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Research Article

Structure and Morphology Characteristics of Fullerene C_{60} Nanotubes Fabricated with *N*-Methyl-2-pyrrolidone as a Good Solvent

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Fullerene C_{60} nanotubes (FNTs) were prepared via liquid-liquid interfacial precipitation using *N*-methyl-2-pyrrolidone (NMP) as solvent and isopropyl alcohol (IPA) as precipitation agent at 8°C. C_{60}-saturated NMP solutions were exposed to visible light to promote the growth of FNTs. Scanning electron microscopy revealed that fibers prepared in the NMP/IPA system show three different morphologies. On the basis of the different morphologies of fullerene C_{60} nanofibers (FNFs), a possible growth mechanism to describe the formation process of FNTs is proposed.

1. Introduction

Since the discovery of carbon nanotube (CNT), one dimensional (1D) nanometer-scale materials have extensively been studied owing to their unique structures and physical properties which lead them to a range of potential applications in the field of nanometer-scale devices. On the other hand, C_{60} is a well-known fullerene prototype, and zero-dimensional structure has been generally accepted for C_{60} fullerene [1]. If it was possible to modify such a zero-dimensional structure of C_{60} into a self-assembled 1D tubular structure, novel optoelectronic and magnetic properties might be expected. Therefore, FNFs has attracted much attention in recent years among the various crystalline forms [2–5].

Recently, various synthesis methods have been developed for the preparation of FNTs, such as solution evaporation [2], template technique [3], surfactant-assisted method [6], and liquid-liquid interfacial precipitation method (LLIP) [7, 8]. Compared with other synthesis method, the LLIP method is a simple and financially viable approach for directly growing FNTs that can be achieved at around room temperature and without the need for catalysts or surfactants. Due to such merits, this work adopts the LLIP method to prepare FNTs.

In typical LLIP method, pyridine was used as a good solvent and IPA was used as a precipitation agent [9, 10]. However, in the process of preparing FNTs, pyridine shows high toxicity and irritant smell, which is unsuitable for mass or industrial production. In this paper, we report another solvent, NMP, to replace pyridine as the good solvent to prepare FNTs, which shows good solubility for C_{60} and relatively low price. We reported that FNFs was prepared in NMP/IPA system with different morphologies for the first time. The different morphologies of FNFs in the NMP/IPA system were revealed by scanning electron microscopy. On the basis of the different morphologies of FNFs, a possible growth mechanism to describe the formation process of FNTs is proposed.

2. Experimental

The FNTs were prepared at ambient pressure and temperature using C_{60} fullerene powder (99.5% purity, MER Ltd.) based on the experimental procedures described in [7–10]. In this work, the method was further modified by using another solvent NMP to replace pyridine. After ultrasonication for 10 min in the ice water bath, a red purple NMP solution

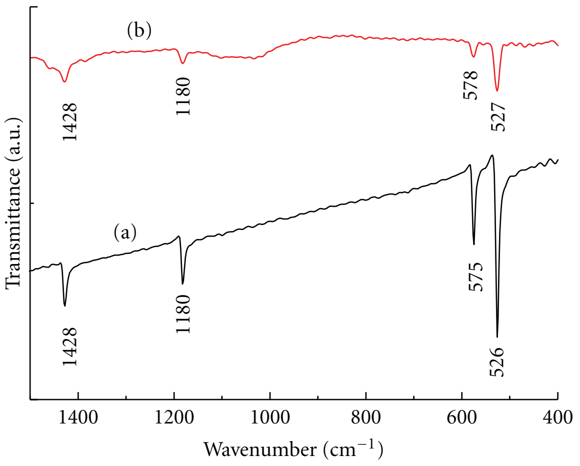


Figure 1: FT-IR spectra of pristine C_{60} powder (a) and FNTs (b).

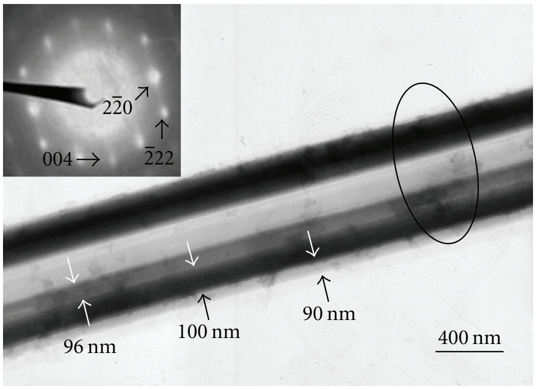


Figure 2: TEM image of C_{60} FNT grown in the C_{60}-saturated NMP and IPA system. Inset is a selected area electron diffraction (SAED) pattern of enclosed part indicating that the tube wall is single crystalline. Three layers of the tube wall are indicated by arrows.

saturated with C_{60} was prepared. In order to promote the growth of the FNFs, the solution was exposed to visible light such as blue light with the center wavelength of 468 nm [11, 12]. After irradiation, the red purple NMP solution turned into brownish red solution immediately. Two mL of this brown NMP solution was put into a transparent 25 mL glass bottle, and 18 mL of IPA was added. To obtain suitable diffusion at the interface, the glass was vigorously vibrated in an ultrasonic bath for 1 min before being stored at 8°C. After about 12 hours, golden-brown cluster fibers were suspended in the solutions.

Infrared spectroscopy was performed for the specimen dried at temperature and the pristine C_{60} powder with KBr using an FTIR apparatus (Bruker Vertex 70). Hollow structure of the C_{60} FNFs and different morphologies were characterized by using transmission scanning electron microscope (TEM, JEOL JEM-2000EX) and scanning electron microscope (SEM, JEOL JSM-6700F). For the purpose of electron microscopic measurement, the specimens were placed on silicon wafer substrates or copper microgrid with carbon film. The color change of C_{60}-NMP solution was recorded by using the UV-visible spectrophotometer (SHIMADZU UV-2400PC).

3. Results and Discussion

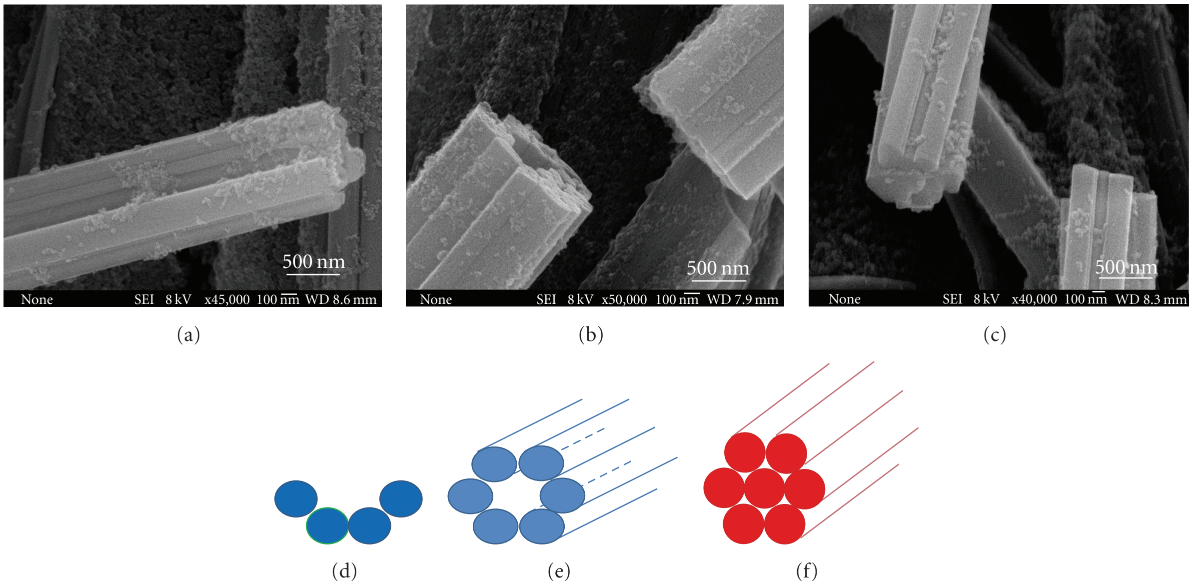
Figure 1 shows FT-IR spectra of pristine C_{60} powder (a) and FNTs (b). Both of the spectra showed sharp absorption peaks characteristic of C_{60} (527, 576, 1182, and 1428 cm^{-1}), confirming that the nanotubes are composed of C_{60} molecules [13]. However, in spectra (b), some modification of the base line was observed even after drying in vacuum, which may be related to the presence of solvent NMP or IPA molecules.

Figure 2 shows a TEM image of typical FNTs precipitated in the C_{60}-saturated NMP and IPA system. The C_{60} FNTs show tubular structure with outer diameters of about 760 nm and inner diameter of about 200 nm. The acquired SAED pattern of an FNT inset in Figure 2 indicates that the FNT has a local single-crystal and face-centered cubic (fcc) structure. The growth direction of the FNT is [110], which is a close-packed direction of an fcc fullerene C_{60} crystal [8]. Furthermore, there was an interesting phenomenon that the wall of the tube was not a monolayer structure. The wall consists of many shell structures. As shown in Figure 2, the tube wall consists of three layers, that is, the outer surface layer A, 90 nm in thickness, and the inner surface layer C, 96 nm in thickness. The morphology of the tube indicates that the FNT might be formed by several fibrel microstructure around the grow axis along the direction [110] but not an integrity structure.

To confirm the consequence on the wall structure of the FNT, the morphologies of FNT were further characterized by SEM, from which we can see the wall structure clearly. Figures 3(a)–3(c) show three different morphologies of FNFs prepared in NMP/IPA system, and Figures 3(d)–3(f) give the corresponding schematic diagrams of the three morphologies.

From Figure 3(a), we can see several nanorods bundled together and form a groove structure, just as the schematic diagram (d) shows us. Figure 3(b) is a cross-section image of the FNT. In this picture, we can see the wall structure of the tube clearly, which is formed by several slender nanorods. We can see the slender nanorods bundled together and self-assembled to form a tubular structure along the direction of grow axis of the FNT. Beside the groove and tubular structure, we also find the solid fiber structure. Just like Figure 3(b), several slender nanorods bundled together and self-assembled in Figure 3(c), but there is a solid fiber formed, not a tubular structure.

In the process of preparing FNTs, we find that the freshly prepared C_{60}-NMP solution exhibits purple-pinkish at the beginning, but turns into burgundy over time. Interestingly, the color change process can speed up the color change process if the C_{60}-NMP solution is exposed to visible light. However, such color change is not observed in the C_{60}-toluene or C_{60}-m-xylene solution [14, 15]. The color change of C_{60}-NMP solution was recorded by using the UV-visible spectrophotometer (Figure 4).



(a) (b) (c)

(d) (e) (f)

FIGURE 3: SEM images (a–c) of FNFs with different morphologies prepared using NMP as solvent, and schematic diagrams (d–f) of the three morphologies.

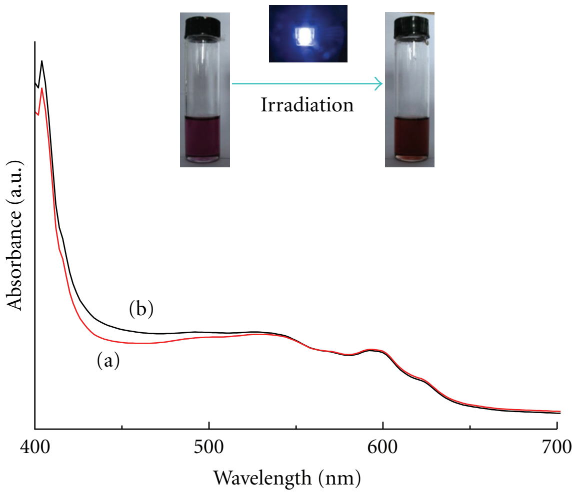


FIGURE 4: UV-vis spectra of C_{60}-NMP solution. (a) Freshly prepared purple-pinkish solution and (b) burgundy solution irradiated by blue light (468 nm) for 30 min.

As shown in **Figure 4**, after light irradiation, the absorbance of the freshly prepared purple-pinkish solution (trace a) increases visibly in the region of 400–500 nm (trace b), consistent with the observed color change, just like the color change process of C_{60}-pyridine solution [14]. The color change process after irradiation is probably related to the formation of the C_{60}-NMP charge transfer (CT) complexes. Fullerene C_{60} is ready to accept multiple electrons, making it become a potential electron accumulator [16]. On the other hand, NMP molecule has a nitrogen atom which allows the molecule to be an electron donor. It is reasonable that CT complex should exist in the C_{60}-NMP system under certain condition. C_{60}-NMP CT complexes form immediately after light irradiation, which plays an important role in the C_{60} dissolvability in NMP and nucleation process.

On the basis of the different morphologies of FNFs and the observed change of UV-visible absorption spectra accounted for the observed color change of C_{60}-NMP solution, a possible growth mechanism to describe the formation process of C_{60} FNTs is proposed.

After light irradiation, C_{60}-NMP CT complexes were formed immediately, which play an important role in dissolvability of C_{60} in NMP and the nucleation process. Similar to the previous work [17–19], when IPA was injected into NMP solution-saturated with C_{60}, crystal seeds with narrow size distributions were formed immediately. Due to the highly anisotropic nature of these crystal seeds [18], the growth direction was largely confined to the [110] direction as indicated in **Figure 2**, resulting in one-dimensional structure [20]. So a large amount of slender nanorods were formed. Then, the slender nanorods self-assembled and three different morphologies of C_{60} FNFs were formed. During the self-assemble progress after nanorods formation, the one-dimensional structures prefer the corners of the hexagonal cross-section, as indicated by the red nanorods in **Figure 5**, because the corner sites have a relatively higher free energy [21]. The secondarily preferable sites for nanorods are the edges of the hexagonal cross section, as indicated by the blue nanorods. Finally is the central portion of the hexagonal cross section, and this self-assemble growth process will end when the nanorods are too few to form the C_{60} FNFs. When there are too few nanorods to form the wall structure of C_{60} FNTs, the groove structure nanofiber, or the precursor of the FNTs as shown in **Figure** 3(a), will be formed. On the contrary, when the amount of nanorods is large enough to supply the central portion of the hexagonal cross section, the overmatured FNTs, or solid fullerene nanowhiskers (FNWs), are formed. Only when the amount of nanorods is not too

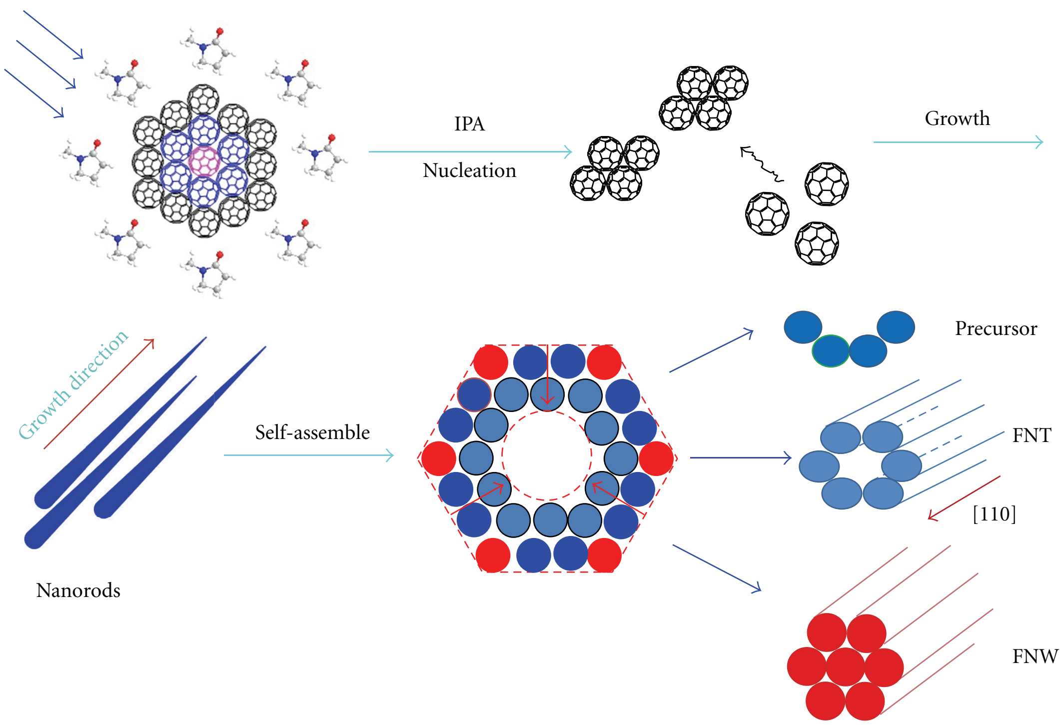


Figure 5: Schematic of the formation process of C_{60} 1D FNFs.

large or too small, just reaching the equilibrium point to form fence-shaped tube wall but not block inner tube, the hollow tubular nanofiber or called C_{60} FNTs are formed, as indicated in Figure 3(b).

4. Conclusions

For the first time, we have succeeded in preparing C_{60} FNFs using C_{60}-saturated solutions in NMP and isopropyl alcohol by an LLIP. The acquired SAED pattern of a FNT indicates that the FNT has a local single-crystal and face-centered cubic (fcc) structure with the growth direction [110]. Scanning electron microscopy revealed that fibers prepared in the NMP/IPA system shows three different morphologies. On the basis of the different morphologies of FNFs and the observed change of UV-visible absorption spectra accounted for the observed color change of C_{60}-NMP solution, a possible growth mechanism to describe the formation process of FNTs was proposed.

Acknowledgments

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