Growth of Manganese Filled Carbon Nanofibers in the Vapor Phase

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We report the vapor phase growth of partially filled graphitic fibers, 20–30 nm in diameter and up to a micron in length, during a manganese catalyzed carbon electric arc discharge. The fiber morphology resembles that of catalytic chemical vapor deposited carbon filaments but the inside hollow contains intermittent precipitates and continuous fillings of Mn that at times occupy > 50% of fiber lengths. Transmission electron microscopy and electron energy loss *line spectra* show that the fillings form as solid cores and may correspond to pure metal.

Recent developments show that nanometer size closed hollow carbon tubules can be grown in multilayer configurations [1] or with single shells [2], depending on the conditions used during synthesis. It has been shown that these tubules can be opened by oxidation [3] and the inside hollow can be filled [4] with inorganic phases creating unique nanocomposite materials. The electrical and mechanical properties of these tubules are predicted to be extremely interesting [5] and with different inorganic phases trapped inside, the material should provide a fascinating system for both theory and future applications as composites. The tubules are grown during an electric arc discharge between two carbon electrodes and the products formed also consist of fullerenes [6] and carbon soot. Various other forms of larger carbon fibers exist commercially and are used in a variety of applications [7]. One important way of making such fibers is by catalytic chemical vapor deposition (CCVD) [7–9]. In this Letter, we show that by using a manganese catalyst under typical fullerene forming conditions, partially filled nanometer size graphite fibers can be grown in the gas phase; the large extent of fillings suggest that the fibers might exhibit true composite character.

We use for the electric arc discharge a pure graphite cathode, but a hole is drilled in the graphite anode and filled with a mixture of graphite and Mn powders in the ratio 2:1 by weight. The voltage and current used for the discharge were ∼25 V and ∼100 A and the He pressure inside the chamber was ∼200 mbars. The soot formed during the discharge is dispersed in ethanol and observed in a transmission electron microscope (TEM) (TOPCON 002B; 200 keV) and a VG scanning TEM (STEM) (100 keV).

Along with fullerenes and carbon soot [6] and particles of codeposited Mn (5–25 nm in size), we observe in moderate quantities filaments of carbon with hollow inside (Fig. 1). The diameter of these fibers ranges narrowly between 20–30 nm and lengths extend up to a micron. The fibers are slightly twisted with the diameter and the cross section of the outer walls and of the inside hollow varying across the length; the graphite (002) planes

that make up the walls have spacing of 0.34 nm (rather broad peak at 0.337 nm in x-ray diffraction) and remain parallel for 10 to a few 100 nm. Low magnification image in Fig. 1(a) contrasts with the straight and perfect alignment of multilayers for practically entire lengths in carbon nanotubes grown on the cathode surfaces [1,2]. The fibers here resemble those [7,8] grown (by CCVD) at high temperatures using transition metal catalysts such as Fe, Co, or Ni. But unlike in the latter where the presence of a hydrocarbon gas or hydrogen is essential for growth, the fibers here are grown in inert gas atmosphere.

We observe that the tips of the fibers contain catalyst particles [Fig. 1(a)] suggesting that the growth is driven
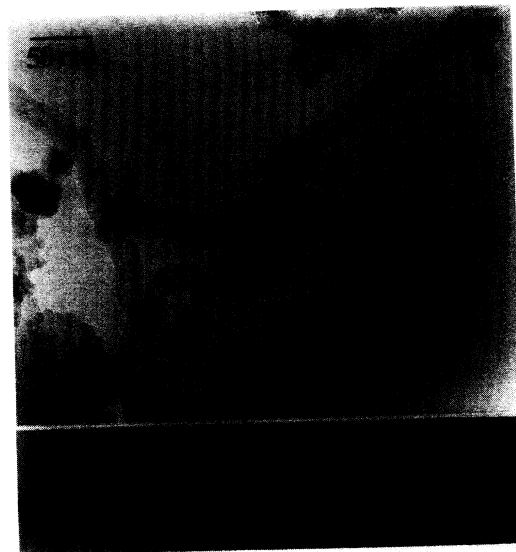

FIG. 1. (a) Low magnification image of twisted capsulated carbon fibers formed under conditions described in the text. The thin arrows indicate the positions of Mn capsulations that are present in the inside hollow of the fibers. The thick arrow shows the position of a large Mn particle present at the tip of one of the fibers. (b) Image of a single fiber with the inside hollow filled for most of its length.

by some form of a Mn catalyst as in typical CCVD fila-
ment growth [7,8]. But the puzzling case here is the en-
capsulated Mn inside the hollow core [marked by arrows
in Fig. 1(a)], which is present at more than one position
along the fiber length, in all fibers. In some cases the
filling extends for a substantial portion of the fiber length;
say > 50% [Fig. 1(b)]. Figures 2(a) and 2(b) show, at
higher resolution, the smaller encapsulations that are
trapped inside the hollow. The inclusions are wrapped
around by graphitic planes, similar to the filled carbon
nanoparticles that have been made recently [10,11] using
La and Fe. Here the graphite layers have formed around
the capsulations but outer layers have grown and overshot
to produce extended growth of the fibers [Figs. 2(a) and
2(b)]. Such overshooting during growth is common in
multishell carbon nanotubes, producing inside termina-
tions of layers [12] and often closed carbon cages inside
cylindrical tubules. Evidence for traces of yttrium car-
bide inside carbon nanotubes [13] and iron-nickel car-
bides in carbon filaments found in interplanetary dust

[14] was reported before. We do not observe any encap-
sulations inside particles and tubes grown in the cathode
deposits under the conditions reported here.

Images in Figs. 2(c) and 2(d) reveal the morphology of
extended fillings and interfaces. The diameter of the
fillings corresponds to the size of the inside hollow (< 10
nm) but the cross sections vary across the length [Figs.
2(c) and 2(d)]. The fillings extend up to a few hundred
nanometers, sometimes starting from the tip of the fiber.
Electron diffraction from individual filled fibers and lat-
tice fringes from encapsulations [Figs. 3(a) and 3(b)]
show that the fillings are crystalline and some of them
correspond to γ-Mn phase. Figure 3(b) shows microdif-
fraction from the portion of a fiber containing filling and
is indexed as a superposition of diffraction from a graph-
ite tube [7] and Mn of a body centered tetragonal struc-
ture (c/a ratio of 1.33) [15]. Weak arcs of intensity due
to (hkl) reflections are seen in the diffraction patterns
from some tubes suggesting that 3D ordering between the
planes is not well established [7].

We identify the chemical composition of the trapped
species inside the fibers at high spatial resolution by scan-
ning the electron beam (in a VG STEM) across a trans-
verse section of the fiber-filling interface and collecting
energy-loss spectrum from each point along the line of
scan. Figure 4(a) represents the 2D plot of a sequence of
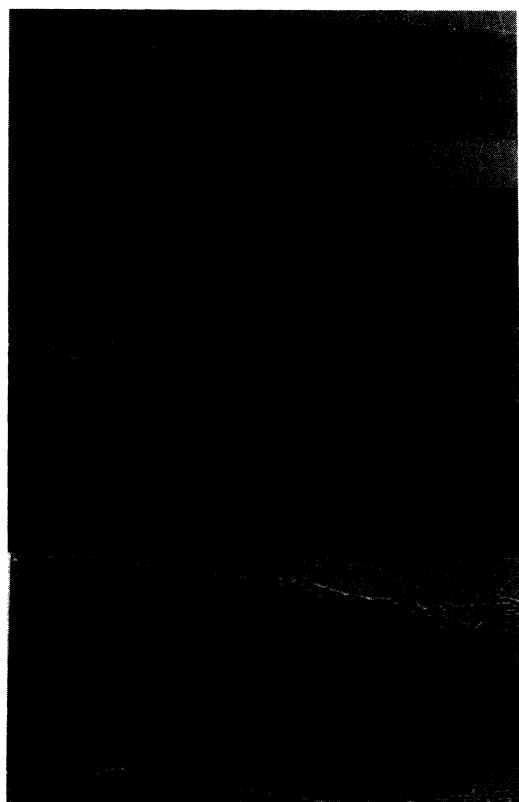128 spectra taken across a tube of ~25 nm with a filling

FIG. 2. (a),(b) High resolution images showing small pre-
cipitates of manganese trapped inside the fiber hollow and sur-
rounded by graphite layers. (c),(d) Images showing the mor-
phology of extended Mn fillings inside carbon nanofibers. Fil-
ling in (d) is slightly wavy but straight segments are seen in (c).
Scale is 0.34 nm between the graphite basal planes (horizontal
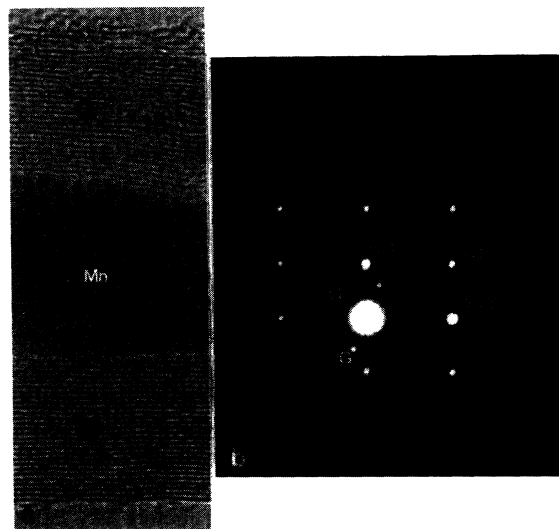fringes) that make the fiber walls.

FIG. 3. (a) A thin transverse section of a fiber showing crys-
talline filling (labeled Mn; showing (011) type fringes 0.213 nm
apart) inside graphitic walls (labeled G). (b) Microdiffraction
pattern from the portion of a fiber with filling. The pattern is a
superimposition of diffraction from the graphite tube [(002)
spots are indexed as "G"; there are more than one orientations
for the (002) planes due to the twisted fiber morphology] and
Mn (indexed by miller indices). The Mn pattern corresponds to
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of Mn of 7 nm. These sequences of spectra are accumulated typically with a 0.5 nm probe, 0.3–0.4 nm pixel increment across the specimen and a 1 sec acquisition time per pixel [16]. Figure 4(b) displays the profile of the relative intensity of these characteristic peaks after background subtraction, following the standard quantification procedure discussed before [17]. Figure 4(c) shows the summed energy loss spectra of the core-loss edges of C (K) and Mn ($L_{2,3}$). Over this energy range no other elements are detected.

As the beam scans across the fiber, the intensity of the energy-loss peaks corresponding to the K edge in graphite (window: 280–325 eV) increases [Fig. 4(b)] corresponding with the increasing number of carbon atoms in a column that the beam encounters (shows that the fiber has cylindrical geometry), dips in the middle due to the inside hollow and follows the same pattern on the other side. The intensity of energy loss from the L edge due to Mn (635–665 eV) correlates well with the position of the central hollow of the fiber and the peaking of intensity in the center clearly indicates that the manganese is formed as a solid cylindrical core and is not just wetting the inside surface. Some of the Mn particles deposited with the soot and the particles that are present at the tip of the fibers show traces of oxygen in their electron energy loss spectra. The ratio of the L_2 and L_3 peaks in the spectra, which indicates the oxidation state of Mn [18], is different for the Mn trapped inside the tubes compared to the Mn particles outside or at the fiber tips and is close to that of pure metal. The C-K edge [Fig. 4(c)] corresponds to graphite and shows no indication for the presence of any carbide species [19] in the filled portions. The high temperature structure of Mn seems to be retained [15] for at least some of the capsulations, similar to that of Co catalyst [2] which is deposited in the soot as the high temperature fcc structure.

The growth mechanism for such encapsulated fibers seems to be an interesting problem. The particles at the tip indicate that the growth is driven by the active catalytic graphitization of the carbon in the plasma by Mn species. Growth models for CCVD graphite filaments [7] suggest that growth proceeds through the dissolution and diffusion of carbon around a seed catalyst particle until the particle becomes chemically poisoned. Such a model will not be able to explain the multiple intermittent fillings that we have seen. However, it could be envisaged that each of the capsulations has acted as separate growth fronts during the growth history of the fiber. Overshooting of the outer graphite layers and subsequent activation by a second catalyst particle could produce such a growth. The large lengths of filled species that we observe would mean that the addition of carbon and manganese should take place continuously and simultaneously. As the catalytic mechanism of manganese in fiber growth seems to be quite different from that of the usual fiber forming transition metals, it may be tested by using the metal under typical CCVD conditions.
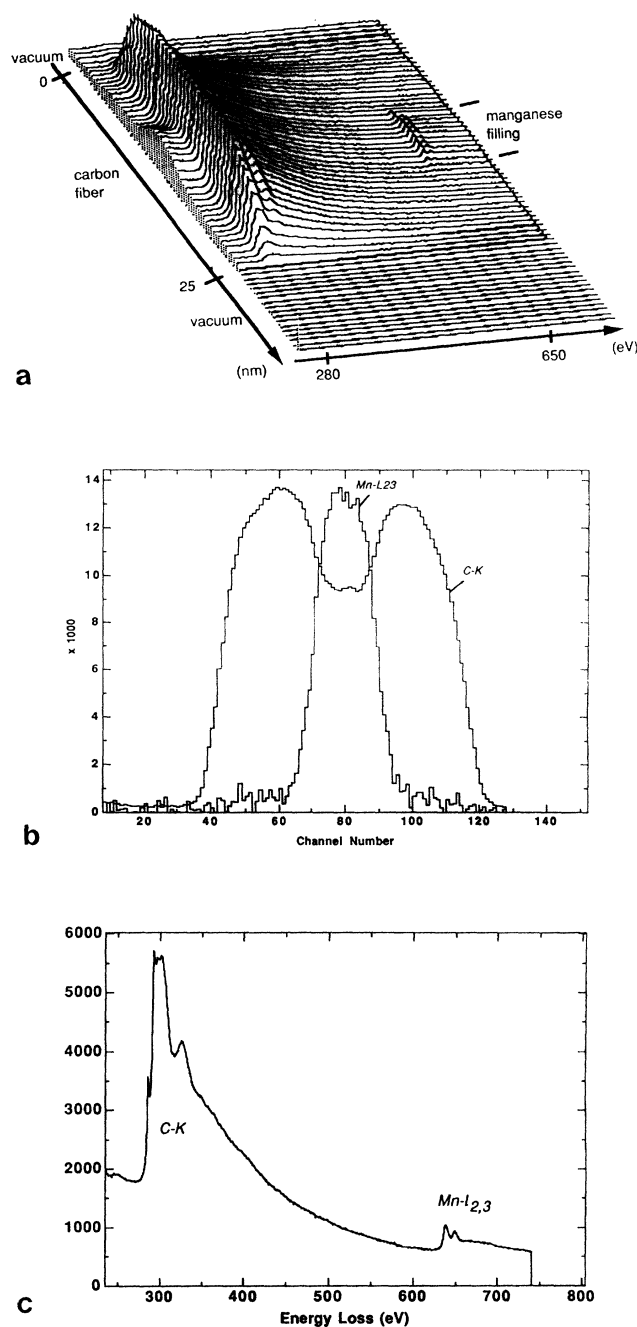

FIG. 4. (a) 2D plot of a line spectrum (128 spectra) as the probe beam scans across approximately 40 nm space from vacuum through a 25 nm fiber with filling and then to vacuum. Horizontal scale represents the energy-loss values. (b) The variation of intensity of the characteristic C-K and Mn-L edges as the beam is scanned across the fiber. The shape of the curves correlates well with an approximate cylindrical geometry of the fiber with an inside hollow and with a solid core of Mn filling. About 100 channels on the horizontal scale corresponds to 30 nm. (c) The electron energy-loss spectrum summed for all beam positions during acquisition. The carbon K (typical graphite) and Mn $L_{2,3}$ peaks are clearly seen and no other peak is detected.

The twisted morphology of the filaments is due to growth in the vapor phase compared to the perfectly straight carbon nanotubes which are grown with a template effect [20]. Also the much higher temperatures near the electrodes create better 3D ordering between layers in nanotubes compared to the filaments here which are formed among soot that condenses in the colder regions of the chamber. Many fibers have a good portion of the length filled and hence they would exhibit properties relating to a true composite material. To test any properties, the fibers have to be separated from the soot and Mn particles. This may be achieved by growing these endohedral fibers preferentially and in substantial amounts by fine tuning the conditions used during preparation.

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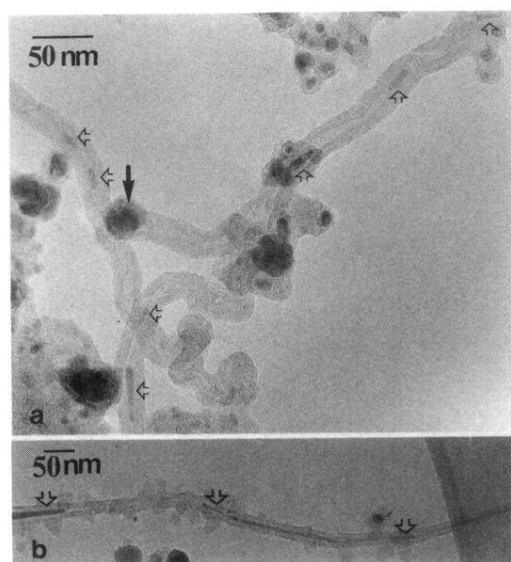[20] T. W. Ebbesen et al., Chem. Phys. Lett. **209**, 83 (1993).

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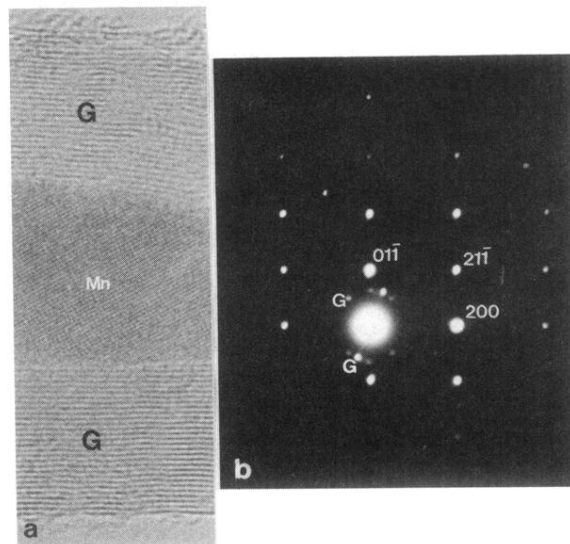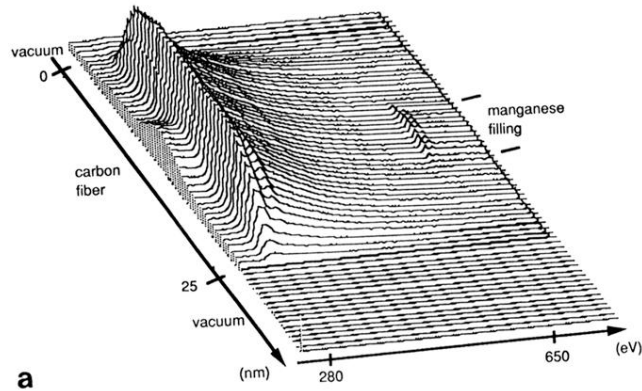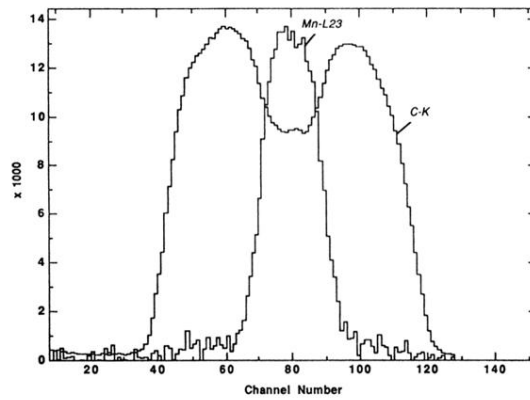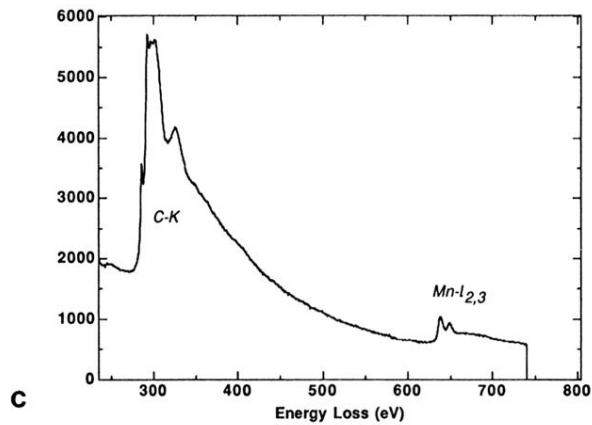
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