Chem. Mater. **2008,** *20,* 1667–1669

Vertically Well-Aligned C_{60} Microtube Crystal Array Prepared Using a Solution-Based, One-Step Process

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Received October 17, 2007
Revised Manuscript Received January 11, 2008

Fullerene, C_{60}, which was discovered in 1985,[1] is a relatively new member of the carbon family, and its chemical derivatives are attractive candidates for new functional materials in the field of organic electronics and solar cells.[1–3] C_{60} is a good electron acceptor with a relatively high electron mobility and a stable structure, and considering its high electron affinity, it should be reactive in redox-type reactions.[3] However, in order for C_{60} and its derivatives to be used in different applications, it must be possible to assemble them into specific structures and shapes with controlled dimensionality. There are several methods for assembling C_{60}-based molecules in a designed manner, such as supramolecular approaches,[4] controlled precipitation,[5–10] and template approaches.[11,12] For instance, one-dimensional C_{60} nanostructures, prepared via various routes, including liquid–liquid interface precipitation (LLIP),[5–10] growth within templates,[11,12] and other precipitation processes,[13–16] have brought about the possibility of developing new C_{60}-based materials with desired structures. However, only long, entangled whiskers or tubes[5–10] have been produced using the LLIP process, and nanorod-shaped powders have been produced using other rapid precipitation processes.[13–16] Therefore, the preparation of a well-defined array of C_{60} structures covering most of the surface of a substrate still remains an unexplored area of research despite the need for them in various applications, such as organic electronics, sensors, redox-type microreactors, and biological substrates.

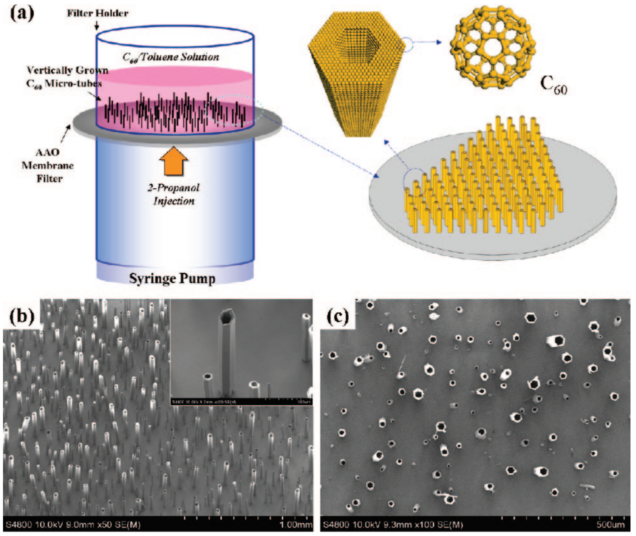

Figure 1. (a) Schematics of apparatus used for preparing vertically grown C_{60} microtube arrays and the substrates on which the vertically aligned C_{60} microtubes were grown. (b) Side and (c) top views of vertically grown C_{60} microtube arrays viewed with SEM. The inset in (b) shows a close-up of C_{60} microtubes on the substrate.

In this communication, we report a simple one-step solution-based process for preparing vertically aligned crystalline C_{60} microtube arrays. A large area of the substrate could be covered with vertically aligned C_{60} microtube crystals that had a hexagonal cross-section and were highly oriented along a crystallographic direction. We believe that the fabricated vertically aligned C_{60} microtube crystals will be useful for applications involving C_{60}-based materials. In addition, the fabrication process can be used to prepare vertically aligned crystals of other organic materials and to develop new candidates for the next generation of materials.

A schematic for fabricating vertically aligned crystalline C_{60} microtube arrays is shown in Figure 1a. In previous studies, 2-propanol has been used to precipitate one-dimensional C_{60} crystals from toluene solutions of C_{60} by using several methods,[5–10,13–15] because of the poor solubility of C_{60} in toluene/2-propanol mixtures. In the current process, 2-propanol was injected slowly into a C_{60}/toluene solution from the bottom through an AAO membrane, mixing with the toluene solution to induce supersaturation of C_{60}. This is similar to the LLIP process, except that the 2-propanol is

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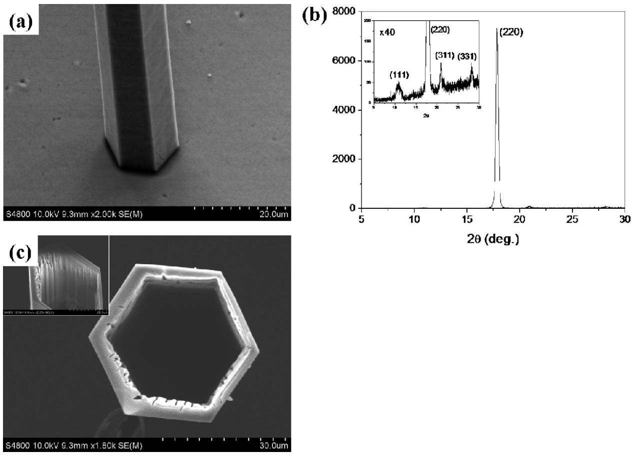

Figure 2. (a) SEM micrograph showing the root of a vertically grown C_{60} microtube in contact with the AAO membrane substrate. (b) X-ray diffraction patterns of a vertically aligned C_{60} microtube array. (c) Top and (inset) side view of a SEM micrograph of a vertically grown C_{60} microtube showing inner-tube structure.

added from the bottom through the AAO membrane. During the injection of 2-propanol, supersaturation near the substrate, i.e., the AAO membrane, results in the heterogeneous nucleation of C_{60} crystals, because the membrane has suitable heterogeneous nucleation sites. Note that the vertically aligned C_{60} microtube crystals could only be prepared using a 2-propanol injection rate of less than 0.05 mL/min when an AAO membrane with a diameter of 25 mm was used. When the injection rate exceeded this value, C_{60} crystals formed in the C_{60}/toluene solution and not on the substrates. The entire surface of the AAO membrane could be covered with vertically aligned C_{60} microtube crystals, as shown in Figure 1b. A top view of the aligned C_{60} microtube array, shown in Figure 1c, clearly shows that all of the aligned C_{60} crystals were tubular in shape. The outer diameter of the microtubes ranged from 10 to 30 μm, and the wall thickness ranged from 1 to 3 μm when fabricated with a 2-propanol injection rate of 0.02 mL/min into 2 mL of a C_{60}/toluene solution. The length of the microtubes was about 500 μm.

Note that the shape and size distributions of the C_{60} microtube crystals were independent of the membrane pore size; that is, the length and the width of the C_{60} microtubes were almost the same when AAO membranes with a pore size of either 20 or 200 nm were used. This indicates that the nucleation and growth of the C_{60} microtubes occurred on the membrane surface and not within the channels. In other words, the C_{60} microtubes formed without templates. This is further supported by observing the surface of the substrate where the bottom of a C_{60} microtube met it. As shown in Figure 2a, the C_{60} microtube grew on the substrate with a clear facetted outer surface. X-ray diffraction images of the vertically aligned C_{60} microtube crystals, shown in Figure 2b, indicated that they were highly crystalline. The magnified diffraction patterns showed that the vertically aligned C_{60} microtubes had a fcc crystal structure. The lattice parameter of the C_{60} microtube crystals was estimated to be approximately 1.41 nm, which is close to the reported value for a fcc C_{60} crystal.[4,6] In particular, the strong diffraction from (220) planes of the microtube array implies that the vertically aligned C_{60} microtube crystals grow in the [110] direction, which is similar to C_{60} nanowhiskers and nanotubes prepared by using the LLIP process.[5–10] Each microtube had a hexagonal cross-section, as shown in Figure 2c.

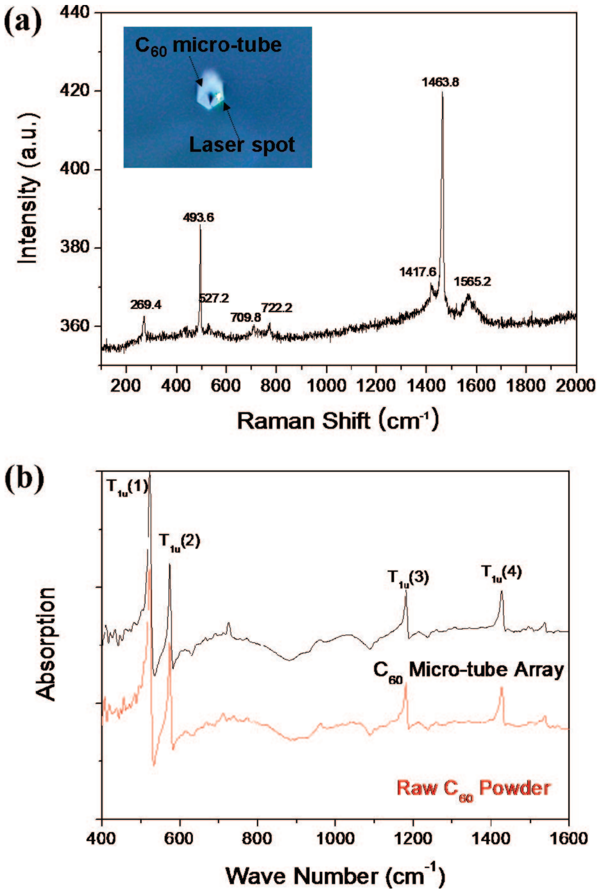

Figure 3. (a) Raman spectrum of the vertically aligned C_{60} microtubes and (inset) an optical micrograph of a single C_{60} microtube during acquisition of the Raman spectra. (b) FT-IR spectra of vertically grown C_{60} microtubes.

The Raman spectrum of the vertically aligned C_{60} microtube array showed peaks at 269.4, 493.6, 709.8, 772.2, 1417.6, 1463.8, and 1575.2 cm^{-1} (Figure 3a), which should correspond to the symmetry modes $H_g(1)$, $A_g(1)$, $H_g(3)$, $H_g(4)$, $H_g(7)$, $A_g(2)$,and $H_g(8)$, respectively. In comparison to the reported Raman lines from isolated C_{60} molecules or pristine C_{60} crystals,[17] the observed Raman spectra were slightly shifted. For example, the $A_g(1)$ mode, which is from the symmetric oscillation of a C_{60} molecule, was shifted from 496 to 493.6 cm^{-1}. In the case of the $A_g(2)$ mode, which is due to the oscillation of pentagons in the C_{60} molecule, the Raman line was shifted from 1469 to 1463.8 cm^{-1}. In addition, a new signal at 527.2 cm^{-1} was observed near the $A_g(1)$ peak. The changes in the Raman spectra are very similar to those of C_{60} nanowhiskers or nanotubes fabricated by using the LLIP process, during which the possibility of polymerization of the C_{60} molecules has been suggested.[5–10] However, the FT-IR spectra of the vertically aligned C_{60} microtube arrays are identical to those of sublimated C_{60} crystals (Figure 3b), and showed no evidence of polymerization. Therefore, the

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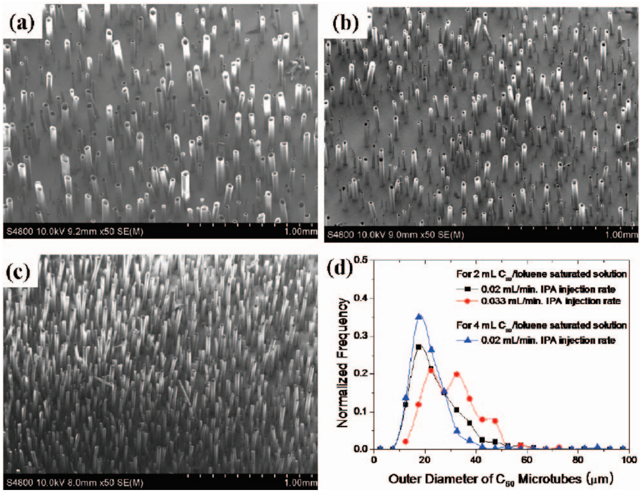

Figure 4. Side view SEM micrographs of vertically aligned C_{60} microtube array fabricated by injecting 2-propanol at a rate of (a) 0.033 and (b) 0.02 mL/min to 2 mL of a C_{60}/toluene saturated solution, and (c) 0.02 mL/min into 4 mL of a C_{60}/toluene saturated solution. (d) Normalized distribution of the outer diameter of vertically aligned C_{60} microtubes with different injection rates of 2-propanol and amounts of the C_{60}/toluene solution.

shifts in the Raman spectra could come from polymerization of the C_{60} molecules during the measurement. In addition, the FT-IR spectra indicated that no solvent remained in the microtubes.

The diameter and density of the C_{60} microtubes could be controlled to some extent by changing the growth conditions, such as the injection rate of 2-propanol and the amount of the C_{60}/toluene saturated solution, as shown in Figure 4. When an injection rate of 0.033 mL/min and 2 mL of a C_{60}/toluene saturated solution were used, the average outer diameter of C_{60} microtubes was 30.4 μm, whereas it was 24.8 μm when an injection rate of 0.02 mL/min was used. At the same time, as shown in images a and b in Figure 4, the density of the vertically aligned C_{60} microtubes on the substrate increased with a decrease in the injection rate of 2-propanol. In addition, the size distribution of the C_{60} microtubes became narrower with a decrease in the injection rate, as shown in Figure 4d. When the amount of the C_{60}/toluene saturated solution was doubled while using the same injection rate of 2-propanol (0.02 mL/min) the average outer diameter of C_{60} microtubes slightly decreased to 21.9 μm, whereas the size distribution became much narrower with a higher density of C_{60}microtubes, as shown in image c and panel d in Figure 4. (See the Supporting Information, Figure S1, for top views of vertically aligned C_{60} microtube arrays grown under different conditions.)

In summary, we developed a one-step, solution-based process for fabricating vertically aligned C_{60} microtube crystals over a large surface area. The large surface area of an AAO membrane could be covered with vertically aligned C_{60} microtube crystals with hexagonal cross-sections that were oriented in a single crystallographic direction. We believe that the fabricated vertically aligned C_{60} microtube crystals will increase the application of C_{60} crystals in, for example, organic electronics, actuators, and microreactors for redox-type reactions. In addition, the fabrication process can be used to prepare vertically aligned crystals of other organic materials and develop new candidates for the next generation of materials.

Supporting Information Available: Detailed experimental procedures and additional SEM figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgment. We extend our deepest thanks to Dr. Cherry Ringer and Dr. Lee, Kyong Ho, for their help in acquiring the Raman spectra and with size measurements. This study was supported by Special Coordination Funds for Promoting Science and Technology of MEXT, Japan.

CM702986F