Metal Nanowires and Intercalated Metal Layers in Single-Walled Carbon Nanotube Bundles

A. Govindaraj,[†,‡] B. C. Satishkumar,[‡] Manashi Nath,[‡] and C. N. R. Rao*[,†,‡]

CSIR Centre of Excellence In Chemistry, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India, and Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

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Nanowires of Au, Ag, Pt, and Pd (1.0−1.4 nm diam) have been produced in the capillaries of single-walled carbon nanotubes (SWNTs). The nanowire is single-crystalline in some cases. Dispersions of the nanowires in alcohol show longitudinal plasmon absorption bands at different wavelengths, suggesting the presence of a distribution of aspect ratios. A novel phenomenon involving the intercalation of metal layers (∼0.5 nm thick) in the intertubular space of SWNT bundles has been observed. SWNTs decorated by metal nanoparticles are formed in some of the preparations.

Introduction

Electron transport in low-dimensional materials is not only of academic interest but also holds promise in nanoelectronics. The synthesis of metal nanowires therefore assumes considerable significance. Carbon nanotubes[1] provide an excellent host matrix for the preparation of metal nanowires. Quantum wire behavior has been reported in single-walled carbon nanotubes (SWNTs) at very low temperatures.[2] Preparation of metal nanorods covered by carbon and other materials has been reported in the recent literature.[3,4] Hsu et al.[5] have reported the electrolytic formation of carbon-sheathed Sn−Pb nanowires with diameters in the 40−90 nm range. We have explored the preparation of thin metal nanowires by filling SWNTs by metals. It may be recalled that multiwalled carbon nanotubes have been opened by acids and filled with various metals.[6,7] Single-walled carbon nanotubes (SWNTs) are also readily opened by acids and filled with metals.[8,9] Sloan et al.[10] have just reported that SWNTs can be filled up to 50% by silver, by employing the KCl−UCl_4 and AgCl−AgBr eutectic systems, to produce nanowires. We have found that a variety of metal nanowires of 1.0−1.4 nm diameter can be readily prepared by employing SWNTs opened by acid treatment prior to the filling with metals. In addition, we have also found evidence of the incorporation of thin layers of metals in the intertubular space of the SWNT bundles.

Experimental Section

SWNTs were produced by the direct current arc-discharge method using a composite graphite rod containing Y_2O_3 (1 atom %) and Ni (4.2 atom %) as the anode and a graphite rod as the cathode,[11] under a helium pressure of 660 Torr with a current of 100 A and 30 V. The web produced from the arc discharge predominantly contained SWNT bundles and amorphous carbon along with metal-encapsulated carbon particles. It was heat-treated at 573 K in air for 24 h to remove the amorphous carbonaceous materials. The heat-treated material was stirred with concentrated nitric acid at 333 K for about 12 h and washed with distilled water to remove the dissolved metal particles. The SWNT material so obtained was suspended in ethanol by using a ultrasonicator and filtered through a micropore filter paper (0.3 μm) from Millipore to remove the polyhedral carbon particles present. The product was then dried at 423 K for about 12 h. Purified SWNT samples so obtained were heat-treated at 623 K for 30 min to remove the acid sites on the surface of the tubes. This treatment is known to open the nanotubes.[8,9] High-resolution electron microscopic (HREM) observations showed that the SWNTs with an average diameter of 1.4 nm were present in bundles of 5−50 nanotubes. The pore size (inner tube diameter) of these nanotubes has been established to be ∼1.4 nm by gas adsorption measurements.[12]

To prepare gold nanowires, 5 mg of purified SWNTs was mixed with ∼10 mg of $HAuCl_4 \cdot xH_2O$, and the mixture was dried in a 10 mm diameter quartz tube at 373 K for 2 h under

* E-mail: cnrrao@jncasr.ac.in.
† Jawaharlal Nehru Centre for Advanced Scientific Research.
‡ Indian Institute Of Science.

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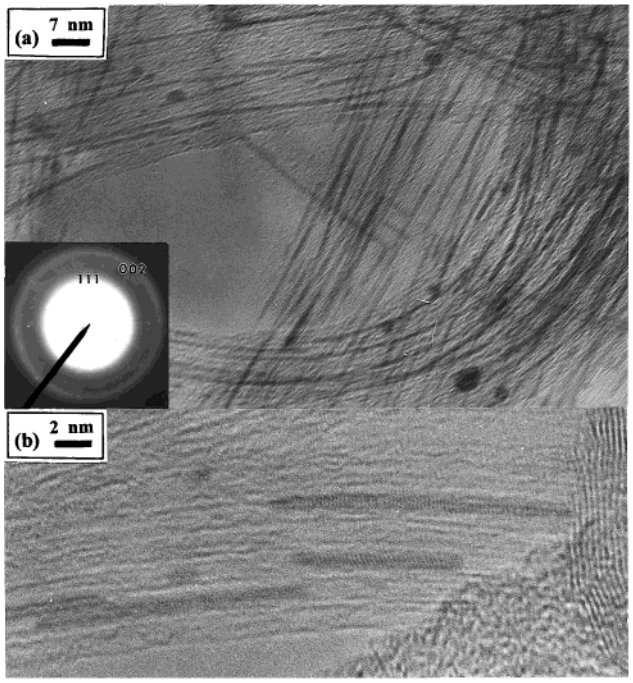

Figure 1. (a) TEM image of Au nanowires inside SWNTs obtained by the sealed-tube reaction. Inset shows an SAED pattern of the nanowires. (b) HREM image showing the single-crystalline nature of some of the Au nanowires.

vacuum (10^{-3} Torr). The quartz tube was sealed under vacuum and heated at 643 K (decomposition temperature of $AuCl_3$ is 527 K) for 20 h. To prepare Pt nanowires, a mixture of SWNTs (5 mg) with $H_2PtCl_6 \cdot 6H_2O$ (10 mg) was dried at 393 K for 2 h under vacuum and the sealed quartz tube containing the mixture was heated in a furnace at 773 K (melting point of $H_2PtCl_6 \cdot 6H_2O$ is 333 K) for 20 h. In a similar manner, $PdCl_2$ (10 mg) was mixed with the SWNTs (5 mg), heated at 373 K for 2 h, and sealed under vacuum. The sealed tube was maintained at 873 K (decomposition temperature of $PdCl_2$ is 773 K) for 20 h. In all of the sealed-tube reactions, the temperature was maintained at ~100 K above the decomposition (or melting point) temperature of the respective metal salt. After treatment with metal salts, the sealed tubes were broken open, and the product was treated with hydrogen at 723 K for 1 h to reduce any metal salt present. The hydrogen treatment was not found to be essential in the case of gold nanowires. To prepare Pt nanowires, we have employed a simple solution method as well. The mixture of SWNTs (5 mg) and $H_2PtCl_6 \cdot 6H_2O$ (10 mg) was refluxed in concentrated HCl or HNO_3 (2 mL) for 1 h. The product was washed with distilled water, dried, and treated with hydrogen at 723 K for 1 h. We have also attempted to prepare metal nanowires by sonochemical means,[13] wherein SWNTs in $AgNO_3$ solution were sonicated (35 MHz ultrasound treatment) for a few hours in a hydrogen atmosphere. It should be noted that SWNTs generally get filled by the metal salt/metal through the open ends.

The products obtained from the various processes discussed above were dispersed in carbon tetrachloride and deposited onto holey carbon copper grids for transmission electron microscope (TEM) observations with a JEOL JEM-3010 operating at 300 kV. Plasmon absorption bands of the dispersions of the nanowires in alcohol were recorded using a Hitachi U3400 spectrometer.

Results and Discussion

In Figure 1a, we show a TEM image that reveals the presence of a large number of gold nanowires obtained from the sealed-tube reaction. The image clearly shows extensive filling of SWNT tubes. The length of the gold nanowires is in the range 15−70 nm, and the diameters are in the range 1.0−1.4 nm. Detailed TEM observations show that the extent of filling of Au nanowires inside the SWNTs is in excess of 50%. Selected area electron diffraction (SAED) patterns taken from the region of nanowires (see inset of Figure 1a) show diffuse rings due to small polycrystalline metal particles. The diffraction rings correspond to the (111) and (002) reflections of gold. In some of the nanowires, however, we have found the metal to be single crystalline, as shown in the HREM image of Figure 1b. This image reveals the resolved lattice of gold with a spacing of ~0.23 nm, corresponding to the (111) planes. Polycrystalline Au aggregates could be transformed into the single-crystalline form by suitable annealing.

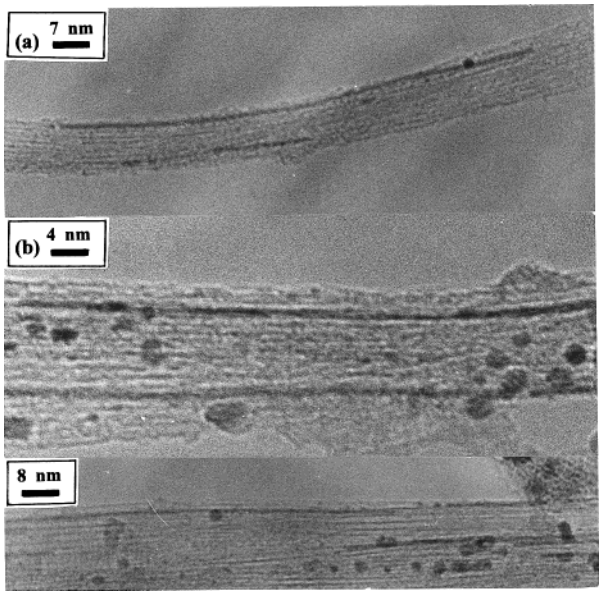

Figure 2. TEM image of Pt nanowires inside SWNTs obtained (a) by the sealed-tube reaction and (b) by the solution method.

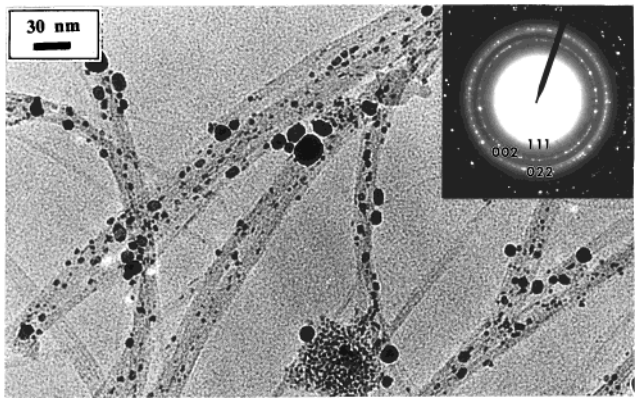

Figure 3. TEM image of SWNT bundles decorated by Pt nanoparticles. Inset shows an SAED pattern of the metal nanoparticles.

We have obtained platinum nanowires by the sealed-tube reaction, as shown in the TEM image in Figure 2a. The image shows a nanowire, 90 nm long and ~1 nm in diameter. Long nanowires of Pt were obtained by the solution method as well. In Figure 2b, we show a TEM image of Pt nanowires obtained on refluxing the

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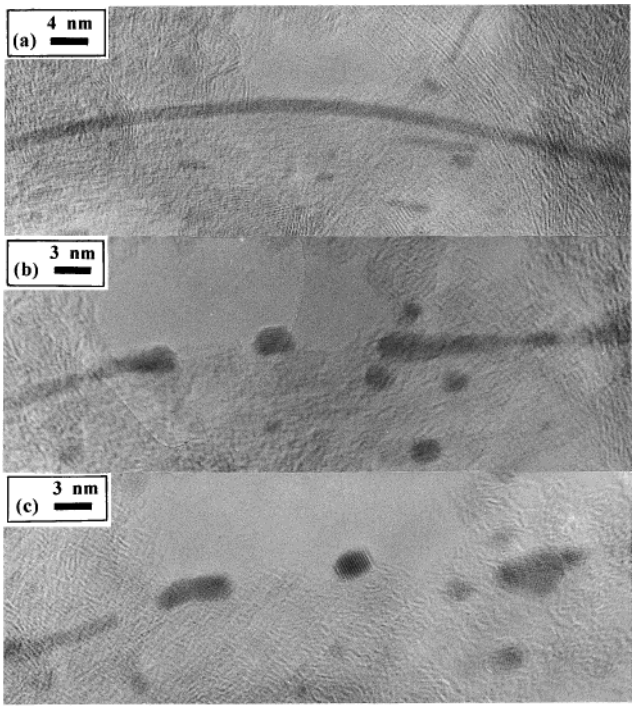

Figure 4. TEM images showing the breakup of a Au nanowire to nanoparticles on continuous exposure to an electron beam at 300 kV (at magnifications >600 000×). SWNTs are also damaged under these conditions.

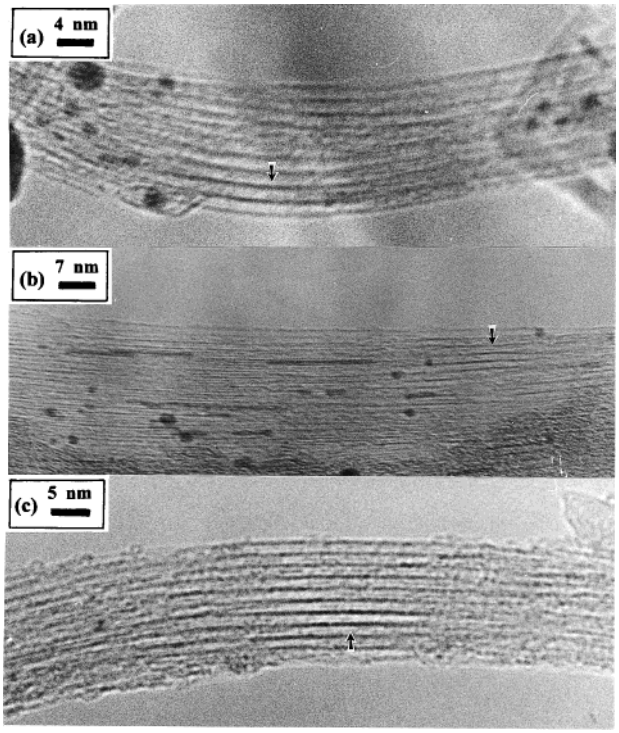

Figure 5. HREM images of metals intercalated in the intertubular space of SWNT bundles: (a) intercalated Pt obtained by the sealed-tube reaction, (b) intercalated Pt (coexisting with nanowires) obtained by the solution method, and (c) intercalated Pd obtained by sealed-tube reaction. Arrows point to the intercalated metal layers.

SWNTs with the metal salt and concentrated HCl. The length of the nanowires here is ∼70 nm, with the diameter remaining at ∼1 nm. We could obtain platinum nanowires by refluxing SWNTs with H_2PtCl_6 and HNO_3. Palladium nanowires could also be obtained by

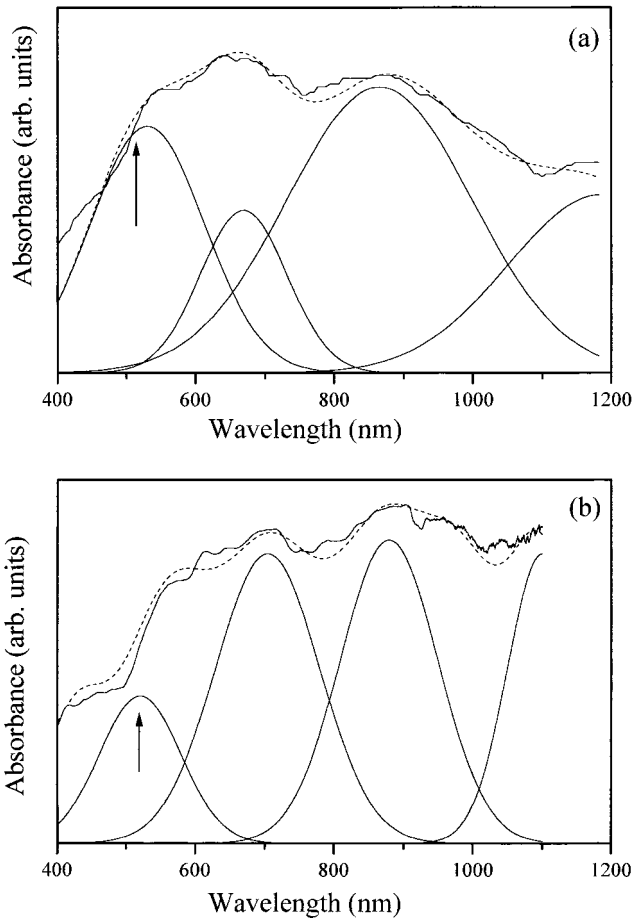

Figure 6. Optical absorption spectra of two alcohol dispersions of Au nanowires in SWNTs. The band around 520 nm corresponds to the transverse plasmon absorption. The other bands are longitudinal plasmon absorption bands.

the sealed-tube reaction, but these were not as long as those of gold or platinum. We could obtain silver nanowires by heating the SWNTs obtained after sonication in $AgNO_3$ solution at 623 K for 1 h, in a $Ar-H_2$ atmosphere.

The products of the sealed-tube reaction occasionally contained metal-decorated SWNTs along with the encapsulated-metal nanowires. The metal nanoparticles (3−20 nm diam) were uniformly dispersed on the nanotube surface (Figure 3). The nanotube surface, having been acid treated, contains active centers[14,15] that can bind the nanoparticles. The SAED patterns showed spotty rings corresponding to (111), (002), and (022) reflections of platinum (Figure 3), arising from the fairly large metal nanoparticles.

During the course of our investigations of gold nanowires by transmission electron microscopy, we have found the nanowires to disintegrate into particles on continuous exposure to an electron beam, when we attempted to examine them under high magnification. We have been able to photograph the sequence of changes with exposure and show a typical set of images in Figure 4. The nanowire in Figure 4a breaks up into smaller fragments, as shown in parts b and c of Figure

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4, after exposure to the beam for 30 and 60 s, respectively. While the microscope is operated at high magnifications (>600 000×), the electron beam energy gets concentrated on a very small region of the sample (in this case, the Au nanowire), causing breakup and melting as a result of the beam-induced heating. The nanoparticles thus produced often exhibit single-crystalline character, as revealed in parts b and c of Figure 4. These images show lattice fringes corresponding to the (111) planes of gold.

An interesting phenomenon that we have observed in the process of filling of the SWNTs with metals is the incorporation of metal layers in the intertubular space of the SWNT bundles. Such intertubular intercalation in the SWNT bundles is demonstrated by the TEM images in Figure 5. Figure 5a shows platinum-intercalated SWNTs obtained in a sealed-tube reaction. The solution method also gives rise to such intercalated SWNTs. Figure 5b shows a TEM image of intercalated platinum coexisting with the nanowires. A HREM image of a SWNT bundle intercalated with palladium is shown in Figure 5c. In all of the images, we notice an increase in the intertubular spacing or the diameter of the SWNT bundle due to intercalation. The thickness of the intercalated metal layer present in the intertubular spacing is generally between 0.4 and 0.5 nm. This is slightly larger than the van der Waals spacing (∼0.3 nm) between the single-walled nanotubes.

We have recorded the electronic absorption spectra of dispersions of gold nanowires in ethanol. The spectra show transverse and longitudinal plasmon absorption bands.[16] Although the transverse absorption band (∼520 nm) does not vary with the aspect ratio of Au nanowires as pointed out by Link et al.,[16] the position of the longitudinal absorption band varies markedly with the aspect ratio and the medium dielectric constant. Decomposition of the observed band envelopes indicates that the dispersions of Au nanowires are characterized by the bands around 670, 860, and 1150 nm due to the longitudinal absorption (Figure 6). These bands indicate that there is distribution of aspect ratios in the nanowire dispersion, with the aspect ratio corresponding to the longest wavelength being rather large. We estimate the range of aspect ratios in the nanowire dispersions examined by us to be 3−6. Clearly, more detailed studies of the plasmon bands of metal nanowires would be worthwhile.

Conclusions

Nanowires of metals such as gold, silver, platinum, and palladium with diameters in the range of 1.0−1.4 nm have been prepared in the capillaries of single-walled carbon nanotubes by simple chemical or sonochemical methods. The nanowires can be polycrystalline or single crystalline. The nanowires exhibit transverse and longitudinal plasmon absorption bands in the electronic spectra, with the latter showing the presence of nanowires with a distribution of aspect ratios. An interesting phenomenon found along with the formation of the nanowires is that of metal intercalation in the intertubular space of the SWNT bundles causing an increase in the diameter of the bundles. Metal-decorated nanotubes have been found to occur in some of the preparations.

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