Research Article

Fabrication of C₆₀ Fullerene Nanofibers by Volatile Diffusion Method

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C₆₀ fullerene nanofibers (FNFs) were for the first time prepared by a volatile diffusion method using toluene as solvent and isopropyl alcohol as precipitation agent in room temperature, 25°C. FNFs with different lengths, aspect ratios, and morphologies could be fabricated by changing incubation time. Meanwhile, as for a crystal growth process, a possible mechanism of the formation of the crystal of FNFs was proposed in which the short and thin FNFs are the result of crystal growth, and self-assembly happens between the short fibers and thus leads to the formation of thick and long bundles of the FNFs.

1. Introduction

Very recently, a series of novel one-dimensional (1D) nanocrystals, with individual C₆₀ molecules as building blocks, have set off a renaissance in scientific research, and vast endeavor has been made to find a controllable method to fabricate high quality 1D C₆₀ nanocrystals or to exploit its potential application in catalyst carriers [1], solar cells [2], electronic devices [3], superconductor [4] and so on [5, 6]. Up to date, the self-assembly techniques that have been reported mainly include (1) reprecipitation method, where mixing of the fullerene saturated solution with alcohol would result in the direct precipitation of fullerene crystals [7, 8] (2) template method via injecting alcohol through anodized aluminum oxide membranes to C₆₀ solution where self-assembly happens [9, 10], (3) liquid-liquid interface precipitation (LLIP) method, where both nucleation and growth of FNFs take place at the interface between good and bad solvents [11–14], and (4) evaporation method, where, by evaporating C₆₀-solvents on a substrate or C₆₀-solution slowly, C₆₀ crystals would separate out [15, 16].

Despite the extensive exploring 1D FNFs preparation approaches, however, it is still desirable to develop more promising methods to fabricate the structures with specific shapes and controlled dimensionality.

Herein, we further developed volatile diffusion method [17] to prepare FNFs. In this method, FNFs with both micro- and millimeter in length could be obtained by room temperature stationary culture. Interestingly, self-assembly happened among FNFs and resulted in the formation of bundles of FNFs submerged in the bottom. Compared with the self-assembly techniques mentioned previously, this method is shadowed with congenitally deficiency of long cultivation cycle, however, highlighted with the varieties of length, aspect ratio, and even morphologies and its vast potential application as microdevices. Meanwhile, it is worthy noticing that the poor solvents used by this method could be reused, which is meaningful in industry development.

2. Experimental

FNFs were prepared via volatile diffusion method by putting an unsealed smaller glass bottle (15 mL, inner diameter is 17 mm) filled with 0.5 mg/mL C₆₀-toluene solution (6 mL) into a sealed bigger bottle (100 mL, inner diameter is 35 mm) containing 25 mL isopropyl alcohol (IPA) and making sure the level of IPA is not high enough to pour into the unsealed bottle. Under these conditions, the whole equipment was kept standing for at least 3 days at room temperature (RT,

FIGURE 1: Experimental scheme of volatile diffusion method.

FIGURE 2: POM images of FNFs cultured for 7 days (a), 1 month (d), and 2 months (g). SEM images of FNFs cultured for 7 days ((b) and (c)), 1 month ((e) and (f)) and 2 months, ((h) and (i)).

FIGURE 3: Raman spectrum of FNF.

approximately 25°C) for stationary culture of FNFs. Figure 1 shows the experimental scheme.

The morphology and structure of C_{60} FNFs were characterized by using polarizing optical microscope (POM, Leica DM2500P), scanning electron microscope (SEM, JEOL, JSM-7500F), transmission scanning electron microscope (TEM, JEOL, JEM-2100), Raman spectroscope (Renishaw 2000 spectrometer, 785 nm laser), and Fourier transform infrared spectroscope (FT-IR, Bruker, Hyperion 1000/2000). X-ray diffraction experiment was performed on a Rigaku diffractometer (XRD, Rigaku, D-Max 2500/PC, Ni-filtered $Cu-K_{\alpha}$ radiation, $\lambda = 1.5418 \text{ \AA}$). Before XRD analysis, the sample was dried at 100°C in a vacuum oven (Memmert, VO200) for 1 h.

3. Results and Discussion

Figure 2 shows the morphologies of fullerene nanofibers with different incubation times. After about 7 day's stationary culture, the length of the fibers is appropriately 10–20 μm , and the diameter is about 1 μm . (see Figures 2(a)–2(c)). Moreover, the fibers become much longer with hundreds of micrometers in length if the cultivation continued to a month (see Figures 2(d)–2(f)). With time prolonging, much longer and thicker fibers could be fabricated. The fibers are visible to the naked eyes and the length could even reach a centimeter (see Figures 2(g)–2(i)). And from the long fibers, due to the blocky size, it is easy to find the imprint of self-assembly. Quite a lot of discussions expanded go around the formation mechanism of the 1D FNFs in the former research, and Miyazawa et al. [11] attributed this phenomenon in LLIP method to the polymerization in axial.

However, as shown in Figure 3, the Raman peaks appearing at 270, 430, 569, 771, 1099, 1250, 1425, and 1574 cm^{-1} are attributed to 8 H_g -modes of C_{60} molecule, respectively. The other peaks at 494 and 1468 cm^{-1} are responsible for

A_g -breathing and the A_g -pinch mode of C_{60} molecule. Compared with the pristine C_{60} powder, no special shift of those peaks has been observed, especially for the $A_g(2)$ mode, which is connected with intermolecular bonding and vastly used to discuss the structural and electronic properties of C_{60} molecules [18], and this phenomenon reveals that crystallization but not polymerization has happened during the formation of FNFs [19].

Hereof, from Figure 4, for the XRD pattern of the fiber in air, it can be seen that FNFs prepared by this method are well crystallized with an FCC system with a cell dimension of $a = 1.44 \text{ nm}$. Previous studies of FNFs prepared by solution evaporation method or LLIP one demonstrate the same result after the fiber dried in vacuum when toluene was used [11, 20]. With the common view that solvents have an influence on the crystal structure, further research is needed.

Meanwhile, anisotropic nuclei and selective growth of crystal are the causes of the 1D structure formation [21, 22]. Therefore, a possible formation mechanism of the FNFs is proposed as shown in Figure 5.

After 7 days of stationary culture, the volume of C_{60} -toluene solution is unchanged. For the common sense, solution exchange must have happened, which means that a slight amount of IPA has diffused into the C_{60} -toluene solution and meanwhile a slight amount of toluene did the same. Due to the incompatibility of solvents ($\epsilon_{\text{toluene}} = 2.38$ and $\epsilon_{\text{IPA}} = 19.93$), liquid-liquid microinterface is formed. Based on the previous research, very short fibers could be fabricated and those fibers are small enough even to play the role of nuclei [23]. From the phenomenon that the volume of the C_{60} -toluene solution is still reducing after a month, it is speculated that the evaporation of toluene solution gains the upper hand during this period, which leads to a dynamic fluctuation which offers the driving force of the continuing growth of the fiber of the system.

A month later, the solution becomes fairly crowded full of long and thin fibers. For stable presence, self-assembly

FIGURE 4: XRD pattern of FNFs prepared by volatile diffusion method.

FIGURE 5: Schematic diagram of the formation path of FNFs.

happens among FNFs and there come the results—long and thick fibers formed and sunk in the bottom (see Figure 5(c)).

4. Conclusions

FNFs with different lengths, aspect ratios, and morphologies were prepared by using volatile diffusion method. After about 7 day's stationary culture, the length of the FNFs is appropriately 10–20 μm , and the diameter is about 1 μm . The

diffusion into C_{60} solution of IPA leads to the formation of nuclei, and after a one-month growth, self-assembly happens among the thin fibers which results in the formation of thick fibers. Raman spectrum reveals the impossibility of polymerization but not crystallization of C_{60} in the FNFs.

Conflict of Interests

The authors declare that they have no conflict of interests.

Acknowledgments

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