# High-pressure induced polymerization of C<sub>60</sub> nanorods

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#### Abstract

 $C_{60}$  nanorods, about 200 nm in diameter and several micrometers in length and with a rectangular cross section, have been synthesized by a simple solution-growth method. Raman spectroscopy and TEM indicate that the  $C_{60}$  nanorods have a fcc crystalline structure similar to that of pristine  $C_{60}$ . Nanorods were polymerized at high temperature and high pressure below 2 GPa. Two different polymeric structures, orthorhombic and tetragonal as determined by Raman spectroscopy, have been obtained under different high temperature and high pressure conditions. The high-pressure induced polymeric samples keep the original nanometer scale rod shape.

Key words: C<sub>60</sub>, solution-growth method, C<sub>60</sub> nanorod, HPHT

### Introduction

As one of the most important novel materials in the carbon family, one-dimensional C<sub>60</sub> has attracted much attention due to its unique structure and physical properties as well as its potential application in the field of nanometer scale devices. Synthesis of highly crystalline C<sub>60</sub> nanorods or wires with various structures is of great interest in this field. It is well known that C<sub>60</sub> is converted into a pure carbon polymer with covalent intermolecular bonds when it is subjected to a combination of high pressure and high temperature. Linking nearest neighbors in the C<sub>60</sub> fcc lattice can lead to at least three polymerized crystal structures under high pressure below 6 GPa, including orthorhombic (linear-chain), tetragonal and rhombohedral structures (Sundqvist 1999, 2004). High pressure and high temperature treatment thus give us an effective tool to obtain various crystalline structures of C<sub>60</sub> (Rao et al., 1993; Wågberg et al. 1999). Very recently,  $C_{60}$  nanowhiskers with diameters of 250 –500 nm, more than 100  $\mu$ m in length and with star-like cross sections, were grown by a liquid-liquid interfacial precipitation method (Miyazawa et al. 2002) and photo-polymerized by irradiation with laser light during growth, forming a mixed polymeric phase (Tachibana et al. 2003). In this work, we synthesized C<sub>60</sub> nanorods with a fcc crystalline structure, similar to that of pristine bulk C<sub>60</sub> crystal. The C<sub>60</sub> nanorods were then polymerized under various high pressure and high temperature conditions. Two polymeric phases, the orthorhombic and tetragonal phases of C<sub>60</sub>, have been obtained in the nanorods studied.

#### Experimental

 $C_{60}$  nanorods were grown by a liquid solution method.  $C_{60}$  powder (99.9%) was used as raw material. A special solvent was found to easily make a  $C_{60}$  solution.  $C_{60}$  nanorods were then grown by slowly evaporating the solution on substrates, such as Mo foil and silicon (Wang et al. 2005).

The C<sub>60</sub> nanorods were polymerized in silicone oil using a piston–cylinder device. Nanorods deposited on Mo or glass substrates were loaded into the pressure cell and were treated under different conditions for over 2 hours. One set was treated at a pressure of 1.5 GPa and a temperature of 573 K, and another at a pressure of 2 GPa and a temperature of 700 K.

The as-grown nanorods were characterized with Raman spectroscopy (Renishaw 1000, UK), transmission electron microscopy (JEM-2010, Japan), and Atomic Force Microscopy (AFM, Nanoscope IV, US). The polymerized sample was washed with pentane and alcohol several times, and analyzed with Raman spectroscopy and AFM. In the Raman spectroscopy measurement, the sample was irradiated with a 514 nm excitation wavelength using a 100 X objective lens. The irradiation power was less than 0.26 mW. The exposure time was less than 10 s, to avoid photo-polymerization of the sample.

#### **Results and discussion**

A typical AFM image of an as-grown sample deposited on a Mo substrate is shown in fig.1. It is obvious that the sample is in the shape of rods with widths of nanometers and with rectangular cross sections. The majority of the nanorods have a width of 200 nm, and the average length is of the order of several micrometers. The rectangular section different from cross is that of nanowhiskers obtained by liquid-liquid interfacial precipitation. From AFM images, we can also estimate the thickness of the nanorods. The thickness of a rod with a width of 200 nm is about 50 nm.

Raman spectroscopy is a powerful tool to



Fig.1 AFM image of as-grown  $C_{60}$  rods on a Mo substrate.

determine the structure of  $C_{60}$ . Typical Raman spectra for nanorods are shown in Fig. 2. For comparison, pristine  $C_{60}$  powder was studied under the same conditions. The Raman spectrum of  $C_{60}$  usually contains 10 peaks, including eight Hg modes and two Ag modes. Among these peaks, the pentagonal pinch mode  $A_g(2)$ , normally observed at 1469 cm<sup>-1</sup>, is a characteristic mode for the monomeric fcc phase. Our Raman data clearly show that nanorods have spectroscopic features very similar to those of the pristine sample, indicating that  $C_{60}$  nanorods and the pristine  $C_{60}$  powder have the same fcc structure.

To further identify the structure of the  $C_{60}$  nanorods we analysed samples by electron diffraction. A diffraction diagram is shown together with a TEM image of a single nanorod in fig. 3. The figure clearly shows a rectangular rod with a width of about 200 nm. The selected area electron diffraction (SAED) pattern shows that the nanorod is a single crystal of  $C_{60}$ . The

SAED spots can be indexed as the (220) and (311) peaks of a fcc structure, the same structure as for pristine  $C_{60}$  powder. From this pattern, it is seen that the preferred growth direction of the nanorod is (110).

To obtain  $C_{60}$  nanorods with various crystalline structures, we then carried out polymerization of  $C_{60}$  nanorods under high pressure and high temperature with a piston–cylinder device. According to previous studies of polymerization in  $C_{60}$  bulk samples, the resulting polymerized structure depends on pressure, temperature and time, and also depends on the treatment path, i.e. whether pressure was applied before heating or after. It is



Fig.2 Raman spectra of (A) pristine  $C_{60}$ , (B) as-grown rods, (C) rods polymerized at 1.5 GPa, 573K, (D) rods polymerized at 2.0 GPa, 700K

known that heating before pressurization will give more pure polymeric phases (Sundqvist 2004). Nanorods were treated at two different conditions in our experiment. One was at a pressure of 1.5 GPa and a temperature of 575 K, at which the orthorhombic (linear-chain) structure is formed in bulk  $C_{60}$ . In our experiment, the sample was first pressed to 0.5 GPa, then heated to 575K and finally the pressure was increased to 1.5 GPa for 4 h. The second used a pressure of 2 GPa at 700K, at which conditions pure tetragonal phase is usually formed in bulk  $C_{60}$ . A similar procedure as before was used:  $C_{60}$  nanorods were first pressed to 0.5 GPa for 4 h.

The recovered samples were cleaned before Raman measurements. Raman spectroscopy is a very powerful tool to distinguish between polymeric phases of  $C_{60}$ . The isolated  $C_{60}$  molecule possesses  $I_h$  symmetry. When  $C_{60}$  molecules are linked together, forming polymeric phases, the formation of intermolecular covalent bonds dramatically

reduces the molecular symmetry and gives rise to pronounced changes in the vibrational spectra. Such a lowering of symmetry results in frequency shifts and splitting of vibrational modes. Generally,  $C_{60}$  polymer phases can be distinguished by the frequency shift of the pentagonal pinch mode Ag(2) (Sundqvist 1999, 2004). Curves C and D in Fig. 2 show typical Raman spectra for nanorods HPHT treated at 1.5 GPa, 575K and at 2.0GPa, 700K, respectively. In curve C, the pinch mode shifts from 1469 cm<sup>-1</sup> to 1458 cm<sup>-1</sup>, which is a characteristic feature for the orthorhombic phase. The  $C_{60}$  nanorods have thus transformed from monomeric fcc structure to an orthorhombic polymeric phase after treatment at 1.5 GPa, 573 K. In curve D, the  $C_{60}$  pinch



Fig.3 TEM image of  $C_{60}$  rod, and inset is the selected area ED pattern.

mode shifts to a lower frequency and splits into three distinguishable peaks, at 1462, 1446 and 1428 cm<sup>-1</sup>. The intensity of the 1446 cm<sup>-1</sup> peak is lower than that of the peak at 1462 cm<sup>-1</sup>. From previous studies, it has been found that the peak at 1446 cm<sup>-1</sup> is a characteristic feature

for the tetragonal phase in bulk  $C_{60}$ , together with a peak at about 1465 cm<sup>-1</sup>. Usually the intensity of the 1446cm<sup>-1</sup> peak is higher than that of the 1465 cm<sup>-1</sup> one in pure tetragonal phase (Sundqvist, 2004). Our result shows that tetragonal polymer was formed in our  $C_{60}$  nanorod sample at 2.0 GPa, 700 K. From our spectral data, the intensity at 1462 cm<sup>-1</sup> is higher than at 1446 cm<sup>-1</sup> in our sample, indicating that other phases exist in this sample. At the treatment conditions used, a pure tetragonal phase of bulk  $C_{60}$  samples has been obtained by many researchers, but others have found traces of the rhombohedral (R) phase which is usually formed at even higher temperatures and pressures (Sundqvist, 1999, 2004). However, spectrum D in fig.2 shows no characteristic peak for the R phase. Usually, peaks at 1462 cm<sup>-1</sup> and 1424 cm<sup>-1</sup> can be observed in Raman spectra for the dimer phase of bulk  $C_{60}$  (Davydov et al. 2000). A comparison with our spectra shows that there is probably a

contribution from dimers to the peaks at 1462 cm<sup>-1</sup> and 1428 cm<sup>-1</sup> in our samples, indicating that dimers probably also have been formed in the  $C_{60}$  nanorods. Such a difference between bulk samples and  $C_{60}$  nanorods treated under the same conditions is probably caused by surface effects in our nanoscale sample. Fitting three peaks to curve D in fig. 2 we find that the samples treated at 2.0 GPa and 700 K contain about 70% tetragonal phase.

To verify whether the rod survived the HPHT treatment we performed AFM measurements with the result shown in Fig.4. It is clearly seen that the sample still has a rectangular shape with an average width similar to that of pristine samples.



Fig.4 AFM image of the high pressure-induced nanorod polymer.

There is no obvious change in width and length compared with those of monomeric nanorods. This result indicates that HPHT treatment will be a very powerful tool to obtain various new structures of  $C_{60}$  nanorods.

## Summary

 $C_{60}$  nanorods have been synthesized by a simple solution-growth method. The as-grown  $C_{60}$  nanorods are about 200 nm in width and several micrometers in length, with a rectangular cross section. Raman spectroscopy indicates that  $C_{60}$  nanorods have a fcc crystalline structure similar to that of pristine  $C_{60}$ .  $C_{60}$  nanorods were polymerized at 1.5 GPa , 573 K and at 2 GPa, 700 K, respectively. Raman spectroscopy on the HPHT treated samples shows characteristic features for orthorhombic and tetragonal polymer phases. The high-pressure induced polymeric sample keeps the original nanometer scale rod shape.

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