

Filling Carbon Nanotubes with Small Palladium Metal Crystallites: the Effect of Surface Acid Groups

R. M. Lago, S. C. Tsang, K. L. Lu,† Y. K. Chen and M. L. H. Green

The Catalysis Centre, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR

The filling of carbon nanotubes with palladium metal crystallites is described and it is shown that when the carbon nanotube samples are opened using nitric acid, surface acid groups (CO₂H and OH) are present on both the nanotubes and nanoparticles and these interact strongly with palladium ions: ultrasound pre-treatment of the carbon nanotube samples prior to the oxidation with nitric acid increases the number of these groups.

The carbon nanotubes discovered by Sumio Iijima¹ can have their end caps selectively removed by treatment with CO₂,² O₂,³ and (very efficiently) nitric acid.⁴ The opened tubes may be partially filled with certain metal oxides.⁴ Here, we present evidence for surface acid groups (CO₂H and OH) on tube samples opened using nitric acid and their role in the filling of nanotubes with small palladium metal crystals.

Closed nanotubes were prepared by the arc vaporization method.² TEM examination of the nanotube-rich carbon distillate showed it to consist of closed nanotubes (*ca.* 30%) with the remainder being nanoparticles: this carbon mixture is designated **C**-tubes. Standard samples of opened and dried nanotubes were obtained by suspending a sample of **C**-tubes in refluxing nitric acid for 24 h. The opened tube samples were washed thoroughly with distilled water and dried in air at 100 °C. TEM examination of the sample showed that more than 90% of the tubes were selectively opened in the cap region. These opened tubes samples are designated as **E**-tubes and also contain the nanoparticles.

The presence of a substantial concentration of surface acid functionalities on the **E**-tubes has been demonstrated by acid–base titration[‡] and by temperature-programmed decomposition (TPD) experiments.[§] The data are consistent with a concentra-

tion of surface acid groups of *ca.* 1.0×10^{20} acid sites per g. The proposal of the presence of surface acid groups, mainly carboxylic and phenolic, on **E**-tubes is supported by previous studies on acid-oxidised graphite and amorphous carbons which indicate the presence of *inter alia* CO₂H and OH groups.^{5–7} Crystalline graphite treated with nitric acid under the same condition used for the **E**-tubes showed a lower concentration of acid sites (*ca.* 5.3×10^{19} sites per g).

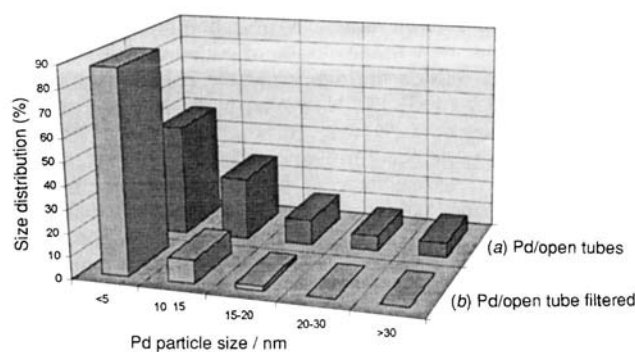


Fig. 2 (a) Pd-tubes, 10% *m/m* Pd, *d* = 20 nm. (b) Pd-tubes, pre-concentrated and dried with pressed filter papers, 2.1% *m/m* Pd, *d* = 3.3 nm.

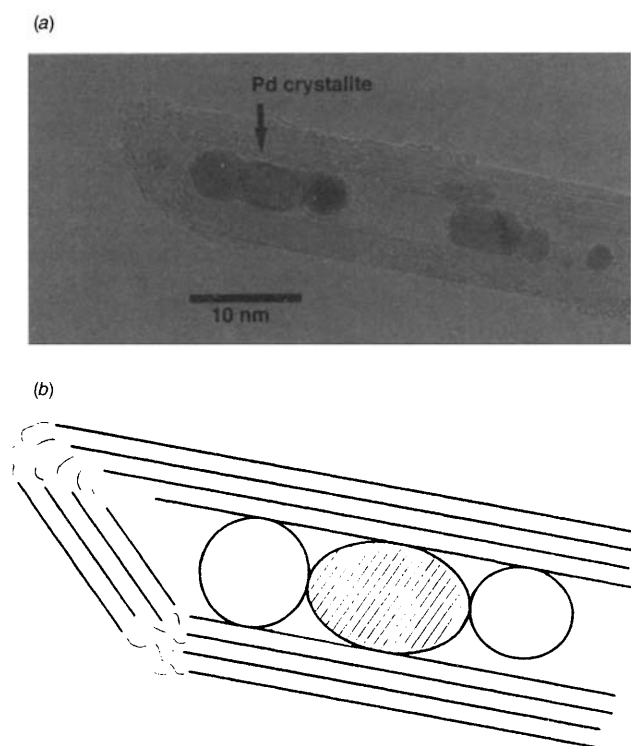


Fig. 1 (a) HRTEM of Pd-tubes showing palladium crystallites in a nanotube, Pd (111) lattice fringes of 0.226 ± 0.005 nm (lit. *d* = 0.2245 nm) can be clearly seen on original photographic prints. The angle of the (111) plane with respect to the tube axis varies with individual crystals. (b) A tracing of the (111) layer planes is provided for clarity.

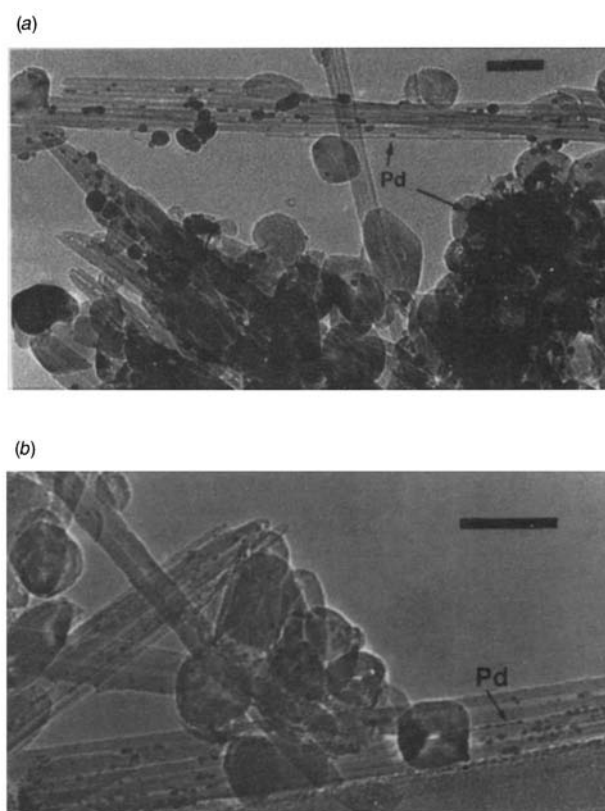


Fig. 3 (a) TEM image of Pd-tubes. (b) TEM image of Pd-tubes after drying with pressed filter paper. Scale bar = 50 nm.

Palladium metal filled nanotubes (**Pd-tubes**) have been prepared from **C-tubes** (1.0 g) using nitric acid (20.0 g) containing 0.1 g of Pd(NO₃)₂ and the same procedure as for **E-tubes**. After draining the excess of nitric acid solution the sample was dried in air and then reduced using H₂ at 250 °C. A HRTEM picture of palladium single crystals in a **Pd-tube** sample is shown in Fig. 1 where lattice fringes corresponding to a Pd (111) layer separation of 0.226 ± 0.005 nm can be seen clearly. Particle size counting from TEM micrographs revealed that 48% of the metal particles were smaller than 5 nm in diameter and the smaller particles were mainly found inside the nanotubes [Fig. 2(a)]. The TEM study showed that there were also large palladium particles deposited outside the carbon nanotubes [Fig. 3(a)]. The average particle size (diameter) of the palladium crystals assuming spherical shape, determined by the methods of CO titration⁷ and by the broadening of the Pd (111) peak at 40° ($d = 0.2245$ nm) in the X-ray powder diffraction (XRD) measurements,⁸ was 20 nm.

The presence of these large particles external to the tubes reflects an incomplete separation of the nitric acid palladium nitrate solution from the freshly prepared **Pd-tube** sample. An attempt to remove the exterior palladium material by washing the dried **Pd-tubes** with water (30 ml) before the hydrogen reduction resulted only in the elution of palladium nitrate from both inside and outside the tubes and the palladium loading decreased from 10 to 0.3%. However, if the HNO₃-PdNO₃-**C-tubes** product mixture was concentrated under reduced pressure until a paste was formed which was then placed on a filter paper, and excess solvent then removed by pressing several filter papers onto the top of the residue, then the palladium content was only reduced from 10 to 2.2% *m/m*. After hydrogen reduction a TEM study showed an average palladium particle size of 3.3 nm with 88% of the palladium particles being smaller than 5 nm, and there were only traces of large external palladium particles [Figs. 2(b) and 3(b)].

We have also studied the absorption of palladium ions from aqueous solution using opened tube samples formed from **C-tubes** which had undergone a prior ultrasound treatment (**SE-tubes**). Sonication of **C-tubes** by high energy ultrasound[¶] readily creates small local defects in the tubes, including buckling, bending and lattice dislocations on the surface.⁹ Indeed, extended exposure to ultrasound can destroy both the

nanotubes and the nanoparticles. TPD study shows that the **SE-tubes** have a higher concentration of acid sites compared to **E-tubes** (Table 1). The **SE-tubes** were filled with palladium, as described for **Pd-tubes**, and dried with filter papers. The resulting **SPd-tubes** had 3.0% *m/m* of palladium, and a reduced average particle size of 2.6 nm.

The adsorption equilibria between **E-tubes** and a range of metal ions in aqueous solutions have been studied. In a typical experiment a sample of **E-tubes** (27 mg) was treated with a solution of palladium nitrate (10 ml at 60 ppm), and after stirring for 20 h the sample was filtered and sucked to dryness. The concentration of the palladium ions in the filtrate was determined by ICP analysis. The data for the absorption of all the various metal ions onto **E-carbon** are given in Table 2. They show a strong correlation of the uptake of the metal ions with the stability constants for the complex formation of the same metal ions with carboxylate and related ligands. Palladium ions are the most strongly absorbed. It may be noted that there is a very good linear relationship of the amount of surface acid groups on the graphite, **E-tubes** and **SE-tubes** with the amount of palladium ions absorbed (correlation coefficient = 0.9925). This suggests that each surface acid site corresponds to one palladium atom.

In conclusion, we have prepared pure palladium metal crystallites of nano-dimensions on the outer and inner surfaces of opened nanotubes. There are acidic groups present on the surfaces of the nanotubes and nanoparticles of the **E-tubes** samples which can bind palladium ions strongly.

We wish to thank the CNPq (Brazilian Government) and the British ORS Award (to R. M. L.).

Received, 18th April 1995; Com. 5/02423D

Table 1 Surface acid groups determined by TPD

Material	Acidity ^{†,§} (acid sites per g)
Closed nanotubes	< 2.0 × 10 ¹⁸
Graphite/HNO ₃	5.3 × 10 ¹⁹
E-tubes	1.1 × 10 ^{20§}
	1.7 × 10 ^{20‡}
Sonicated and opened SE-tubes	1.3 × 10 ²⁰

Table 2 Amount of metal ions adsorbed from a solution on opened nanotubes and stability constants^a for the complex with different acid containing ligands (K_1) MeCO₂⁻ and (K_2) HO₂C-CO₂^{-11,12}

Metal ion	mmol of metal per g of nanotube	K_1 /mol l ⁻¹	K_2 /mol l ⁻¹
Pd ²⁺	0.029	4.80	8.72
Cu ²⁺	0.015	2.22	4.50
Co ²⁺	0.011	1.46	3.20
Ni ²⁺	0.010	1.43	3.80
Fe ²⁺	0.006	1.40	2.30
Pr ³⁺	0.007	2.01	—
UO ₂ ⁺²	0.005	2.61	6.00

^a Stability constant: $K = [M-L]/[M][L]$.

Footnotes

† Permanent address: Institute of Chemistry, Academia Sinica, Taipei, Taiwan.

‡ In a typical experiment a sample of **E-tubes** (heated to 120 °C under vacuum for 4 h) was suspended in 20–100 ml of sodium hydroxide (0.001 mol dm⁻³) overnight and the mixture was titrated with hydrochloric acid (0.001 mol dm⁻³) using methyl orange as indicator.

§ A sample of **E-tubes** was heated from ambient temperature to 900 °C at 5 °C min⁻¹ under a nitrogen stream and quantitative GC analysis used to monitor the formation of CO and CO₂.

¶ The sonication of the nanotubes prior to nitric acid treatment was carried out using a high energy sonication horn (Heat Systems Ultrasonics W-375) for 30 min in a suspension of closed tubes (1.0 g) in 20 ml of deionised water. The delivery power was estimated to be 17 W by calorimetric measurements.¹⁰

References

- S. Iijima, *Nature*, 1991, **354**, 56.
- S. C. Tsang, P. J. F. Harris and M. L. H. Green, *Nature*, 1993 **362**, 520.
- P. Ajayan, T. W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki and H. Hiura, *Nature*, 1993, **362**, 522.
- S. C. Tsang, Y. K. Chen, P. J. F. Harris and M. L. H. Green, *Nature*, 1994, **372**, 159.
- H. P. Boehm, E. Diehl, W. Heck and R. Sappok, *Angew. Chem.*, 1964, **76**, 742.
- D. J. Suh, T. J. Park and S. K. Ihn, *Ind. Eng. Chem. Res.*, 1992, **31**, 1849.
- C. P. Burguete, A. L. Solano, F. R. Reinoso and S. M. Lecea, *J. Catal.*, 1989, **115**, 98.
- Solid State Chemistry Techniques*, ed., A. K. Cheethan and P. Day Oxford Scientific, Oxford, 1987, p.80.
- K. L. Lu, R. M. Lago, S. C. Tsang, Y. K. Chen, P. J. F. Harris and M. L. H. Green, unpublished observation.
- T. J. Mason, *Practical Sonochemistry*, Ellis Horwood, Chichester, 1991, p. 46.
- A. E. Marthel and R.M. Smith, *Critical Stability Constants*, vol. 3, Plenum, New York, 1977.
- D. D. Perrin, *Stability Constants of Metal Complexes*, IUPAC Chemical Series, vol 22, Pergamon, New York, 1979.