Nickel nanowires of 4 nm diameter in the cavity of carbon nanotubes

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Nickel nanowires of 4 nm diameter were formed in the cavity of carbon nanotubes with an inner diameter of 20 nm.

There has been an increasing interest in the fabrication of ferromagnetic metal nanowires in terms of their fundamental importance as well as potential application in magnetic recording technology. Recently, such nanowires have been often prepared by a template technique[1] that involves electrochemical deposition of metal into nanometer-wide channels of anodic aluminium oxide films,[2,3] polycarbonate track etched membranes[4,5] or nanochannel array glass.[6] The obtainable lowest diameter by such methods is restricted by the lowest attainable inner diameter of the nanochannels in the template materials. None of the nanochannels in the above host materials can easily reach an inner diameter of < 10 nm. Therefore, the template method does not allow the construction of ferromagnetic metal nanowires with a diameter of < 10 nm. Here we report a unique nickel nanowire formation by metal–organic chemical vapor deposition (MOCVD) in the cavity of carbon-coated nanochannels of anodic aluminium oxide film. The diameter of the nickel nanowires prepared by this method is uniformly 4 nm, which is much smaller than the inner diameter (*ca.* 20 nm) of the carbon-coated nanochannels.

Previously, we demonstrated that monodisperse carbon nanotubes with uniform size (length, diameter and thickness) can be prepared by the following template carbonization technique;[7,8] pyrolytic carbon deposition in the uniform and straight channels of anodic aluminium oxide film and then liberation of the carbon from the film by dissolving the template. With a similar method, but using a catalyst, Martin and coworkers prepared more highly crystallized carbon nanotubes.[9] Furthermore, by applying this template technique, we and then Martin *et al.* prepared platinum or iron-filled uniform carbon nanotubes in which the metal or metal oxide was present as nanorods or nanoparticles.[10–12] In this study, we attempted to insert nickel into carbon nanotubes. The previously described anodic oxidation[7,8] of an electropolished aluminium plate was used to prepare a porous anodic aluminium oxide film with a channel diameter of *ca.* 30 nm and the film diameter and thickness were 20 mm and *ca.* 75 μm, respectively. The film was subjected to carbon deposition by thermal decomposition of propene (1.2% in N_2) at 800 °C, which resulted in uniform coating of carbon on the channel walls. The resultant carbon-coated film was then subjected to metal–organic chemical vapor deposition (MOCVD) of nickelocene [$Ni(C_5H_5)_2$] in the following manner. Nickelocene was vaporized at 105 °C (corresponding to a vapor pressure of 0.6 kPa) and the film was exposed to the vapor with H_2 gas (50% in N_2) at a total flow rate of 100 cm^3(STP) min^{-1} at 275 °C for 0.25 or 1 h. After the MOCVD, the film was treated with 10 M NaOH solution at 150 °C in an autoclave for 6 h to dissolve the anodic aluminium oxide. Nickel/carbon nanotube composites were obtained as an insoluble fraction. The composites were observed with a transmission electron microscope (TEM; JEOL, JEM-2010) equipped with an energy dispersive X-ray spectrometer (Noran, 644G3SES).

Fig. 1(a) shows a bright field TEM image of the nickel/carbon nanotube composites prepared by MOCVD for 1 h. The image exhibits a carbon nanotube with a diameter of *ca.* 30 nm, containing a single nanowire of 500 nm in length and 4 nm in diameter. Fig. 1(b) shows the electron diffraction pattern taken from the nickel/carbon nanotube composite [Fig. 1(a)]. The pattern presents a pair of arcs from the carbon (002) reflection. In addition to the reflection from the carbon tube, two pairs of sharp diffraction spots were observed, which can be indexed as (111) and (222) reflections from fcc nickel metal. Apart from the sharp spots, there are several spots from nickel metal (220) and (331) reflections. An energy dispersive X-ray spectrum taken from this nanowire confirms the presence of nickel with no signal corresponding to oxygen. Both the diffraction pattern and elemental analyses suggest that the nanowire is pure nickel metal rather than a nickel compound. The appearance of the nickel (111) and (222) reflections not as a ring, but as a pair of symmetrical spots, indicates high orientation of the (111) planes in the nickel nanowire [Fig. 1(a)]. Judging from the positions of (111) and (222) spots, we can conclude that the (111) planes run parallel to the axis of the nickel wire. This was further confirmed by the lattice fringe image discussed below.

Fig. 2 shows a high resolution TEM image of a nanowire-containing carbon nanotube prepared under the same conditions as in Fig. 1(a). In this image, the lattice fringes of the nanowire which are located near the inner wall of the carbon nanotube are clearly observed and the lattice planes are parallel to the wire axis. The regular spacing of the observed lattice planes was 0.20 nm, which corresponds to the separation of (111) planes of fcc nickel metal. For all the nanowires we observed in this study, such preferable orientation of (111) planes was found without any clear grain boundaries. This accords with the result of the electron diffraction [Fig. 1(b)]. From these findings, we concluded that each of these nickel nanowires is a slender single crystal.

In order to examine the formation of nickel nanowire at an early stage, we carried out the MOCVD for a shorter time, *i.e.* 15 min. We observed many nickel nanowires in the cavity of carbon nanotubes as shown in Fig. 3. In some cases, short nanowires are present at an angle to the tube axis. The length of

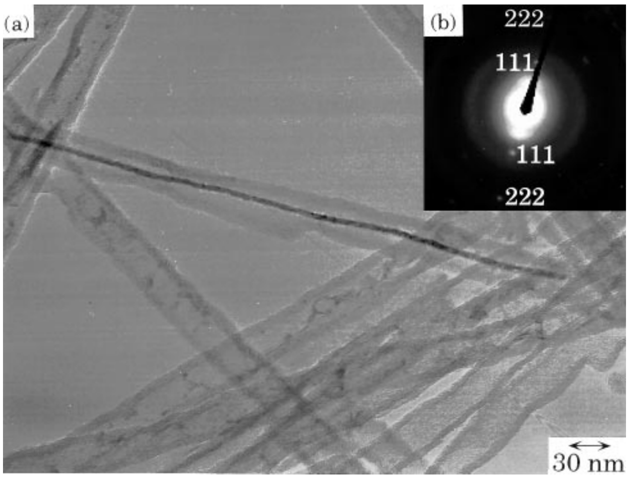

Fig. 1 (a) Low-magnification TEM image of a nickel/carbon nanotube composite prepared by MOCVD for 1 h at 275 °C. (b) Electron diffraction pattern taken from the nanowire-containing carbon nanotube (a).

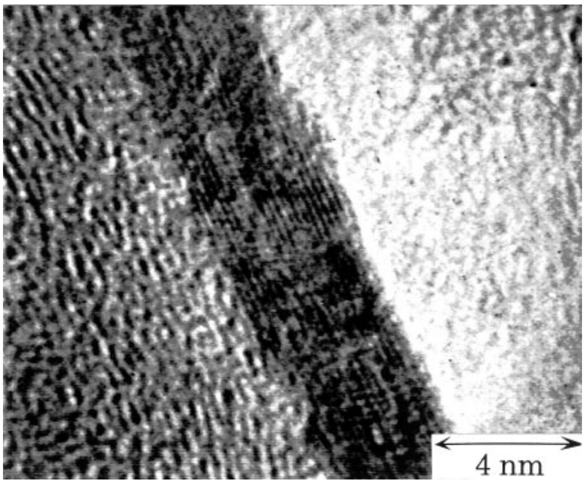

Fig. 2 High-resolution TEM image of a nickel wire near the inner wall of carbon nanotubes. The carbon nanotube/nickel nanowire composites was prepared by MOCVD for 1 h at 275 °C.

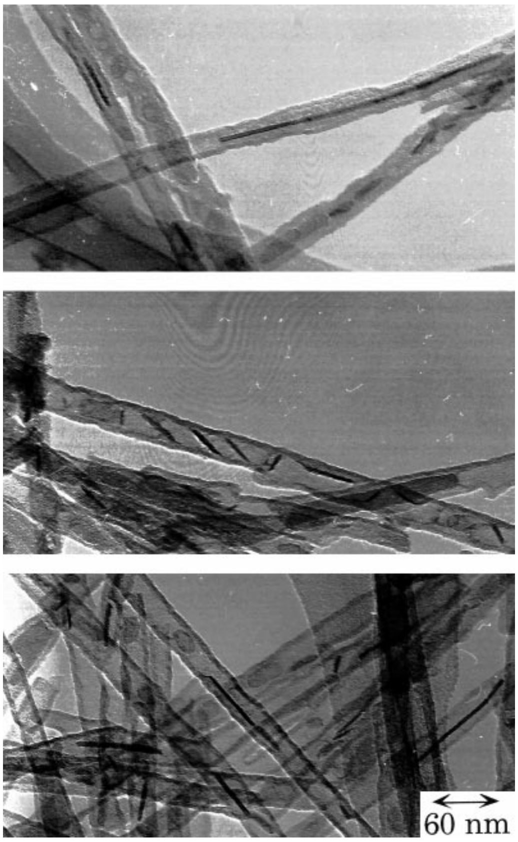

Fig. 3 Bright field TEM images at different areas for carbon tubes/nickel nanowire composites prepared by MOCVD for 15 min at 275 °C.

the nanowires varies from ten to a few hundred nm and the average length is less than that in Fig. 1(a). It was found that the nanowire diameter is rather uniform at *ca.* 4 nm irrespective of the MOCVD time period. This finding suggests preferred nanowire growth toward the direction parallel to (111) plane.

Among all the tubes we have examined with TEM, more than 50% of the tubes contained nickel nanowires with a uniform diameter of 4 nm. However, we did not observe any nanowires in the cavity of carbon nanotubes near their open ends. This implies that the growth of nickel nanowires occurred inside the carbon-coated nanochannels. Even though the nickel metal was formed in the nanochannels, the diameter of the resultant nanowires was less than the inner diameter of the nanochannels. At the present moment, we do not have a reasonable explanation for the formation of such thin nanowires, but we presume that the coated carbon plays some role in producing them.

The template method is considered to be a promising approach for the fabrication of metal nanowires of very small size.[2–6,13] In this method, the obtainable diameter of nanowires is, however, regulated by the inner diameter of the nanochannels in the template materials. To the best of our knowledge, the formation of metal nanowires with diameters smaller than that of the template has not been previously reported. Another important feature in our method is that nickel nanowires are always evident as encapsulated nanowires in the hollow interiors of uniform carbon nanotubes. Since metal-filled carbon nanotubes could have a variety of industrial applications,[14] there have been many attempts towards the production of carbon nanotubes filled with metal or metal compounds as nanowires.[15–20] However, as stated above, the diameter of the nanowires is always the same as the inner diameter of carbon nanotubes. Thus, the nanowire formation we have discovered here is a quite unique phenomenon and can provide a novel methodology for future nanofabrication technology.

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