Nanoporous Fullerene Nanowhiskers

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Carbon-based materials have received enduring attention from various scientists due to their unique properties, diverse morphology, and wide applications. Fullerene (C_{60}), the most interesting candidate in the carbon family, has peculiar structural characteristics over other members. Indeed, it has various applications like other carbon materials in fields such as sensors, catalysis, and optical devices. The recent development in one-dimensional nanostructural materials with assorted morphology like nanotube, nanorods, nanoplates, etc., has further enhanced the utility of these carbon materials.

The self-slow-aggregation of C_{60} molecules into a small cluster in the pure solvent medium is well-known.[1,2] On the basis of this, various crystalline C_{60} crystals were grown in different solvents with dissimilar structure and diverse shapes.[3−5] The nature of the solvent plays a major role in the cluster structure, and the various mechanistic approaches for cluster formation are described.[6] In the earlier reported literature, the obtained C_{60} crystals are a few micrometers or millimeters in diameter and crystallinty is stabilized by the solvent molecule. More recently, the synthesis of C_{60} nanotubes or nanowhiskers has created an enormous amount of expectation due to the nanosize and the tubular morphology similar to that of carbon nanotubes. Unlike other carbon materials, the C_{60} nanotube has solubility in various organic solvents, which adds supplementary advantages to the exploitation of C_{60} nanotubes as a removable template.[7]

Various synthetic strategies have been introduced for the preparation of C_{60} nanowhiskers (or) nanotubes.[8−10] In our earlier study, we introduced liquid−liquid interfacial precipitation of C_{60} and C_{70} nanowhiskers using toluene or *m*-xylene and isopropyl alcohol (IPA) interface.[11−13] It is believed that the porous nanowhiskers preparation could be possible only by our interfacial preparation method. Pursuing our efforts toward the finding of a better solvent system for the synthesis of porous C_{60} nanowhiskers, we have evaluated various combinations of solvents. Finally, the formation of porous C_{60} nanowhiskers have been successfully obtained by mixing of different ratios (v/v) of C_{60} saturated benzene and IPA. Before mixing, the solutions were cooled to 5 °C and the IPA was added slowly to the C_{60}-saturated benzene solution. After the addition, the solution was ultrasonicated for 1 min at 5 °C in an ultrasonic water bath. The resulting mixture was kept in an incubator at 5 °C for 24 h. The optical microscopic image of the C_{60} nanowhiskers produced at the benzene−IPA interface is shown in Figure 1. Very thin nanowhiskers few hundred micrometers in length were observed. This can also be seen from the microscopic image that the nanowhiskers are uniform in size throughout the length of the tube. Unlike the nonporous nanowhiskers reported earlier by our group and other researchers, in the present case, nanowhiskers with very fine pores have been observed. Although the pore size and shape vary, they were insignificant compared to the whole view.

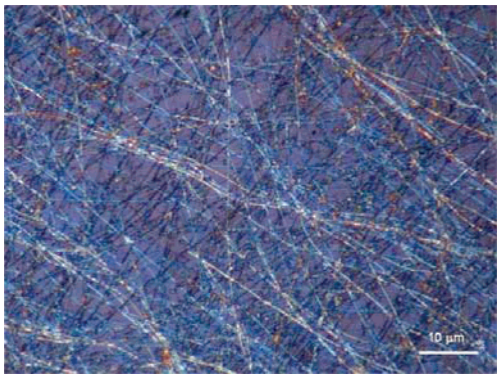

Figure 1. Optical microscopic image of C_{60} nanowhiskers.

The morphology of the prepared C_{60} nanowhiskers has been further analyzed by FE-SEM analysis. Figure 2 shows the FE-SEM images of the prepared porous nanowhiskers at different magnification. Very long C_{60} nanowhiskers (more than 100 micrometers) with uniform size were observed in the mesh. The average size of nanowhiskers is around 100 nm in diameter. However, because of the Pt sputtering, the morphology of pores on the surface could not be seen clearly.

Figure 3 shows a representative set of scanning transmission electron microscopy (STEM) images of the C_{60} nanowhiskers prepared at the benzene−IPA interface. The ob-

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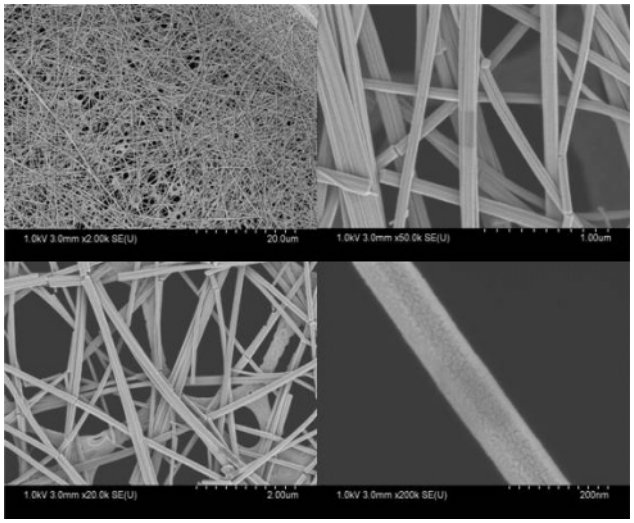

Figure 2. FE-SEM images of platinum sputtered C_{60} nanowhiskers.

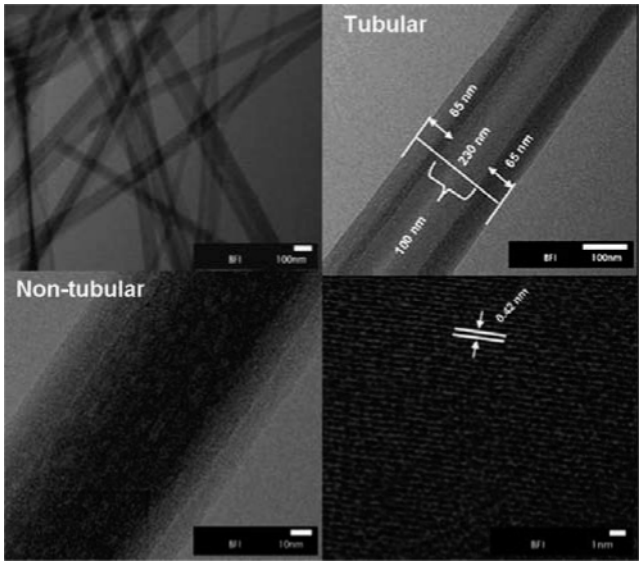

Figure 3. STEM images of C_{60} nanowhiskers.

nanowhiskers in the range of 100−300 nm in diameter. In the case of tubular nanowhiskers, the inner diameter of the tube is ∼100 nm and the wall thickness is 65 nm. Regardless of the inner diameter, the wall thickness is found to be constant in the range of 65−75 nm for the other tubular nanowhiskers. In the case of nontubular nanowhiskers, a very thin layer of amorphous surface was found. The size of the nontubular nanowhiskers was found to be smaller when compared to tubular nanowhiskers. A clear lattice fringing has been observed for the nontubular nanowhiskers with a lattice plane spacing of 0.42 nm. This obtained value has good concordance with the *d* value of the (311) plane. The length of the nanowhiskers is in the range of a few hundred micrometers.

The TEM images of the nanowhiskers are shown in Figure 4. The fine pores on the wall surface of the nanowhiskers are clearly visible (indicated by red circle). The observed pores are not uniform in size and shape. It is presumed that during the formation process of C_{60} nanowhiskers, the solvent molecule occupies the space inside the pores of the tubes. The solvent molecules that present inside the tubes get

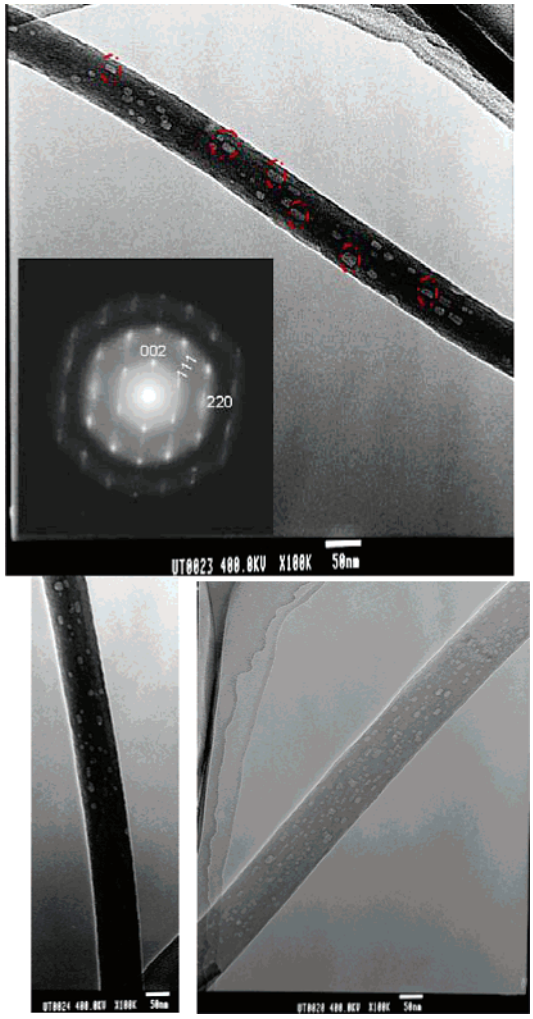

Figure 4. TEM images of nontubular porous C_{60} nanowhiskers.

evaporated during the drying process. The evaporation of solvent makes the pores on the walls of the nanowhiskers. It is speculated that the solvent-evaporation process has a crucial role in the structure direction and leads to tubular and nontubular nanowhisker formation. The nanowhiskers that are smaller in size (<100 nm) become nontubular and the nanowhiskers with a larger size (>100 nm) surmount the tubular structure. Certainly, the observed porous nanowhiskers with a size less than 100 nm are nontubular, which supports the above speculation that solvent evaporation in the small nanowhiskers makes nontubular nanowhiskers. However, there is no comprehensible evidence for the formation of tubular and nontubular nanowhiskers. The formation of pores has been further confirmed by the observed higher specific surface area of 376 m^2/g, whereas the specific surface area of pristine C_{60} powder is 20 m^2/g.

The inset of Figure 4 shows the selected area electron diffraction pattern of porous C_{60} nanowhiskers, the acquired pattern shows that the nanowhiskers are face-centered cubic in structure.[11] The crystalline nature has been further confirmed by X-ray diffraction pattern (XRD) analysis. The XRD pattern (see the Supporting Information) of room-temperature dried C_{60} nanowhiskers shows three major peaks at 2θ values of 10.7, 17.6, and 20.6 corresponding to (111), (220), and (311) plane reflections, respectively. The obtained XRD pattern can be indexed for the fcc crystal system.[14,11]

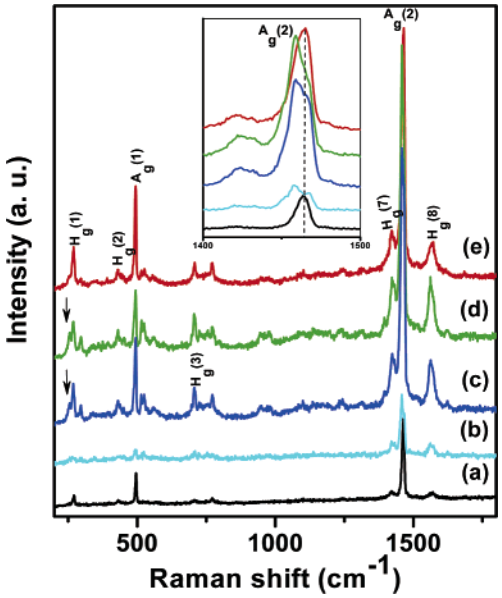

Figure 5. Raman spectroscopy of (a) pristine C_{60} and porous C_{60} nanowhiskers prepared at (b) 1:9, (c) 1:8, (d) 1:6, and (e) 1:4 benzene:IPA ratios.

However, the reflection corresponding to the (200) plane was not observed for the porous nanowhiskers. Likewise, the absence of the 200 reflection is typical for pristine fcc C_{60} crystals.[15]

To understand the effect of solvent ratio on the C_{60} nanowhisker formation, the C_{60}-saturated benzene to IPA ratio has been varied between 1:3 to 1:12 with 1 mL intervals. The growth of nanowhiskers has been observed for all ratios up to 1:9; however, above this ratio, formation of nanowhiskers was not observed even after 1 week's time. It is commonly accepted that the solvent ratio has a crucial role in the growth of nanowhiskers. Also, the effect of temperature on the growth rate has been studied at 5, 10, 15, and 25 °C for the 1:4.5 ratio of C_{60}-saturated benzene and IPA. Interestingly, the effects of temperature on the growth of the C_{60} nanowhiskers have been observed at the interface. The growth rate has an inverse dependence with increase in temperature. As the temperature increases, the growth time also increases and the yield of the nanowhiskers decreases gradually. However, there is no formation of nanowhiskers at room temperature (25 °C), even after a very long time. Regardless of the temperature and solvent ratio, the obtained nanowhiskers show very fine and narrow pores in nontubular morphology.

The C_{60} nanowhiskers prepared at different ratios of the solvent have been scrutinized using Raman spectroscopy. Figure 5 shows the Raman spectra of the nanowhiskers and pristine C_{60} powder.

The observed Raman lines at 267, 429, 494, 707, 1423, 1459, and 1562 cm^{-1} are attributed to $H_g(1)$, $H_g(2)$, $A_g(1)$, $H_g(3)$, $H_g(7)$, $A_g(2)$, and $H_g(8)$ modes for C_{60} molecules,[16] respectively. Among the Raman active lines, the most significant one is the line at 1469 cm^{-1}, which corresponds to the "pentagonal pinch" mode or $A_g(2)$ mode. This has been used extensively as an analytical probe for the structural and electronic properties of C_{60} molecules.[16] This mode is very susceptible to intermolecular bonding. Although there is no significant difference between Raman spectra of nanowhiskers prepared with different solvent ratios, a noticeable peak shift for the $A_g(2)$ mode has been observed at 1459 cm^{-1} for the nanowhiskers compared to the pristine C_{60} powder. Figure 5 (inset) shows the Raman lines of the $A_g(2)$ mode for the nanowhiskers and pristine C_{60}. A very clear downshift was observed for the porous nanowhiskers. Indeed, the shift in the peak position is negligible for the nanowhiskers prepared with a lower solvent ratio (1:4), but at a higher solvent ratio (1:6 and above), the shift is very significant. The observed downshift from 1469 cm^{-1} for the nanowhiskers can be attributed to the polymerization of C_{60} molecules in the nanowhiskers.[17] A similar observation in the downshift has been observed for the photoassisted polymerization of C_{60} solid.[18,19] Hence, it is speculated that the polymerization possibly will occur during the laser irradiation, which is used for the Raman spectroscopic measurements (Figure 5). In addition, the peak around the 267 cm^{-1} shows a clear splitting (shown by arrow in Figure 5) in the lower-frequency region for the nanowhiskers prepared at 1:6, 1:8, and 1:9 ratios. The peak splitting hints to the polymerization C_{60} molecule in the nanowhiskers. However, this splitting may also occurs because of the good crystalline nature of the nanowhiskers. Thus, detailed investigation is necessary to account for the above splitting in the Raman lines.

In summary, we have succeeded in the preparation of porous C_{60} nanowhiskers using the liquid−liquid interfacial precipitation method. The prepared nontubular nanowhiskers contain nanopores over the wall surface. The porous nanowhiskers show higher specific surface area than pristine C_{60} powder. The preparation of porous tubular nanowhiskers is our ultimate aim, as a template for the preparation of various metal/metal oxide nanowire or nanotubes. The electron diffraction and XRD pattern reveals the fcc crystalline nature of the prepared porous nanowhiskers. Raman spectroscopic studies on the porous nanowhiskers show the polymerization of C_{60} molecules (due to laser light irradiation). We are currently exploiting the nanoporus nanowhiskers for various applications, particularly as an anode material for the fuel cell and template for the preparation of metal-oxide nanostructures.

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Supporting Information Available: Experimental details and XRD pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

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