

液液界面反应制备 C₆₀ 微米管阵列及其上转换荧光性能研究

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摘要: 采用 C₆₀/甲苯溶液和异丙醇作为原料, 通过液液界面渗透反应在 AAO 模板上制备了垂直定向排列的 C₆₀ 微米管阵列。通过 SEM、XRD、Raman、荧光光谱(PL)对材料的结构和性能进行测试表征。结果表明 C₆₀ 微米管阵列由 C₆₀ 分子聚合而成, 为面心立方结构, 微米管直径 5~10 μm, 壁厚 1~3 μm。在 1 064 nm 近红外入射光激发下样品在红光区域发生了上转换发光, 分析表明这是由多壁碳管丰富的能级所造成。

关键词: 富勒烯; 微米管阵列; 上转换发光

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Preparation of Up-Conversion C₆₀ Microtube Arrays by Liquid-Liquid Interfacial Precipitation Method

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Abstract: Vertically aligned C₆₀ microtube arrays were synthesized at ambient pressure and temperature by using the modified liquid-liquid interfacial precipitation(LLIP) method in the system of C₆₀/toluene and isopropyl alcohol (IPA). The C₆₀ microtube arrays were structurally characterized by SEM, XRD, Raman scattering and photoluminescence(PL) measurements. The results reveal that the C₆₀ microtube arrays are formed by polymerization of C₆₀ molecules with an fcc crystal structure, hexagonal cross-section of 5 to 10 μm and the wall thickness of 1 to 3 μm. When excited at 1 064 nm near infrared region, the up-conversion luminescence was seen in the infrared region due to different energy levels of multiwalled carbon tubes.

Key words: fullerene; microtube arrays; up-conversion

The recent development in structural materials with specific morphology has further extended the application of C₆₀ and its derivatives. There are several methods to assemble C₆₀-based molecules with controlled dimensionality, such as controlled precipitation, and template approaches^[1~3]. It was reported that the fullerene whiskers and nanotubes were prepared at the interface between a solution of good solvent and a poor solvent of fullerenes^[4~6] by the liquid-liquid inter-

facial precipitation(LLIP) method^[7~9].

Recently, the optical properties of carbon tubes have attracted much attentions, and the studies of photo excited states and emission properties of carbon tubes have advanced remarkably. Several years ago, Riggs et al. reported that carbon nanotubes in solution were luminescent in the visible-light range, which had been confirmed by other research groups subsequently^[10~13]. Both the multi-wall and single-wall carbon tube are lu-

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minescent, however the study on nonlinear photoluminescence in multi-wall carbon tubes is insufficient^[14,15]. Fullerenes, which can be considered as diminutive versions of carbon tubes, are well known to possess large and fast nonlinear optical properties^[16].

In this work, a simple one-step solution-based process for preparing vertically aligned C_{60} microtube arrays is reported. The surface morphology is observed by SEM. XRD and Raman scattering measurements are used to structurally characterize the formation of C_{60} microtube arrays. Finally, the up-conversion luminescence spectra of these arrays are investigated.

1 Experimental

1.1 Synthesis

All reagents were of analytical grade and used without further purification. The instrument for preparing vertically aligned C_{60} microtube arrays based on Seung I. Cha group^[7] is shown in Fig.1. At first, The C_{60} powders(99.9% purity, Yongxin Technology CO., Ltd.) were dissolved in toluene(99.5% purity, Shanghai Laboratory Reagent CO., Ltd.) to achieve a C_{60} -saturated solution of 0.3% concentration by weight. The dissolution of the fullerene was obtained through magnetic stirring for 15 minutes before illumination with 365 nm UV for 24 h. Then isopropyl alcohol (99.5 % purity, Shanghai Kaidi Chemical Reagent CO., Ltd.) was injected slowly into the C_{60} /toluene solution from the bottom through an anodic aluminum oxide (AAO) membrane, mixing with the toluene solution to induce supersaturation of C_{60} . The experimental temperature was controlled below 15 °C, and the isopropyl alcohol(IPA) injection rate was less

than 0.05 mL·min⁻¹.

1.2 Characterization

The morphology of arrays was inspected by using JSM-5900 SEM. The crystalline phase was analyzed by ARL XTRA power X-ray diffraction system with Cu $K\alpha$ radiation source($\lambda=0.154\ 056\ \text{nm}$) operated at 45 kV and 35 mA, and the scan rate(2θ) of 10°·min⁻¹ was applied to record the pattern in the 2θ range of 5°~25° by means of a solid detector and a scintillation counter. The intermolecular bonding in C_{60} microtubes was examined by means of Raman spectroscopy. The Raman spectra of C_{60} microtubes on the glass plate at 294 K in air were measured by Renishaw invia Laser Raman Spectroscopy. The spectra excitation was provided with a semiconducting laser of a wavelength of 514 nm. The spot size of laser light on the sample was controlled with a 20× objective lens. In addition, the irradiation time to obtain a Raman spectrum was only 30 s. The photoluminescence spectra were measured at room temperature with a spectrophotometer (Jobin Yvon Fluorolog 3-221) using a Xe lamp (450 W) as excitation source, and focused by off-axis mirror for maximum efficiency at all wavelengths.

2 Results and discussion

2.1 structural characterizations

Fig.2 shows the SEM images of the prepared vertically aligned C_{60} microtube arrays at different magnifications. The surface of AAO membrane is covered with vertically aligned C_{60} microtube crystals(Fig.2a). The multiwalled structure could be observed distinctly by Fig.2b which shows a microtube grown incompletely. A legible view of a single vertical C_{60} microtube, shown in Fig.2c, clearly shows that the aligned C_{60} crystals grown along vertical direction were tubular in shape with a hexagonal cross-section. The outer diameter of the microtubes ranges from 5 to 10 μm , and the wall thickness ranges from 1 to 3 μm when fabricated by injecting IPA into 2 mL of C_{60} /toluene solution with an injection rate less than 0.05 mL·min⁻¹. It should be noticed that the nucleation and growth of the C_{60} microtubes occur on the surface and not within the channels of AAO membrane, so the shape and size

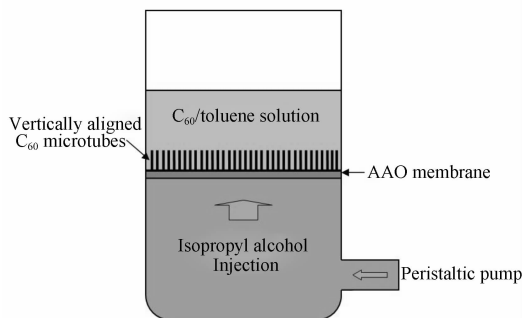


Fig.1 Schematics of setup used for preparing vertically grown C_{60} microtube arrays

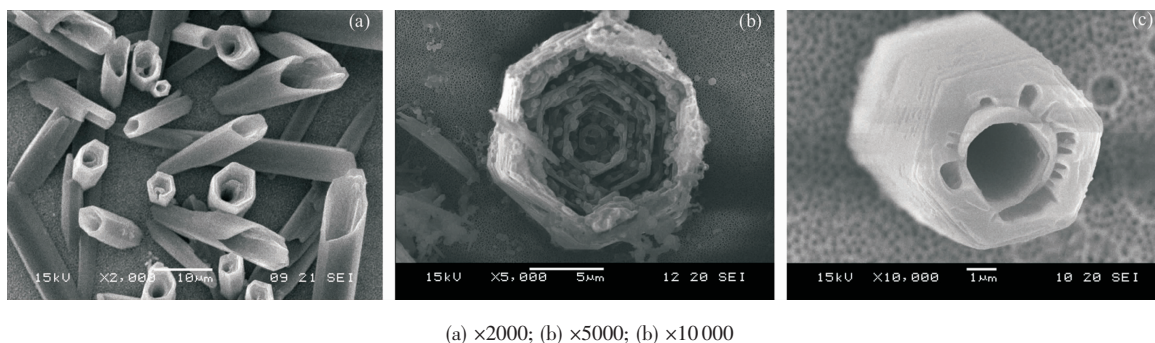


Fig.2 SEM images of vertically aligned C_{60} microtube arrays

distributions of the C_{60} microtube crystals are independent of the pore size of the membrane. Pore size of either 20 or 200 nm was used in this work.

The XRD pattern (Fig.3) of room-temperature dried C_{60} microtubes shows three major peaks at 2θ values of 10.7° , 17.6° , and 20.6° corresponding to (111), (220), and (311) plane reflections, which are typical for pristine fcc C_{60} crystals. The strong diffraction from (220) planes of the microtubes implies that the C_{60} microtube crystals grow in the (110) direction, which is similar with C_{60} nanowhiskers and nanotubes prepared by using the LLIP process^[17,18]. Furthermore, the other small peaks like the small peak at $2\theta=10.2^\circ$ which is the neighborhood of (111) reflection peak in the XRD pattern for the C_{60} microtubes, may be related to a structural imperfection such as stacking faults and/or the presence of hexagonal closest packing phase^[18].

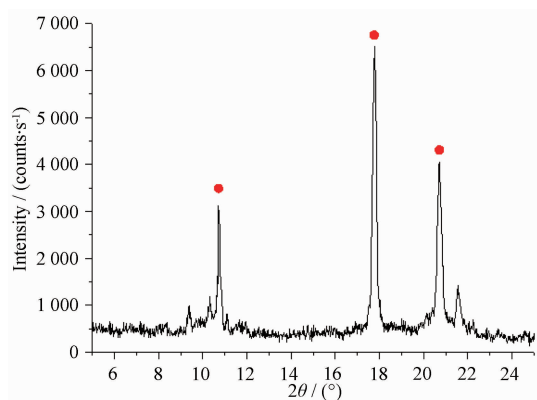


Fig.3 XRD pattern of C_{60} microtubes grown in C_{60} -saturated toluene and IPA system

The C_{60} microtubes have been scrutinized by using Raman spectroscopy (Fig.4). The observed Raman peaks of C_{60} microtubes at 268, 429, 492, 709, 770, 1420.6, 1463, 1575 cm^{-1} are attributed to Hg(1), Hg

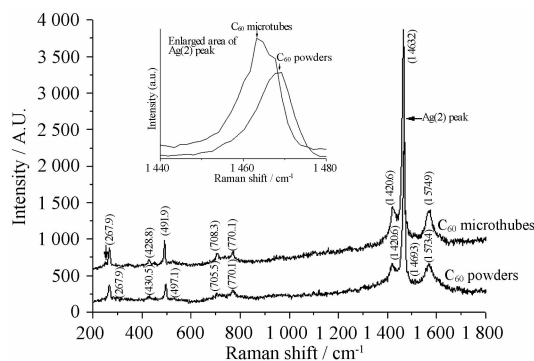


Fig.4 Raman spectra of the C_{60} microtubes and C_{60} powders

(2), Ag(1), Hg(3), Hg(4), Hg(7), Ag(2), Hg(8) modes for C_{60} molecules, respectively. Among the Raman active peaks, in comparison to the Raman peaks from pristine C_{60} crystals, the observed Raman spectrum of C_{60} microtubes slightly shifts. The most significant one is the peak corresponding to the “pentagonal pinch” mode or Ag(2) mode. This mode is very susceptible to intermolecular bonding. From the inset in Fig.4, it can be found that this peak slightly shifts from 1469 to 1463 cm^{-1} . The observed downshift from 1469 cm^{-1} for the microtubes can be attributed to the polymerization of C_{60} molecules in view of the symmetry conditions for the proposed 2+2 cyclo-addition polymerisation mechanism^[19]. In the case of the Ag(1) mode attributed to the symmetric oscillation of a C_{60} molecule, the peak is also shifted from 496 to 492 cm^{-1} . In addition, the peak around 268 cm^{-1} shows a clear splitting (shown by arrow in Fig.4) in the lower-frequency region. The peak splitting hints to the polymerization C_{60} molecule in the microtubes^[4]. However, this splitting may also occur because of the good crystalline nature of the nanowhiskers. Thus, detailed investiga-

tion is necessary to account for the above splitting in the Raman lines. These changes in the Raman spectra are very similar to those of C_{60} nanowhiskers or nanotubes fabricated by using the LLIP process^[4,5]. The possibility of the C_{60} molecules polymerization in the process has been suggested in related reports^[19-21].

Consequently, the growth mechanism of C_{60} microtubes through polymerization is proposed. The polymerization mechanism is suggested to be 2+2 cycloaddition. This involves the breaking of parallel double bonds on adjacent C_{60} molecules and their reformation into four-membered, cross-linking rings (Fig. 5). Such bonding can occur to various degrees, giving rise to polymerized C_{60} structures with cross-linking bonds in 1-, 2- and 3-dimensions. The reduction in the number of double bonds following 2+2 cycloaddition reduces the strain energy in the C_{60} structure, allowing molecules to elongate in directions parallel to the new cross-links. The replacement of intermolecular Van der Waals bonds for covalent C-C bonds, increases the strain associated with the polymer structure. And this leads to the formation of a series of dimer and 1-dimensional “pearl chain” structures as indicated by a reduced intermolecular spacing along the growth direction of C_{60} microtubes^[20,21]. Differences in surface energy between IPA and C_{60} /toluene generate a pressure gradient across the interface, which varies inversely with the radius of curvature. The pressure within the liquid-liquid interface, is thus considered to be large enough to induce cycloaddition reactions at room temperature. This principle can not be ruled out certainly, as 1D chains of polymerized C_{60} are known to be formed under high pressure conditions without high temperatures^[22]. Lateral bonding

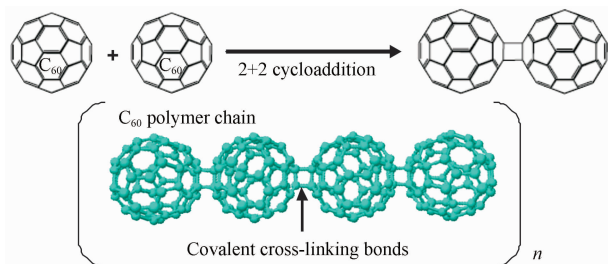


Fig.5 Polymerization between adjacent C_{60} molecules: a possible mechanism for the growth of C_{60} microtubes via LLIP

between individual chains is assumed to be through Van der Waals interactions, as is the case in bulk C_{60} crystals, because no indication of chemical bonding is observed in other directions^[5,20]. Fig.5 indicates the manner in which C_{60} molecules polymerize via 2+2 cycloaddition, leading to the formation of a dimer and a 1D chain.

2.2 Photoluminescence

Under the excitation of 1 064 nm light, the emission spectra of samples are shown in Fig.6. The dashed line corresponds to the fluorescence spectrum of AAO membrane, which has a sharp peak at 709 nm. This peak is considered to be the 2/3 multiple of excited 1 064 nm light. The dotted line relates to the emission spectrum of C_{60} powders, which has no peak from 600 nm to 950 nm. The solid line shows that AAO membrane covered with vertically aligned C_{60} microtube arrays has a broad emission around 750 nm besides the peak at 709 nm similar with AAO membrane. It is evident that the vertically aligned C_{60} microtube arrays can get red emissions at visible light area with near infrared 1 064 nm light excitation. It is novel that this up-conversion carries out a wide band luminescence excited with a homogeneous light.

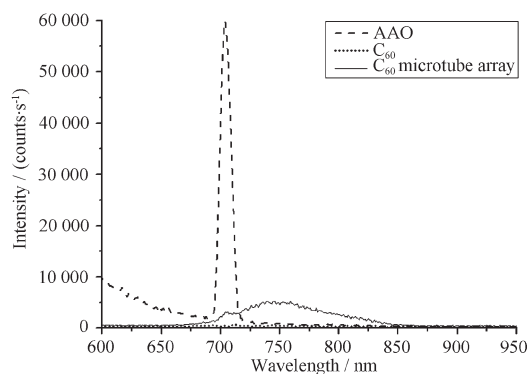


Fig.6 Emission spectra of AAO, C_{60} and vertically aligned C_{60} microtube array under 1 064 nm excitation

The vertically aligned array in Fig.2 is constructed of multiwalled carbon microtubes obviously. It is well known that multiwalled carbon tube is formed by a series of layers with different diameters, and the bandgaps in different diameter layers are absolutely distinguishable. The bandgaps of inner layers are broader than the outer ones. There are coupling ef-

fects caused by van der Waals forces between these carbon tube layers. The broader bandgaps of inner layers are coupling with the narrower bandgaps of outer layers by these effects. The broader energy levels of inner layers are similar with electronic energy levels of the molecule, and the narrower energy levels of outer layers are analogous with vibration levels of the molecule in the same way. There are two possibilities of transition from high energy level to low energy level when the multiwalled carbon microtubes are excited to excited state. The first one is radiation-free transition corresponding to vibration levels of outer layers, and the other one is radiation transition relative to the broad energy levels of inner layers. The mechanism of up-conversion is speculated as follows: electrons are excited to high-energy state by photon absorption, then radiation-free transit to lower energy state by vibration levels. Subsequently, the density of states increase sharply when electrons arrive this lower energy state, and it leads to easier radiation transition than radiation-free transition^[23]. Wherefore the up-conversion photoluminescence comes out. So the wide band luminescence is caused by the multi-layer structure of multiwalled carbon tubes.

3 Conclusions

The liquid-liquid interfacial precipitation process reveals a good method for obtaining vertically aligned C₆₀ microtube arrays. SEM images show that the C₆₀ microtube has a multi-layer structure, the outer diameter of the carbon microtubes ranges from 5 to 10 μm with hexagonal cross-sections, and the wall thickness ranges from 1 to 3 μm . XRD results show that the C₆₀ microtubes have an fcc crystal structure. Raman spectroscopy analysis indicates the polymerization C₆₀ molecule in the microtubes, and their polymerization mechanism has been discussed. Finally, the wide band up-conversion luminescence due to different energy levels of multiwalled carbon tubes is recorded clearly.

References:

- [1] Wang L, Liu B, Yu S, et al. *Chem. Mater.*, **2006**,**18** (17): 4190~4194
- [2] Liu H, Li Y, Jiang L, et al. *J. Am. Chem. Soc.*, **2002**,**124** (45):13370~3371
- [3] Jin Y, Curry R J, Sloan J, et al. *J. Mater. Chem.*, **2006**,**16** (37):3715~3720
- [4] Sathish M, Miyazawa K, Sasaki T. *Chem. Mater.*, **2007**,**19** (10):2398~2400
- [5] Ringor C L, Miyazawa K. *Diam. Relat. Mater.*, **2008**,**17**(4~5): 529~534
- [6] Asaka K, Kato R, Yoshizaki R, et al. *Diam. Relat. Mater.*, **2007**,**16**(11):1936~1939
- [7] Cha S I, Miyazawa K, Kim J D. *Chem. Mater.*, **2008**,**20**(5): 1667~1669
- [8] Tachibana M, Kobayashi K, Uchida T, et al. *Chem. Phys. Lett.*, **2003**,**374**(3~4):279~285
- [9] Shinohara K, Fukui T, Abe H, et al. *Langmuir*, **2006**,**22**(15): 6477~6480
- [10] Riggs J E, Guo Z, Carroll D L, et al. *J. Am. Chem. Soc.*, **2000**,**122**(24):5879~5880
- [11] Guldi D M, Holzinger M, Hirsch A, et al. *Chem. Commun.*, **2003**,**10**:1130~1131
- [12] Banerjee S, Wong S S. *J. Am. Chem. Soc.*, **2002**,**124** (30): 8940~8948
- [13] Sun Y P, Zhou B, Henbest K, et al. *Chem. Phys. Lett.*, **2002**, **351**(5~6):349~353
- [14] Luo Y S, Xia X H, Liang Y, et al. *J. Solid State Chem.*, **2007**,**180**(6):1928~1933
- [15] Baibarac M, Baltog I, Lefrant S, et al. *Diam. Relat. Mater.*, **2008**,**17**(7~10):1380~1388
- [16] Brennan M E, Coleman J N, Panhuis M, et al. *Synthetic Met.*, **2001**,**119**(1~3):641~642
- [17] Minato J, Miyazawa K. *Carbon*, **2005**,**43**(14):2837~2841
- [18] Minato J, Miyazawa K. *Diam. Relat. Mater.*, **2006**,**15** (4~8): 1151~1154
- [19] Chambers G, Byrne H J. *Chem. Phys. Lett.*, **1999**,**302**(3~4): 307~311
- [20] Miyazawa K, Kuwasaki Y, Obayashi A, et al. *J. Mater. Res.*, **2002**,**17**(1):83~88
- [21] Miyazawa K, Kuwasaki Y, Hamamoto K, et al. *Surf. Interface Anal.*, **2003**,**35**(1):117~120
- [22] Moret R, Launois P, Wagberg T, et al. *Eur. Phys. J. B*, **2000**, **15**(2):253~263
- [23] YUAN Yan-Hong(袁艳红), MIAO Run-Cai(苗润才), BAI Jin-Tao (白晋涛), et al. *Acta Photonica Sinica (Guangzi Xuebao)*, **2005**,**34**(11):1651~1653