Carbon-atom chain formation in the core of nanotubes

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Here we report the observation of a linear carbon-atom chain, synthesized using an arc discharge from a graphite double anode. We use high-resolution TEM to evidence the formation of a carbon-atom chain along the axis of a needlelike structure consisting of concentric cylindrical graphitic shells. The atomic chain in the core of the innermost cylinder, by calculations on the basis of van der Waals interactions, demonstrates an extremely high thermal stability (up to 4200 K) and exhibits high mechanical strains.

From theoretical[1,2] and experimental[3–5] investigations, it is evident that C_n atomic chains hold substantial promise for use as emitting structures of atomic-scale field emitters,[6] atomic-scale electronic devices,[2,7] etc. However, these have been much less studied in part due to difficulties in producing such one-dimensional carbon structures. Therefore, the most important step in the realization of these fascinating materials for fundamental scientific measurements and technological applications is the synthesis of high-quality carbon-atom chains. Recently, the generation of carbon-atom chains by chemical synthesis,[3] and β-SiC surface-supported formation[4] have been reported. To our knowledge, carbon-cluster structures can be built by existing carbon-atom bonding, so another possibility of discovering carbon-atom chains growth may be through direct observation of carbon specimens produced in fullerene synthesis.[3]

Carbon-atom chain samples were prepared by a double-anode arc-discharge method. The anode existing side by side with two graphite rods 6 mm in diameter was employed, and the cathode consisted of a graphite plate of 30×30 mm^2. The gap between the electrodes was maintained at ~1 mm. During the carbon arc-discharge vaporization, operating under a helium atmosphere of ~500 Torr at a current density of ~200 A/cm^2 and 25 V potential difference between the electrodes, the deposit formed on the cathode was ground to a fine powder, ultrasonically dispersed in ethanol and put on a grid for observation using a high-resolution transmission electron microscope (HRTEM) (JEM-200CX) with 200 keV accelerating voltage.

The majority of the nanostructures imaged by HRTEM were consistent with previous observations: closed or nearly closed complex three-dimensional structures of graphitic sheets, and multiwalled nanotubes. But we also observed needlelike structures different from conventional nanotubes. Figure 1(a) shows a typical example of such a structure that is observed in our studies with the TEM and Fig. 1(b) exhib-its a schematic image of a carbon atom in the core of an innermost tube. We note that TEM studies published to date have not revealed the presence of such a needlelike structure. On initial examination, this structure looks like a collapsed carbon nanotube. However, on the basis of these new experimental findings on needlelike morphologies, we propose that this structure is in fact a carbon needle consisting of coaxial tubes of graphite sheets. This idea can be considered in more detail as follows.

To rule out the possibility that we observe only flattened tubes in the HRTEM images, we performed a careful sample
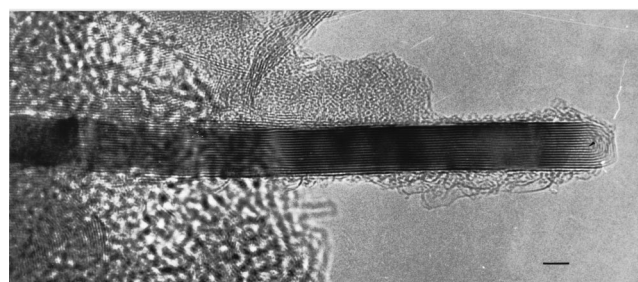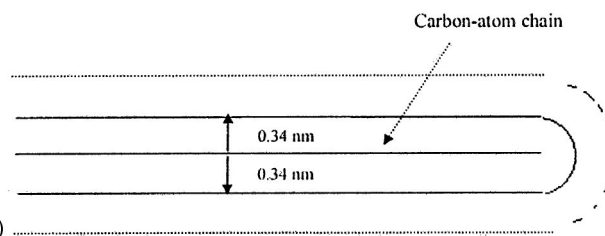
FIG. 1. (a) HRTEM image of carbon needlelike structure, showing a carbon-atom chain in the core of an innermost tube (pointed out by an arrow). Note the smooth transition from the curved right cap to the cylindrical graphitic tube walls. Scale bar 3.3 nm. (b) Schematic image of a carbon atom in the core of an innermost tube.
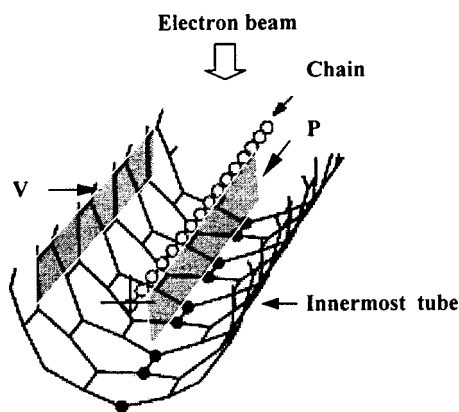
FIG. 2. Clinographic view of a carbon-atom chain in the core of an innermost tube of a needlelike carbon structure. The meaning of the labels V and P is explained in the text.

rotation examination. The entire specimen grid was rotated *in situ* inside the TEM through angles in excess of 20°. The width (diameter) of such a structure shows no change when tilted along an axis paralleled to the needlelike axis, supporting the idea of a coaxial arrangement of graphitic tubes. Another notable feature is that the needlelike structure in Fig. 1(a), consisting of 19 lattice fringes (corresponding to graphite sheets separated by 0.34 nm) exhibits distinctively capped hemisphere end. In this end of the needlelike structure, the curved shells did not grow to completion, but the trend of the concentric shells is faintly visible. If the carbon nanotube is in the imaging plane, two parallel sets of equal-numbered lattice fringes, separated by a gap, should be observed. However, such a structure in a TEM image, a total of 19 lattice fringes, with no gap is observed. It seems to us that from the outer later the ninth lines are two lattice fringes at both sides of the innermost tube of the needle like structure. This smallest tube with an observed hemisphere end is ~0.68 nm in diameter and filled with a black line in the core. In other words, such a needlelike structure is indeed a multiwalled carbon nanotube consisting of nine concentric cylindrical graphite shells with a lattice fringe inside its gap.

Significantly, two parallel fringes of the innermost tube are separated by a black line [fringe image marked by an arrow in Fig. 1(a)] that is a smoothly continuous straight line and is terminated abruptly near the capped end of the tube. Because the diameter of the innermost tube is ~0.68 nm, the spacing between the inner tube wall and black line is calculated as ~0.34 nm. In other words, this black line is perfectly aligned along the innermost tube axis. We consider that the black line inside the tube may be a lattice fringe of a carbon-atom chain and the van der Waals interactions between the atom chain and the inner wall of the innermost tube may act as an adhesive keeping the carbon chain stable in this special space. One of the key questions about the TEM observation for the carbon-atom chain is how the lattice fringe can be formed from a carbon-atom chain alone. As shown in Fig. 2, indicated by shading, plane P (including atom chain and bonding carbon atoms in a hexagon net) and two side portions of the innermost tube shading and labeled V (Ref. 8) are oriented so that these planes may satisfy the imaged condition for the incident electron beam, and thus the plane P projection forms a black line—carbon-atom lattice fringe.

The growth of the carbon-atom chain during self-assembly can be explained in two steps. First, a graphite arc-discharge produces C_2 moieties (these C_2 units are assumed to be building blocks for the nanotubes) bonded to the active sites of a soot particle, and the C_2 units binding to one other formed half-fullerene (C_{60}). That half-C_{60} cage can initiate the formation of a single-wall nanotube. If the central axis of that half-C_{60} cage is a threefold or a fivefold rotation axis, a (9,0) or a (5,5) tubule will start growing. Second, once a carbon atom enters into the center of half-C_{60} cage, this atom can be stabilized by van der Waals force and remains an unsaturated bond binding to other carbon atoms, showing that this atom will become the first atom in the chain and that the formation of a carbon-atom chain will be synchronized with the growth of a nanotube graphene sheet. In general, that half-C_{60}, when extruded from the soot particle, can either grow to a complete C_{60} or initiate the formation of a single-wall nanotube. Perhaps, the presence of the first carbon atom in the chain hinders the development of a C_{60} cage.

To get a better understanding of the thermodynamic properties and stability of this carbon-atom chain in the core of the nanotube (about 0.68 nm in diameter, we perform molecular-dynamics (MD) simulations using the interaction models. TLHT model[9] is similar to the models of Tersoff[10] and Brenner,[11] which are suitable to simulate the graphite structure as well as the fullerene. The LJ model[12] for the van der Waals interactions between chain atoms and a single-wall carbon nanotube has been successfully used to investigate the second virial coefficient, the compressibility, the lattice vibrational specific heat, the vacancy formation energy, and the energy of the separation of two closely packed surfaces. The equations of motion for each of the nonrigid atoms are integrated by using a leapfrog form of the Verlet algorithm[13] over time steps $\Delta t = 0.08$ fs. We increase the temperature of the heat bath in steps of $\Delta T = 200$ K from 0 K to the final temperature 4200 K, and let the tube and chain equilibrate for 1000 time steps at each new temperature.

To study thermodynamic properties of the carbon-atom chain, we first construct a carbon-atom chain in the core of a single-walled tube [see Fig. 3(a)]. Figure 3(b) shows that the carbon-atom chain is heated up to a high temperature of 4200 K exceeding the melting point of graphite, and clearly exhibits that the chain remains intact without dissociation although the disordered structure appears in the tube wall. As a comparison, we also construct a carbon-atom chain in the free space and then heat the chain to 3000 K [Fig. 3(c)], and find that the chain tends to curl itself up and decomposes with several broken bonds. As is evident to the eye, this is mainly due to van der Waals force between the atomic chain and the wall of the nanotube, which makes the chain withstand very high thermal temperature, resisting bond breaking.

In order to investigate the mechanical stability of the carbon-atom chain, we perform MD simulation for the collision of the C_{60} molecule with the tube and surprisingly find that the chain may stand very high mechanical strains without dissociation although it bends severely. Figure 4 shows the typical snapshots of the atomic positions as a function of the simulation time. During the collision event, both the carbon-atom chain and single-walled tube bend to large
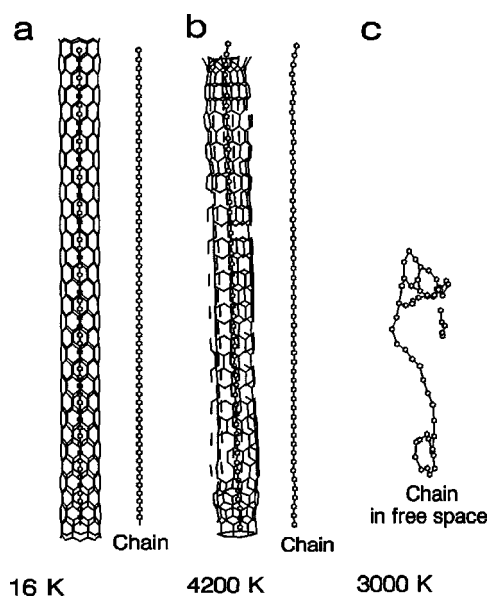
FIG. 3. Snapshots illustrating the geometry of a carbon-atom chain in the core of a single-walled nanotube (a) and (b) and in the free space (c) at different temperatures. (a) The initial structures of the carbon-atom chain in the core of the tube with diameter of 0.68 nm at temperature 16 K. (b) The atom chain and the small tube are heated to 4200 K. (c) The carbon-atom chain in the free space is heated to temperature 3000 K.

FIG. 4. Simulated snapshots of the atomic positions at various times for the collision of a C_{60} molecule with a single-walled tube filled with a carbon-atom chain. (a) The initial positions of the incident molecule C_{60} (90 eV) and the carbon-atom chain in the core of the single-walled nanotube with diameter of 0.68 nm. (b) and (c) The carbon-atom chain and single-walled tube bent to large angles owing to the repulsive forces from the incident molecule. (d) Upon further bending, the carbon-atom chain keeps intact without dissociation.

angles owing to the bending force from the incident molecule C_{60}. Upon further bending, the carbon-atom chain keeps a linked chain without dissociation.

From the above investigations, we draw two conclusions from our results. First, clear evidence is provided that the lattice fringe inside the innermost needlelike tube is indeed a carbon-atom chain. Second, we demonstrate that van der Waals forces will be very important in determining the high thermal and mechanical stability of the carbon-atom chain.
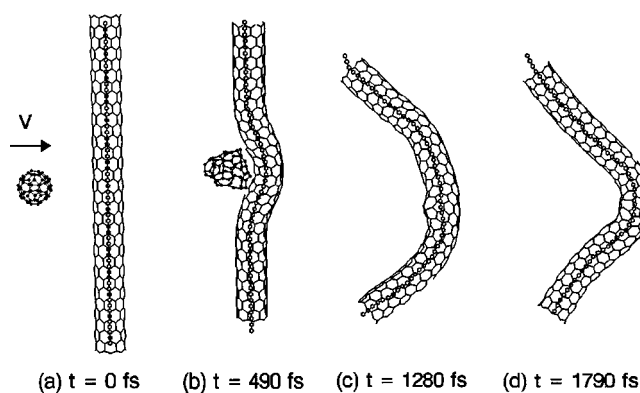
We predict that the linear atom chains of the other materials should be observable at least for very small tubes that satisfy van der Waals interactions between the linear atom chains and the inner wall of the small tubes. These systems, atomic chains in nanometer-sized channels, may be called an ''atom electric cable.'' Therefore, we estimate the fabrication of this type of stable carbon-atom chain system will be significant for the development of atom-sized electronic technologies.

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