Y-junction carbon nanotubes

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Carbon nanotubes with junctions are considered to be of potential value in nanoelectronics. A simple pyrolysis procedure for producing *Y*-junction carbon nanotubes is described. The method involves the pyrolysis of the organometallic precursor, nickelocene, along with thiophene at 1273 K. Tunneling conductance measurements showed that at the *Y* junction, the *I*-*V* characteristics are asymmetric with respect to zero bias as in a junction diode. [S0003-6951(00)04942-1]

The possible use of carbon nanotubes in nanoelectronics has aroused considerable expectations. For such applications it is important to be able to connect the nanotubes of different diameters and chirality.[1–5] The complex three-point nanotube junctions have been proposed as the building blocks of nanoelectronics. For this purpose, *Y* and *T* junctions have been considered as prototypes. The *Y*- and *T*-type junctions appear to defy the conventional models in favor of an equal number of five- and seven-membered rings to create nanotube junctions. It has been suggested that *Y* junctions can be created with an equal number of five- and eight-membered rings.[6] To date, there have been no practical devices made of real nanotube junctions, although junctions consisting of crossed nanotubes have been fabricated to study their characteristics.[7] The only report of synthesis of *Y*-junction nanotubes has made use of *Y*-shaped nanochannel alumina templates, in which small quantities of cobalt particles were electrochemically deposited; the nanotubes were then formed in the channels by the pyrolysis of acetylene, after the reduction of the catalyst.[8] By this means, *Y*-junction nanotubes of 15–100-nm-diam and micrometer lengths were produced. We have been able to produce *Y*-junction carbon nanotubes in good quantities, by carrying out the pyrolysis of an organometallic precursor along with thiophene. It may be recalled that the pyrolysis of a hydrocarbon in mixture with thiophene over nickel particles yields coiled carbon nanofibers and nanotubes with knees and shoulders.[9,10] The *Y*-junction nanotubes so produced show interesting *I*-*V* characteristics.

The experimental setup employed by us for the synthesis of the *Y*-junction carbon nanotubes consists of stainless steel gas flow lines and a two-stage furnace system fitted with a quartz tube (10 mm inner diameter), as shown in Fig. 1. The flow rates of gases were controlled using UNIT mass flow controllers. A known quantity ($\sim$100 mg) of the nickelocene (Sigma Aldrich) was taken in a quartz boat and placed at one end of a quartz tube, such that the nickelocene boat was located in the first furnace. The temperature of this furnace was raised to 623 K at a controlled heating rate ($\sim 10°$/min). Argon gas was passed through the quartz tube at a desired flow rate. Hydrogen was bubbled at the same time through thiophene and these vapors along with nickelocene vapors were introduced into the pyrolysis zone of the second furnace maintained at 1273 K. The flow rates for argon and hydrogen were 240 and 10 sccm, respectively (sccm=standard cubic centimeter per minute). Carbon deposits accumulated at the inlet and outlet ends of the second furnace. These deposits were removed and examined by transmission electron microscopy (TEM) with a JEOL JEM-3010 microscope operating at 300 kV.

TEM observations show that the deposits at the inlet end of the second furnace in Fig. 1 contained little of carbon, and had mainly metal-encapsulated graphite nanoparticles. The carbon deposits at the outlet, however, consisted of carbon nanotubes, a large majority of which had *Y* junctions. In Fig. 2(a), we show the TEM image of a typical *Y*-junction carbon nanotube. This is a multi-walled carbon nanotube with an inner diameter of 8 nm and an outer diameter of 40 nm. The angle enclosed between the upper arms of the *Y*-junction nanotube is close to 90°. In the clockwise direction, the angles enclosed between the other pair of the *Y*-junction arms are 120° and 150°. The TEM image of another *Y*-junction nanotube with an outer diameter of 50 nm is shown in Fig. 2(b). The enclosed angles in all three arms of *Y* junction are 120° each. At the bottom of the *Y* junction we see the beginnings of another *Y* junction $\sim$500 nm from the top one. This image shows how multiple *Y* junctions can exist, suggesting possible multiple tunnel devices on a single carbon nanotube.[6]

A TEM image revealing the presence of several *Y*-junction carbon nanotubes is shown in Fig. 2(c). Many of the nanotubes possess multiple *Y* junctions as can be seen from the TEM image in Fig. 2(d). The occurrence of *Y* junctions in the carbon nanotubes prepared by the pyrolysis method employed by us was common, the yield of such structures in typical preparations being of the order of 70%. While nickelocene acts as the common source for catalytic nickel nanoparticles as well as carbon, the role of thiophene impurity appears to go beyond yielding unusual graphitic morphologies. A high resolution transmission electron microscope image taken at the *Y* junction in a nanotube is shown in Fig. 3. The image shows the fishbone-type stacking of the graphene sheets, followed by a hollow in the center.

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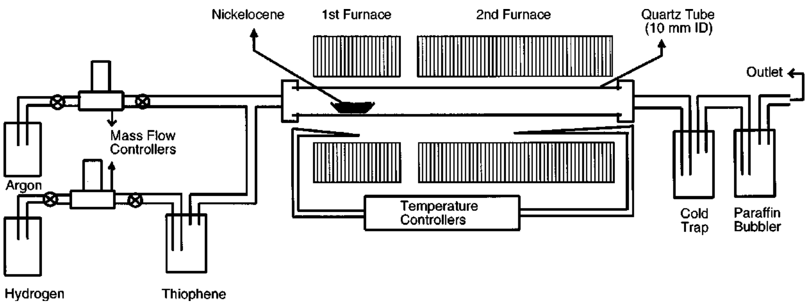

FIG. 1. Pyrolysis setup for the synthesis of carbon nanotube *Y* junctions employing nickelocene and thiophene.

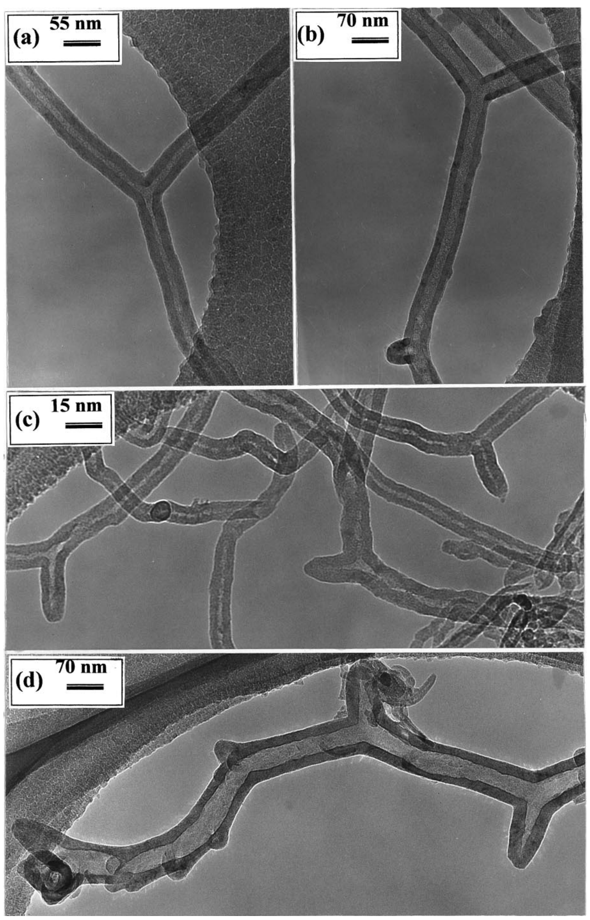

FIG. 2. TEM images of (a) a typical *Y*-junction carbon nanotube, (b) a *Y*-junction nanotube showing the beginning of another *Y* junction; (c) several nanotubes with *Y* junctions and (d) a nanotube with multiple *Y* junctions along the length.

FIG. 3. HREM image of a *Y* junction showing the fishbone-type stacking of graphene sheets ($d_{(002)}$~3.4 Å).

The interlayer separation is ~3.4 Å, indicative of graphitic stacking.

Tunneling conductance measurements were carried out by positioning the tip atop a *Y* junction (the point of contact between the three arms) as well as on the individual arms of the *Y*-junction nanotubes. A typical *I*-*V* curve obtained along the arms of the *Y* junction is shown in Fig. 4(a). This should be compared with the *I*-*V* curve obtained from atop the *Y* junction in a *Y* junction nanotube as shown in Fig. 4(b). We notice that both the curves are typical of metal-insulator-metal junctions with the current values displaying a threshold around zero bias. The curve in Fig. 4(a) is symmetric about the zero bias. The tunnel current has the same magnitude (~19 nA) at bias voltages of +1700 and −1700 mV. The inset in the figure giving the plot of differential conductance versus bias gives a gap of ~760 mV, symmetric with respect to zero bias. In Fig. 4(b), however, the threshold bias voltage is ~190 mV in the positive bias. The tunneling current rises exponentially beyond this bias voltage, reaching a maximum of ~28 nA at 1700 mV. Under a negative bias, there is a gradual rise in the tunneling current beyond a relatively large threshold bias (~440 mV). The tunneling cur-

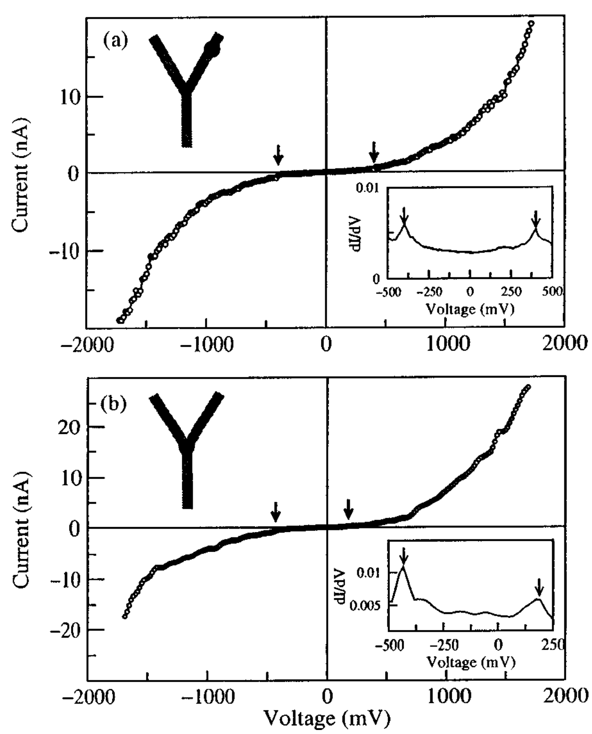

FIG. 4. *I*-*V* curves collected from different points in a *Y*-junction carbon nanotube; (a) from the junction of the three arms and (b) from one of the arms away from the junction. Insets show plots of dI/dV vs bias voltage. The observed gaps are indicated by arrows.

rent reaches a value of ~18 nA at a negative bias of 1700 mV, which is far less than that for the positive bias. Thus, the *I-V* plot is asymmetric with respect to bias polarity. The plot of differential conductance (dI/dV) versus bias shown in the inset of Fig. 4(b) also clearly demonstrates the asymmetry about zero bias. Such asymmetry is characteristic of a junction diode and this in turn indicates the existence of intramolecular junction in the carbon nanotubes. It is to be noted that the asymmetry found in the *Y* junction is somewhat comparable to that reported in the case of intramolecular junctions.[11]

In conclusion, the preponderant formation of *Y* junctions in the carbon nanotubes produced by the pyrolysis of nickelocene in the presence of thiophene is worth noting. It would appear that the process involves not only the *in situ* formation of catalytic nickel nanoparticles, but also the simultaneous formation of nanotubes with *Y* junctions, due to the catalytic effect of the thiophene present in gas stream. Since one can manipulate carbon nanotubes using atomic force or scanning tunneling microscopy, the ready availability of such nanostructures opens up possibilities in developing nanoelectronic devices. The asymmetry in the *I-V* curve around zero bias found at the *Y* junction suggests that the nanotubes obtained in the present study may be of use in this direction.

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