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Sol–gel synthesis of an array of C_{70} single crystal nanowires in a porous alumina template

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An ordered array of C_{70} single crystal nanowires was prepared by a sol–gel template method which is composed of three steps: generation of the C_{70} sol; deposition of C_{70} sol particles in the pores of the alumina membrane; and annealing of the resulting C_{70} composite in an argon atmosphere.

Fullerene-C_{70} chemistry[1] has been established since first detection of these species by Kroto *et al.*[2] and the subsequent macroscopic preparation by Krätschmer *et al.*[3] Photophysical properties,[4–7] conductivity,[8] photoconductivity[9] and optical limiting performance[10,11] of C_{70} have been reported frequently in the literature. Recently, C_{70} self-organization into short- and long-range order[12,13] has aroused great interest among scientists, but there has been little work on C_{70} nanostructures such as nanowires and nanotubules. As we all know, one-dimensional (1D) structures with nanometer diameters, such as nanotubes and nanowires, have a great potential for the testing and understanding of fundamental concepts about the roles of dimensionality and size in, for example, optical, electrical and mechanical properties and for applications ranging from probe microscopy tips to interconnections in nanoelectronics.[14] But developing the techniques for synthesizing and characterizing nanostructures is one of the grand challenges to chemists.

Here, we report the first generation of an ordered array of C_{70} single crystal nanowires obtained by a sol–gel template method. This is a key step for the construction of molecular devices.

A simple method to generate an aqueous colloidal solution has recently been developed by our group:[11] 8.0 mg C_{70} powder (99% purity), 100 mg Al–Ni alloy (excess) and 400 mg solid NaOH pellets were put in a bottle, which was evacuated and filled with argon; then 10 ml THF (distilled from sodium–benzophenone in a Schlenk system) were added with stirring. With the exception of C_{70}, which is slightly soluble in THF, the other starting materials do not dissolve. NaOH solid pellets dissolve with accompanying effervescence after the addition of 3 ml of deoxygenated water. The colour of the THF layer turned from slightly yellow to red–orange. After 1 h the red–orange THF solution was separated from the colourless aqueous caustic NaOH solution. Then, the solution of C_{70}^- in THF was added dropwise to 50 ml of undegassed distilled water. The THF was removed under reduced pressure to give an aqueous colloidal solution of containing 0.45 mg l^{-1} C_{70} (0.54 mM).[11]

An alumina template (Anodise®) made by Whatman Inc. (SEM images revealed a pore diameter ranges of 100–300 nm) was immersed in the C_{70} sol for 4–5 h under *ca.* 1.3 atm at ambient temperature. The template was then taken out from the C_{70} sol and dried at *ca.* 75 °C for 30 min. The deposits on both faces of the alumina membrane were removed by polishing with alumina powder, and annealed under argon atmosphere with the temperature ramping up to 500 °C for 5 h, before ramping back down to room temperature.

Fig. 1 shows scanning electron microscope (SEM)† images of the sample which was treated with a 6 M NaOH solution for *ca.* 3 min in order to dissolve the top layer of alumina. Without tetrabutylammonium hydroxide (TBAH) as catalyst, C_{70} cannot form C_{70} fullerol; also, without a reducing agent, C_{70} cannot form C_{70} anions in aqueous caustic solution. It can be seen that the C_{70} nanowires are well ordered and are perpendicular to the alumina template.

Fig. 2(a) is a transmission electron microscopy (TEM)† image of selected C_{70} nanowires. The diameter varies from 100 to 300 nm, which corresponds to the pore diameter of the alumina template. Bright field TEM images revealed that the

Fig. 1 Scanning electron micrograph of an array of C_{70} nanowires embeded in the alumina template matrix: (a) general cross-section view; (b) and (c) part view, magnifying power ×4000 and ×12 000, respectively.

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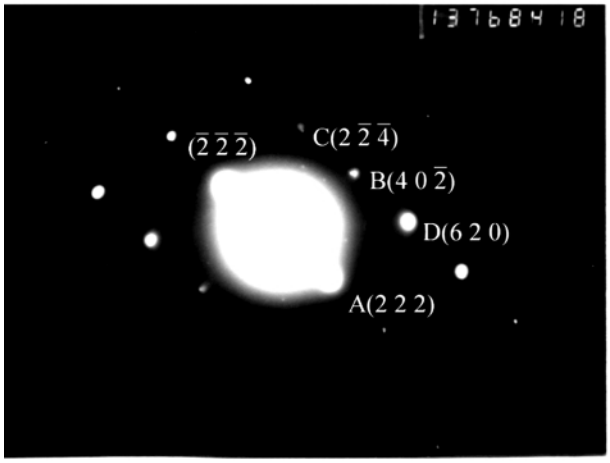
(a)



(b)

Fig. 2 (a) Transmission electron micrograph (TEM) images of a piece of *ca.* 150 nm diameter C_{70} nanowire after removing the alumina matrix, scale bar is 100 nm; (b) fcc [1$\bar{3}$2] zone axis electron diffraction pattern of corresponding C_{70} nanowires.

C_{70} nanowires were stable under the 200 keV electron beam. Fig. 2(b) is an electron diffraction pattern of the selected C_{70} nanowires. The ratio of $R_A^2:R_B^2:R_C^2:R_D^2 \approx 12:20:24:40$, R corresponding to the distance between the reflection spot and the reflection pattern center. These results suggest that the C_{70} crystal is of cubic structure, whose reflection spots may be indexed as A(222), B(40$\bar{2}$), C(2$\bar{2}\bar{4}$) and D(620), and the zone axis is [1$\bar{3}$2]. The sharp [1$\bar{3}$2] zone axis pattern contains D(620) reflections at *ca*. 44°, B(40$\bar{2}$) reflections at *ca*. 78°, and C(2$\bar{2}\bar{4}$) reflections at *ca*. 120° from A(222). Hence, the C_{70} single crystal samples prepared by this method, similar to the samples prepared by sublimation, are face-centered cubic, and thermal annealing is in favor of the fcc phase forming. This result is in accordance with the observation by Heiney and coworkers,[15] *i.e.* that the fcc phase is the equilibrium state of pure C_{70} above 300 K.

In conclusion, the sol–gel template method is a convenient and powerful method for generation the array of single-crystal C_{70} nanowires. The morphology and structure of the C_{70} nanowires array were studied by SEM and TEM. The C_{70} nanowires are single crystals with fcc structure and the zone axis is along the [1$\bar{3}$2] direction. The morphology of the array of C_{70} nanowires is brush-like and well ordered and is stable under a 200 keV electron beam.

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Notes and references

† SEM images were obtained using a Hitachi, X650/EDAX, PV9100 scanning electron microanalysis instrument. TEM images were obtained using a Transmission Electron Microscope JEM-200CX, JEOL. The accelerating voltage of the electron beam was 200 keV.

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