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Synthesis and Solid-State Studies of Self-assembled C_{60} Microtubes

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Abstract

C_{60} microtubes were fabricated by a modified solution evaporation method, evaporating a solution of C_{60} in toluene in an atmosphere of m-xylene at room temperature. The C_{60} microtubes have outer diameters ranging from 2-8 micrometers. IR spectra, TG analysis and x-ray diffraction showed a solvated structure for the as-grown C_{60} microtubes. Through a gentle heat-treatment in vacuum, pure C_{60} microtubes with single crystalline fcc structure were obtained after the elimination of solvents. It is suggested that the C_{60} microtubes form through self-assembly from several individual C_{60} nanorods.

Keywords: C_{60}, microtube, solid-state studies, self-assembly.

Introduction

Since its initial discovery in 1985 [1], fullerene C_{60} has attracted significant attention due to its unique physical and chemical properties. Very recently, a series of novel one-dimensional nanocrystals, with individual C_{60} molecules as building blocks, have set off a renaissance in the scientific research [2-4]. Much effort has been made to find a controllable method to fabricate high quality one-dimensional C_{60} nanocrystals, resulting in the discovery of the liquid–liquid interfacial precipitation method (LLIP) [5,6], the template method [2] and the solution evaporation method [3,7,8]. In particular, tubular nanocrystals received great interest for their unique structure and for potential applications, such as storage materials. As far as we are aware, C_{60} nano/micro tubes were only obtained using the LLIP method and the template method [2,5]. However, for applications as devices, there remained two challenging tasks: (1) to synthesize tubular C_{60} crystals with high purity (constituted with pure C_{60}) and high crystallinity, and (2) to fix the nanocrystals on substrates with good dispersibility. The solution evaporation method has been successfully employed to fabricate well dispersed C_{60} nanorods with high purity and high crystallinity, and in this process m-xylene plays a vital role as an effective shape controller [3,7]. This study indicates that the solution evaporation method might be an effective way to fabricate nanotubes meeting these requirements. However, no tubular C_{60} nanocrystal has been synthesized from pure m-xylene solution with this method, probably due to the close packing of molecules. Here, we provide a new effective approach to the synthesis of C_{60} nanotubes by using a modified solution method in which we introduce m-xylene into another good solvent for C_{60}. This approach is the opposite of the LLIP method, in which poor solvents (alcohols) are added to a rich solution of C_{60}, resulting in a liquid-liquid interface [5,6]. In the present study, we found that toluene is an effective shape tuner together with m-xylene. Because of the good solubility of C_{60} in toluene and m-xylene the growth process involves no interface and thus avoids the formation of entangled structures. We have successfully obtained well dispersed C_{60} nanocrystals with a regular tube shape by properly adjusting the ratio of toluene to m-xylene.

Crystallization from solutions usually produces C_{60} solvated structures [9-12]. It has been found that C_{60} nanorods fabricated from solutions of C_{60} in m-xylene have a single-crystalline C_{60}*1m-xylene solvated structure [7]. This particular structure exhibits a highly enhanced luminescence compared to a pure C_{60} nanorod [7]. However, it is still an open question whether C_{60} microtubes obtained from toluene and m-xylene solutions also form solvated structures and if there is any difference between these and single-crystalline C_{60}*1m-xylene. This study is important for understanding the formation mechanism of the special tubular shape and how the two solvents tune the shape. Therefore, in this work we also carried out solid-state studies of our fabricated C_{60} nanotubes by using infrared spectroscopy (IR), x-ray diffraction (XRD) and thermal gravimetric analysis (TGA). It is found that C_{60} nanotubes form a solvated structure with toluene and m-xylene, and that the molar ratio of the components is 1:2:3 in the order toluene, m-xylene and C_{60}. The structure found was slightly different from that of C_{60}*1m-xylene, due to the introduction of toluene. A tentative mechanism is also proposed to explain the formation of the particular morphology observed.

2. Experiment

C_{60} (purity>99.9%) was purchased from Wuda Sanwei Carbon Cluster Corporation, China, toluene was purchased from Beijing Chemical Plant China, and m-xylene (purity>99.0%) was purchased from Phentex Corporation USA.

A saturated toluene solution of C_{60} was deposited as small drops on a substrate and the same volume of m-xylene was placed in the same way about one centimeter away on the same substrate. An inverted glass beaker, about 80ml in volume, was then used to cover both. After slow evaporation of the C_{60} toluene solution in the m-xylene atmosphere under the cover, we obtained C_{60} microtubes on the substrate. Different substrates, including Si, glass, aluminum foil, etc. have been tested and all substrates that are chemically inert to the solvents have been found useful for crystal growth.

C_{60} microtubes on a silicon substrate were examined by means of a scanning electron microscope (SEM, SSX-550 SAIMADZU, Japan). When the solutions were dropped directly onto a copper mesh with carbon microgrids to produce C_{60} microtubes, a transmission electron microscope (TEM, JEM-2010, Japan) could be employed to study their morphology. X-ray powder diffraction were performed by a Rigaku D/max-RA, using CuKα1 radiation with λ = 1.5406Å, Raman spectroscopy studies were performed by a Raman spectrometer (Renishaw inVia, UK) with an 830 nm laser as excitation to avoid photo-polymerization. IR absorption spectroscopy (Nicolet Avatar 370 DTGS) and TGA (Perkin-Elmer) were also carried out to study the composition of the samples.

3. Result and discussion

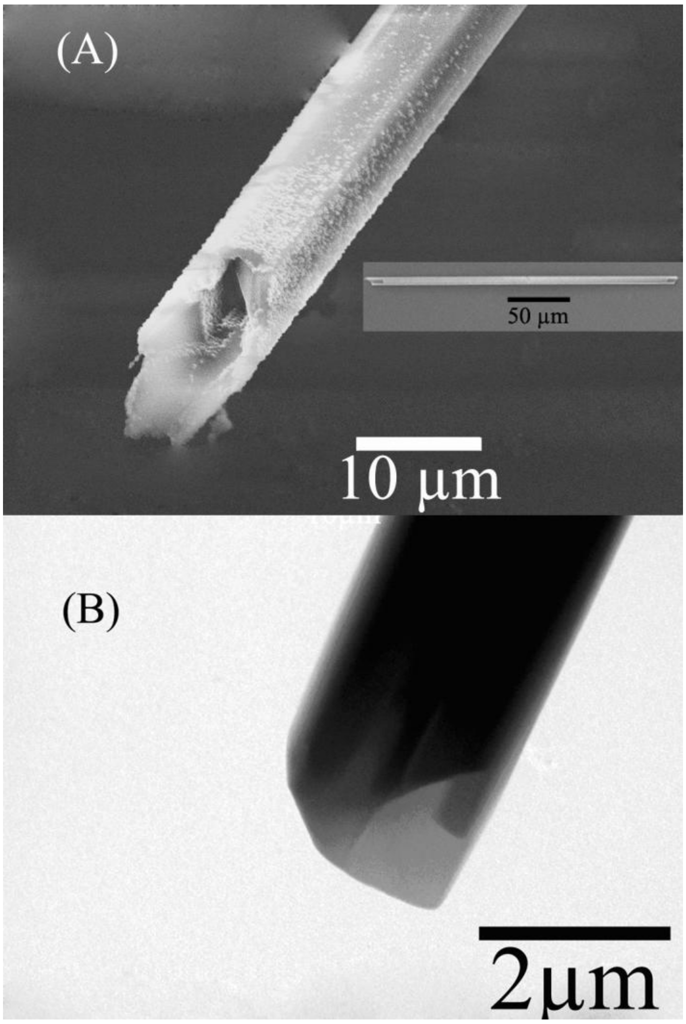

Fig. 1. SEM (A) and TEM (B) images of a single C_{60} microtube. Insert in part (A) was the image of one single C_{60} microtube after heat treated at 150^{o}C in vacuum.

A SEM image of a C_{60} microtube is shown in Fig.1A. The outer diameters of the C_{60} microtubes are about 2 to 7 micrometers, and the inner diameters are 1 to 3 micrometers. The wall thickness is about one micrometer. When a single C_{60} microtube was imagined, its detailed features were apparent. The microtubes had a hexagonal cross section and an open end without a regular shape. Insert in Fig. 1A shows the image of one single C_{60} microtubes heat treated at 150 ^{o}C, which indicated that the microtube morphologies can maintain under this condition. The TEM image in Fig. 1B shows a relatively small C_{60} microtube with an outer diameter of about 2 micrometers, and the TEM image of the tip also shows a tubular shape.

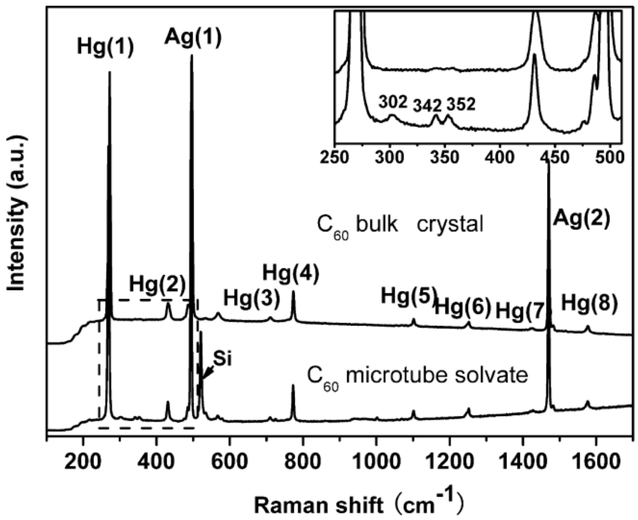

Fig. 2. Raman spectra of C_{60} bulk crystals (top) and as-grown C_{60} microtubes (bottom).

Raman spectroscopy is a powerful tool to analyze C_{60}. It is well known that there are ten Raman peaks for C_{60}, eight of which are Hg modes and two are Ag modes [13, 14]. In this study, Raman spectra were collected to characterize the microtubes as shown in Fig. 2, where the spectra of C_{60} bulk crystal are also shown for comparison. The Raman spectra of as-grown C_{60} microtubes also have ten peaks at the positions 270, 430, 495, 711, 773.4, 1101.5, 1250, 1427, 1470 and 1576.4 cm^{-1}, these peaks indicated that the microtubes consist of C_{60}. The peak located at 520 cm^{-1} is contributed by the silicon substrate, showing that the obtained spectrum is reliable. A direct comparison of the two spectra shows that the microtubes have spectroscopic features very similar to those of pristine C_{60}, indicating that the microtubes really consist primarily of C_{60}. Furthermore, the Raman spectra show that the Ag (2) pentagonal pinch mode of the C_{60} microtubes is found at 1470 cm^{-1}, which is characteristic for pristine C_{60}. It is well known from the literature that this line will shift to lower frequencies in polymerized C_{60} [15-17], indicating that the microtubes consist of monomeric C_{60}. In addition, several new weak peaks were detected at 342, 353, and 537 cm^{-1}, and the C_{60} peaks normally found at 496 and 272 cm^{-1} were shifted to 494 and 269 cm^{-1}, respectively. Similar shifts and new peaks have also been found in the Raman spectra of C_{60} solvates formed with toluene and m-xylene.[7,18] The new peaks and the shifts described above further confirmed that solvent molecules have been introduced into the C_{60} lattice, where they interact with C_{60} molecules and lower the local symmetry.

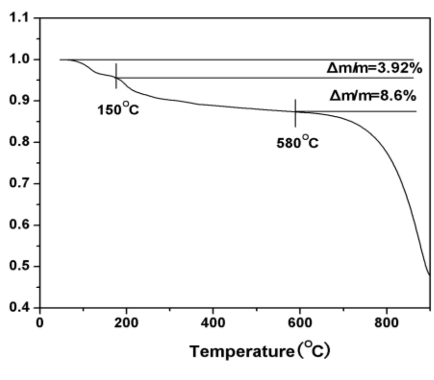

Fig. 3. TGA curve of as-grown C_{60} microtubes.

Although the Raman spectra show that solvent molecules are incorporated into the as-grown C_{60} microtubes, the kind and stoichiometry of solvents is not clear. To determine the molar ratio between C_{60} and solvent molecules in the as-grown microtubes, thermogravimetry analysis (TGA) was employed. The temperature was ramped from 40 ℃ to 900 ℃ at a rate of 5 ℃/min in an N_2 atmosphere. This procedure should also help us to study the thermal behavior of the as-grown solvate microtubes. The TGA curve is shown in Fig. 3. Clearly, there are three mass loss regions in the studied range of temperature, indicating that there are at least three components in the samples. From a careful analysis of the curves, it is found that the first mass loss starts as soon as the study begins. Considering the possible components of the samples, this mass loss should be due to the vaporization of toluene. This indicates that the toluene in the solvate is not air-stable. In the higher temperature region, just above the first mass loss region, the second mass loss starts at about 150^{o}C. This temperature is close to the boiling temperature of m-xylene (135^{o}C), indicating that this mass loss was due to the evaporation of this component. In the highest temperature region there is a last mass loss beginning at about 580^{o}C, which is close to the sublimation temperature of C_{60} in N_2 atmosphere. This indicates that the last mass loss can be identified with sublimation of the C_{60}. Furthermore, it is also found that the mass losses of toluene and m-xylene correspond to about 3.92% and 8.6% of the total weight, respectively, while the mass loss of C_{60} is about 87.48%. From this we can ascertain that the molar ratios of the solvate components are 1:2:3 for toluene, m-xylene and C_{60}, respectively. This suggests that there is one solvent molecule for each C_{60}. From a comparison with the composition of the C_{60}·1m-xylene nanorods obtained from pure m-xylene solution, it can be speculated that toluene has replaced m-xylene in some of its positions in the lattice of the as-grown C_{60} microtubes.

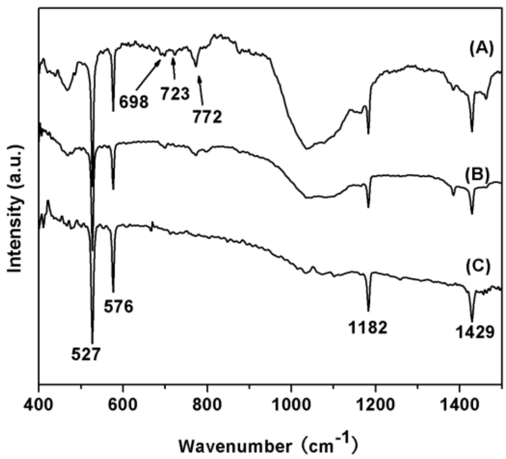

Fig. 4. IR spectra for C_{60} microtubes stored in air for (A) one day, (B) two months and for microtubes (C) heat-treated at 150°C in vacuum.

Knowledge about the stability of the C_{60} solvates in air at room temperature is important for both practical applications and for our understanding of the formation mechanism of C_{60} microtubes. To confirm the stability of the solvents in as-grown C_{60} microtubes, IR spectroscopy was also carried out on samples kept in air for one day, for two months, and heat-treated at 150°C in vacuum, respectively. The spectra A, B and C in Fig. 4 show sharp absorption peaks, characteristic for C_{60}, at the positions 527, 576, 1182 and 1429 cm^{-1}, indicating that the specimens were primarily composed of C_{60} molecules. However, for the as-grown sample, three additional peaks at 698, 772 and 723 cm^{-1} were found (curve A). The former two absorption peaks are characteristic for m-xylene and the peak at 723 cm^{-1} for toluene. This result again indicates that the as-grown microtubes are solvates containing m-xylene and toluene, consistent with the TGA results.

In the IR spectrum shown as curve B in Fig. 4, for the sample kept for two months in air, the two peaks at 698 $cm^{-1}$and 772 cm^{-1} are still observed, but the absorption peak at 723 cm^{-1} has disappeared. Combining this with the TGA results, the disappearance should be due to the loss of toluene. The result further confirms that toluene in the crystals is not stable at room temperature, but that the solvent m-xylene is. The IR spectrum of a sample treated at 150^{o}C for 5 hours in vacuum (10^{-4} Pa) is shown as curve C in Fig. 4. No characteristic absorption peaks for solvents were observed, indicating that all the solvents in the samples were removed under these conditions, and that we have obtained pure microtubes consisting of only C_{60}.

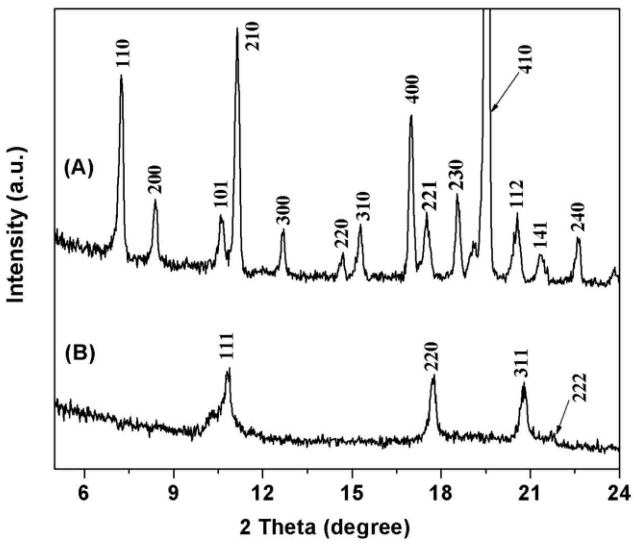

Fig. 5. XRD patterns from (A) as-grown C_{60} microtubes and (B) C_{60} microtubes treated at 150^{o}C in vacuum.

To investigate the structure of the solvated and pure C_{60} microtubes, X-ray diffraction (XRD) has been carried out. As shown by curve A in Fig. 5. the structure of as-grown C_{60} microtubes has been indexed by a hexagonal system with cell dimensions a = 2.411 nm and c = 0.930 nm (a/c = 2.593), which is slightly different from the parameters of C_{60} nanorods obtained by evaporation of a solution of C_{60} in pure m-xylene. [2,7] This slight difference in the values of cell parameters is attributed to the presence of toluene in some m-xylene positions. XRD patterns for microtubes heat-treated at a temperature about 200°C in vacuum of about 10^{-4} Pa, which according to the TGA and IR results should consist of pure C_{60}, are presented as curve B in Fig. 5. As expected, the microtubes have XRD features very similar to those of pristine bulk C_{60} [19,20]. Peaks have been indexed as the (111), (220), (311) and (222) diffraction peaks from a fcc lattice, indicating that the C_{60} microtubes have the same fcc structure as pristine C_{60}. This result suggests that single crystalline pure C_{60} microtubes were obtained under these gentle treatment conditions.

Fig. 6A shows SEM images of a selected incomplete microtube found among our samples, a side-view SEM image of the morphology of the tip of incomplete C_{60} microtubes is exhibited. The SEM image of the incomplete microtube reveals that neighboring individual nanorods are assembled together, resulting in a bundle with the morphology of a fence. To confirm this proposed growth mechanism we have designed two similar experiments differing in the evaporation rates of the solution. First, the solution of C_{60} in toluene was kept in the atmosphere of m-xylene for only five minutes, and was then opened in the aerator to make the solvent evaporate rapidly (in about five minutes). SEM images of the obtained samples are shown in Fig. 6C. The SEM images reveal C_{60} crystals with rodlike morphologies and diameters in the range of 100 to 300 nm. In the other experiment, the solution was evaporated at a temperature of -10^{o}C to slow down the evaporation rate. The SEM image shown in Fig 6B shows that a microtube-like structure has been synthesized on the Si substrate. Individual C_{60} microrods have diameters in the range of 1 to 2 μm, which is smaller than the diameters of C_{60} microtubes but much larger than those of C_{60} nanorods. In addition, the tips of the C_{60} microrods consist of several C_{60} nanorods assembled together. These results indicate that the morphology of the C_{60} crystals grown have a close relationship with the evaporation rates.

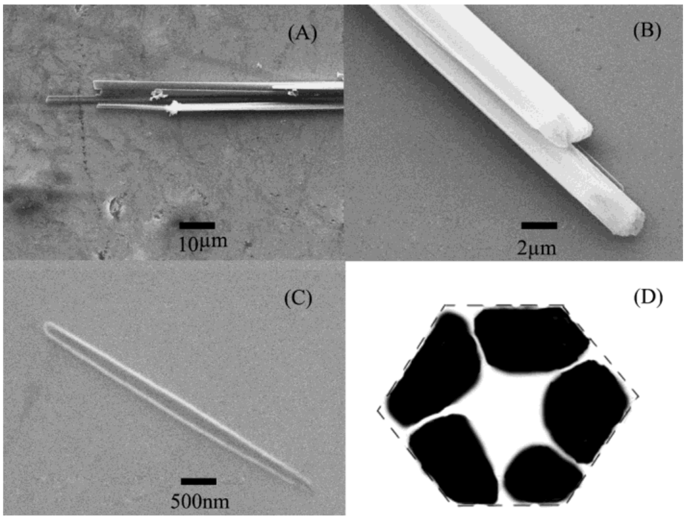

Fig. 6. SEM images of (A) incomplete C_{60} microtubes synthesized at room temperature, (B) C_{60} microrods synthesized at -10^{o}C and (C) C_{60} nanorods obtained by rapid evaporation of solution. Part (D) shows the proposed model for the cross section of C_{60} microtubes.

In our previous work, we have found that m-xylene is an effective shape controller for C_{60} nanorods [2,7], forming a single crystalline solvated structure with C_{60}. In this work m-xylene was also introduced into the lattice of C_{60}, as shown by the TGA and

IR results, the presence of m-xylene is attributed to its being dissolved into the toluene solution, where it can take part in the formation of 1D fullerene structure. Considering the experiments with different evaporation rates mentioned above, we believe that single nanorods are the first step in the fabrication of C_{60} microtubes and rods. It is reasonable that the incomplete C_{60} microtubes correspond to early stages in their growth, which may also result in the formation of hexagonal prismatic tubular morphologies at the final growth stage. From SEM observations of the C_{60} microtubes we propose the dotted line model of C_{60} microtubes shown in Fig. 6D, suggesting that the C_{60} microtubes are formed by the coalescence of neighboring nanorods. This mechanism is similar to that of ZnO microtubes [21]. However, in the case of rapid evaporation there was not enough time for the nanorods to aggregate together, and only individual nanorods were obtained. In the opposite case, when the solution evaporated more slowly, the C_{60} nanorods were packed more closely and solid microrods were obtained instead of microtubes.

4. Conclusion

In summary, C_{60} microtubes were fabricated by modifying the facile solution evaporation method developed earlier through evaporating toluene solution in an atmosphere of m-xylene at room temperature. The microtubes have hexagonal cross sections and outer diameters ranging from 2 to 8 micrometers. The as-grown samples consisted of C_{60} solvated with toluene and m-xylene, and the molar ratios of the components were 1:2:3 for toluene, m-xylene and C_{60}, respectively. The as-grown samples have an hcp structure (a = 2.411 nm and c = 0.93 nm). After heat-treatment at 200^{o}C in vacuum the solvents were removed and pure C_{60} single crystalline microtubes with an fcc structure (a = 1.428 nm) were obtained. Moreover, a reasonable growth mechanism was proposed, suggesting that C_{60} microtubes were self-assembled from several individual nanorods.

Acknowledgment

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