*J. Am. Chem. Soc.* **1994,** *116,* 397–398

## Encapsulation of Palladium Crystallites in Carbon and the Formation of Wormlike Nanostructures

Ying Wang

*Contribution no. 6599*
*Central Research and Development*
*DuPont Company, P.O. Box 80356*
*Wilmington, Delaware 19880-0356*

*Received October 25, 1993*

Since the discovery of carbon nanotubes[1,2] and large, onionlike, nested fullerenes,[3] several metals,[4,5] and metal carbides[6–8] have been included into these carbon nanostructures. Here I report the successful inclusion of cubic palladium crystals inside giant carbon clusters and the formation of novel wormlike carbon nanostructures (nanoworms). The head of the "worm", typically 20–50 nm in diameter, consists of palladium encapsulated in carbon, and the body of the "worm", several hundred nanometers in length, consists of many sections of carbon tubes with cone-shaped internal voids.

The technique used to generate carbon-encapsulated palladium is the familiar electric arc method reported before.[2,6] In an arc chamber filled with flowing 500 Torr of helium, a $^1/_2$-in.-diameter stationary carbon rod is connected to the negative electrode and a $^1/_4$-in.-diameter translatable carbon rod is connected to the positive electrode. The $^1/_4$-in.-carbon rod has a 2.7-mm hole drilled through. Before each experiment, the hole was filled with PdO/graphite cement paste and dried in an oven at 100 °C overnight. The wt % of PdO to carbon varies from 0.05% to 1%. The arc experiment was performed with 125–150 A of DC current, and the gap of the electrodes was maintained to be 1–2 mm.

After each arc experiment, the deposit formed at the tip of the negative carbon electrode was collected for analysis. Transmission electron microscopy (TEM) of the central portion of the deposit is shown in Figure 1. The micrographs reveal the presence of many wormlike carbon nanostructures, typically 20–50 nm in diameter and several hundred nanometers in length. Each wormlike structure consists of many sections of carbon tubes, with mostly cone-shaped internal voids. At the head of the wormlike structures, a material showing a darker TEM image is encapsulated inside the carbon shell.

Energy dispersive X-ray analysis of the head region indicates the existence of Pd in the material. Selected area electron diffraction (covering a circle of 400 nm in diameter) on a single nanoworm shows discrete diffraction spots. In addition to those expected from carbon,[1] several spots, corresponding to lattice constants of 2.36, 1.38, and 1.19 Å, can be observed. These spots are not symmetrically arranged and vary from picture to picture, depending on the orientation of the crystallite. The latter two lattice constants, 1.38 and 1.19 Å, can be identified with the (220) and (311) planes of cubic palladium crystals, respectively.[9] The 2.36-Å lattice constant, which is tentatively assigned to the (111) plane of Pd, is about 5% larger than that expected from (111) of Pd, 2.246 Å. Such uncertainty is not uncommon for small area electron diffraction, especially if defects exist in the crystallites. This assignment is confirmed by the X-ray diffraction data (Figure 2), which provide more precise measurements of the lattice constant. Peaks corresponding to lattice spacing of 3.418, 2.122, and 1.71 Å are due to carbon nanotubes and nested carbon clusters. The two additional peaks, at lattice spacing of 2.248 and 1.942 Å, match precisely with those expected from the (111) and (200) planes of cubic palladium crystals, respectively.[9] The observed electron diffraction and X-ray diffraction data cannot be attributed to PdO, and there is no known phase of palladium carbide.[10] I therefore conclude that a palladium nanocrystal is encapsulated in carbon as shown by the TEM images in Figure 1. Among the micrographs examined so far, Pd is not present in the triangular void, although there is no intrinsic reason why it should not be there.

Several additional observations on the wormlike nanostructures are summarized below. (1) The formation of these structures is extensive (Figure 1a), even though the palladium content in the starting anode rod is only 0.05%. (2) These wormlike structures are mostly observed in the core of the cathode deposit. Such structures are rarely seen in the shell of the deposit and are absent in the soot collected from the surface of the bell jar top. The soot contains palladium nanocrystals mixed with amorphous carbon. (3) On the basis of surveying several dozens of such nanoworms, I found that if the encapsulated palladium is regarded as the head of the "worm", then the tips of the cone-shaped internal voids *always point at the tail*, which does not contain palladium. This indicates that the encapsulated palladium is the seed for the growth of such structure. (4) Occasionally, one observes a nanoworm missing a palladium head (Figure 3). The appearance of a wormlike body with a cone-shaped internal void indicates that palladium crystallite was once present in the head. This shows that the carbon shell surrounding the palladium can be opened under certain conditions.

It is interesting to speculate on the possible growth mechanism of such wormlike nanostructures. Recall that a cone-shaped tip is a commonly observed morphology for carbon nanotubes.[1,2] A model of open-end growth of carbon nanotubes has been proposed before.[11] The growth starts with a nucleus, and the subsequent tube morphology depends on the formation of hexagonal, pentagonal, and heptagonal rings on the periphery of open tube ends. Hexagonal rings lead to the formation of straight tubes; pentagonal rings lead to a positive disinclination of the growth direction; and heptagonal rings lead to a negative disinclination of the growth direction. The closure of the tube and the formation of a cone-shaped tip is due to the presence of pentagonal rings.

The extension of this model can be used to explain qualitatively the growth of the nanoworms observed here. The cone-shaped internal void is formed by tube closure due to pentagonal rings. Each closure is followed by new growth from the outer layer which forms the next section. The presence of palladium seems to cause a more frequent appearance of the pentagonal ring and a more frequent tube closure. This periodical closure and regrowth eventually leads to the formation of a wormlike structure. However, the origin of the apparent periodicity is not clear. Also, the formation of such structures depends on the metal used. In the previous cases of metal-encapsulation,[4–8] no such structure has been seen. Recently, cobalt was used to catalyze the formation of single-wall carbon nanotubes.[12] Again, no wormlike structure was observed. Ferromagnetic metals such as Fe, Co, and Ni are commonly used catalysts for the growth of carbon fiber.[13] To the best of my knowledge, there is no report on the observation of nanoworms in these carbon fibers (see note at the end of the

---

(1) Iijima, S. *Nature* **1991**, *354*, 56–58.
(2) Ebbesen, T. W.; Ajayan, P. M. *Nature* **1992**, *358*, 220–222.
(3) Ugarte, D. *Nature* **1992**, *359*, 707–709.
(4) Ajayan, P. M.; Iijima, S. *Nature* **1993**, *361*, 333–334.
(5) Ugarte, D. *Chem. Phys. Lett.* **1993**, *209*, 99–103.
(6) Ruoff, S. R.; Lorents, D. C.; Chan, B.; Malhotra, R.; Subramoney, S. *Science* **1993**, *259*, 346–348.
(7) Seraphin, S.; Zhou, D.; Jiao, J.; Withers, J.; Loutfy, R. *Nature* **1993**, *362*, 503.
(8) Yosida, Y. *Appl. Phys. Lett.* **1993**, *62*, 3447.
(9) JCPDS-ICDD powder diffraction data base, 1990.
(10) *Binary Alloy Phase Diagrams*; Massalski, T. B., Ed.; The Materials Information Society: Metals Park, Ohio, 1990; Vol. 1, p 869.
(11) Iijima, S.; Ajayan, P. M.; Ichihashi, P. *Phys. Rev. Lett.* **1992**, *69*, 3100.
(12) Bethune, D. S.; Klang, C. H.; de Vries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, *363*, 605–607.
(13) Baker, R. T. K.; Harris, P. S. In *Chemistry and Physics of Carbon*; Walker, P. L., Jr., Thrower, P. A., Eds.; Dekker: New York, 1978; Vol. 14, p 83.

0002-7863/94/1516-0397$04.50/0

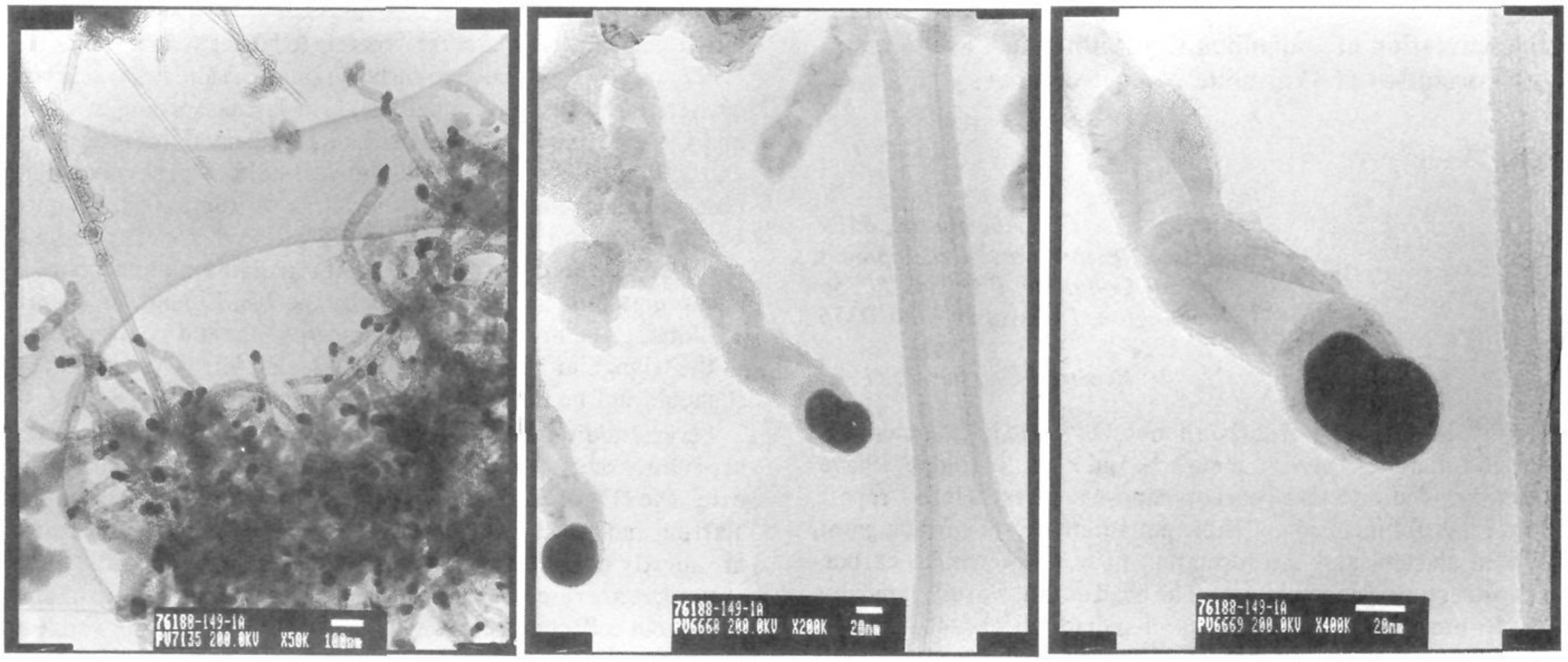

**Figure 1.** Electron micrographs of the core of the cathode deposits, showing many wormlike nanostructures with carbon-encapsulated palladium heads. (a, left) A magnification ratio of 125 000, (b, middle) a magnification ratio of 500 000, and (c, right) a magnification ratio of 1 000 000 showing the palladium head. Although the carbon shell looks amphorous in the micrographs, the electron diffraction and X-ray data show that it has the same lattice constants as the carbon nanotube and polyhedra. It is possible that the shell has some defects or is covered by other carbon which obscures the lattice image.

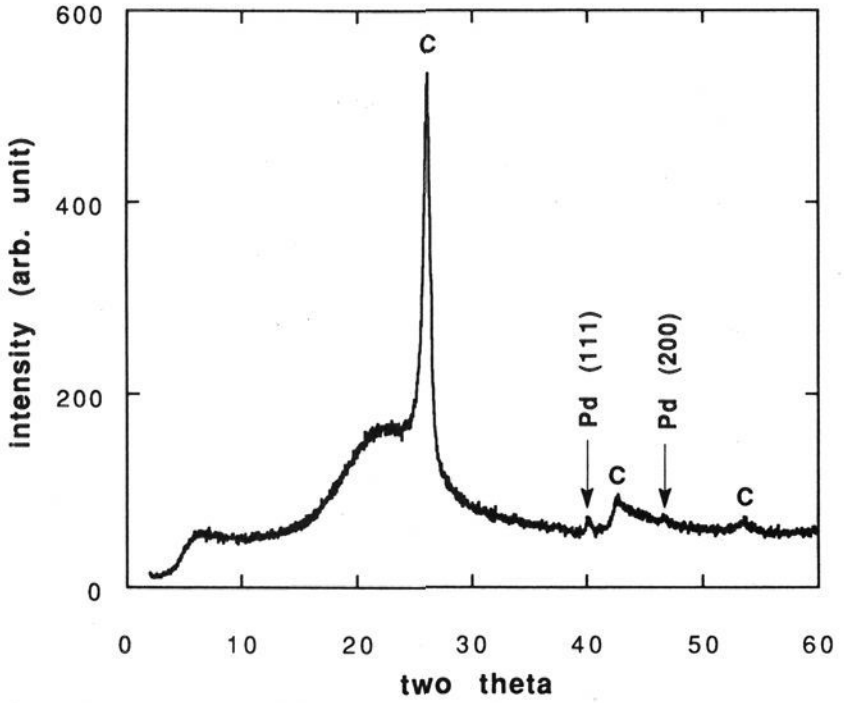

**Figure 2.** Powder X-ray diffraction data of the core of the cathode deposits, containing carbon-encapsulated palladium. Cu$\alpha$ radiation was used. The broad bumps at ~22° and ~6° are due to amphorous material of unknown nature.

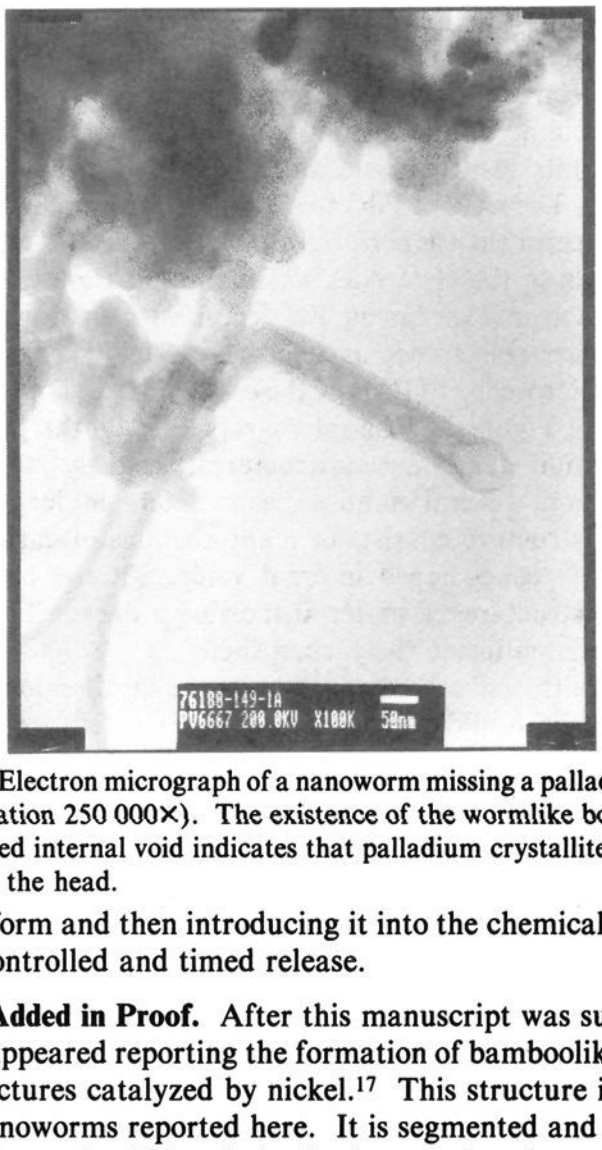

**Figure 3.** Electron micrograph of a nanoworm missing a palladium head (magnification 250 000×). The existence of the wormlike body with a cone-shaped internal void indicates that palladium crystallite was once present in the head.

paper). It should also be noted that not all of the organics in the graphite cement were driven out of the carbon rods. Their effects on the formation of nanoworms need to be studied. However, the fact that many other metals tried in this laboratory, prepared under the same conditions, did not generate nanoworms suggests that the effect due to organic impurities is small. The interaction between metal and carbon is clearly important but not understood.

Palladium is an important catalyst for many chemical reactions.[14] Carbon-encapsulated palladium can be released under certain conditions in the arc experiment (Figure 3). It has also been reported that electron beam irradiation[5] and chemical methods can be used to open the ends of carbon nanotubes and nanoparticles.[15,16] Therefore, encapsulation of palladium in carbon may provide a novel means of protecting palladium in its pristine form and then introducing it into the chemical reaction with a controlled and timed release.

**Note Added in Proof.** After this manuscript was submitted, a paper appeared reporting the formation of bamboolike carbon nanostructures catalyzed by nickel.[17] This structure is similar to the nanoworms reported here. It is segmented and periodic, but the internal void is tubular in shape rather than triangular as in the case of the nanoworm. There is no indication whether the formation of bamboolike structures is as massive as the formation of nanoworms observed here. Nickel does form a metastable carbide phase, while palladium does not.[10] The effect of metals on the formation of these exotic carbon nanostructures is clearly an interesting subject for future study.

**Acknowledgment.** I thank M. J. Van Kavelaar for performing electron microscopy and S. Harvey for preparing carbon rods for the arc experiments.

---

(14) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Berlin, 1980.

(15) Tsang, S. C.; Harris, P. J. F.; Green, M. L. H. *Nature* **1993**, *362*, 520–522.

(16) Ajayan, P. M.; Ebbesen, T. W.; Ichihashi, T.; Iijima, S.; Tanigaki, K.; Hiura, H. *Nature* **1993**, *362*, 522–525.

(17) Saito, Y.; Yoshikawa, T. *J. Cryst. Growth* **1993**, *134*, 154.