



TEMPLATE SYNTHESIS OF CARBON NANOTUBES

G.L. Hornyak¹, A.C. Dillon¹, P.A. Parilla¹, J.J. Schneider²,
N. Czap², K.M. Jones¹, F.S. Fasoon¹, A. Mason¹, and M.J. Heben¹

¹ National Renewable Energy Laboratory 1617 Cole Blvd., Golden, Colorado 80401 USA

² Institut für Anorganische Chemie, Universität Essen, 45117 Essen, Germany

Abstract -- *The template synthesis and characterization of carbon nanotubes (CNTs) formed in porous alumina membranes (PAM) by the thermal chemical vapor decomposition (CVD) of propylene (Pr) gas are described. We found that the graphitic character of CNTs improved as CVD temperature was increased from 500 to 800 °C. Samples showed progressive increases in metallic appearance and layered tube wall structure and decreases in electrical resistance. No further enhancement of graphitization was observed among samples formed at 800, 900 and 1000 °C. X-ray diffraction (XRD) indicated that long-range order was absent in all CNTs tested. Localized crystalline domains of graphitic carbon, however, were detected by Raman spectroscopy and seen in light and dark field transmission electron microscopy (TEM) images. CNTs formed in the presence of catalytic Fe and Co particles at 600 and 700 °C with a Pr/N₂ flow rate of 94 sccm (standard cubic centimeters per minute) showed slightly lower electrical resistance than CNTs formed in control experiments. The catalytic effects of Fe and Co were observed for samples made at 800 °C with a 50 sccm Pr/N₂ flow rate as “nanotubes within nanotubes” were formed. No major differences were found between catalyst-containing and control samples formed at temperatures greater than or equal to 800 °C at 94 sccm.*

©1999 Acta Metallurgica Inc.

INTRODUCTION

Single-wall CNTs formed by an arc-discharge process were shown here at NREL to stabilize adsorbed hydrogen at moderate temperatures (1) and to demonstrate selectivity of CO₂ over CH₄ in gas separation experiments (2). Study of transport and adsorption properties of CNTs would be greatly facilitated, however, if nanotubes could be aligned within a well-defined matrix. PAMs, formed by the anodic electrolysis of aluminum, consist of hexagonally packed parallel pore channels and offer a possible means of achieving an ordered array of CNTs. Control over anodization parameters can produce pore diameters ranging from 2 to 500 nm, porosities from 20 to 70% and pore densities from 10⁷ to 10¹² cm⁻² (3). The resulting PAMs are optically transparent in the visible range of the spectrum, resistant to most chemicals except for strong acids and bases and stable to temperatures in excess of 1000 °C (3). Template synthesis of nanotubes by CVD has been investigated during the past five years by a handful of research groups (4-6). We are now interested in the fabrication and characterization of ordered arrays of CNTs for applications that include their use as a medium for hydrogen storage, as lithium battery electrode materials and as natural gas purifiers. The degree of graphitization of template synthesized CNTs as a function of CVD conditions and catalysts is of great interest.

EXPERIMENTAL

PAM templates were formed by anodizing high purity aluminum plates in a 10 wt.% sulfuric acid solution at 20 V for 4 h at 0 °C (3). PAMs were removed from the aluminum plate surface by a voltage reduction procedure with subsequent acid detachment (3). The resulting membranes were approximately 30 μm thick and 30% porous with an average pore diameter of 32 nm. Selected membranes that were heat-treated at 900 °C for 5 h between quartz plates to enhance flattening yielded a pore diameter of *ca.* 50 nm. Robust PAMs, with thickness greater than 200 μm , were fabricated in 20 wt.% H_2SO_4 at 20 V for 12 h at -5 °C.

Chemical vapor deposition was accomplished in a 3-zone furnace by: 1) purging in N_2 for 1 h at 500 °C, 2) heating in forming gas for 2 h at temperatures ranging from 500 to 800 °C and 3) heating in 2.5 vol.% Pr in N_2 for 2 h at temperatures ranging from 500 to 1000 °C. The flow rate of the gas was fixed at either 94 (high) or 50 (low) sccm. Samples for TEM, XRD, SEM (scanning electron microscopy), EPMA (electron probe microanalysis) and Raman spectroscopy were prepared by removing the host alumina by ultrasonication in concentrated HF. The resulting suspension was centrifuged, decanted, rinsed and suspended in ethanol.

The degree of graphitization was evaluated by light and dark field TEM imaging, measurement of the transverse electrical resistance of the membrane (along the length of the CNTs) with 0.31 cm^2 contacts, Raman spectroscopy, XRD and sample appearance. Cobalt catalysts were formed *in situ* by aqueous incipient wetness impregnation (AIWI) of PAM pore channels with 0.3M CoSO_4 or $\text{Co}(\text{NO}_3)_2$ (6). Fe_2O_3 nanoparticles were formed by the low temperature decomposition of *bis*(η -toluene) $\text{Fe}(0)$ at -78 °C (7). These catalyst precursors were converted into metals by reduction in forming gas at temperatures of 600 to 800 °C.

RESULTS and DISCUSSION

Figure 1 shows an SEM image of a nanotube array formed in a robust PAM with thickness of *ca.* 200 μm . The alumina matrix was dissolved in concentrated HF *without* ultrasonication. The array remained intact after HF treatment due to the presence of the carbonaceous surface layers. The CNTs were formed at 600 °C without catalysts for a 3 h Pr deposition time at 94 sccm. As expected, the tubes are 200 μm in length and have a diameter of *ca.* 30 nm. The aspect ratio of the CNTs in this array is nearly 7000.

In Figure 2a, a TEM image of CNTs formed at 800 °C without the aid of catalysts is shown. These tubes were liberated from the alumina template by dissolution in HF *with* ultrasonication. Numerous single and bundled CNTs are evident. Nanotubes formed at 500 and 600 °C did not survive ultrasonication during HF treatment. In these cases, TEM images revealed agglomerations of unstructured carbon. CNTs formed at 800 °C or greater survived ultrasonication but were found by EPMA to contain as much as 50 wt.% alumina.

Qualitative evaluation of the degree of graphitization of non-catalytic samples is given in Table 1. Sample surface appearance proceeded from “shiny black” to “silvery reflective” as CVD temperature was increased from 500 to 800 °C. Above 800 °C, the appearance became a duller gray-metallic as thicker surface layers were formed at higher deposition rates. Layering in nanotube walls was first observed in TEM images of 700 °C samples (600 °C specimen CNT structures did not survive HF with ultrasonication). The degree of layering improved in samples formed at higher temperatures (Figure 2b), but graphitization was still confined to a length scale



Figure 1. Robust array of carbon nanotubes (aspect ratio *ca.* 7000) formed at 600 °C.

less than a few nm. No major differences in terms of CNT wall layered structure were detected among samples made at 800, 900 and 1000 °C. Transverse electrical resistance of samples decreased dramatically as CVD temperature was increased from 500 to 800 °C, but no significant differences in electrical resistance were detected among samples formed at 800 °C or higher.

Raman spectra for samples formed at various temperatures (Figure 2c) revealed a broad feature at *ca.* 1360 cm^{-1} , associated with disorder within a graphite lattice, and a broad feature at *ca.* 1600 cm^{-1} , attributed to one of the fundamental Raman modes of crystalline graphite (8). The fact that the two peaks have nearly identical magnitude indicates the presence of nanocrystalline graphite with domain size less than 10 nm (8). Compared to the 600 and 700 °C sample spectra, the 800 and 1000 °C spectra showed an attendant decrease in signal intensity in both peaks. Dark field TEM image data also confirmed the presence of crystalline domains in samples formed at 700 °C (Figure 2d) or greater.

TABLE 1

CVD Temperature	Surface Appearance	Structure of CNT Wall	Electrical Resistance	Raman Analysis	XRD Analysis
500 °C	Shiny Black	Amorphous	$>10^6 \Omega$	Insuff. Sample	Insuff. Sample
600 °C	Glassy Black	Amorphous	$>10^3 \Omega$	+ Nanographite	Insuff. Sample
700 °C	Shiny Slate	Incipient Layers	$<100 \Omega$	+ Nanographite	Insuff. Sample
800 °C	Reflective Silver Mirror	Well-Defined Layers	$<2 \Omega$	+ Nanographite	No Long-Range Order
900 °C	Dull Metallic Gray	Well-Defined Layers	$<1 \Omega$	No Sample	No Long-Range Order
1000 °C	Dull Metallic	Well-Defined	$<1 \Omega$	+ Nanographite	No Sample

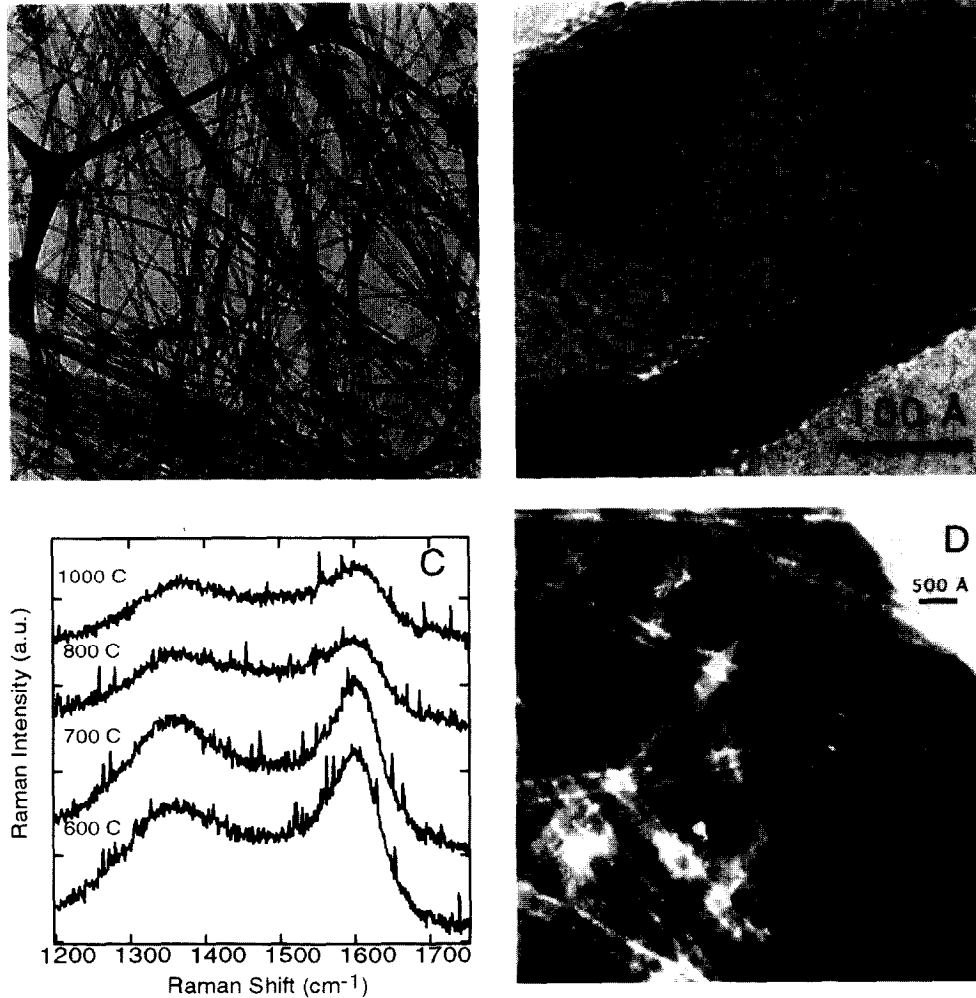


Figure 2. (A) TEM image of carbon nanotubes formed at 800 °C CVD conditions and liberated from the PAM by immersion in concentrated HF with ultrasonication. These CNTs have aspect ratio exceeding 1000 and vividly demonstrate the result of the template synthesis process. (B) TEM image of a tube wall of a CNT formed by CVD at 900 °C with the aid of Fe catalysts. The wall thickness is ca. 8 nm. Although layering is evident, long-range order is absent. (C) Raman spectra of CNTs obtained with laser excitation at 488 nm. The features apparent at 1360 cm⁻¹ and 1600 cm⁻¹ indicate the presence of nanocrystalline graphite. Peak intensity was diminished in the 800 and 1000 °C sample spectra. The presence of more turbostratic graphite and alumina may have interfered with the signal. (D) TEM dark field image of tube walls of CNTs formed at 700 °C. The bright centers along the pore channel walls correspond to crystalline domains. These domains were not well pronounced in CNTs formed at temperatures lower than 700 °C. The image indicates that the domain size is small.

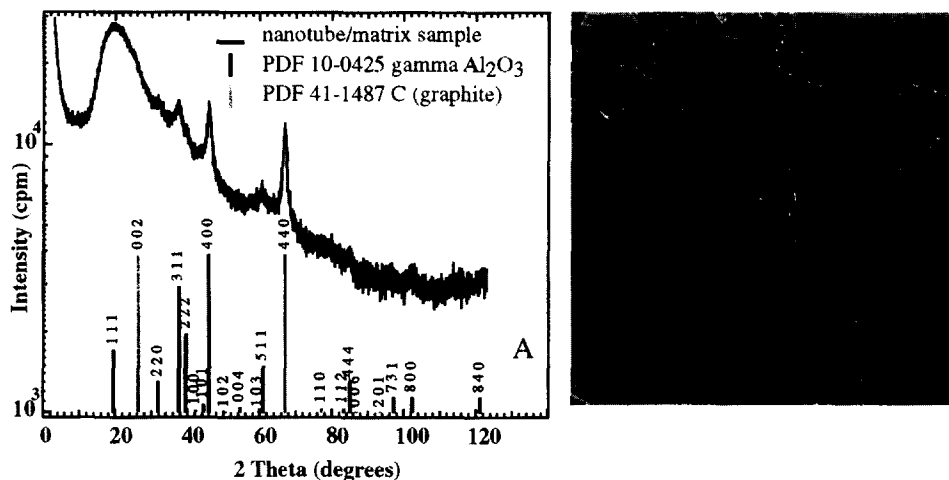


Figure 3. (A) XRD spectrum of a sample formed at 800 °C shows several γ -alumina peaks (black numbers) but no signal from the primary [002] peak for graphite (gray numbers). This suggests that long-range order is absent in CNTs prepared by our method and that the population of graphitic crystallites is small. (B) “Nanotubes within nanotubes” are shown. These small CNTs were formed with the aid of catalytic Fe nanoparticles. The smaller nanotubes have an outer diameter of *ca.* 10 nm and wall thickness less than 2 nm. Cobalt doped PAMs also generated smaller nanotubes within the major CNT formed in the PAM channel.

XRD data showed that long-range order was absent in all samples tested. The XRD spectrum shown in Figure 3a corresponds to a sample formed at 800 °C CVD that underwent immersion in concentrated HF with ultrasonication. The features at [311], [400] and [440] of the XRD spectrum displayed in Figure 3a do not correspond to graphite but rather to γ -alumina. Amorphous hydrated alumina, found initially in PAMs, is converted to the γ -alumina phase during exposure to temperatures greater than 500 °C.

Under low flow rate CVD conditions (50 sccm, 800 °C), Co and Fe catalyst particles induced the growth of smaller nanotubes (Figure 3b) within the major CNT tube defined by the template PAM pore channel wall. The smaller nanotubes were highly curled and were found in the majority of pore channels. No such catalytic effects were observed for samples formed at the higher flow rate (94 sccm). A slight decrease in the electrical resistance of catalyst-influenced samples with respect to controls was detected for the 600, 700 and 800 °C CVD sets, but no significant differences were found between catalytic and control samples formed at higher temperatures. EPMA results indicated the presence of *ca.* 1 wt.% sulfur as well as alumina in HF-treated CNT samples. The CNTs, whether in the PAM or not, exuded a strong sulfur odor when ground with mortar and pestle. The presence of sulfur is not surprising since the PAMs are formed in a sulfuric acid electrolyte and 10 to 15 wt.% sulfate is incorporated (3).

CONCLUSIONS

Ordered arrays of carbon nanotubes with aspect ratios from 1000 to 7000 have been successfully synthesized in porous alumina templates by CVD reactions. The degree of

graphitization, however, of samples formed from 800 to 1000 °C was not as high as expected. Although TEM images showed that the relative degree of order in the layers improved and that electrical resistance decreased in samples formed at increasing CVD temperatures, no further improvement was observed in samples formed at temperatures greater than 800 °C. Tomita *et al* (5) concluded, in reference to samples made by a similar procedure, that the average domain size was less than 10 nm and that their CNTs were not well graphitized. Accordingly, XRD, Raman and TEM results jointly agreed that long-range order was lacking in the high temperature CVD samples. Perturbations induced by the non-uniform nature of the pore channel walls of PAMs may preclude the formation of layered graphite with long-range order. Localized order was evident, however, in TEM light and dark field images and was demonstrated in Raman spectra of samples formed at 600 °C or greater.

The shape and relative intensity of the Raman peaks indicated that nanographite domains were less than 10 nm in size. In fact, the Raman spectra are very similar to those of glassy carbon prepared by the thermal decomposition of phenolic resins (9). The surprising decrease in intensity of the peak at 1360 cm⁻¹ with increasing temperature is consistent with the formation of larger nanocrystals, but an expected sharpening of the peak at *ca.* 1600 cm⁻¹ was never observed. The presence of *ca.* 50 wt.% alumina and turbostratic surface graphite in the samples formed at higher CVD temperatures may have interfered with Raman signal acquisition. Post-CVD heat treatments have been suggested as a means of enhancing graphitization (5,6).

Fe and Co nanoparticle catalysts induced the growth of “nanotubes within nanotubes” under low flow rate conditions at 800 °C in what was essentially a one-step process. No internal nanotubes were formed, however, at 94 sccm. The rate of carbon deposition at higher CVD gas flows and temperatures may have overwhelmed the competing process of metal-mediated nanotube formation. In addition, the generation of reduced sulfur compounds at higher temperatures may have poisoned catalysts (10). Future work will focus on the catalytic effects of Co, Fe and Ni nanoparticles at temperatures ranging from 600 to 800 °C, the use of non-sulfur bearing PAMs and the study of CNT growth mechanisms using other CVD gases.

ACKNOWLEDGMENTS

This work was supported by the Office of Energy Research (Advanced Energy Projects Division) of the US Department of Energy under Contract No. DE-AC36-83CH10093.

REFERENCES

1. Dillon, A.C.; Jones, K.; Bekkedahl, T.; Kiang, C.; Bethune, D.; Heben, M. *Nature* **1997**, *386*, 377.
2. Dillon, A.C.; Heben, M.J. **1997**, Unpub. Results.
3. Hornyak, G.L. *Ph.D. Dissertation*, **1997**, Colorado State University.
4. Yang, D.; Baughman, R.; Hornyak, G.L.; Martin, C.R. *Allied Signal* **1993**, Unpub. Results.
5. Kyotani, T.; Tsai, L.; Tomita, A. *Chem. Mater.* **1996**, *8*, 2109.
6. Che, G.; Lakshmi, B.B.; Martin, C.R.; Fisher, E.R. *Chem. Mater.* **1998**, *10*, 260.
7. Schneider, J.; Czup, N.; Hornyak, G.L.; Heben, M.J., *Nano '98 Bk. of Abs.* **1998**, P1-10, 210.
8. Tuninstra, F.; Kocing, J.L.; *J. Phys. Chem.* **1970**, *53*, 1126.
9. Tallant, D.R.; Parmeter, J.E.; Simpson, R.L. *Diamond & Rel. Mater.* **1995**, *4*, 191.
10. Motojima, S.; Hasegawa, I.; Kagiya, S.; Momiyama, M. *Appl. Phys. Lett.* **1993**, *62*, 2322.