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The effect of light irradiation on the growth of C\textsubscript{60}-C\textsubscript{70} nanofibers

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1. Introduction

Fullerene C\textsubscript{60} nanofibers (FNFs) are one form of fullerene crystal with 1-dimensional (1-D) structure. This special crystal gets many attentions since they do not only own the characteristic of fullerene C\textsubscript{60} monomer, but also their size and dimension as 1-D material. [1]

Consequently, many researches focused on the application designs of this material based on the property or structure of those fibers. For example, due to their larger specific surface area, FNFs have been vastly reported as catalyst carriers. [2, 3] With the nature of semiconductor and higher Young’s modulus compared to C\textsubscript{60} crystals [4], FNFs could be used as electron devices. [5] The discovery of their superconductivity established on electron acceptor characteristic by Takeya et al. through intercalation of potassium extends their application in maglev, radiation detectors, microwave generator and so on. [6] At the same time, FNFs polymer hybrid with potential application in electromagnetic shielding materials, highly hydrophobic materials, and antistatic materials emerged. [7, 8] Even, a new nanoporous carbon 1-D material, which is the thermal conversion of FNFs, shows excellent electrochemical capacitance and superior sensing properties for aromatic compounds compared to commercial activated carbons. [9]

Due to their marvellous potential application in many areas, several methods have been developed for the construction of FNFs. They are (1) solution evaporation [10, 11], (2) template technique [12, 13], (3) surfactant-assisted method [14], volatile diffusion method [15], and (4) LLIP method. [16, 17] With the advantages of no requirement of physical templates and catalysts, LLIP method generally acknowledged as the way of great promise for self-assembly to construct this 1D structure. [18, 19] Meanwhile, great attentions have been paid to the growth of this 1-D materials and the further development of this method, not only in the morphologies, such as aspect ratio, tube containing rate, formation mechanism discussion [20], but also their compositions. Various FNFs composed not only C\textsubscript{60}, but also C\textsubscript{70}, C\textsubscript{60}[C(COOC\textsubscript{2}H\textsubscript{5})\textsubscript{2}]\textsubscript{2}(\textsubscript{2}5-C\textsubscript{60})Pt(PPh\textsubscript{3})\textsubscript{2} or even C\textsubscript{60}-C\textsubscript{70} mixture have been successfully fabricated using LLIP method. [21-24] Indeed, constructing C\textsubscript{60}-C\textsubscript{70} FNFs have been widely studied, since C\textsubscript{60}-C\textsubscript{70} mixture is much cheaper than C\textsubscript{60} or C\textsubscript{70} and low-cost fullerene fibers are mostly studied to practical application. The Young’s moduli of C\textsubscript{60}-C\textsubscript{70} FNFs were tested by a transmission electron microscope equipped with atomic force microscope functionality and were found to increase with increasing C\textsubscript{70} content in the mother solutions [25, 26]. However, quantitative analysis of C\textsubscript{60}-C\textsubscript{70} ratio in solid C\textsubscript{60}-C\textsubscript{70} FNFs was still urgent problem and quite meaningful for better understanding of the Young’s moduli, optical properties or even the formation process of C\textsubscript{60}-C\textsubscript{70} FNFs.

Herein, based on our former researches about the significant relationships between the formation of FNFs and the charge transfer (CT) adducts [27, 28], we used the CT complex, formed between C\textsubscript{60} or C\textsubscript{70} and pyridine, which are susceptible to light irradiation, to fabricate C\textsubscript{60}-C\textsubscript{70} nanofibers with different C\textsubscript{60}-C\textsubscript{70} ratio. By changing the irradiation time, we fabricated FNFs with different but linearly C\textsubscript{60}-C\textsubscript{70} ratio characterised by using high-pressure liquid chromatography analysis (HPLC). Besides, changing the irradiation time may well be a method to control the length or diameter of those fibers through polarizing optical microscope (POM) and scanning electron microscope (SEM) analysis. Ultraviolet-visible (UV-Vis) spectrometer was used to analysis the mechanism.

2. Experimental

2.1 Synthesis of C\textsubscript{60}-C\textsubscript{70} FNFs
Firstly, a pyridine-saturated colloid with C$_{60}$-C$_{70}$ (C$_{70}$ 22mlo%; MER Corp, Tucson, AZ, USA) was prepared by filtering 10ml 1mg/ml C$_{60}$-C$_{70}$-pyridine colloid according to literature. [18,19] Then, the colloid was exposed to white light in the region of 300–700 nm (20W, irradiation distance: 8cm) at 8 °C for 0, 30, 60 and 90min. A typical procedure for the preparation of the FNFs is as follows: 1ml of C$_{60}$-C$_{70}$-pyridine colloid was poured into 20ml transparent glass bottle and 9ml of (isopropyl alcohol) IPA was added. The mixture of colloid solution was kept at 8 °C and floating batting of metallic luster fibers appeared after 48h.

2.2 Characterization of C$_{60}$-C$_{70}$ FNFs

The FNFs obtained were characterized by using polarizing optical microscope (POM, Leica DM-2500P), scanning electron microscope (SEM, JEOL JSM_6700F), high-pressure liquid chromatographic instrument (JAI HPLC-9104) and UV-Vis spectrometer (SHIMADZU UV-2450). For the purpose of electron microscopic measurement, the specimens were placed on aluminium foil as substrate. In HPLC analysis, Buckyprep column chromatography was used and toluene was selected as mobile phase. The detection wavelength was 310nm and column pressure is 48-51Pa.

3. Results and discussion

3.1 Morphology analysis

![Fig. 1 Optical microscope images of C$_{60}$-C$_{70}$ FNPs prepared in C$_{60}$-C$_{70}$-pyridine colloid with different time of light irradiation (a: 0min; b: 30min; c: 60min; d: 90min)](image)

Fig. 1 shows the optical microscope images of FNPs prepared in C$_{60}$-C$_{70}$-pyridine colloid with (a) 0min, (b) 30min, (c) 60min and (d) 90min irradiation. For their 1-D morphology, it is acknowledged that the anisotropy of nuclei and the selective growth of crystal are the causes. [17, 29]

These C$_{60}$-C$_{70}$ fibers are quite long and some of them could reach millimetre scale. In comparison, the fibers in Fig.1 (b), (c) and (d) are similar, which all tend to be fine and tangles. Relativity, a few crude and straight fibers emerged in Fig.1 (a). That’s to say that fibers without light irradiation have larger distribution in diameters. Thus, we hold the views that the light irradiation may have good effects on the fine morphology of the C$_{60}$-C$_{70}$ nanofibers.

3.2 Component analysis

![Fig. 3 HPLC of C$_{60}$-C$_{70}$ soot (a) and FNPs prepared in C$_{60}$-C$_{70}$-pyridine colloid with different time of light irradiation (b: 60min; c: 60min; d: 90min)](image)

Fig. 3 shows the HPLC images of soot (a) and FNPs prepared in C$_{60}$-C$_{70}$-pyridine colloid with (a) 0min, (b) 30min, (c) 60min and (d) 90min light irradiation, respectively. The surfaces of the fibers are flat. Meanwhile the diameters of those fibers tend to be a wild distribution from hundreds of nanometers to several microns. A random statistical analysis of FNPs shows that the average diameters of fibers prepared in C$_{60}$-C$_{70}$-pyridine colloid with 0, 30, 60 and 90min irradiation are 690, 680, 450 and 360nm, separately. The longer irradiation does, the thinner those fibers would be. And from the SEM images we can see that some of them are hollow structures. Also, with enlarging the irradiation time, the diameter distribution of the FNPs is getting smaller.

In fact, the size distribution of C$_{60}$ FNPs aroused great attention since the discovery of those 1-D materials. Solvent ratio, growth temperature [20], solution volume [30], operation process [17], and even the area size of the interface. [31] But for C$_{60}$-C$_{70}$ nanofibers, the composition becomes another important factor, apparently, has connections with the morphologies distribution.

![Fig. 2 SEM images of C$_{60}$-C$_{70}$ FNPs prepared in C$_{60}$-C$_{70}$-pyridine colloid with different time of light irradiation (a: 0min; b: 30min; c: 60min; d: 90min)](image)
0min, c: 30min, d: 60min, e: 90min)

Fig. 3 shows the HPLC traces of C_{60}-C_{70} soot and FNFs prepared in C_{60}-C_{70}-pyridine solution with different irradiation time on the C_{60}-C_{70}-pyridine solution. The retention time (t) of C_{60} and C_{70} are 12.3min and 20min, respectively. [25, 26, 32] The component percentages of C_{60} and C_{70} are given by the ratio of the areas of the two peaks in Fig. 3. [33] The C_{70} content in FNFs that have not been irradiated by light is as high as 28mol%, however, the C_{70} content in fibers that have been irradiated for 90min is only 11mol%. Combining the C_{70} content in FNFs with 30 and 60min light irradiation, which are 20mol% and 15mol%, separately, a linear relationship could be found between C_{70} content in FNFs and the length of white light irradiation, as follows:

\[ y_{C_{70} \text{ content}} = 0.19t + 26.90 \] (1)

**3.3 Mechanism analysis**

The consistency of subsequent steps suggests that the differentiation occurs in light irradiation. As a matter of fact, during white light irradiation, a slight colour change from brown-red to dark brown has been observed. For analysing of this process and based on our former researches [27, 28], we conducted UV-Vis spectra analysis of this C_{60}-C_{70} system, as shown in Fig. 4.

![Graph showing the relationship between irradiation time and C_{70} content of FNFs.](image)

**Fig. 4 Relationship between irradiation time and C_{70} content of FNFs**

By increasing the length of light irradiation, the C_{70} content in FNFs decreased from 28mol% to 11mol%. The values of C_{70} content (\(y_{C_{70} \text{ content}}\)) were shown in Fig. 4 and fitted by the following curve as a function of length of light irradiation (t).

\[ y_{C_{70} \text{ content}} = 0.19t + 26.90 \] (1)

In Fig. 5, four peaks emerged in the region of 350nm-700nm in the UV-Vis spectra in the C_{60}-C_{70}-pyridine solution. The absorption at 380nm and 600nm are the characteristic of C_{60}. [34] And the peak at 406nm corresponds to C_{70} molecule. [35] Additionally, in UV-Vis spectra of C_{60}-C_{70}-pyridine solution, a strong absorption at the region of 400-500nm appears. It should be noted that the absorption in this region refers to CT adducts. [36, 37]. Similar absorption has been reported for various thin films of C_{60} and C_{70} and attributed to aggregate of fullerene molecule. Fullerene C_{60} or C_{70} have the ability to accept multiple electrons [38, 39]. On the other hand, pyridine has a nitrogen atom with lone pair, which allows the molecule to be an electron donor [37, 40]. So, it’s possible that CT adducts should exist in the C_{60}-C_{70}-pyridine system in this condition. Charge transfer reactions through photo excitation between C_{60}, C_{70} and pyridine happened [37] as follows:

![Image of C_{60}, C_{70}, and pyridine with arrows indicating charge transfer reactions.](image)

**Fig. 5 UV-Vis spectra of C_{60}-C_{70}-pyridine solution with different irradiation time (a: 0min; b: 30min; c: 60min; d: 90min)**

In Fig. 5, the absorbance at 350nm-700nm in the UV-Vis spectra in the C_{60}-C_{70}-pyridine solution. The absorbance at 380nm and 600nm are the characteristic of C_{60}. [34] And the peak at 406nm corresponds to C_{70} molecule. [35] Additionally, in UV-Vis spectra of C_{60}-C_{70}-pyridine solution, a strong absorption at the region of 400-500nm appears. It should be noted that the absorption in this region refers to CT adducts. [36, 37]. Similar absorption has been reported for various thin films of C_{60} and C_{70} and attributed to aggregate of fullerene molecule. Fullerene C_{60} or C_{70} have the ability to accept multiple electrons [38, 39]. On the other hand, pyridine has a nitrogen atom with lone pair, which allows the molecule to be an electron donor [37, 40]. So, it’s possible that CT adducts should exist in the C_{60}-C_{70}-pyridine system in this condition. Charge transfer reactions through photo excitation between C_{60}, C_{70} and pyridine happened [37] as follows:

Such interaction between C_{60}, C_{70} and pyridine in the pressure of light may have influence of fullerene cluster, which serves as nucleation site or building materials for larger structure. [41] Thus, when different length of light irradiation is offered, different balance between C_{60} and C_{70} and pyridine established. From the figure, we can see that the content of CT is increasing with enlarging the length of light irradiation time. We supposed that CT can only serve C_{60} molecules for crystal growing, while not for crystal nucleating. [28] When the content of CT is increasing, the speed of crystal growing will slow down. According to the theory of H. Ji [17], C_{60} molecules prefers the corners of the hexagonal cross section, then the edges of the hexagonal cross section, lastly the center portion of the hexagonal cross. As the existence of CT, the C_{60} molecules can choose the growing sites more independently, then the selectivity of C_{60} molecules attached to the crystal seeds will be better, the diameter distribution tends to be uniform. Additionally, we suppose that C_{60} is easier to form CT complex with pyridine compared to C_{70}, and it can explain the reason why there is a decreasing of C_{70} content as the longer irradiation time. Meanwhile, the differentiation of each balance in cluster structure or concentration leads to the distinction of size and component ratio of FNFs.

**Conclusions**

C_{60}-C_{70} soot was used in the article to fabricate C_{60}-C_{70} FNFs by LLIP method. With the increase of length of light
irradiation, the diameter of FNFs tends to be thinner, meanwhile, the content of C\textsubscript{70} in FNFs drops. We ascribed those phenomena to the formation of C\textsubscript{60} and C\textsubscript{70} pyridine charge-transfer adducts, which is sensitive to light.

### Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.


Charge transfer reactions between $C_{60}$, $C_{70}$ and pyridine

White light (20W) on $C_{60}/C_{70}$-pyridine colloid

0 min

$+IPA$ for 12 h

$C_{70}$ content

30 min

$+IPA$ for 12 h

Average diameter

60 min

$+IPA$ for 12 h

90 min

$+IPA$ for 12 h