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The effect of trichlorobenzene solvent geometry on the morphologies of C_{60} nano/microcrystals produced from solution

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ABSTRACT

C_{60} nano/microcrystals were synthesized from fullerene dissolved in three different trichlorobenzene isomers, to investigate the role of solvent as both shape and morphology controller in the synthesis of C_{60} nanocrystals. Various C_{60} nano/microcrystals, in particle-, sheet-, cuboid- and rod morphologies have been selectively fabricated at 80 °C using either solution evaporation or solution mixing method. The molecular structure of trichlorobenzene solvent plays a key role in the formation of different crystal morphologies, and also affects the crystal structure of synthesized samples.

1. Introduction

The unique physical and chemical properties of fullerenes together with the increasing interest in nanomaterials make C_{60} nano/microcrystal a highly attractive material, which could be used in electrical and optical devices, solar cells and even medical devices [1–3]. Thus, the controlled synthesis of C_{60} nanocrystals has become a focus topic in recent years [4–6]. Several methods have been used to control the morphology of C_{60} crystals, such as the use of templates [7], solvent-assisted methods on substrate or in solution [4,5,8] and vapor–solid processes [6]. Among these methods, solvent-assisted methods (including solution evaporation and liquid–liquid interfacial precipitation) have been found to be the most facile and efficient. The previous studies show that the morphology and structure of C_{60} crystals depend on the solvent used [4,8,9]. Wang et al. found m-xylene was a good solvent to obtain one dimensional C_{60} namocrystals with solution method, which also control the crystal structure of solvated materials [4]. Yao et al. reported that the morphologies of C_{60} nanocrystals could be tuned by different kind of dichlorobenzene [8]. Geng et al. found that 1,2,4-trimethylbenzene has a novel role in the regulation of the molecular packing process that leads to a preferential stacking of C_{60} molecules along different lattice planes [9]. However, further investigation is still necessary to understand the controlling mechanism of C_{60} crystal morphology by solvent.

As known, the carbon atoms in a C_{60} molecule have their valences satisfied by two single bonds and one double bond leading to an electron configuration where the surface is covered with π electrons and appears to be aromatic. This special molecular electronic property makes strong interactions possible between C_{60} molecule and other molecules with aromatic rings. Interestingly, compounds having at least one aromatic ring have been reported to be efficient for the shape control of fullerene crystals [8,10,11]. However, the mechanism for shape control of C_{60} nanocrystals by different aromatic compounds is still unclear. It is well known that to study the solvent polarity is an effective way to investigate the formation of solvation shell around fullerene molecules and the mechanism of nanocrystal [12,13]. To the best of our knowledge, the shape control effect of aromatic hydrocarbons were carried out on several solvents, such as xylene by Wang et al. [4,14], dichlorobenzene by Yao et al. [8], mesitylene by Geng [9] and Park et al. [10]. No research was carried out on the C_{60} nanocrystal morphology tuning effect of trichlorobenzene isomers, which has various molecule morphologies and polarities. A systematic investigation on trichlorobenzene isomers was important for better understanding the formation of different morphologies.

In this work, C_{60} nanocrystals with different morphologies were fabricated using 1,2,3, 1,2,4 and 1,3,5-trichlorobenzene as shape controllers, respectively. Both solution evaporation and solution mixing methods (at 80 °C) have been used. With both methods, C_{60}

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nanosheets and nanoparticles were fabricated using 1,2,3 and 1,2,4 type solvents, respectively. C_{60} nanocuboids were fabricated by evaporating saturated C_{60}/1,3,5-trichlorobenzene solution, and C_{60} nanorods were obtained by mixing C_{60}/1,3,5-trichlorobenzene solution with isopropanol. Our results suggest that the morphologies of C_{60} nanocrystals can be effectively controlled by selecting the type of trichlorobenzene, and C_{60} crystal morphologies have a close relationship with the structures of solvent molecules.

2. Experimental

2.1. Materials

C_{60} (purity >99.9%) was purchased from Wuda Sanwei Carbon Cluster Corporation, China, and the 1,2,3/1,2,4/1,3,5-trichlorobenzene were obtained from Aladdin Chemical Co. Led.

2.2. Material preparation

The fullerene solution was prepared by placing a mixture of C_{60} powder and solvent (either solid or liquid) in a glass bottle (25 ml in volume), which was heated at 80 °C for one hour. The resulting fullerene solution was then deposited as small drops on a substrate and slow evaporation resulted in the growth of C_{60} crystals at 80 °C. Different substrates, including Si, glass, metal foil, etc. have been tested. All substrates are chemically inert to the solvent that can be used for the crystal growth. For comparison, we have also prepared C_{60} nanocrystals by directly adding isopropanol (IPA) as a precipitant into the liquid solution containing C_{60}. With the evaporation method it usually takes ~1 h to grow C_{60} nanocrystals, while a brown aggregate of C_{60} crystals was instantaneously produced as soon as IPA was added at 80 °C.

2.3. Characterization

The crystals were characterized by Scanning Electron Microscopy (SEM, Hitachi S-4800), Raman spectroscopy (Renishaw inVia) using an excitation wavelength of 830 nm, IR spectroscopy (Bruker Vertex80 V FTIR spectrometer), X-ray diffraction (Rigaku D/max-RA, using CuKα1 radiation with λ = 1.5406 Å), and Transmission Electron Microscopy (JEM-2010, Japan). The samples used for characterizations were prepared by evaporating saturated C_{60}/solvent solution on Si substrate and all measurements were carried out at room temperature.

3. Results and discussion

3.1. Morphologies of C_{60} crystals

Fig. 1 a, c and e shows the SEM images of C_{60} nano/microcrystals obtained by evaporating C_{60} solutions containing 1,2,3, 1,2,4 and 1,3,5-trichlorobenzene at 80 °C, respectively. As shown in Fig. 1a, evaporating a saturated C_{60} solution containing 1,2,3-trichlorobenzene results in the formation of C_{60} nanosheets with thickness ranging from 100 nm to 300 nm. It is clear that most of the nanosheets have a hexagonal shape (irregular). A typical image of the samples obtained by evaporating C_{60} solutions in 1,2,4-trichlorobenzene on the substrate is shown in Fig. 1c. These particles in diameter from 500 nm to 1 μm have a flower-like shape with holes in the center. Fig. 1e shows samples obtained through evaporating a saturated solution of C_{60} in 1,3,5-trichlorobenzene. The resulting crystals have cuboidal morphologies in lengths of 1–2 μm.

For comparison, SEM images of C_{60} micro/nanocrystals obtained by mixing C_{60} solutions containing different kinds of trichlorobenzene with IPA at 80 °C are shown in Fig. 1b, d and f. As shown in Fig. 1b, when using 1,2,3-trichlorobenzene, hexagonal nanosheets in an average diameter of about 5 μm and an average thickness of about 250 nm can be obtained. The hexagonal morphology of C_{60} nanosheets in this case was more regular than that of the nanosheets obtained by solution evaporating method. Fig. 1d shows an image of the samples obtained using 1,2,4-trichlorobenzene. It is seen that the resulting nanoparticles have a "bowlike" structure in dimeter of about 200 nm. The size distribution is much more uniform and the crystals are smaller than those obtained from the solution evaporation process. Fig. 1f shows that the C_{60} forms nanorods having round tips with uniform diameters of about 250 nm and lengths of about 1–4 μm when 1,3,5-trichlorobenzene/C_{60} saturated solution was added into IPA.

3.2. Structure studies of C_{60} crystals

To study the structure of as-grown C_{60} nanocrystals with different morphologies obtained by solution evaporation method, XRD patterns were recorded for crystals grown on Si substrate. The results are presented in Fig. 2. As shown in Fig. 2b, d and f, all the samples obtained by solution evaporation method have a face-centered-cubic (fcc) structure, with lattice parameters a = 1.449 ± 0.005 nm, 1.428 ± 0.005 nm and 1.428 ± 0.005 nm, respectively. Curves a and c in Fig. 2 show the XRD patterns from samples fabricated by solution mixing method using 1,2,3/1,2,4-trichlorobenzene solvents. Both of these can also be well indexed with an fcc structure. In contrast, C_{60} nanorods obtained by mixing 1,3,5-trichlorobenzene solution with IPA have a hexagonal structure (shown in Fig. 2e) with parameters $a = 2.074 \pm 0.005$ nm and $c = 1.074 \pm 0.005$ nm. Interestingly, for the nanosheets obtained from 1,2,3-trichlorobenzene by solution evaporation method and solution mixing method (see Fig. 2a and b), the relative intensity of (1 1 1) and (2 2 2) diffraction peaks are much higher than those from other samples indicating that (1 1 1) plane is preferentially oriented parallel to the substrate. To explain this phenomenon, a Selected Area Electron Diffraction (SAED) was recorded during our TEM observations and the pattern was shown in Fig. 2 as an inset. From the pattern we can prove that the terminated surface of C_{60} nanosheets fabricated with these methods were (1 1 1) planes. The reason for occurrence of this terminated surface may be related to the growth mechanism and morphologies of the crystals.

3.3. IR studies of C_{60} crystals

To further explore the shape tuning mechanism of solvents, it is necessary to investigate the components of as-grown samples. IR spectroscopy is an effective tool to detect organic solvents, and was therefore used to study the components of our as-grown C_{60} crystals. Fig. 3 shows typical IR spectra for the as-grown nanocrystals obtained by both solution evaporation method and solution mixing method using these three kinds of trichlorobenzene. In the range from 500 to 1500 cm^{-1}, four peaks, at the positions of 527 cm^{-1}, 577 cm^{-1}, 1183 cm^{-1} and 1428 cm^{-1}, respectively, were found in all the spectra. These peaks are all characteristic absorption peaks for C_{60} [11] and confirm that all the samples consist of C_{60}. Furthermore, another two absorption peaks marked with stars were found at the positions of 874 cm^{-1} and 1385 cm^{-1}, and can be assigned as the absorption peaks of trichlorobenzenes. The appearance of these peaks indicated that trichlorobenzene molecules have been introduced into C_{60} crystal lattice during the synthesis. It is clear that among all the samples, relative intensity of the peak at 1385 cm^{-1} is the highest for the samples fabricated using 1,3,5-trichlorobenzene, indicating that these crystals contain more solvent (1,3,5-trichlorobenzene) than the others.