Filling of Carbon Nanotubes with Silver, Gold, and Gold Chloride

Andrew Chu,† Jessica Cook,† Rufus J. R. Heesom,† John L. Hutchison,‡ Malcolm L. H. Green,*,† and Jeremy Sloan†

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK, and Department of Materials, Parks Road, Oxford OX1 3PH, UK

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The synthesis of carbon nanotubes filled with silver, gold, and gold chloride is described. The resulting materials have been studied by high-resolution electron microscopy, X-ray powder diffraction, and energy-dispersive spectroscopy (EDS). The EDS data were obtained using a high-resolution electron microscope equipped with a field emission gun which allowed for X-ray analytical data to be obtained on individual particles located within the carbon nanotubes using a 0.7 nm probe.

Introduction

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. Several different approaches to the problem of filling nanotubes have been taken. Early work on bismuth and lead relied upon capillary action to pull liquids into the hollow nanotube cavities.[6,7] Certain lanthanide and transition-metal carbides have been trapped in nanotube cavities by the arc-evaporation of metal-doped carbon rods.[8−13] Metal nitrates were encapsulated by refluxing closed nanotubes in HNO_3 in the presence of the soluble nitrates.[5] Herein we describe the filling of carbon nanotubes with Ag and Au crystallites via a two-step method and the subsequent characterization of the nanotube.

Results and Discussion

A two-step method employing wet chemistry techniques was used to prepare carbon nanotubes filled with Ag and Au metal. The nanotubes previously opened by oxidation with HNO_3[5] were stirred overnight with a concentrated aqueous solution of either $Ag(NO_3)$ or $AuCl_3$. After concentration of the mixture and separation of the resulting tube samples from the excess of the solution, they were calcined in a furnace at 250 °C (for $Ag(NO_3)$) and at 160 °C (for the $AuCl_3$ sample). At these temperatures, $Ag(NO_3)$ (>160 °C) and $AuCl_3$ are decomposed to give the elements.[14] $AuCl_3$ decomposed at temperatures less than 150 °C to give AuCl which dissociates into the elements at higher temperatures.[14]

Although it has been reported that the yields of filled tubes using a two-step preparation are lower than those obtained using a one-step method, in the cases of Ag and Au, we observed a relatively high percentage of opened nanotubes being filled with the metals (∼70%).[5,6] The overall yields of filled nanotubes were roughly estimated by the visual inspection of portions of the sample using TEM.

The annealed Ag and Au samples were examined by high-resolution transmission electron microscopy (HRTEM), analytical energy-dispersive spectroscopy (EDS), and X-ray powder diffraction (XRD). Preliminary HRTEM images of the Ag sample showed that small crystallites of Ag metal were present inside and outside of the carbon nanotubes. A typical carbon nanotube containing several small Ag crystals is shown in Figure 1. The crystals observed in Figure 1 range in size from 35 to 85 Å. An HRTEM image of the tip of a nanotube in which an unusually large single crystal of Ag (190 Å) is encapsulated is shown in Figure 2. This Figure 2 also shows a smaller crystal of Ag located on the outside wall. The *d* spacing of the lattice for the encapsulated large crystal and the small spherical crystal was measured to be 2.361 ± 0.05 and 2.369 ± 0.05 Å, respectively, which both correspond to the reported value for the {111} plane of 2.359 Å.[15]

Figure 3 shows the HRTEM image of a small gold crystal located within a nanotube which, assuming a perfect sphere, is estimated to contain 3000 ± 200 atoms of gold. The measured regular *d* spacing of the observed planes of the lattice is 2.325 ± 0.05 Å, which corresponds to the {111} planes of Au (lit. value = 2.355 Å).[15] Most of the gold encapsulated within the carbon nanotubes was found to consist of these spherical crystallites of

† Inorganic Chemistry Laboratory.
‡ Department of Materials.
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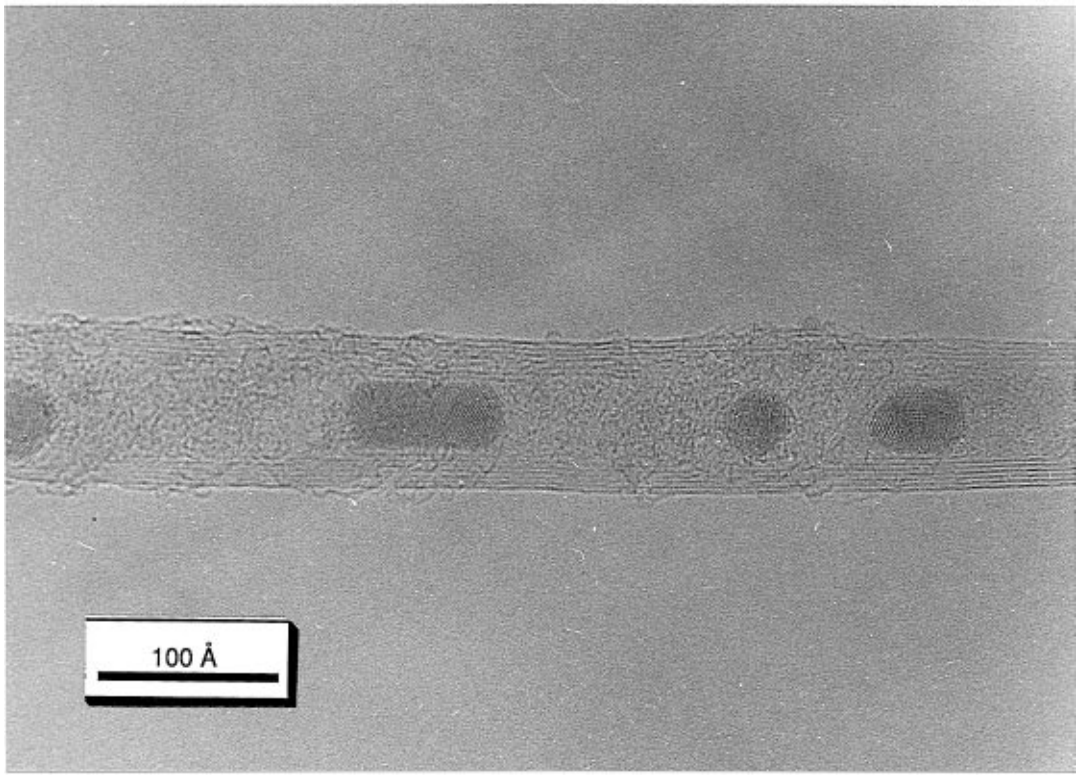

Figure 1. HRTEM image of a carbon nanotube filled with small, spherical Ag crystals.

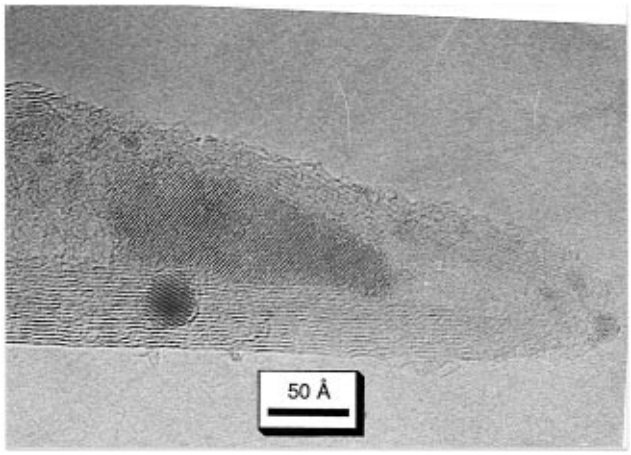

Figure 2. HRTEM image of large crystal of Ag encapsulated within the tip of a nanotube. A representative smaller Ag crystal located on the outside of a carbon nanotube is also observed.

gold ranging from 10 to 50 Å in diameter. Furthermore, a few of the carbon nanotubes were found to be filled with small amounts of AuCl. These reflect the incomplete reduction of the initial gold(III) chloride. In one example, a sample of AuCl was observed as a trilayer coating located on the outside of the carbon nanotubes as shown in Figure 4. In this coating the observed lattice fringes have a spacing of 3.35 ± 0.05 Å which correspond to the {200} planes of AuCl.[15] Further annealing of the initial gold containing sample under H_2 at 300 °C resulted in the complete conversion of the AuCl to Au metal as confirmed by XRD measurements.

Another interesting feature of the sample shown by the solid arrow in Figure 3 is the presence of amorphous gold chloride material intercalated into the gaps in the nanotube wall. The presence of both gold and chlorine was shown by EDS scans. Ajayan et al.[16] observed a similar intercalation behaviour for V_2O_5-filled nanotubes.

We have studied the carbon nanotubes filled with gold using a recently developed high-resolution TEM equipped with a field emission gun (FEG) as a source. This has a minimum probe size of 0.7 nm and therefore makes it possible to obtain analytical EDS data on individual particles located within nanotube cavities with a very high degree of spatial discrimination. In Figure 5b, an EDS spectrum of the Au particle (Figure 5a) is presented. The strong Cu peaks are due to the copper grid supporting the lacey carbon film. Only a small amount of the carbon present in the walls of the nanotube is observed relative to gold. It is an excellent example of the high spatial resolution of the FEGTEM since no chlorine was detected in this analysis, despite the presence of a crystal of AuCl located directly adjacent to the Au crystal.

Colloidal particles of silver and gold been prepared in a wide range of sizes by a number of different methods. Traditional methods for synthesizing colloidal metal particles involve the chemical reduction of aqueous metals salts, which typically give particles >100 Å in diameter.[17] Recent work has focused on the development of new methods of preparation which give uniform, ultrasmall colloidal particles which are of the order of 50 Å or less in diameter.[18]

Nanoclusters of silver are of interest for their potential optical properties and applications to solar energy conversion.[19−21] Silver nanoclusters, which are of similar dimensions (~50 Å) to those described in this paper, have recently been prepared using reverse micellar mediums.[22,23] In such systems, the size of the clusters

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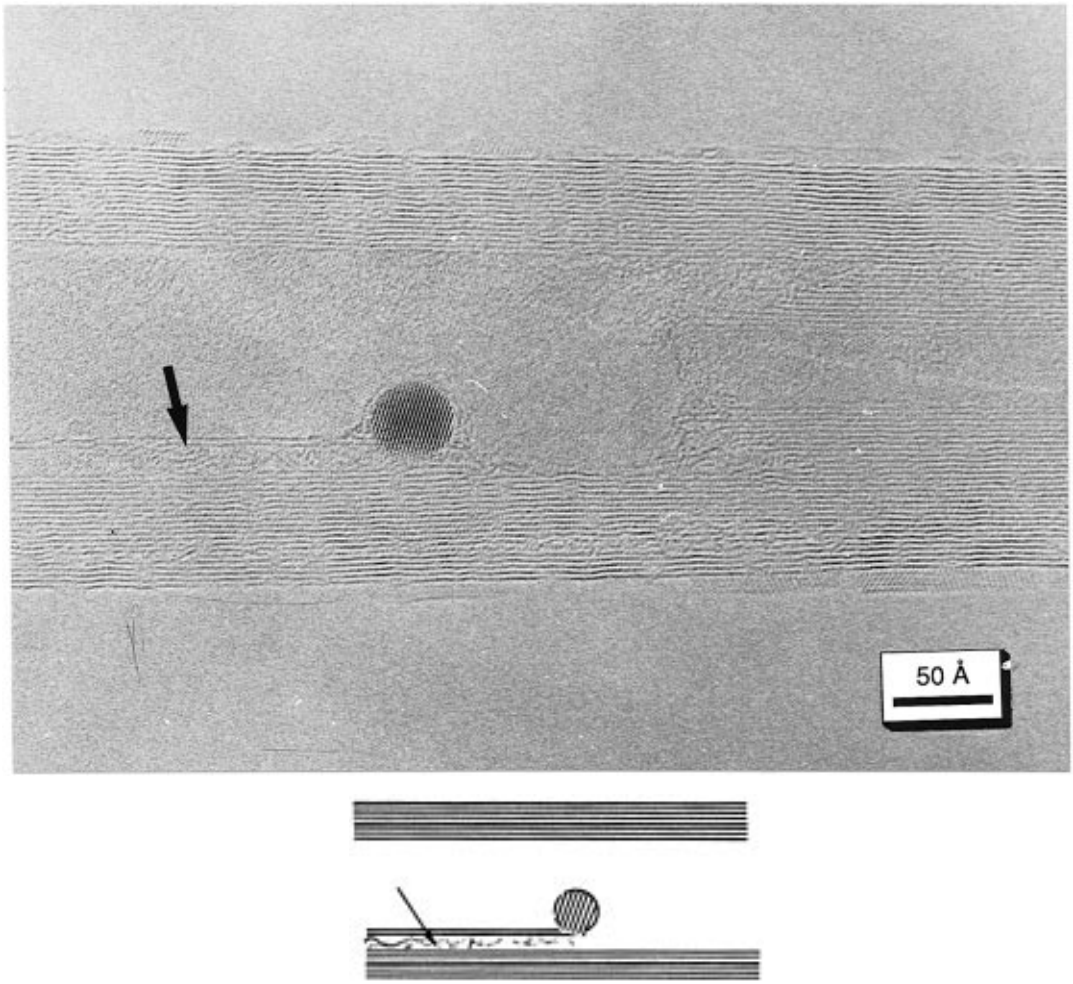

Figure 3. HRTEM image of a carbon nanotube filled with a spherical Au crystal. The observed fringes of 2.325 ± 0.05 Å correspond to the {111} planes of Au (lit. value = 2.355 Å). The solid arrow indicates where there has been intercalation into the gaps where carbon layers are missing.

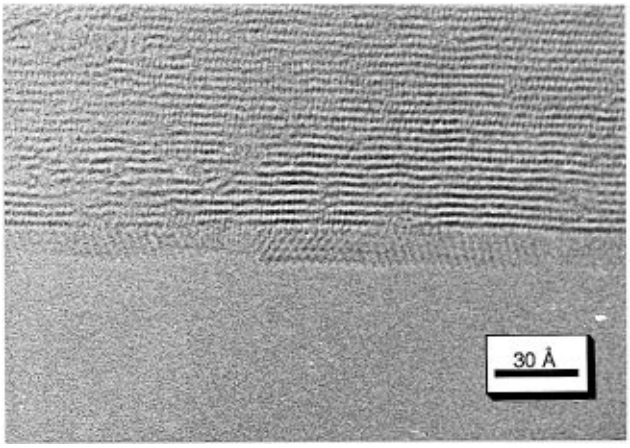

Figure 4. Partial coating of the exterior of the nanotube with a trilayer of AuCl.

can be altered by varying parameters such as water content, the reducing agent concentration, and the solvent. For example, the dimensions of Ag nanoclusters synthesized in AOT reverse micelles using hydrazine or $NaBH_4$ as a reducing agent, vary from 13 to 130 Å, with the majority of particles ranging from 30 to 80 Å in diameter.[23] Similar work carried out on the synthesis of Au nanoclusters from $HAuCl_4$ solubilized in PEGDE (pentaethylene glycol dodecyl ether)/hexane/water mixtures gave particles with diameters ranging from 25 to 100 Å.[24]

Molecular clusters of silver have also been synthesized in the cages and channels of zeolites.[21] The structure and size of the Ag cluster is dependent on the zeolite host, with hexasilver clusters being formed in completely Ag^+-exchanged zeolites; tri- or tetratsilver clusters being formed in partially Ag^+-exchanged zeolites; and linear trisilver clusters being formed in reduced faujasites.[21]

Conclusions

A two-step method for filling carbon nanotubes with Ag and Au metal results in a high percentage of filled opened nanotubes has been described. The use of a FEGTEM with a 0.7 nm probe for the EDS data has resulted in analytical data being obtained on individual crystals located within the hollow cavity of nanotubes.

Experimental Section

Production of Carbon Nanotubes. Carbon nanotubes were prepared by the arc-discharge method in 0.13 atm of helium using a dc voltage of 30 V and a current of ~180 A.[25] The nanotubes were opened at the tips by oxidation with HNO_3

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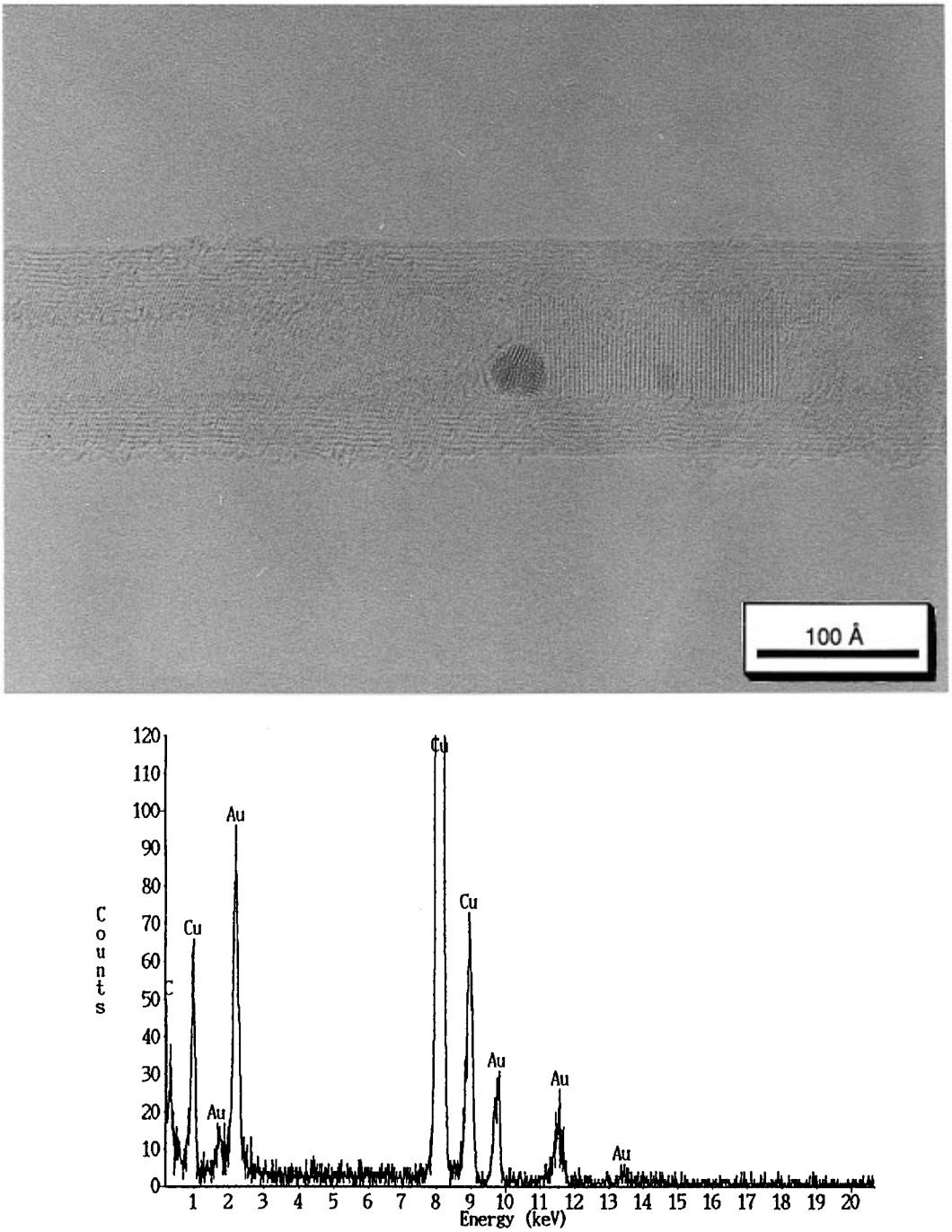

Figure 5. (a) Typical crystallite of Au metal encapsulated within the hollow cavity of a carbon nanotube. (b) Analytical EDS spectrum of the Au particle shown in Figure 3a obtained on a JEOL 2010F electron microscope equipped with a field emission gun (probe size = 0.7 nm).

at 130 °C for 24 h.[5] The tubes were then filtered onto glass filter paper, washed copiously with deionized water, and then dried in the air in an oven overnight at 60 °C.

Silver Filled Nanotubes. Opened nanotubes (0.5 g) were added to $Ag(NO_3)$ (2 g) in deionized H_2O (5 mL). The resulting suspension was stirred at room temperature for 24 h and then pipetted dropwise onto glass filter paper (Whatman's size 1 μm). After the filter paper was allowed to dry overnight at 160 °C, the black solid material was ground in a pestle and mortar and redried overnight in air at 250 °C.

Gold/Gold Chloride Filled Nanotubes. Opened tubes (1 g) were added to $AuCl_3$ (1 g) in deionized H_2O (5 mL). The mixture was stirred for 4 days in air until the bulk of the water had evaporated leaving a black paste. The paste was poured onto glass filter paper and dried in the oven at 160 °C overnight. The black solid was then calcined in a furnace under Ar at 600 °C for 4 h.

Electron Microscope Studies. Samples of carbon nanotubes were dispersed in CH_2Cl_2 and deposited onto a lacey carbon film. High-resolution electron microscopy was performed using a JEOL 4000FX instrument operated at optimum defocus with an accelerating voltage of 400 kV. EDS was performed on a JEOL 2010 F microscope operating at 200 kV using the smallest available probe. A Philips PW1710 diffractometer with Cu Kα radiation operating in the $\theta-2\theta$ mode was used for the XRD measurements.

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