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Pure and Clean Double-Walled Carbon Nanotubes

Novel Physical Phenomena may arise from co-axial nanotube structures

Highly crystalline and pure double-walled carbon nanotubes (DWNTs) are needed in order to probe electronic properties, thermal transport and mechanical behavior of individual DWNTs. Here we report the fabrication of a new type of a paper-like material consisting of high-purity DWNTs in high yields using a catalytic chemical vapor deposition (CVD) method in conjunction with an optimized purification treatment. These tubes are hexagonally packed in bundles and show a narrow diameter distribution.

DWNTs, which consist of two concentric graphene cylinders, have attracted the attention of numerous scientists because these hybrid structures [lying between single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs)], may exhibit intriguing electronic and mechanical properties that have not been reported hitherto. Therefore, various attempts to produce high purity DWNTs have been published[1-7]. Unfortunately, these reports usually generate mixtures of DWNTs and SWNTs, in addition to metal particles, amorphous carbon and multi-layer carbon nanotubes. The CCVD method is considered to be most efficient in dealing with the large-scale production of nanotubes[8, 9]. Arc-discharge methods and thermal treatments of C_{60} peapods result in DWNTs as well as unwanted carbon nanomaterials[1, 4], and the cross-sections of the DWNTs (using high resolution transmission electron microscope (HRTEM)) were never shown because the uniformity and purity of the DWNT material has not yet reached that of SWNTs[1-7].

The synthesis of DWNTs was carried out using a conditioning catalyst (Mo/Al_2O_3) on one end of the furnace, and the nanotube catalyst (Fe/MgO) in the middle part of the furnace (see supplemental information). Subsequently, a CH_4+Ar gas mixture (1:1) was fed into the reactor for 10 minutes at 875°C. When using the conditioning catalyst[10], preferential growth of DWNTs over SWNTs occurred, possibly due to an increased portion of active carbon species. In order to obtain a pure DWNT paper (Fig. 1a), a two-step purification process was applied to the synthesized products. In particular, HCl treatments (18wt%HCl, 373K, 10hrs) were carried out in order to remove iron catalyst and the supporting material, followed by air oxidation at 500^{o}C for 30 minutes. The latter process is used to remove amorphous carbon and chemically active SWNTs. After a filtering process, we obtained a dark and stable paper-like sheet, which is very flexible and mechanically stable (tough) (Fig. 1a). Careful HRTEM (JEOL JEM-2010FEF) observations revealed an extremely high-yield of DWNTs (more than 95%) arranged in bundles

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(Fig. 1c).

The DWNT paper (see Fig. 1b and 1c) contains nanotubes with a narrow diameter distribution, exhibiting a hexagonal packing (Fig. 1d). Raman studies were carried out in order to determine the radial breathing mode (RBM) frequency, which is inversely related to the tube diameter. Raman peaks appear above 250cm^{-1} (corresponding to the inner shells of DWNTs), and below 250cm^{-1} (usually associated with the outer shells of DWNTs). Using the equation $\omega_{RBM} = 234/d_t + 10$, where d_t is the tube diameter (nm) and ω_{RBM} being the RBM frequency (cm^{-1})[11], it is possible to define two pairs of DWNTs; (inner diameter: outer diameter) = (0.77nm:1.43nm) and (0.9nm:1.60nm), respectively (see supplementary information).

With the availability of this pure material available, researchers will now be able to answer: (1) Do DWNTs behave as quantum wires?; (2) Is there a chirality relationship between the concentric tubes during growth?; (3) Is there any significant effect of the concentric tubes on the electronic conductance?; (4) What are the adsorption properties of co-axial nanotube ropes?, etc.

In addition to fundamental research, we envisage this material to be useful in the fabrication of novel sensors, nanocomposites, field emission sources, nanotube bi-cables and electronic devices[12, 13]. It is expected that DWNTs will replace SWNTs or MWNTs for various specific applications due to their *expected* superior mechanical properties, thermal conductivity and structural stability derived from their unique coaxial structure.

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Figure 1 a, A photograph of a DWNT paper produced in the present study, **b**, FE-SEM image and **c**, Low-magnification TEM image (insert image exhibiting high resistance to bending of a single bundle) of DWNT paper, revealing the presence of bundles of carbon nanotubes. Note that impurities are notably absent in the former images, **d**, Typical HRTEM images of a different bundle, showing the perfect structures both in cross-section and side view. It is noteworthy that the tubes appear to be "perfect" and the bundles always reveal a hexagonal packing structure.

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