

# Formation of platinum nanorods and nanoparticles in uniform carbon nanotubes prepared by a template carbonization method

Takashi Kyotani,\* Li-fu Tsai and Akira Tomita

Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Sendai 980-77 Japan

## Template technique makes it possible to prepare Pt metal-filled uniform carbon nanotubes in which the metal is present as either nanorods or nanoparticles.

Carbon tubes at the nanometre level have now been characterized as a new carbon material. Specifically, metal-filled carbon nanotubes could have a variety of industrial applications, as reviewed by Freemantle.<sup>1</sup> Thus the preparation and application of such filled nanotubes are now becoming a very challenging area of research. Carbon nanotubes have been prepared thus far mainly using an arc-discharge evaporation technique<sup>2,3</sup> or by thermal decomposition of benzene vapour,<sup>4</sup> and there have been several attempts to insert metal into the tubes prepared by the arc-discharge evaporation technique.<sup>5–8</sup> Recently, we have prepared carbon nanotubes by a template carbonization technique using an anodic aluminium oxide film,<sup>9,10</sup> which has an array of parallel and straight channels with a diameter of nanometre level and has been often utilized as a template to synthesize nanomaterials.<sup>11–17</sup> The most striking feature of our carbonization method is that it allows one to produce monodisperse carbon nanotubes with uniform length, diameter and thickness. Here, we attempt to prepare Pt metal-filled uniform carbon nanotubes with the template method using an anodic oxide film.

An oxide film was prepared by electro-oxidation of an aluminium plate (purity 99.99%) at a cell voltage of 20 V in sulfuric acid. The diameter and thickness of the resulting film were 15 nm and 75 nm, respectively, and its channel diameter was found to be *ca.* 30 nm. The film was placed in a vertical quartz reactor. The reactor temperature was raised to 800 °C under N<sub>2</sub> flow and then propene gas (2.5% in N<sub>2</sub>) was passed through the reactor. The thermal decomposition of propene in the uniform straight channels of the anodic oxide film resulted in carbon deposition on the channel walls. After 3 h decomposition the reactor was cooled to room temp. and the film was taken out. Pt was loaded on this carbon-deposited film by the following evaporation method. The film was impregnated with an ethanol solution of hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) at room temp. for 3 h and then ethanol was evaporated at 80 °C under an N<sub>2</sub> flow with the film immersed in the solution. The reduction of chloroplatinic acid in the channels was performed by the following two methods; heat treatment at 500 °C under H<sub>2</sub> flow or stirring with an excess of a 0.1 M NaBH<sub>4</sub> aqueous solution at room temperature. After the reduction, the carbon-deposited film was washed with an excess of a 46% HF solution at room temp. to dissolve the anodic aluminium oxide template. As a result, a Pt metal/carbon nanotube composite was obtained as the insoluble fraction.

Fig. 1(a) and (b) show bright-field TEM images at different magnifications for the Pt/carbon tube composite prepared at 500 °C. These two images indicate the presence of uniform carbon nanotubes and their outer diameter and wall thickness can be estimated to be 30 nm and *ca.* 5 nm, respectively. Although some of the tubes are empty, the others are filled with many rod-like materials which are observed as dark images. The low-magnification TEM image [Fig. 1(a)] indicates that these nanorods are more abundant in the end of the tube hollows, where some of them are > 1 μm in length. Their structure was

investigated by electron diffraction and X-ray powder diffraction (XRD). Fig. 1(c) shows the electron diffraction pattern which was taken from the TEM image [Fig. 1(b)]. The pattern presents the diffraction from Pt metal crystallites as clear spots together with carbon 002 diffraction as a pair of strong arcs. Some of the spots from the fcc structure of Pt metal and carbon 002 arcs are labelled in the figure. This pattern confirms the dark material to be Pt metal. The appearance of the diffraction for Pt as clear spots, not as rings, indicates the high crystallinity of the Pt nanorods. The small number of these diffraction spots suggests the presence of only a few Pt crystallites in the area of Fig. 1(b). The XRD analysis also confirmed the reduction of chloroplatinic acid to Pt metal. From the peak width of the Pt(111) diffraction, the average crystallite size was calculated to be *ca.* 30 nm.

The TEM photographs of the composite reduced by NaBH<sub>4</sub> solution at room temp. are displayed in Fig. 2. Like the composites reduced at 500 °C, Pt metal is observed only in the carbon tube hollows and some tubes appear to be completely

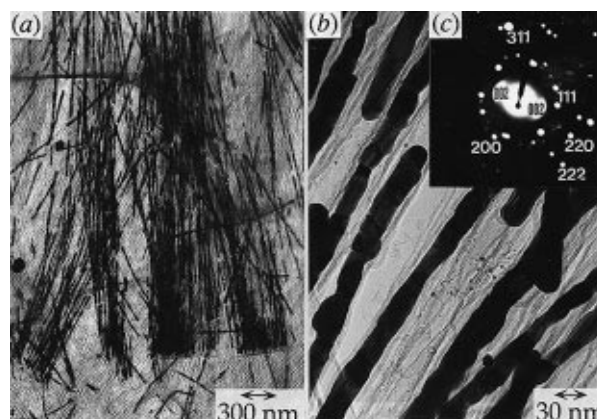


Fig. 1 (a), (b) TEM photographs for Pt/carbon tube composites reduced at 500 °C; (c) electron diffraction pattern taken from the TEM image (b)

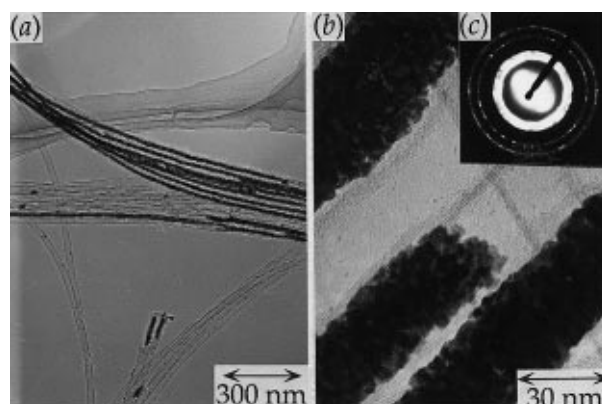


Fig. 2 (a), (b) TEM photographs for Pt/carbon tube composites reduced at room temp; (c) electron diffraction pattern taken from the TEM image (b)

filled with the metal. There is, however, some difference in microscopic features between the two Pt metals prepared at different temperatures [Figs. 1(b) and 2(b)]. The Pt metal reduced at room temp. appears to consist of very fine particles of size 2–5 nm, which is in good agreement with the calculated value from the XRD analysis. The electron diffraction pattern of the Pt metal gives further information on its structure. The pattern [Fig. 2(c)] exhibits a set of diffraction rings from Pt metal (these rings can be indexed [from the inside as] 111, 200, 220, 311 reflectance fcc Pt), together with a pair of carbon 002 arcs. It is noteworthy that the diffraction from Pt metal did not appear as clear spots, but as concentric rings, each of which consists of a large number of very small spots. This finding suggests that the metal reduced by NaBH<sub>4</sub> solution is comprised of many fine crystallites, which accords with the microscopic difference between the two types of Pt metal.

For the above two types of composites, Pt was loaded by the evaporation to dryness method. On the other hand, when the impregnated film was removed from the chloroplatinic acid solution and then dried, less Pt was loaded in the carbon tubes. Fig. 3 shows the bright-field TEM image of the composite prepared by this loading method, where the reduction of Pt was performed with NaBH<sub>4</sub> solution at room temp. The image does not reveal rod-like Pt metal, but rather, very fine Pt particles in the hollows. Some of Pt particles form agglomerates with each other and the size varies from 1 to 4 nm.

Although the carbon nanotubes prepared by our template technique are not structurally perfect, their length, diameter and

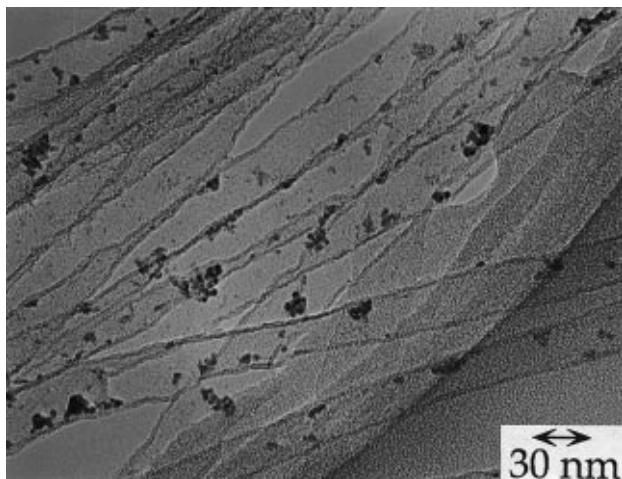


Fig. 3 Bright-field TEM image of Pt nanoparticles in carbon tubes

thickness are controllable and monodisperse. Here, by applying the template technique, we have succeeded in preparing Pt metal-filled uniform carbon nanotubes in which the metal is present as either nanorods or nanoparticles. It should be noted that no Pt metal was observed on the outside wall of the tubes. This is due to the preparation procedure, *viz.*, chloroplatinic acid as the Pt metal precursor was loaded into the carbon-deposited alumina film before dissolution of the alumina by HF; thus there is no other space for Pt to be loaded except within the channels.

We thank the High Voltage Electron Microscope Laboratory of Tohoku University for microscopical analysis. This study was partly supported by Special Coordination Funds for Promising Science and Technology from Science and Technology Agency, Japan, the Ministry of Education, Science, Sports and Culture of Japan (07650777) and the Mitsubishi Foundation.

#### Footnote

\* E-mail: kyotani@icrs.tohoku.ac.jp

#### References

- 1 M. Freemantle, *Chem. Eng. News*, 1996, **74**, 62.
- 2 S. Iijima, *Nature*, 1991, **354**, 56.
- 3 T. W. Ebbesen and P. M. Ajayan, *Nature*, 1992, **358**, 220.
- 4 M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi and H. W. Kroto, *J. Phys. Chem. Solids*, 1993, **54**, 1841.
- 5 P. W. Ajayan and S. Iijima, *Nature*, 1993, **361**, 333.
- 6 S. C. Tsang, Y. K. Chen, P. J. F. Harris and M. L. H. Green, *Nature*, 1994, **372**, 159.
- 7 R. M. Largo, S. C. Tsang, K. L. Lu, Y. K. Chen and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1995, 1355.
- 8 B. C. Satishkumar, A. Govindaraj, J. Mofokeng, G. N. Subbanna and C. N. R. Rao, *J. Phys. B: At. Mol. Opt. Phys.*, 1996, **29**, 4925.
- 9 T. Kyotani, L. Tsai and A. Tomita, *Chem. Mater.*, 1995, **7**, 1427.
- 10 T. Kyotani, L. Tsai and A. Tomita, *Chem. Mater.*, 1996, **8**, 2109.
- 11 W. Liang and C. R. Martin, *J. Am. Chem. Soc.*, 1990, **112**, 9666.
- 12 C. J. Brumlik and C. R. Martin, *J. Am. Chem. Soc.*, 1991, **113**, 3174.
- 13 J. D. Klein, R. D. Herrick II, D. Palmer, M. J. Sailor, C. J. Brumlik and C. R. Martin, *Chem. Mater.*, 1993, **5**, 902.
- 14 C. R. Martin, *Science*, 1994, **266**, 1961.
- 15 B. Xiaohua, L. Feiyue and R. M. Metzger, *J. Appl. Phys.*, 1996, **79**, 4866.
- 16 P. Hoyer, *Langmuir*, 1996, **12**, 1411.
- 17 R. V. Parthasarathy, K. L. N. Phani and C. R. Martin, *Adv. Mater.*, 1995, **7**, 896.

Received in Cambridge, UK on 17th December 1996; Com. 6/08439G