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Imaging As-Grown [60]Fullerene Nanotubes by Template Technique

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Fabrication of nanometer-scale components in desired geometries is significant for the new generation of optics, electronics, and other areas.[1] Nanotubes can be made from a variety of materials including carbon, ceramics, metals, and organic polymers that have been discussed in several reviews.[2] It is also fundamentally interesting to develop specific structural architectures using material with unique structure and properties that are structurally different from previously reported ones. The ready availability of [60]fullerenes as novel electropool π-systems has increasingly invited exploration of their outstanding physical and chemical properties. In particular, the preparation of fullerene nanotubes is of great interest from both a fundamental and a practical point of view.

Control of size, especially the diameter, is a key factor in the success of nanotube synthesis. Template synthesis has attracted much attention because it is a versatile approach. The size, shape, and structural properties of the nonstructural materials are controlled by the template used. Many groups have used this method to prepare nanoscale materials employing alumina membranes or track-etched membranes as templates.[3]

We have developed a useful and experimentally easy way to directly fabricate C_{60} nanotubes with a monodisperse size distribution and uniform orientation using C_{60} powders. When a pure solvent is evaporated from a wettable surface, the liquid remaining forms complex two-dimensional patterns.[4] Comparing the pure solvent to the behavior compound solution, the evaporation or drying of saturated compound solution is more complex. Similar phenomena occur if porous templates are brought into contact with solution:[5] the small pores of the templates allow or promote the formation of three-dimensional patterns as the solvent evaporates from flat surfaces. It is likely that the imperfections in the surface of the template (the error in observed pore diameter is approximately 10%) play a role in the effects of wetting by creating a meniscus at points along the pore which, when fired, creates the transecting regions of the tubules.

We believe that the morphologies of the C_{60} tubes resulting from our processes remains within the confining template when the solvent has been completely evaporated. If the template is of monodisperse size distribution when it is aligned, so are the nanotubes, and ordered nanotube arrays can be obtained if the solutions can be formed into nanotubes with a wall thickness of a few tens of nanometers. Owing to its versatility, this approach should be a promising route toward a variety of nanotubes (i.e., polymer, inorganic, and organic compounds).

We used an ordered porous alumina template with narrow pore size distribution.[6] The pores are arranged in a regular hexagonal lattice. Pore densities as high as 10^{11} pores/cm^2 can be achieved. The pores are straight, with a smooth inner surface and with diameters in a broad range of 5−200 nm.[7] For the process, the template was repeatedly dipped into a toluene solution of C_{60}, and the solvent was allowed to dry between dipping. After a number of "dip-and-dry" cycles, the templates were heated to 500 °C for 5 h under an argon atmosphere and then cooled to room temperature. Figure 1 shows the as-grown nanotubes formed from the toluene solution of C_{60} by dip-and-dry. Figure 1A shows that the template filled with C_{60} nanotubes is of a metal sheen and smooth surface. It suggests the template may be a semiconductor. Figure 1B depicts an array of aligned C_{60} nanotubes, which have smooth and clean surfaces with a diameter of 220−310 nm and a length of 60 μm, which correspond to the diameter of the pores of membrane and the thickness of the template used (ca. 60 μm), respectively. After selectively dissolving the template, the remaining nanotube array still exhibits its hexagonal long-range order. The tip of a C_{60} nanotube formed in an alumina template was uncovered by etching the alumina substrate with aqueous sodium hydroxide (Figure 1C). The top of C_{60} nanotubes after removal of the templates displays a monodisperse-size diameter of 30 nm. The nanotubes grown from the membrane exhibit a straight alignment perpendicular to the substrate and are well-ordered. The large surface is not completely removed which makes the C_{60} tubes stick together (Figure 1D).

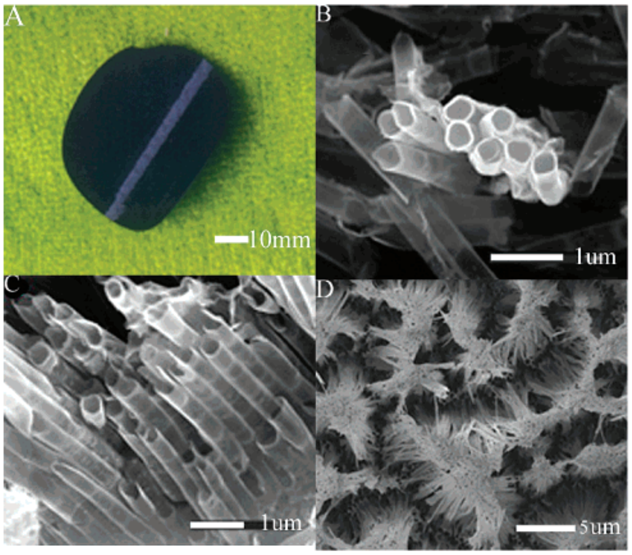

Figure 1. (A) Photography of the alumina template with diameter in 2.5 cm. Scanning electron micrographs of C_{60} nanotubes: (B) Top of C_{60} nanotubes after removal of the alumina templates. (C) Ordered array of C_{60} nanotubes after complete removal of the template. (D) Large area of aligned C_{60} nanotubes.

The production was also characterized by FT-IR spectra (KBr) (Figure 1A in Supporting Information), which provide further

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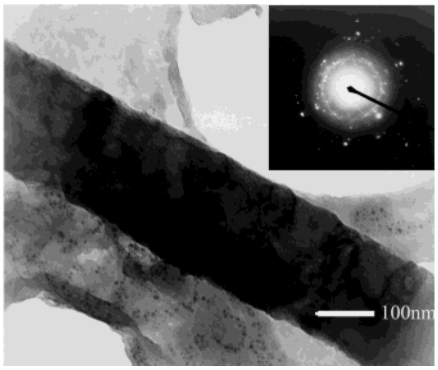

Figure 2. Transmission electron microscopy images of C_{60} nanotubes with diameter of 100−300 nm. Inset: the corresponding electron diffraction pattern of a single C_{60} nanotube.

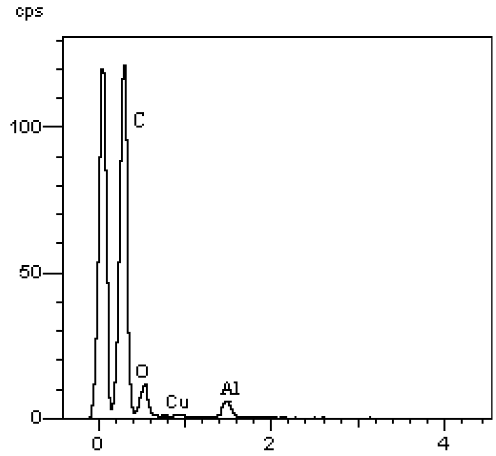

Figure 3. Energy-depressive X-microanalysis of a single C_{60} nanotube.

evidence for bonding. The results show four typical C_{60} absorption bands at 527, 577, 1182, and 1431 cm^{-1}, respectively.

The transmission electron microscopy observations of fullerene nanotubes grown from the template membrane are shown in Figure 2. According to the figure, the surface of C_{60} nanotube was covered with less Al_2O_3. The success of the preparing C_{60} nanotubes was further confirmed by the elemental signature of carbon in the energy-depressive X-microanalysis show in Figure 3. The results indicate unambiguously that these nanotubes are composed of only carbon element. The inset of Figure 2 is an electron diffraction pattern of the selected C_{60} nanotubes. The result shows that the nanotubes are polycrystalline, and the structure of nanotubes is a mixed phase of face-centered cubic and hexagonal close-packed structure.

The morphologies of the tubes did not depend on the concentration of the precursor solution. When the template was dipped only one time in 0.005 M solution, only a small amount of C_{60} was loaded into the template. In these cases, tubules did not form, but rather narrow sheets of C_{60} formed that extended along one wall of the pores. These sheets, as observed by TEM (Figure 1B in Supporting Information), were roughly the same width as the template's pores, but they were not tubular. These observations suggest that the C_{60} is more likely to grow along the length of the pore than around its circumference when there is not enough material present to form the entire tubule.

As demonstrated, we obtained C_{60} nanotubes with uniform orientation from toluene solution of C_{60} by "dip-and-dry". Owing to its versatility, this approach should be a promising route toward a variety of nanotubes (i.e. polymer and inorganic and organic compounds) and should be applicable to any compound that can be dissolved in a membrane-compatible solvent. Especially, this method could be a general technique for thermopolymerization and in situ polymerization under controll of their shape and size.

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Supporting Information Available: Synthetic procedures, FT-IR spectra, and the TEM of a C_{60} sheet (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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