery.²³ The approach we have developed includes CVD-based synthesis of carbon within the pores of an alumina template membrane with or without a nickel catalyst in the pores.^{24,25} The carbon nanofibers are produced at relatively low temperatures. We have found that highly ordered graphitic nanofibers can be obtained when the carbon fibrils are formed and annealed in the presence of a nickel catalyst. Use of other metal catalysts such as Co and Fe has also been explored. The results of these investigations are described here.

Experimental Methods

Materials. Ethylene (9.92% in helium), pyrene, sodium hydroxide, concentrated HF (all from Aldrich), and 9.4% nickel resinate solution (Engel Hard Corp.) were used as received. The alumina template membranes (200 nm diameter pores, 60 μm thick) were obtained commercially (Whatman Anapore filters, Fisher). $\text{Fe}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ (Aldrich) were used as received.

Catalyst Loading and Generation. Organometallic nickel (Engel Hard) was initially prepared for deposition by diluting a nickel resinate solution with toluene, creating solutions with 0.7%, 1.4%, and 3.3% Ni. Immersing the template membrane into these nickel solutions and allowing the solvent to evaporate resulted in deposition of a film of the organometallic nickel compound on the inner wall of the membrane pores. The thickness of the nickel coatings are consistent with the dilution factor. These coated template membranes were then placed in a sealed tube furnace, and the atmosphere was purged with argon at room temperature. With an argon atmosphere, the furnace temperature was adjusted to 400 °C at a rate of ~ 10 °C/min. Maintaining this oven temperature for 15 min thermally decomposed the organometallic compound and resulted in the deposition of a nickel thin film.²⁴ The use of an inert atmosphere minimized oxide formation.

Similarly, immersing the template membrane (200 nm diameter pores) into 0.1 M $\text{Fe}(\text{NO}_3)_2$ or $\text{Co}(\text{NO}_3)_2$ solutions and allowing the water to evaporate resulted in deposition of $\text{Fe}(\text{NO}_3)_2$ or $\text{Co}(\text{NO}_3)_2$ on the inner wall of the pores in the membrane, respectively. These coated template membranes were then placed in a sealed tube furnace, and the atmosphere was purged with H_2 at room temperature. With an H_2 atmosphere, the furnace temperature was adjusted to 580 °C for 3 h to produce Fe or Co inside the pores.

Carbon Nanofiber and Nanotube Synthesis. To prepare the carbon nanofiber and nanotube ensembles, the template membrane, with or without the Ni catalyst in the pores, was placed on a right angle platinum grid in the CVD

reactor. The reactor temperature was increased to 900 °C for the membranes without Ni and to 545 °C for those with the Ni catalyst, both under an argon flow. The carbon nanofibers and nanotubes were synthesized by decomposition of either ethylene or pyrene. With ethylene, the Ar flow was terminated after the temperature had stabilized. Simultaneously, a 10 sccm flow of ethylene was initiated. After deposition, the Ar flow was resumed, the ethylene flow was terminated, and the furnace was turned off and allowed to cool to room temperature. In the case of the pyrene precursor, ~ 50 mg of pyrene was placed in the 200 °C zone of the reactor and Ar (50 sccm) was used as the carrier gas. Other procedures were the same as for the ethylene decomposition.

Electron Microscopy. Scanning electron microscopic (SEM) images were obtained using a Phillips 505 microscope. One surface layer of the membrane was removed by polishing with abrasive paper, and the membrane was glued (Torr-seal epoxy, Varian), polished face up, to a piece of paper towel. The resulting composite was immersed in either 6 M aqueous NaOH (Ni-catalyzed CVD samples) for 10 min or concentrated HF (CVD samples) for 24 h to dissolve the alumina. This yielded an ensemble of carbon tubes or fibrils that protruded from the epoxy surface like the bristles of a brush. Treatment by HF or NaOH does not appear to alter the morphology or microstructure of the fibers. The "brush" sample was then attached to an SEM sample holder, and 20 nm of Au-Pd was sputtered onto the surface using an Anatech sputter coater.

Transmission electron microscopic (TEM) images of the carbon nanostructures were obtained using a JEOL 2000 microscope. Both surface layers were removed, and a piece of the resulting membrane was placed on a carbon-film-coated TEM grid. The 6 M aqueous NaOH solution was then applied to the membrane to dissolve the alumina. After removal of the alumina template membrane in NaOH, the carbon nanofibers were rinsed in water to ensure complete removal of NaOH. The freed nanostructures adhered well to the TEM grid and were easily imaged. Electron diffraction data were obtained using the same instrument. The accelerating voltage of the electron beam was 100 kV, and the focal length was 80 or 120 cm. A gold single crystal was used as a standard to check the camera length.

Heat Treatment of Ni-Catalyzed CVD Carbon Nanofibers. The carbon/Anapore composite membrane synthesized with the Ni-catalyzed CVD method was placed in the tube furnace under an argon atmosphere for 15 min at room temperature. The temperature was then adjusted to 500 °C at a rate of ~ 5 °C/min. Maintaining this oven temperature for 36 h converted the carbon nanofibers into highly ordered graphitic carbon.

Results and Discussion

CVD Carbon Nanotubes and Nanofibers. Figure 1 shows SEM images of CVD carbon nanotubes obtained for a 10 min deposition at 900 °C using ethylene (A) and pyrene (B) as precursors. The deposition creates carbon tubes within the pores of the membrane as well as a thin carbon film on the surface of the membrane. These SEM images were obtained after dissolution of the template membrane in concentrated HF, but without removing the surface carbon layer from the membrane. The following features can be noted from these images. First, both ethylene and pyrene precursors can be pyrolyzed in the pores and deposited on the inner pore wall to form carbon nanotubes under these experimental conditions. There are apparently no macroscopic defects in the carbon nanotubes. Second, the carbon nanotubes have the same outer diameter as that of the pores of the template membrane. Furthermore, these carbon nanotubes are a highly aligned ensemble, which

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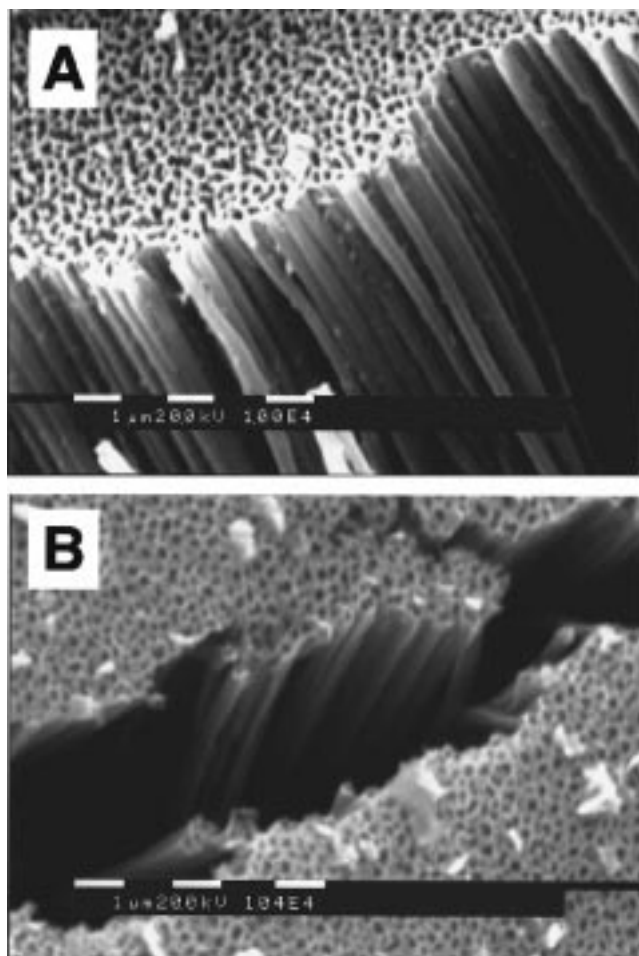


Figure 1. Scanning electron micrographs of CVD carbon nanotubes obtained after 10 min deposition at 900 °C using (A) ethylene and (B) pyrene as precursors.

is advantageous over the random orientation of the carbon nanotubes prepared by either arc discharge²⁶ or other methods.²⁷ Third, these carbon nanotubes are uniform and hollow with open ends.

Solid carbon nanofibers can be formed by increasing the deposition time. SEM images of CVD carbon nanofibers obtained after 40 min deposition at 900 °C using pyrene and ethylene precursors are shown in parts A and B of Figures 2, respectively. These SEM images were obtained after dissolution of the template membrane in concentrated HF and by removing the surface layer by polishing with abrasive paper. These carbon nanofibers have no macroscopic defects and have the same diameter as the pores of the template membrane. Again, these nanofibers (Figure 2) are a highly aligned ensemble.

Fe- and Co-Catalyzed CVD Carbon. The membranes activated with either Fe or Co were exposed to ethylene gas for 30 min at 580 °C. Figure 3A shows an SEM image of Co-catalyzed CVD carbon nanofibers after dissolving the membrane. Although it is clear that some carbon structures are formed, they are not very ordered or symmetric and the tubes tend to fuse together in bundles. No carbon fibers or tubes were observed inside

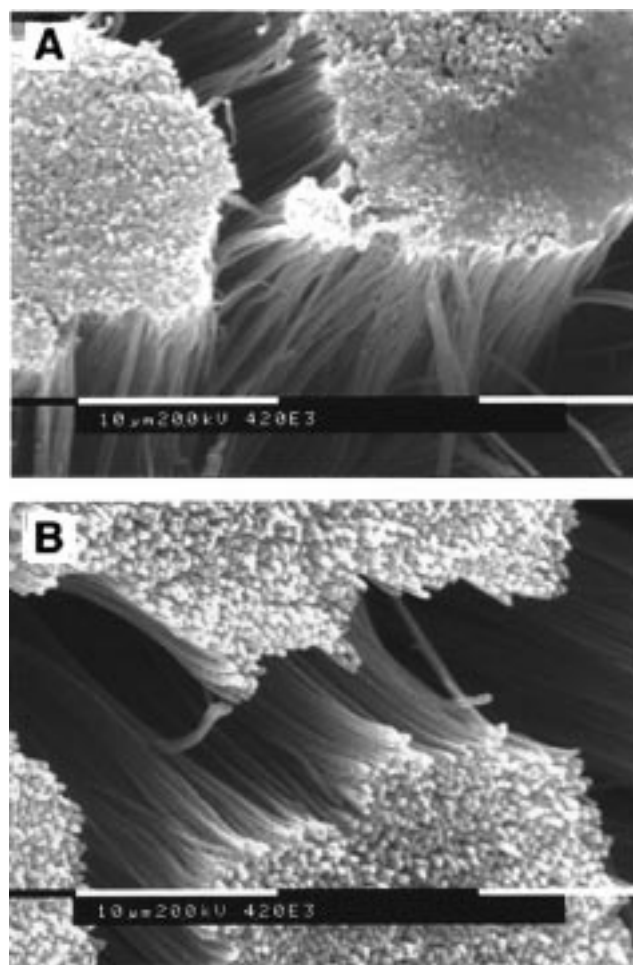


Figure 2. Scanning electron micrographs of CVD carbon nanofibers obtained after 40 min deposition at 900 °C using (A) ethylene and (B) pyrene as precursors.

the membrane containing the Fe catalyst at this temperature. If the Fe-activated membranes were exposed to ethylene gas at 760 °C with a H₂ atmosphere, the carbon nanotubes grew out of the template membrane and across the membrane surface. Figure 3B shows a representative SEM image of Fe-catalyzed CVD carbon nanofibers with 10 nm walls (measured using TEM) formed at 760 °C. The diameter of the carbon nanotubes with closed ends is only 75–100 nm, significantly smaller than the diameter of the pores. This suggests these carbon nanotubes are not templated by the pores in the membrane, but rather are produced only by the catalyst particles.^{14,28}

Ni Catalyst-Activated Membranes. Figure 4 shows SEM images of the Anopore alumina membrane surface before (A, A') and after (B, B') immersing in 0.7% Ni-resinate-toluene solution at two different magnifications. After immersion, the SEM images show no tubes formed inside the pores, and most have the same pore diameter as the bare alumina membrane. These results demonstrate that at this concentration of Ni solution, the nickel does not form a continuous tube in the pore of the alumina membrane. Rather, Ni probably exists as nanoparticles sticking to the inside walls of the pores.²⁹

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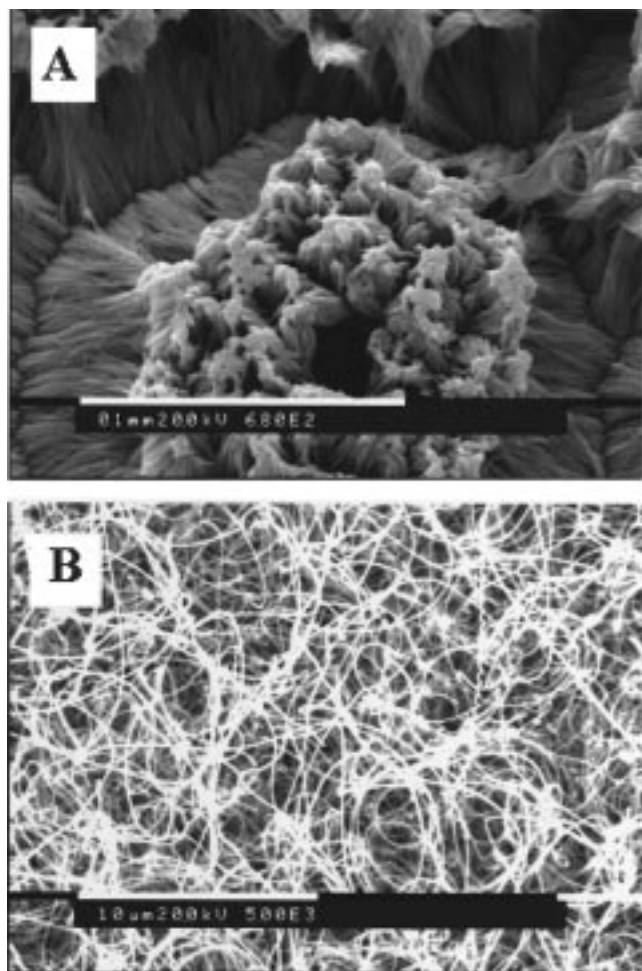


Figure 3. Scanning electron micrographs of (A) Co-catalyzed (580 °C) and (B) Fe-catalyzed (760 °C) CVD carbon nanostructures using ethylene as the precursor.

In contrast, by increasing the concentration of nickel resinate in the solution, nickel is formed in a continuous tube or fiber, as shown in Figure 5 for 1.4%, 3.1%, and 9.4% nickel-resinate solutions. (These images were obtained after liberating the nickel nanostructures from the alumina membrane by dissolution in 6 M NaOH.) It was found that the resultant nickel comprises uniform hollow tubes with open ends (Figure 4A,B). Furthermore, the wall thickness of the tubes was easily controlled by changing the concentration of nickel resinate. If the undiluted nickel-resinate solution were applied, the pores filled to form fibers or capsules (Figure 5C). The nickel-catalyst-activated membranes, which are prepared using 0.7–3.1% Ni-resinate solutions, can be used as templates for carbon nanostructure synthesis. For all experiments described below, Ni-activated alumina membranes made from the 0.7% Ni solution (Figure 4B, B') were used as templates for carbon synthesis.

Ni-Catalyzed CVD Carbon Nanofibers. One of the difficulties associated with CVD of carbonaceous materials is the relatively high temperatures needed for deposition of highly ordered materials. We have devel-

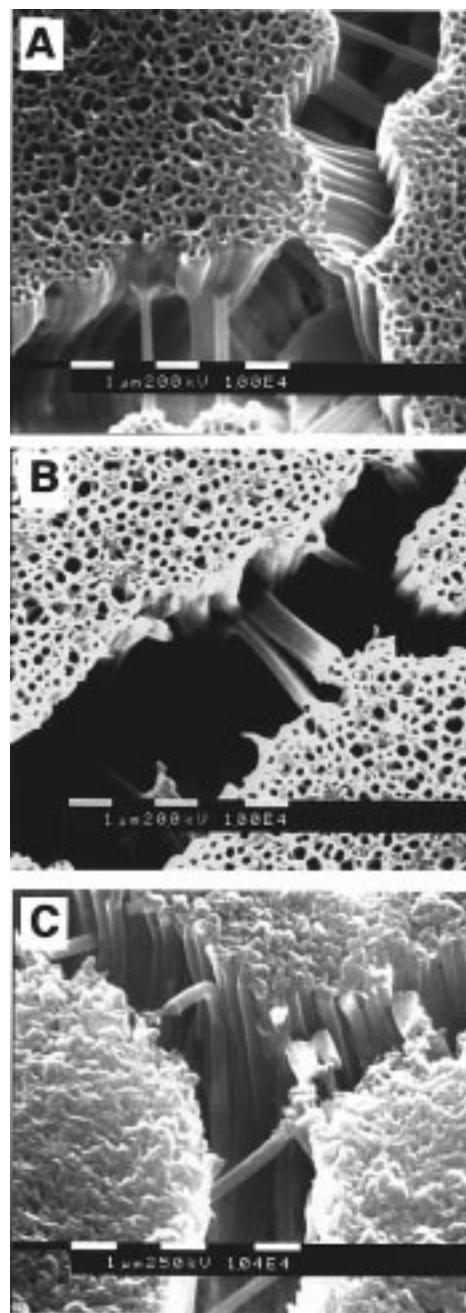


Figure 4. Scanning electron micrographs of Ni-based nanotubes and fibers prepared in Anopore alumina membranes immersed in (A) 1.4%, (B) 3.1%, and (C) 9.4% nickel-resinate solution.

oped a new, low-temperature approach to preparing carbon nanotubes using CVD synthesis within the pores of Ni-catalyzed alumina template membranes. The activated membrane was prepared as described above, placed in a CVD reactor at a temperature of 545 °C, and exposed to ethylene gas or pyrene vapor. Figure 6 shows SEM images of Ni-catalyzed CVD carbon nanofibers obtained after a 20 min deposition using ethylene or pyrene as the precursor. These images were obtained after dissolution of the template membrane in 6 M NaOH and removal of the surface layer.

The carbon nanofibers formed from ethylene (Figure 6A) have no macroscopic defects and have the same diameter as the pores in the template membrane. The nodal structures on the outsides of the fibers are likely

(29) While it is possible that the Ni exists as an extremely thin film on the inside pore diameter, we do not observe formation of complete tubes at the low concentrations of Ni resinate solution (<1.4%).

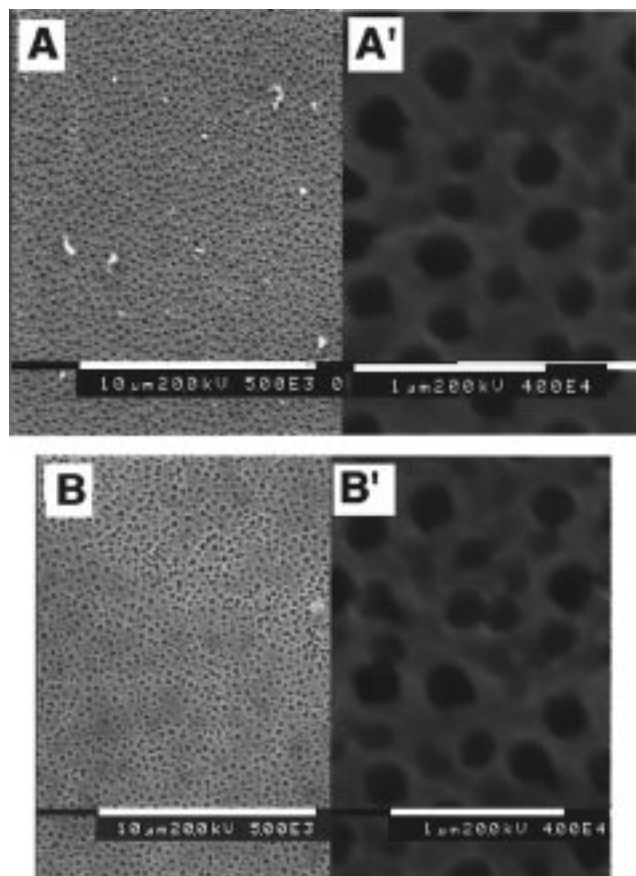


Figure 5. Scanning electron micrographs at two different magnifications of the 200 nm pore diameter Anopore alumina membrane surface before (A, A') and after (B, B') immersion in 0.7% nickel-resinate-toluene solution.

remnants of the nickel catalyst applied to the membrane. Alternatively, this type of nodal structure has been attributed to the transport of carbon vapors to the catalyst particles.³⁰ The pyrene precursor also deposits carbon on the inner wall of the pores under the same conditions as the ethylene precursor, but the resultant carbon is a hollow tube with a very thin wall, even at deposition times up to 40 min. After dissolution of the membrane, all tubes formed from pyrene appear broken (Figure 6B). These results suggest our nickel-catalyst-containing membrane can activate ethylene, but not pyrene.

Conversion to Graphite. Graphite is normally formed at temperatures over 2500 °C.³¹ At lower decomposition temperatures, the degree of ordering in the graphite lattice can be considerably less. For example, on substrates such as quartz and alumina, turbostratic carbon is formed at ~900 °C.³² Oriented graphite can, however, be formed at these lower temperatures if the substrate material is Fe, Co, or Ni.^{33–35} Indeed, Yudasaka and co-workers have shown that graphite thin films are formed on Ni substrates using

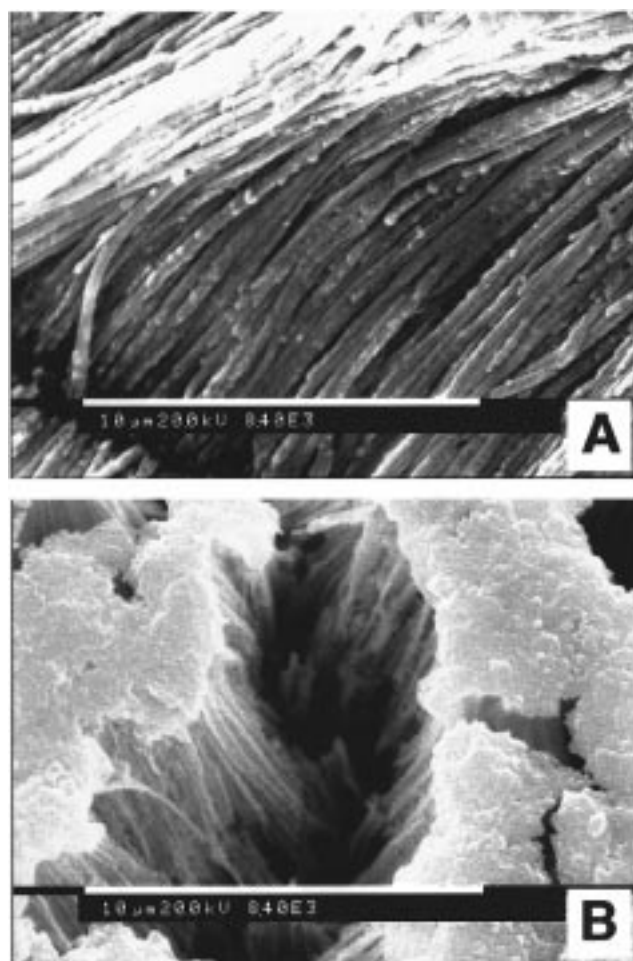


Figure 6. Scanning electron micrographs of Ni-catalyzed CVD carbon nanofibers obtained after 20 min deposition at 545 °C using (A) ethylene and (B) pyrene as precursors.

many different organic materials and substrate temperatures ≥ 800 °C.³⁶ Here, we can obtain highly ordered graphitic nanofibers by first applying a nickel catalyst to our membrane. Figure 7 shows the TEM image of a 200 nm carbon fiber synthesized by Ni-catalyzed CVD in the pores of the template membrane formed at 545 °C. Also shown in Figure 7 is the corresponding electron diffraction pattern. The surface of the fiber is not uniform with both light and dark areas. We believe the dark areas correspond to residual Ni-resinate, as was seen in the SEM images (Figure 6A).

The ring patterns in Figure 7B show that the carbon fibers are not only crystalline but are also somewhat graphitic. The brightest ring corresponds to the 002 reflection of hexagonal graphite. The intensity of this particular reflection is not, however, uniform across the ring, with two bright spots occurring at opposite positions across the ring. The brighter portions are the result of orientation in the fiber. The next continuous ring seen in the diffraction pattern corresponds to the 110 reflection of hexagonal graphite. There is no difference in the intensity in this particular diffracted ring, which suggests that there is no preferred orientation along the a^* - or b^* -axes. The third diffracted ring, however, which corresponds to the 004 reflection of

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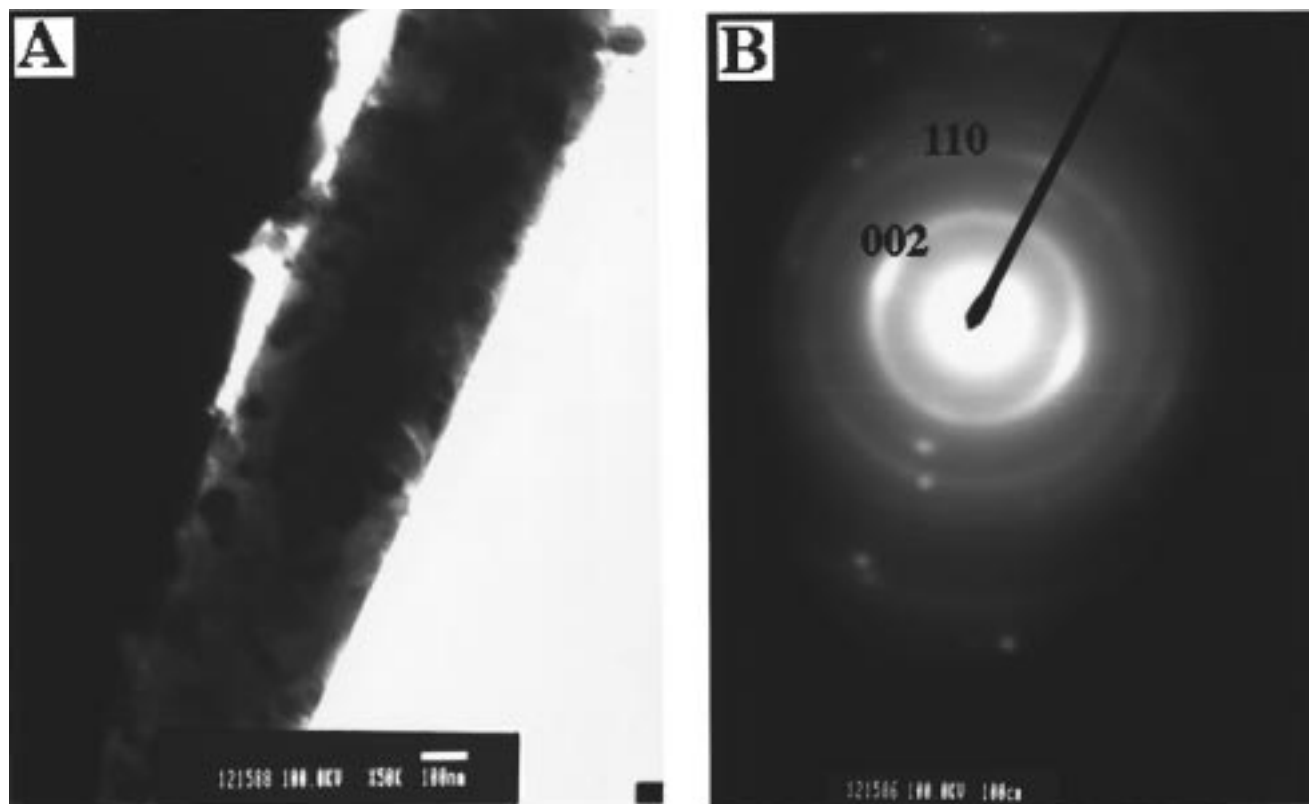


Figure 7. (A) TEM image of Ni-catalyzed CVD carbon nanofibers after synthesis at 545 °C and (B) corresponding electron diffraction pattern.

graphite, is oriented in the same manner as the 002 reflection. Superimposing the diffraction pattern on the TEM image of the fiber shows that the c^* -axis is oriented perpendicular to the long axis of the fiber. The c^* -axis in the graphite unit cell is perpendicular to the stacked layers.³⁷ Therefore, we can conclude that the graphite layers have a preferential orientation parallel to the long axis of the fiber. The layers are not, however, highly ordered as the continuous portions of the ring are also seen. Other reflections, perhaps corresponding to nickel, could not be indexed.

The crystallinity of the fibers formed by Ni-catalysis within the membrane improved upon heating. Annealing the fibers at 500 °C for 12 h gave an electron diffraction pattern with the 002 reflection that appeared as two symmetric arcs of a circle. Further heating for a longer time (~36 h) tremendously improved the orientation of the carbon fibers, Figure 8. The fibers heated for a longer time also showed striations in the TEM images, Figure 8A. The electron diffraction patterns obtained from such fibers showed only oriented patterns, indicative of single-crystalline structures. A representative pattern is shown in Figure 8B. All the reflections in these patterns were indexed to that of hexagonal graphite. The 002 reflections, which occurred as arcs in the diffraction patterns of fibers heated for short times, now occur as spots. Superimposing the diffraction pattern on the TEM image of the fiber shows that the c^* -axis is perpendicular to the long axis of the fiber and the a^* -axis is along the length of the fiber. The zone axis in this diffraction pattern is (010), that

is, the fiber is viewed down the b^* -axis of hexagonal graphite. These results show we have made single-crystalline, hexagonal graphite fibers with the layers oriented parallel to the long axis of the fiber. Electron diffraction patterns taken at different locations along the axis of the carbon fibers were nearly identical with that shown in Figure 8. This suggests the graphitic structure of the carbon extends the entire length of the fibers. Indeed, dark field images show that many of the fibers are crystalline. This is not, however, true for all fibers as the ends of some fibers show small areas of discontinuity in the dark field images, suggesting polycrystalline regions do exist.

Tomita and co-workers have reported the synthesis of ultrafine carbon tubes in an alumina membrane using either carbonization of poly(furfuryl alcohol) or pyrolysis of propylene at 800 °C.¹⁵ In the latter case, they did observe some orientation of the planes in the carbon tubes. Further heat treatment at 2800 °C showed a significant increase in the degree of ordering of the (002) planes. These tubes were not, however, completely graphitized. Furthermore, extremely high temperatures were employed to achieve even minimal ordering.

Yudasaka et al. have reported the formation of multilayer graphite nanotubes by CVD of 2-methyl-1,2'-naphthyl ketone on Ni under very specific reaction conditions.³⁰ Specifically, to achieve graphite nanotubes, temperatures of 700 °C and Ni catalyst particles of 20 to 30 nm diameters were used. At higher temperatures, graphite thin films were formed preferentially over carbon nanotubes. At lower temperatures, the Ni film was not transformed into droplets of the appropriate size needed for catalysis of the carbon. Even under these optimum deposition conditions these

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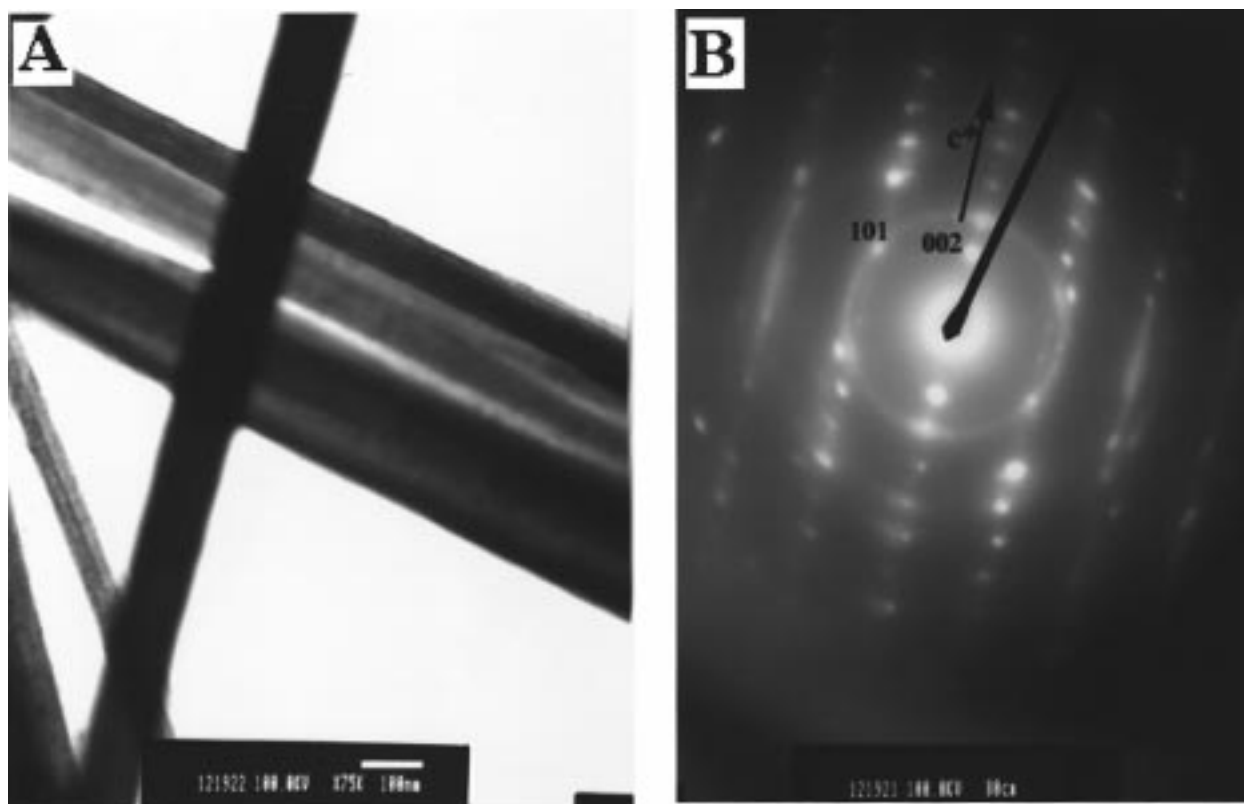


Figure 8. (A) TEM image of Ni-catalyzed CVD carbon nanofibers after 36 h heat treatment at 500 °C and (B) corresponding electron diffraction pattern. The diffraction pattern is for the fiber(s) running across the width of the image.

researchers did not produce highly ordered ensembles of nanotubes.

Our work is the first report of CVD synthesis of graphitic carbon nanofibers directly in the pores of a template membrane. These nanostructures are highly ordered ensembles composed of nanofibers of uniform dimensions. With the addition of a Ni catalyst to our membrane, highly ordered graphite nanofibers were formed at considerably lower temperatures (<600 °C) than these other methods. It should also be noted that we do not require specific dimensions for our Ni particles.

Interestingly, the difference in morphology between the Ni, Co, and Fe-activated carbon nanostructures observed here may be attributed to the catalyst particles. Carbon films formed on Ni substrates are more crystalline than those formed on other substrates.³⁸ Baker and co-workers have shown that both the particle size and the orientation of the catalyst crystal can greatly affect the alignment and morphology of carbon structures.^{21,39} This work has shown that both the choice of catalyst (i.e., Ni or Fe), as well as the ability of the crystallographic faces of the catalyst to decompose hydrocarbons will control the resulting carbon nanofiber structure. Baker and co-workers suggest that an alteration in the crystal structure of the catalyst particles could result in the generation of other structural forms, including coiled and helical configurations.²¹ The role of the catalyst particles trapped in the

membrane in the growth mechanism for the carbon nanofibers in these systems, however, remains an open question.

We make one final note about the formation of Ni-catalyzed graphite nanofibers. The fibers cleave preferentially along the striations observed in the TEM images (Figure 8A). Figure 9 shows TEM images of Ni-catalyzed CVD carbon nanofibers after synthesis at 545 °C (A) and followed by 36 h treatment at 500 °C (B). Since the graphitic layers are stacked parallel to the long axis of the fiber and the interlayer attraction is mainly van der Waals, it is easy to cleave them in layers. This type of cleavage in highly ordered graphite is commonly observed.⁴⁰

dc Conductivity of Carbon Nanofibers. Typical raw conductivity data for carbon nanofibers are shown in Table 1. The carbon nanofibers prepared by CVD and Ni-catalyzed CVD using ethylene as the precursor and CVD using pyrene as the precursor are conducting. The conductivity ranged between 0.1 and 3.0 S/cm. The carbon prepared by Ni-catalyzed CVD using pyrene as the precursor is nonconducting. This could be the result of defects in the thin walled tubes or simply the broken tubes observed in the SEM images, Figure 6B. After heat treatment, the conductivity for all carbon nanotubes decreases. This may also be the result of broken fibers or cleavage of the graphitic layers. Li-ion intercalation studies of these fibers are currently underway in our laboratories.⁴¹

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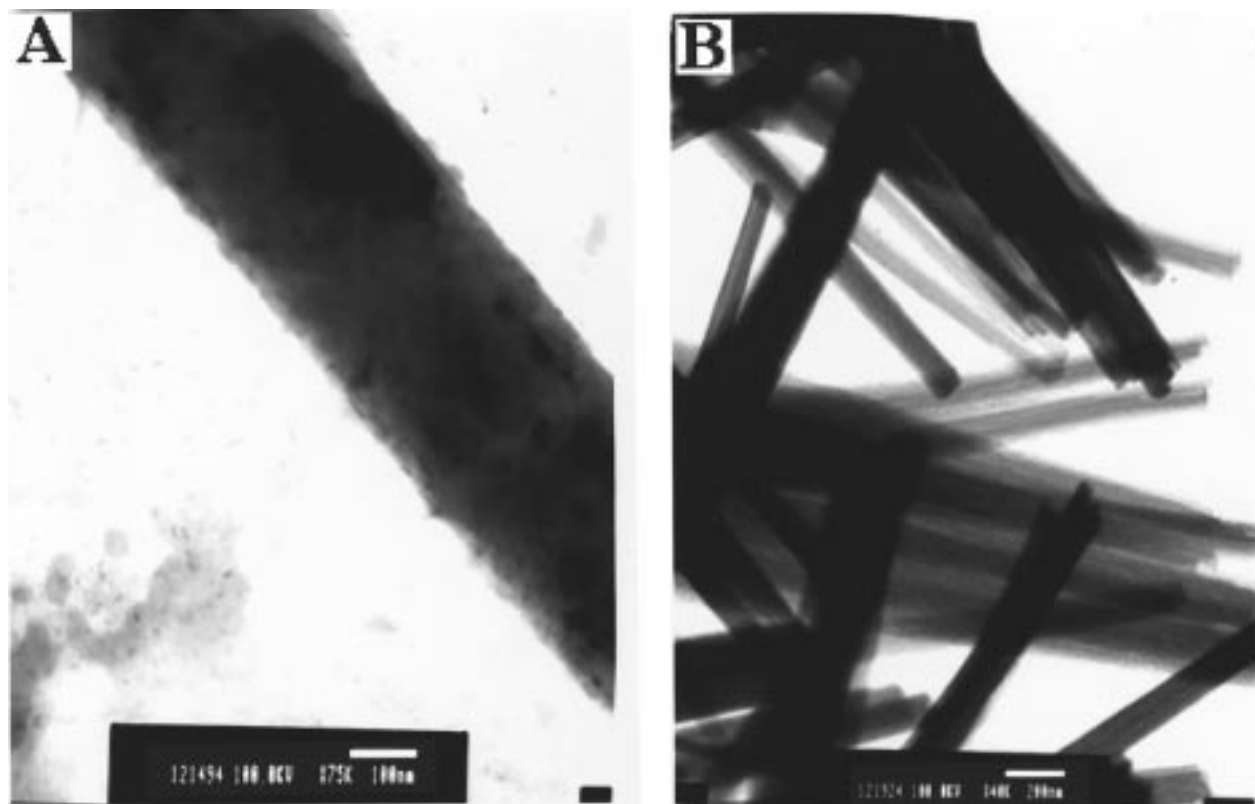


Figure 9. TEM images of Ni-catalyzed CVD carbon nanofibers (A) after synthesis at 545 °C and (B) after 36 h heat treatment at 500 °C.

Table 1. dc Conductivity of CVD Carbon Nanofibers^a

carbon nanofibers	conductivity (S cm ⁻¹)
CVD ethylene (900 °C)	3.0 ± 0.2
CVD pyrene (900 °C)	0.80 ± 0.05
Ni-catalyzed CVD ethylene (545 °C)	0.10 ± 0.02
Ni-catalyzed CVD pyrene (545 °C)	<2.7 × 10 ⁻⁷

^a Measurements made with a two-point probe method.

Conclusion

We have developed a new approach for preparing graphitic carbon nanofiber and nanotube ensembles. This approach entails CVD-based synthesis of carbon within the pores of an alumina template membrane with or without a Ni catalyst. The CVD carbon deposition in the bare alumina membrane (200 nm diameter pores) was exposed to ethylene gas or pyrene vapor at 545 °C. The resultant carbon comprises uniform hollow tubes with open ends. With increasing deposition time, the

carbon tubes can be converted into carbon nanofibers. TEM and electron diffraction data show the graphitic carbon nanofibers synthesized in Ni-catalyst activated membranes are initially not highly ordered. After heating at 500 °C for 36 h, however, the electron diffraction data show a spotted diffraction pattern characteristic of crystalline graphite, and there are striations along the length of the fibers. The electron diffraction data also show the graphitic planes are parallel to the long axis of the nanofibers.

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