Tree-shaped C$_{60}$/C$_{60}$-Ferrocene Crystals by Kinetically Controlled LLIP Process

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Abstract. Among the one-dimensional C$_{60}$ crystals, vertically aligned microtubes on the porous alumina substrates provide several interesting features including their well developed hexagonal cross sections and hollow internal structures. These characteristic structures of vertically aligned C$_{60}$ microtubes are caused by their well developed crystals structures and can be predicted by classical nucleation and growth theory. Therefore, the variation of its chemical composition by doping or alloying or variation of kinetic environments during the growth can causes variety of structural changes from vertically aligned hexagonal microtubes. The morphology of vertically aligned C$_{60}$ microtubes is modified by controlling kinetic factors and including of lattice defects. The controlling kinetic factors by modified injection mode of 2-propanol gives various inner structure of vertically aligned C$_{60}$ microtubes such as filled inner structure, double walled inner structure and porous inner structures. The addition of lattice defects by inclusion of ferrocene doped C$_{60}$ gives tree-shaped C$_{60}$ crystals with many branches consisting of bundles of thin needles.

1. Introduction

C$_{60}$ is an interesting form of carbon to both scientists and engineers [1-3] and recently discovered one-dimensional C$_{60}$ nanostructures should bring about new applications for fullerene materials [4-8]. Several methods have been used to precipitate one-dimensional C$_{60}$ crystals from solution, including nanowhiskers, nanotubes, and nanorods [2]. Among them, the liquid-liquid interface precipitation (LLIP) process has been used to produce long C$_{60}$ nanowhiskers or nanotubes without templates. Moreover, recently introduced vertically aligned C$_{60}$ microtubes on the porous alumina substrate provide new potential application fields by kinetically controlled LLIP process [9].

Among those one-dimensional C$_{60}$ crystals, vertically aligned microtubes on the porous alumina substrates provide several interesting features including their well developed hexagonal cross sections and hollow internal structures. These characteristic structures of vertically aligned C$_{60}$ microtubes are caused by their well developed crystals structures and can be predicted by classical nucleation and growth theory. Therefore, the variation of its chemical composition by doping or alloying or variation of kinetic environments during the growth can causes variety of structural changes from vertically aligned hexagonal microtubes.
In this study, the effect of kinetic variation during the growth and the effect of doping of ferrocene derivative of C\textsubscript{60} to pure C\textsubscript{60} crystals on the morphology are investigated. The variations of kinetic environments during the growth of vertically aligned C\textsubscript{60} microtubes were controlled by controlling the injection of 2-propanol used for precipitation of C\textsubscript{60} crystals from its solution. In addition, the inserting of small amount of ferrocene doped C\textsubscript{60} induces the morphological changes of C\textsubscript{60} crystals hence provide 3-dimensional tree-shaped C\textsubscript{60} crystals.

2. Experimental Procedures

2.1. Preparation of solutions

Saturated C\textsubscript{60} solutions in toluene (dehydrated 99.5%, organic synthesis grade) was prepared by mixing an excess amount of C\textsubscript{60} powder (99.95% sublimated, MTR Ltd.) with toluene, followed by ultrasonication for 30 min. After sonication, the solutions were filtered through 450 nm Teflon syringe filters (Puradisc\textsuperscript{TM}, Whatman Inc). The solution containing 6 mol. % of ferrocene containing C\textsubscript{60} derivatives, as shown in Scheme 1, and C\textsubscript{60} in toluene, called ferrocene doped C\textsubscript{60} solution, was prepared with same route to saturated C\textsubscript{60} solution.

2.2. Preparation of vertically aligned C\textsubscript{60} and ferrocene doped C\textsubscript{60} crystals

In order to fabricate vertically aligned C\textsubscript{60} and crystals and ferrocene doped C\textsubscript{60} crystals, a glass filter holder for filters with a diameter of 25 mm was used. A syringe pump was connected to the lower part of filter holder by Teflon tubes. Anodized alumina (A\textsubscript{2}O) filters (Anodisc 25, 200 nm pore size, Whatman Inc.) were loaded in the filter holder. The solution (2 mL) was mixed with a 2-propanol with controlled rate using syringe pump. The injection rate was 0.02ml/min for vertically aligned crystals. All procedures were conducted in an incubator at 5 °C under ambient light. The amount of injected precipitator was 6 mL for 2 mL of the C\textsubscript{60} solution. The separated C\textsubscript{60} crystals were dried in an incubator at 5 °C in air. SEM micrographs were obtained on a FE-SEM (Hitachi-4800, 10 kV), and HRTEM and STEM were performed on a JEOL (JEM-2100F, 160 kV).

3. Results and Discussions

3.1. Effect of kinetic environments on the morphology of vertically aligned C\textsubscript{60} crystals

The vertically aligned C\textsubscript{60} microtubes can be prepared on the porous alumina substrate as reported before\cite{3}. In this result, on interesting feature is that the outer surface of each microtube is smooth, while the inner surfaces are serrated. The reason is not clear, but it gives possibility to control inner structures.

The inner structure of vertically aligned C\textsubscript{60} microtubes can be controlled by changing the injection mode. When the 2-propanol was injected continuously, the vertically aligned C\textsubscript{60} microtubes with smooth outer surfaces and serrated inner surfaces are formed. One interesting feature is that when the 2-propanol is injected continuously until the vertically aligned C\textsubscript{60} microtubes are formed, which is actually 4 hours injection with rate of 0.02ml/min. to 2ml of saturated C\textsubscript{60} solution in toluene, and
Figure 1. SEM morphology of vertically aligned C$_{60}$ microrods prepared by injection of 2-propanol for 4 hours and incubated for 4 hours to the C$_{60}$/toluene saturated solution followed by holding 2-propanol injection and having incubation time around 4 hours, the inner space of microtubes are filled and they turns into microrods as shown in Fig. 1. It gives an interesting fact that the outer surfaces are formed first and then the inner structures are formed. Considering the serrated structures of inner space in vertically aligned C$_{60}$ microtubes, the inner structures can be modified by changing injection mode.

When 2-propanol was injected with modified mode as shown in Fig. 2(a), reinjection after holding, one-more wall is formed within the C$_{60}$ microtubes as shown in Fig. 2(b). When the 2-propanol was injected in stepwise mode as shown in Fig. 3(a), complex inner structures were formed including small microtubes on the top of large microtubes and porous inner structures. The changes in inner structure of vertically aligned C$_{60}$ microtubes by modification of injection mode give a possibility that the inner structures are mud-like phases, while the outer surfaces are rigid solids.

Figure 2. SEM morphology of vertically aligned C$_{60}$ microtubes with double walled inner structure. (a) 2-propanol injection mode and (b) double walled C$_{60}$ microtubes.
Figure 3. SEM morphology of vertically aligned C_{60} microtubes with complex inner structures including porous inner walls and small tubes on the wall of large tubes. (a) 2-propanol injection mode and (b) double walled C_{60} microtubes.

3.2. Effect of addition of ferrocene doped C_{60} on the morphology of C_{60} crystals
In addition to the kinetic modification, the addition of defects by addition of ferrocene doped C_{60} changes the morphology of C_{60} crystals dramatically as shown in Fig. 4. The tree-shaped structures with many branches composing of bundles of thin rods can be fabricated on the porous alumina substrates.

Figure 4. SEM micrographs of C_{60} trees on the porous alumina substrate prepared from the mixture of C_{60} and ferrocene doped C_{60} by 6 mol. %. (a) Low magnification micrograph showing the forest of C_{60} trees and (b) closer look of C_{60} tree with branches. (c) Closer image near the branches and (d) high magnification of end of branches showing bundles of needle shaped C_{60} crystals.
One interesting feature is that the structure is not affected by the modification of 2-propanol injection rate in the range from 0.01ml/min. to 0.04ml/min. It means that the structure is deeply dependent on the including crystal defect induced by addition of ferrocene doped C\textsubscript{60}, rather than kinetic parameters. The TEM observation shown in Fig. 5(a) gives a factor that each rod forming the bundle is rolled form of thin plate. The thin plates are divided into thin needles with sharp tips as shown in Fig. 5(b). The HRTEM image and diffraction patterns in Fig. 5(c) and (d) shows the thin plates are well crystallized. These structural characters give a possibility that they are formed by splitting and deformation due to the lattice strain due to inclusion of ferrocene doped C\textsubscript{60}. However, to find out the detail mechanisms and structure, more analysis is required.

Figure 5. TEM micrographs of C\textsubscript{60} trees prepared from the mixture of C\textsubscript{60} and ferrocene doped C\textsubscript{60} by 6 mol. %. (a) Low magnification image, (b) high magnification image showing splitting, (c) high resolution TEM image and (d) diffraction pattern.
4. Summary

The morphology of vertically aligned C$_{60}$ microtubes is modified by controlling kinetic factors and including of lattice defects. The controlling kinetic factors by modified injection mode of 2-propanol gives various inner structure of vertically aligned C$_{60}$ microtubes such as filled inner structure, double walled inner structure and porous inner structures. The addition of lattice defects by inclusion of ferrocene doped C$_{60}$ gives tree-shaped C$_{60}$ crystals with many branches consisting of bundles of thin needles.

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