Purification of rhodium-filled carbon nanotubes using reversed micelles

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A method for the selective removal of material from the outside of filled carbon nanotubes is exemplified for rhodium trichloride filled tubes: the purification proceeds by washing with the reversed micelle mixture, dodecylammonium propionate (dap)-solubilized water in benzene; subsequent treatment of the nanotubes containing rhodium trichloride with H_2 at 500 °C for 5 h gives nanotubes filled with discrete crystals of rhodium metal and no metal crystals were detected exterior to the nanotubes.

Theoretical studies on carbon nanotubes suggest that the introduction of foreign materials into hollow nanotube cavities may have interesting effects on the physical and electronic properties of the encapsulated materials.[1–5] It is predicted that filled nanotubes may find practical uses as nanowires, composites and novel catalysts. The procedures used to fill carbon nanotubes, however, result in a large amount of material being deposited on the outside of the nanotubes. The presence of this external material limits the evaluation of properties of the filled nanotubes. Previous attempts to remove this material, for example by washing, resulted in the removal of the encapsulated materials from the internal cavity.[6] Here we describe a method of purification using reversed micelles in non-polar solvents.

Carbon nanotubes were produced by the arc-discharge method and opened by treatment with refluxing azeotropic nitric acid (*ca.* 10 h) as previously described.[4] The opened carbon nanotubes were stirred with a concentrated, aqueous solution of rhodium trichloride. The resulting solid material was allowed to settle, pipetted onto glass filter paper and oven-dried overnight at 60 °C. The rhodium trichloride was then reduced to rhodium metal by heating at 550 °C under a continuous stream of H_2 for 4.5–6.5 h.

Examination of the reduced sample by HRTEM revealed that approximately 70% of the opened nanotubes were filled with discrete crystals of rhodium metal. The overall yield of filled nanotubes was estimated by the visual inspection of portions of the sample using TEM. The absence of detectable chlorine in the sample was confirmed by analytical energy dispersive spectroscopy (EDS). XRD data also support the complete conversion of initial rhodium material in the bulk sample to rhodium metal. Fig. 1 shows an HRTEM micrograph of encapsulated crystallites of rhodium, where the observed lattice fringes of the largest crystal of 2.20 ± 0.05 Å, correspond to the spacing between the (111) planes of rhodium metal (lit.,[7] 2.196 Å). In this micrograph, the labels 1 and 2 indicate where pentagons and heptagons, respectively, have been incorporated into the hexagonal network causing bends in the body of the tube.[8] The size and shape of the encapsulated rhodium particles are varied, with both small, spherical and longer, ellipsoidal crystallites being observed. The spherical crystallites are more common and, unlike the ellipsoidal crystallites, do not fill the entire diameter of the inner cavity. The near spherical nature of the rhodium crystals whose diameters are smaller than the diameter of the internal cavity presumably reflects the high surface tension of rhodium metal. The ellipsoidal shapes of the large particles, whose diameters if spherical would be greater

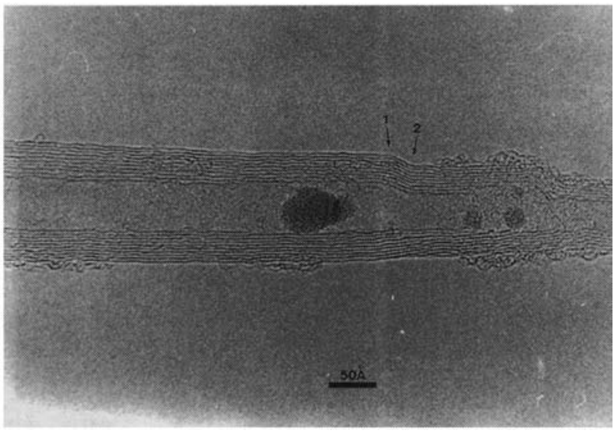

Fig. 1 HRTEM image of typical crystallites of rhodium metal carbon contained with a nanotube. The fringes of 2.20 ± 0.05 Å measured for the large particle correspond to the distances between the (111) planes of rhodium metal (lit.,[7] 2.196 Å).

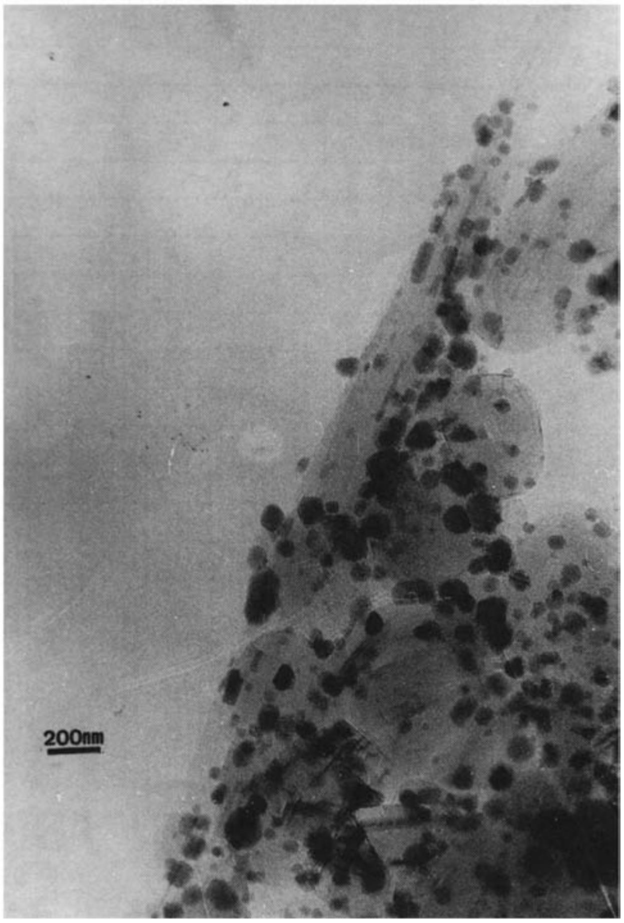

Fig. 2 TEM micrograph showing the presence of rhodium crystallites located on both the inside and the outside of carbon nanotubes

than the internal diameter of the nanotubes, must reflect the size restriction imposed by the carbon walls.

The TEM study also revealed a large number of spherical metal particles deposited outside the carbon nanotubes as shown in Fig. 2. Attempts to remove the external rhodium material, prior to hydrogen reduction, by washing with water resulted in removal of rhodium material from both inside and outside the nanotubes. We searched for a washing medium which would be too bulky to enter into the interior of the nanotubes and for this reason chose to explore the reversed micelle medium formed from dodecylammonium propionate[9] (dap)-solubilized water in benzene $\{[\mathrm{dap}] = 0.512\ \mathrm{M}, [\mathrm{H_2O}] = 0.11\ \mathrm{M}\}$. The critical micelle concentration (cmc) of dap was $(3\text{–}7) \times 10^{-3}\ \mathrm{M}$. After the dap/benzene/water solution had reached equilibrium, 200 mg of unpurified rhodium material filled nanotubes was added. After stirring for 3 days at 30 °C, the nanotubes were isolated by cannula filtration and calcined in a tube furnace at 500 °C under H_2 for 5 h.

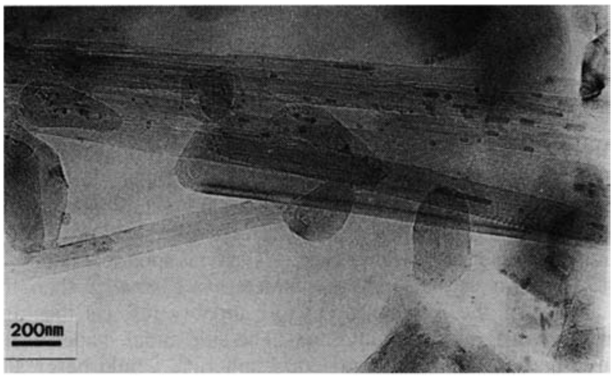

Fig. 3 TEM micrograph of rhodium-filled nanotubes after removal of the externally located rhodium particles by treatment with a reverse micellar solution

HRTEM investigations of the nanotubes showed rhodium metal crystals to be present inside the nanotubes with no crystals exterior to the nanotubes being detected (Fig. 3). Elemental analysis results, obtained after treatment with the reverse micelle solution, show a rhodium content of *ca.* 0.25%, as compared to *ca.* 2% for the unwashed samples.

In conclusion, we have shown that washing with a bulky micellar medium can cause the selective removal of soluble material exterior to filled nanotubes, whilst leaving the encapsulated material essentially unchanged. Studies on the catalytic and physical properties of the rhodium-filled nanotubes are in progress.

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