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Papers

The effect of light irradiation on the growth of C₆₀-C₇₀ nanofibers

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C₆₀-C₇₀ nanofibers (FNFs) were prepared using a modified liquid-liquid interfacial precipitation (LLIP) method in the pyridine solution of C₆₀-C₇₀ soot and isopropyl alcohol (IPA) under illumination with white light in the region of 300–700 nm. The composition of the C₆₀-C₇₀ FNFs was analysed by high-pressure liquid chromatography. It is found that the concentration of C₇₀ in the C₆₀-C₇₀ FNFs is decreased with the increase of irradiation time in the C₆₀-C₇₀-pyridine solution. In morphology aspect, polarizing optical microscope (POM) and scanning electron microscope (SEM) were used and changing the irradiation time may well be a method to control the length or diameter of those fibers. In mechanism analysis, it was speculated that the charge transfer (CT) complexes between fullerenes C₆₀, C₇₀ and pyridine that could be excited by photo was the explanation of this phenomenon.

1. Introduction

Fullerene C₆₀ 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 C₆₀ 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 C₆₀ 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 C₆₀, but also C₇₀, C₆₀[C(COOC₂H₅)₂]_n(_n 2-C₆₀)Pt(PPh₃)₂ or even C₆₀-C₇₀ mixture have been successfully fabricated using LLIP method. [21–24] Indeed, constructing C₆₀-C₇₀ FNFs have been widely studied, since C₆₀-C₇₀ mixture is much cheaper than C₆₀ or C₇₀ and low-cost fullerene fibers are mostly studied to practical application. The Young's moduli of C₆₀-C₇₀ FNFs were tested by a transmission electron microscope equipped with atomic force microscope functionality and were found to increase with increasing C₇₀ content in the mother solutions [25, 26]. However, quantitative analysis of C₆₀-C₇₀ ratio in solid C₆₀-C₇₀ FNFs was still urgent problem and quite meaningful for better understanding of the Young's moduli, optical properties or even the formation process of C₆₀-C₇₀ 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 C₆₀ or C₇₀ and pyridine, which are susceptible to light irradiation, to fabricate C₆₀-C₇₀ nanofibers with different C₆₀-C₇₀ ratio. By changing the irradiation time, we fabricated FNFs with different but linearly C₆₀-C₇₀ 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 C₆₀-C₇₀ FNFs

Firstly, a pyridine-saturated colloid with C₆₀-C₇₀ (C₇₀ 22mole%; MER Corp, Tucson, AZ, USA) was prepared by filtering 10ml 1mg/ml C₆₀-C₇₀-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 C₆₀-C₇₀-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 C₆₀-C₇₀ 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

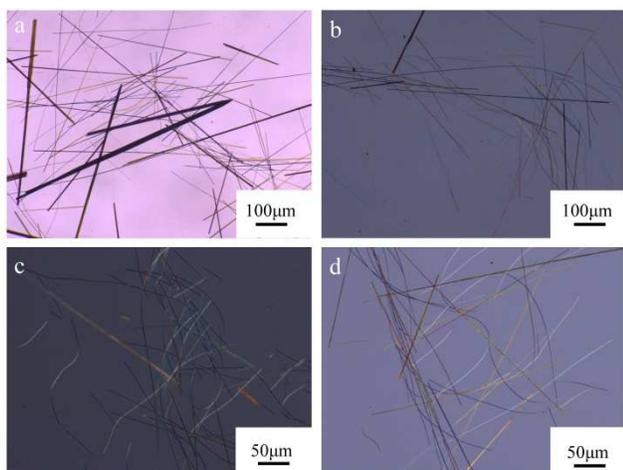


Fig. 1 Optical microscope images of C₆₀C₇₀ FNFs prepared in C₆₀-C₇₀-pyridine colloid with different time of light irradiation (a: 0min; b: 30min; c: 60min; d: 90min)

Fig. 1 shows the optical microscope images of FNFs prepared in C₆₀-C₇₀-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 C₆₀-C₇₀ 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. Relatively, 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 C₆₀-C₇₀ nanofibers.

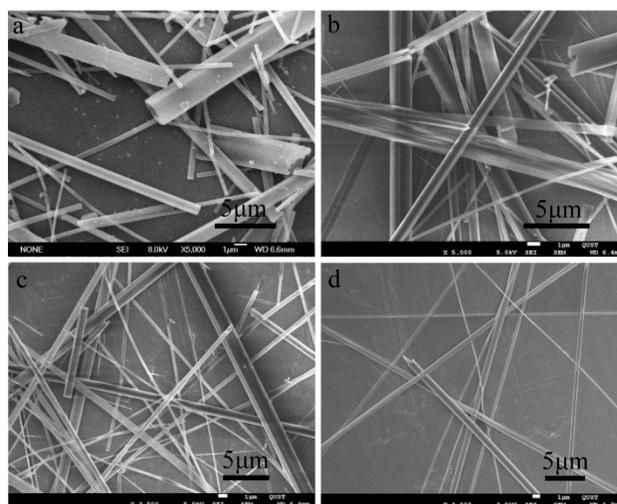


Fig. 2 SEM images of C₆₀-C₇₀ FNFs prepared in C₆₀-C₇₀-pyridine colloid with different time of light irradiation (a: 0min; b: 30min; c: 60min; d: 90min)

Fig. 2 shows the SEM images of FNFs prepared in C₆₀-C₇₀-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 FNFs shows that the average diameters of fibers prepared in C₆₀-C₇₀-pyridine solution 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 FNFs is getting smaller.

In fact, the size distribution of C₆₀ FNFs 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 C₆₀-C₇₀ nanofibers, the composition becomes another important factor, apparently, has connections with the morphologies distribution.

3.2 Component analysis

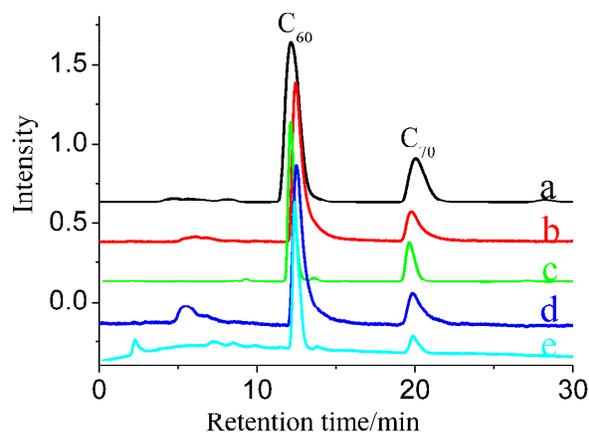


Fig. 3 HPLC of C₆₀-C₇₀ soot (a) and FNFs prepared in C₆₀-C₇₀-pyridine colloid with different time of light irradiation (b):

0min, c: 30min, d: 60min, e: 90min)

Fig. 3 shows the HPLC traces of C₆₀-C₇₀ soot and FNFs prepared in C₆₀-C₇₀-pyridine solution with different irradiation time on the C₆₀-C₇₀-pyridine solution. The retention time (t_r) of C₆₀ and C₇₀ are 12.3min and 20min, respectively. [25, 26, 32] The component percentages of C₆₀ and C₇₀ are given by the ratio of the areas of the two peaks in Fig. 3. [33] The C₇₀ content in FNFs that have not been irradiated by light is as high as 28mol%, however, the C₇₀ content in fibers that have been irradiated for 90min is only 11mol%. Combining the C₇₀ content in FNFs with 30 and 60min light irradiation, which are 20mol% and 15mol%, separately, a liner relationship could be found between C₇₀ content in FNFs and the length of white light irradiation, as follows:

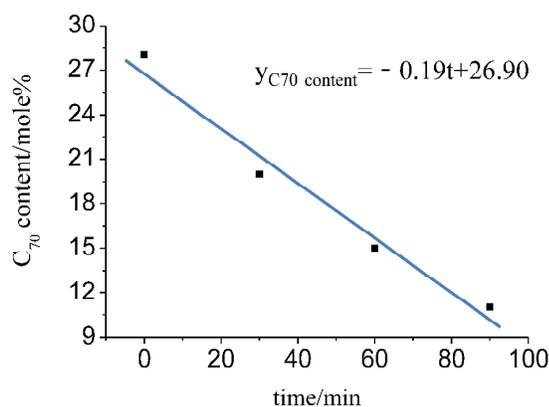


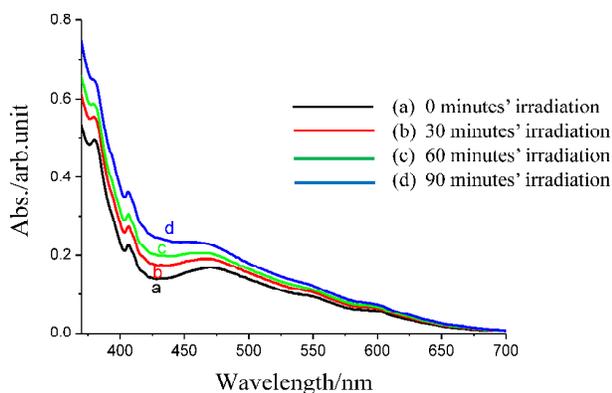
Fig. 4 Relationship between irradiation time and C₇₀ content of FNFs

By increasing the length of light irradiation, the C₇₀ content in FNFs decreased from 28mol% to 11mol%. The values of C₇₀ content (y_{C₇₀ content}) were shown in fig. 4 and fitted by the following curve as a function of length of light irradiation (t).

$$y_{C_{70} \text{ content}} = -0.19t + 26.90 \quad (1)$$

3.3 Mechanism analysis

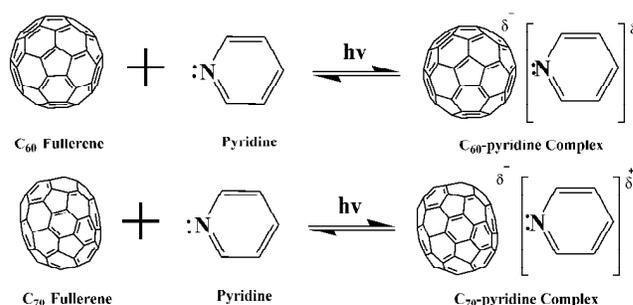
The consistency of subsequent steps suggests that the differentiation occurs in light irradiation. As a matter of fact, during white light irradiation, a slight colour change from brown-red to dark brown has been observed. For analysing of this process and based on our former researches [27, 28], we conducted UV-Vis spectra analysis of this C₆₀-C₇₀ system, as shown in Fig. 5.



30

Fig. 5 UV-Vis spectra of C₆₀-C₇₀-pyridine solution with different irradiation time (a: 0min; b: 30min; c: 60min; d: 90min)

In Fig. 5, four peaks emerged in the region of 350nm-700nm in the UV-Vis spectra in the C₆₀-C₇₀-pyridine solution. The absorption at 380nm and 600nm are the characteristic of C₆₀. [34] And the peak at 406nm corresponds to C₇₀ molecule. [35] Additionally, in UV-Vis spectra of C₆₀-C₇₀-pyridine solution, a strong absorption at the region of 400-500nm appears. It should be noted that the absorption in this region refer to CT adducts. [36, 37]. Similar absorption has been reported for various thin films of C₆₀ and C₇₀ and attributed to aggregate of fullerene molecule. Fullerene C₆₀ or C₇₀ 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 C₆₀-C₇₀-pyridine system in this condition. Charge transfer reactions through photo excitation between C₆₀, C₇₀ and pyridine happened [37] as follows:



Such interaction between C₆₀, C₇₀ 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 C₆₀, C₇₀ and pyridine established. From the figure.5, we can see that the content of CT is increasing with enlarging the length of light irradiation time. We supposed that CT can only sever C60 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], C60 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 section. As the existence of CT, the C60 molecules can choose the growing sites more independently, then the selectivity of C60 molecules attached to the crystal seeds will be better, the diameter distribution tends to be uniform. Additionally, we suppose that C60 is easier to form CT complex with pyridine compared to C70, and it can explain the reason why there is a decreasing of C70 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

C₆₀-C₇₀ soot was used in the article to fabricate C₆₀-C₇₀ FNFs by LLIP method. With the increase of length of light

irradiation, the diameter of FNFs tends to be thinner, meanwhile, the content of C₇₀ in FNFs drops. We ascribed those phenomena to the formation of C₆₀ and C₇₀ pyridine charge-transfer adducts, which is sensitive to light.

Notes and references

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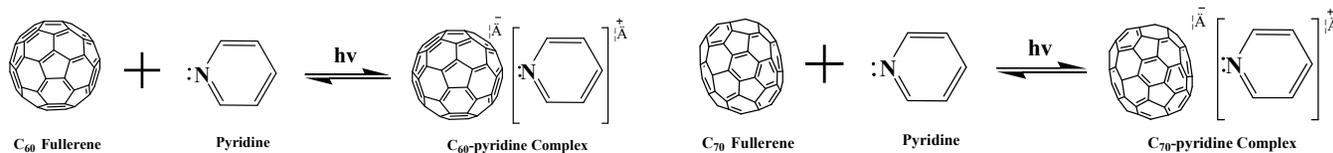
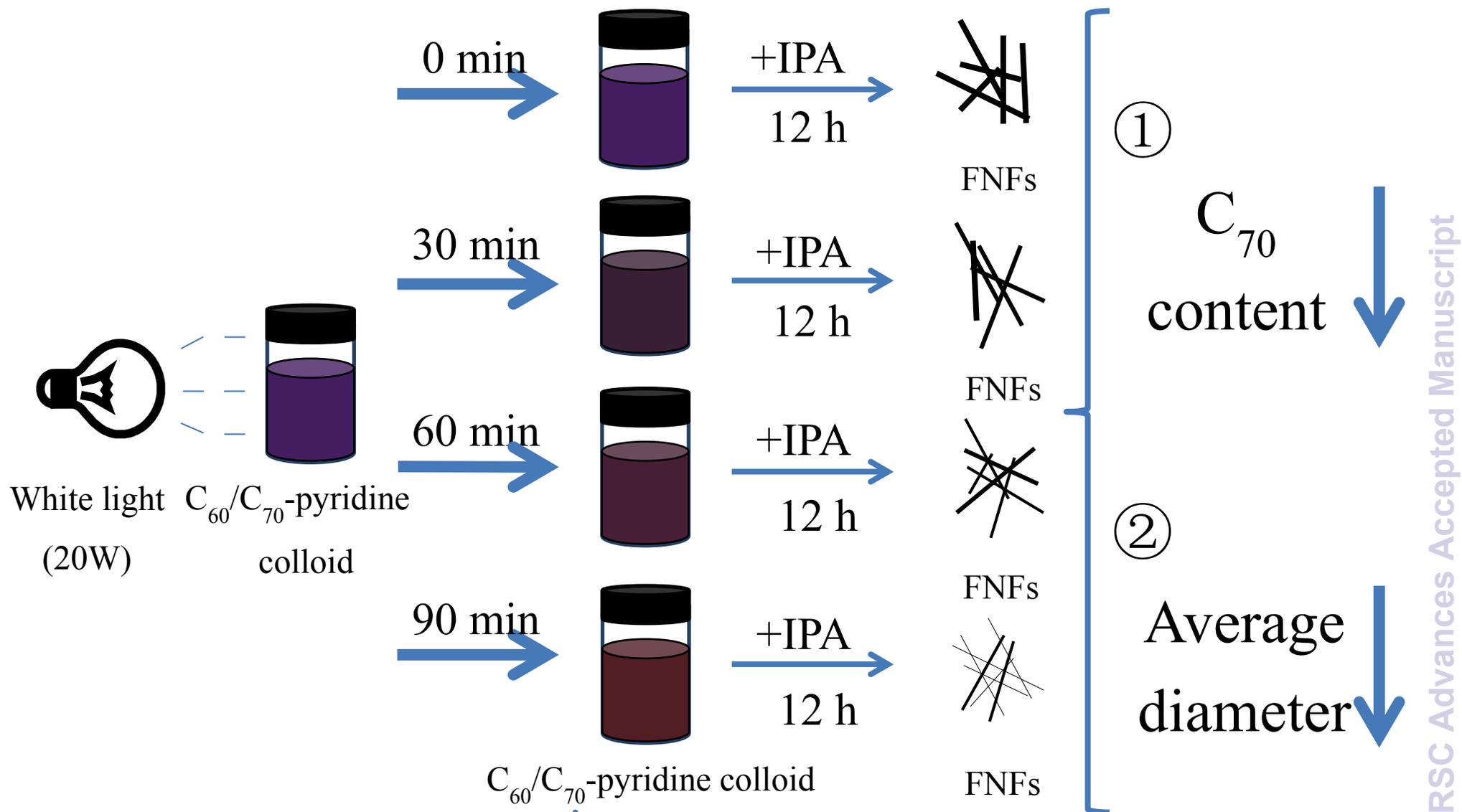
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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ 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.

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