

Fullerene Nanotubes

Fullerene Nanotubes: New Nanoelements with Applications in Organic Electronics

Related to conventional carbon nanotubes in both shape and construction, fullerene nanowhiskers and fullerene nanotubes have received far less attention. The terms “fullerene nanowhisker” and “fullerene nanotube” refer to closely related cylindrical and tube-like structures, respectively. Thus, fullerene nanowhiskers are *solid, cylindrical*, single crystal structures with sub-micron outside diameters and varying lengths while fullerene nanotubes are *hollow, tubular*, single crystal structures, also with sub-micron outside diameters and varying lengths.

Fullerene nanowhiskers were discovered in 2001 by Kun'ichi Miyazawa during the preparation of a sol-gel.¹ Following the addition of a toluene solution of [60]fullerene to a sol that contained isopropanol, thin fibrous structures were observed to grow and were named C₆₀ nanowhiskers. A liquid-liquid interfacial precipitation technique was subsequently developed² in which isopropanol was layered atop a saturated solution of [60]fullerene in toluene. In the same year, Zhu and co-workers reported a method to prepare the first [60]fullerene nanotubes using a porous alumina template.³ The [60]fullerene nanotubes grown on an alumina template possessed outside diameters of 220-330 nm and a length of approximately 60 μm. Miyazawa subsequently demonstrated that [60]fullerene nanotubes could also be grown using the liquid-liquid interfacial precipitation method^{4,5} with pyridine-isopropanol as an especially effective solvent combination for this purpose.

The liquid-liquid interfacial precipitation method is vastly superior to the alumina template method as it does not require a template and produces larger quantities of higher quality [60]fullerene nanotubes. Thus, using the liquid-liquid interfacial precipitation method, both fullerene nanowhiskers and fullerene nanotubes can be prepared with outside diameters ranging from approximately 100 nm to many microns and lengths ranging from several hundred nanometers to millimeters. Using the liquid-liquid interfacial precipitation method,

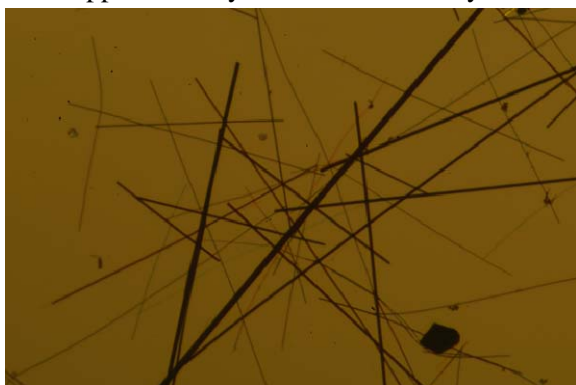


Figure 1. Optical microscope image (100x magnification) of typical [60]fullerene nanowhiskers grown from isopropanol-toluene solution. Nanowhiskers of many different diameters are observed and appear to be colored orange, red, green, grey, blue and brown in the optical microscope, depending upon diameter.

fullerene nanowhiskers and nanotubes are believed to nucleate at the interface between the layered solvents. They are typically grown at or below room temperature with complete growth taking several days. During this time, the isopropanol slowly diffuses into the fullerene rich phase increasing its hydrophilicity. The liquid-liquid interfacial precipitation method is simple but does have limitations including modest yields. Fullerene starting material that is not converted to fullerene nanowhiskers or nanotubes is generally recovered as a black powder. Moreover, the liquid-liquid interfacial precipitation method does not produce nano-structures with uniform diameters. Typically, structures with both micron scale and sub-micron diameters are produced.

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In this project, we developed a method to produce relatively uniform batches of hollow [60]fullerene nanotubes in high yield. We further probed the thermal, sonochemical and mechanical behaviors of [60]fullerene nanotubes by subjecting them to heat, ultrasonic bathing and mechanical stresses induced by an atomic force microscope tip.

Fabrication of Uniform Batches of [60]Fullerene Nanotubes in High Yield. Miyazawa's standard procedures for the formation of [60]fullerene nanowhiskers involve the preparation of saturated solutions of [60]fullerene in toluene followed by the careful layering of an equal volume of isopropanol and storage at room temperature for several days. Optical microscopy illustrates that this simple method produces structures with a range of diameters from several microns to sub-micron (Figure 1). Although Miyazawa reports that toluene-isopropanol conditions lead to [60]fullerene nanowhiskers rather than [60]fullerene nanotubes, we find that both structures form. Replacing toluene with pyridine leads to product that is almost entirely [60]fullerene nanotubes, but again with a relatively wide range of diameters.

We developed a modified technique that produces relatively uniform batches of [60]fullerene nanotubes that are approximately 300 nm in diameter. Using this modified technique, a 9:1 volume excess of isopropanol is layered atop a freshly prepared solution of pyridine containing 1.3 mg/mL of [60]fullerene. The two-phase mixture is stored at 2 °C for 24 hours to allow for the formation of nano-nucleation sites. After 24 hours at 2 °C, the two-phase mixture has not visibly changed. It is shaken quickly to produce a homogeneous solution which is then stored without agitation at 2 °C for several days. On occasion, the freshly shaken solution shows immediate signs of [60]fullerene nanotube growth, but more commonly not. After several days, a feathery, light yellow ball of fine [60]fullerene nanotubes are observed to form (Figure 2). Unlike other preparations, the procedure is high yielding (nearly quantitative). Little if any black [60]fullerene solid is observed to aggregate on the bottom of the vial as is typical with other preparations. The [60]fullerene nanotubes can be filtered, washed with polar solvent and dried.

Optical microscopy of the [60]fullerene nanotubes prepared as described (Figure 3)

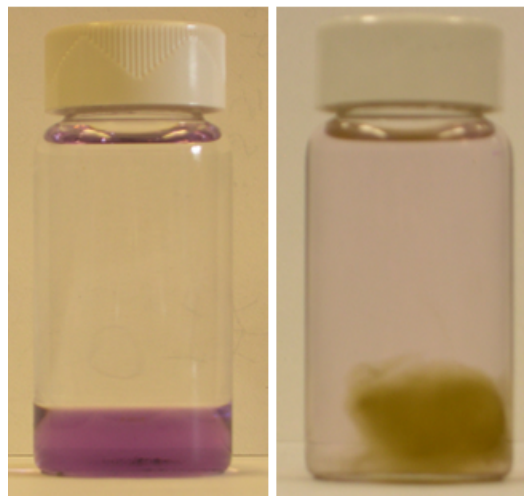


Figure 2. A modified Miyazawa liquid-liquid interfacial precipitation of [60]fullerene nanotubes using pyridine-isopropanol (see text). Left: vial immediately after layering isopropanol atop freshly prepared [60]fullerene-pyridine solution; Right: a feathery, light yellow ball of fine [60]fullerene nanotubes.

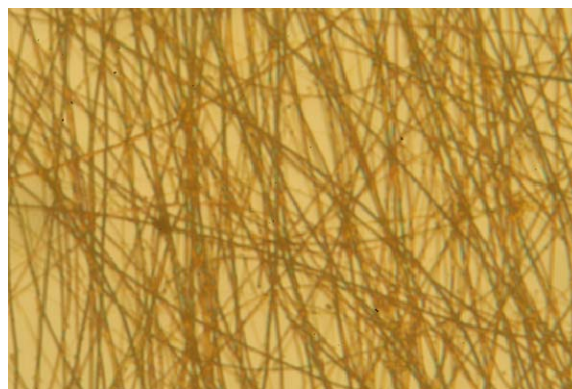


Figure 3. Optical microscope image (600x magnification) of [60]fullerene nanotubes prepared using the modified Miyazawa liquid-liquid interfacial precipitation method described in the text.

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reveals uniform structures which are, on average, smaller in diameter than [60]fullerene nanowhiskers or [60]fullerene nanotubes prepared in other manners. They are also quite clean, almost devoid of carbon particles.

It is interesting to note from the optical microscope images that the 300 nm diameter [60]fullerene nanotubes do not bundle extensively as do conventional carbon nanotubes. This bundling behavior in conventional carbon nanotubes hinders certain applications including the formation of high strength composites and is typically ascribed to favorable van der Waals interactions between the carbon nanotubes. Fullerenes also engage in π - π stacking interactions and this property has been exploited in order to prepare exotic [60]fullerene derivatives in which two or three [60]fullerene moieties sit within van der Waals distance of one another.⁶ Indeed, fullerene crystals including [60]fullerene nanowhiskers and [60]fullerene nanotubes owe their formation and stability to favorable [60]fullerene-[60]fullerene interactions. It is then a surprising but welcome observation that [60]fullerene nanotubes with 300 nm diameters do not experience significant bundling.

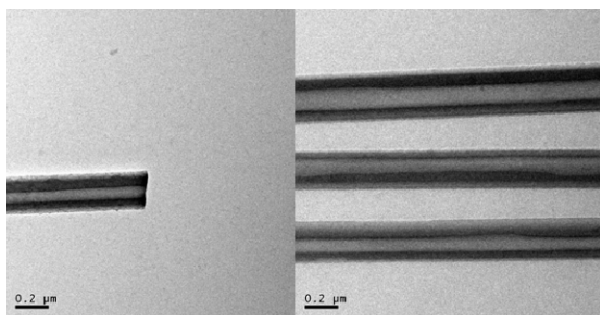


Figure 4. TEM images of [60]fullerene nanotubes prepared using the modified Miyazawa liquid-liquid interfacial precipitation method described in the text. The light regions in the interior of each [60]fullerene nanotubes correspond to hollow space.

Transmission electron microscopy (TEM) analysis of the [60]fullerene nanotubes (Figure 4) reveals several interesting features. First, the [60]fullerene nanotubes are all open ended structures devoid of end-caps as in conventional carbon nanotubes. This suggests the possibility

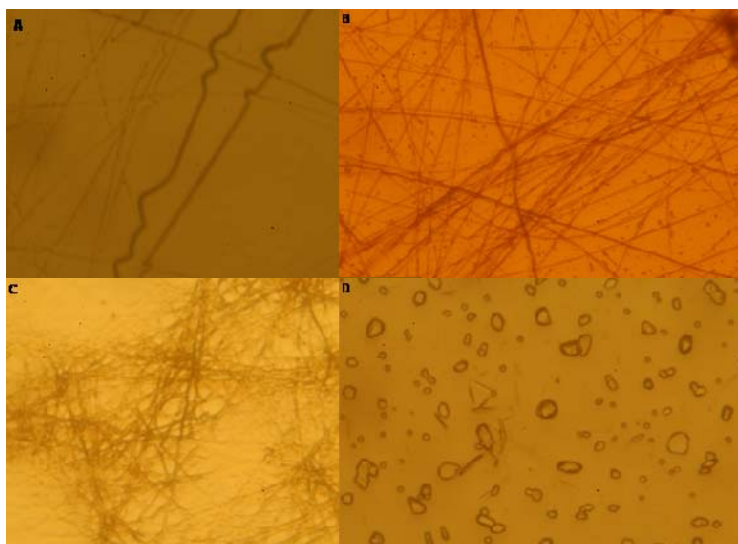


Figure 5. Optical microscope images (600x) of [60]fullerene nanowhiskers heated at 180 °C for varying times. A: 2 d; B: 3 d; C: 5 d; D: 7 d.

of filling the hollow interior space with either organic or inorganic materials, solids, liquids and gases alike. Secondly, the wall thickness of each [60]fullerene nanotube is approximately 100 nm and the width of the hollow interior (i.e., inside diameter) is also approximately 100 nm. Thus, there is ample room within the interior of the [60]fullerene nanotubes to place a significant quantity of organic and inorganic material. It should be possible to perform chemical reactions in this space including but not limited to polymerizations. In this way, the [60]fullerene nanotubes can

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be viewed as reaction chambers in which novel nano-architectures can be built. Thirdly, there is some variation in wall thickness along the long axis of each [60]fullerene nanotube, as illustrated on the right side of Figure 4. That is, [60]fullerene nanotubes do not possess a constant inside diameter along the growth axis.

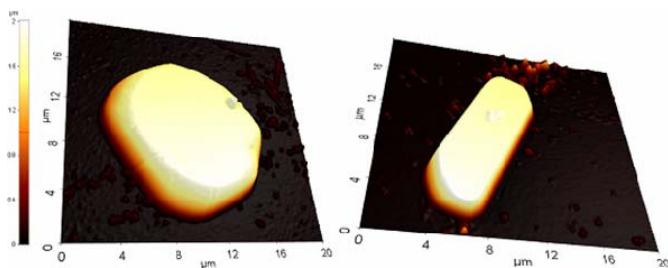


Figure 6. AFM images of a [60]fullerene disc and rod created upon heating [60]fullerene nanotubes to 180 °C on glass for 7 d.

Thermal Stability of [60]Fullerene Nanotubes. The thermal stability of [60]fullerene nanotubes was gauged by preparing a sample on glass and monitoring structural changes via optical microscopy as a function of heat time at 180 °C. Separate samples were heated for a total of 2, 3, 5 and 7 days. Although [60]fullerene nanotubes were previously reported to remain crystalline at temperature up to 650 °C and [60]fullerene nanowhiskers are reported to survive heat treatments of 1100 °C without a loss in electrical properties,^{4,5} we observe [60]fullerene nanotubes to deform within 2 days at 180 °C and become unrecognizable after 7 days at 180 °C (Figure 5). By contrast, conventional carbon nanotubes are stable to at least 700 °C in air.

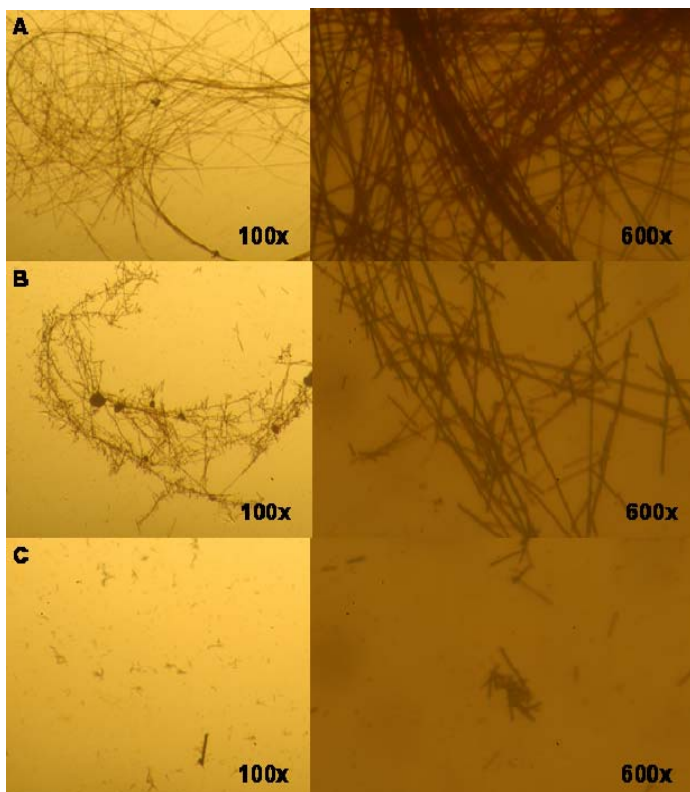


Figure 7. Optical microscope images of [60]fullerene nanowhiskers subjected to 5 seconds (A), 10 seconds (B) and 30 seconds (C) of 40 kHz ultrasonic bathing.

After 2 days at 180 °C, initial deformation of the [60]fullerene nanotubes involves the bending of tubes lying atop one another at the overlap sites (Figure 5A). After 3 days at 180 °C, a noticeable loss of structure and an apparent heat induced ‘swelling’ of the [60]fullerene nanotubes walls is observed concomitant with the formation of micron sized discs that appear as droplet structures in the optical microscope images (Figure 5B). After 5 days at 180 °C, the structural integrity of the [60]fullerene nanotubes walls is all but lost (Figure 5C) and after 7 days, only micron sized discs and rod-like remnants of the [60]fullerene nanotubes remain (Figure 5D). Fullerene molecules themselves are known to be quite stable to this relatively low temperature, so the change in morphology represents a loss in crystallinity, not a chemical transformation. The micron sized

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fullerene discs and rods prepared in this manner have been studied by atomic force microscopy (Figure 6) where diameters ranging from 1 to 20 μm and heights ranging from 500 nm to 2 μm have been observed.

Sonochemical Stability of [60]Fullerene Nanotubes. The sonochemical stability of [60]fullerene nanotubes was gauged by subjecting samples to an ultrasonic bath for varying durations. Prior to ultrasonic bathing, a sample was prepared by placing several milligrams of [60]fullerene nanotubes in a glass vial with a large excess of hexane. The vial was placed inside the well of a 40 kHz, 350 W ultrasonic bath filled with water and subjected to a total of 5, 10, 30 and 60 seconds of ultrasonic cavitation with aliquots removed at each time interval. Optical microscopy reveals that the original [60]fullerene nanotubes are quickly broken into smaller nanotubes, even after 5 seconds of ultrasonic bathing (Figure 7). Progressively longer durations of ultrasonic bathing lead to progressively shorter [60]fullerene nanotubes. Atomic force microscopy images of the [60]fullerene nanotubes subjected to ultrasonic bathing reveal considerable structural damage in addition to shortening lengths (Figure 8). Thus, after only 5 seconds of 40 kHz ultrasound, small [60]fullerene nanoparticles begin to clutter the glass substrate (Figures 7A and 8A), presumably formed via physical disruption of the sidewalls of the [60]fullerene nanotubes. After 10 seconds, the number of [60]fullerene nanoparticles increases dramatically and the sidewall of some [60]fullerene nanotubes reveal long, straight stripes (Figures 7B and 8B). The topology of these striped features indicates that they correspond to pitted regions as if large, thin sections of [60]fullerene nanotube sidewalls were either peeled from the starting structures or pushed inside the hollow interiors. After 30 seconds of sonication, the damage is more complete (Figures 7C and 8C). Sidewall fragments are strewn about the substrate leaving behind structurally compromised remains of [60]fullerene nanotubes and many [60]fullerene nanoparticles.

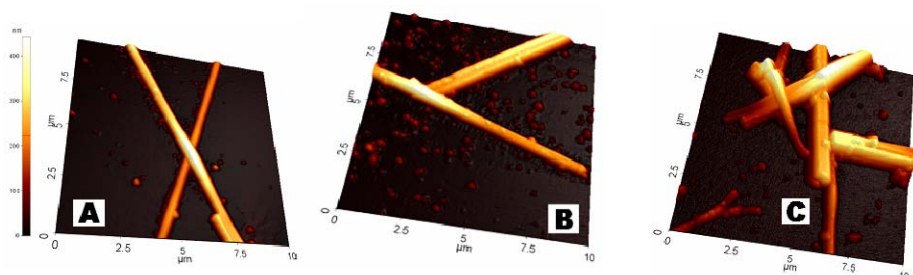


Figure 8. Atomic force microscope images of [60]fullerene nanowhiskers subjected to 5 seconds (left), 10 seconds (middle) and 30 seconds (right) of 40 kHz ultrasonic bathing.

Ultrasonic cavitation involves the creation and implosion of bubbles within a liquid medium. While the temperature inside the imploding bubbles is debated, values in excess of 5000 $^{\circ}\text{K}$ are commonly considered. Because the bubbles are small, the heat rapidly dissipates such that the temperature of the bulk solution is largely unaffected. Cavitation that occurs adjacent to a solid surface leads to an asymmetric implosion with a microjet forming on the side of the bubble opposite the solid surface. These microjets are reported to move at speeds approaching 400 km/h creating enough force to deform or destroy molecules and materials including polymer like polypropylene and polyamide. The [60]fullerene nanotubes prepared and studied here are not covalently attached to one another but rather held together by relatively weak van der Waals forces. As such, they are no match for the forces associated with ultrasonic cavitation.

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Mechanical Stressing of [60]Fullerene Nanotubes and Nanowhiskers Using an Atomic Force Microscopy Tip. Optical microscopy reveals that the modified liquid-liquid interfacial precipitation method is useful for preparing nano-structures with relatively uniform 300 nm diameters. TEM images suggest that the structures formed are hollow as in [60]fullerene nanotubes rather than [60]fullerene nanowhiskers. In order to gain unequivocal evidence for the hollow nature of the nano-structures formed, we turned to mechanical stressing studies using an AFM tip. Thus, we conducted nano-pushing experiments (i.e., mechanical stressing in the X direction) by offsetting a Si AFM tip to the left side of each [60]fullerene nanotube tested, bringing the tip in contact with the glass substrate, and then dragging the tip across the substrate such that it moved through the [60]fullerene nanotubes. Electronic feedback was suspended during this action. Subsequent tapping mode imaging revealed that the [60]fullerene nanotubes were broken in all cases and the breaks were not clean (Figure 9).

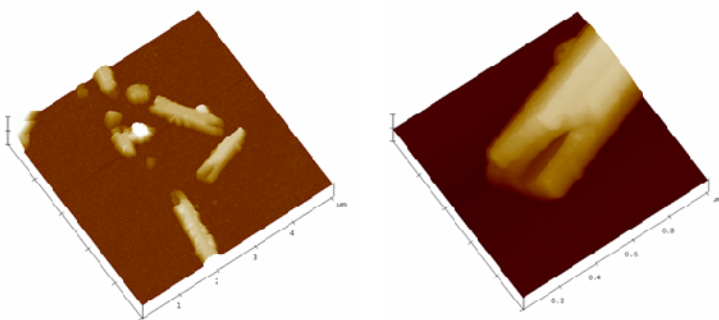


Figure 9. Atomic force microscope images of a [60]fullerene nanotube fragments formed during a nano-push stress test as described in the text. Left: the [60]fullerene nanotube was broken in two places, 1.5 μm apart, using a Si tip traveling at 300 nm/s; right: a close-up view of one of the fragments reveals a hollow interior

Multiple fragments of [60]fullerene nanotubes were typically observed on the glass substrate following each nano-push stress test. Moreover, the fragments lack symmetry and are consistent with a broken multilayer structure in which parallel layers have sheared past one another during rupture. A section analysis of the broken fragments corroborates the TEM analysis (Figure 4) in that both the inside diameters of the [60]fullerene nanotubes and the sidewall thicknesses are approximately 100 nm (Figure 10).

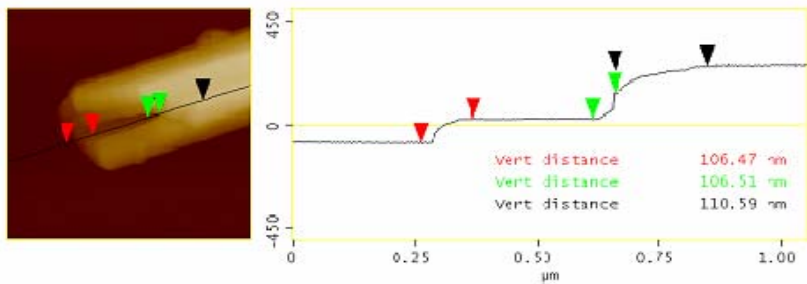


Figure 10. Section analysis of the [60]fullerene nanotube fragment shown in Fig. 9 formed during a nano-push stress test as described in the text

We further performed a nano-indentation study (i.e., mechanical stressing in the Z direction) on a [60]fullerene nanotube. For this experiment, the AFM tip was brought into contact with the same [60]fullerene nanotube at two prescribed locations. The tip was subsequently pressed against the surface at each location using tip loads of 210 nN and 420 nN. The tip load was determined from the bending of the cantilever and from its nominal spring constant. In each case, the Z-push time was 5 seconds. Topographical images of the distressed [60]fullerene nanotubes reveal a 13 nm

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dent at the site of the 210 nN push and a rupture of the [60]fullerene nanotubes at the site of the 420 nN push (Figure 11).

The results of the X-push and Z-push mechanical stressing studies highlight the differences between [60]fullerene nanotubes and conventional carbon nanotubes. Conventional carbon nanotubes are known to have high rigidity and high strength along the axial direction while being quite compressible and deformable in the transversal direction. This is in stark contrast to [60]fullerene nanotubes which are relatively weak, readily deformable and inelastic.

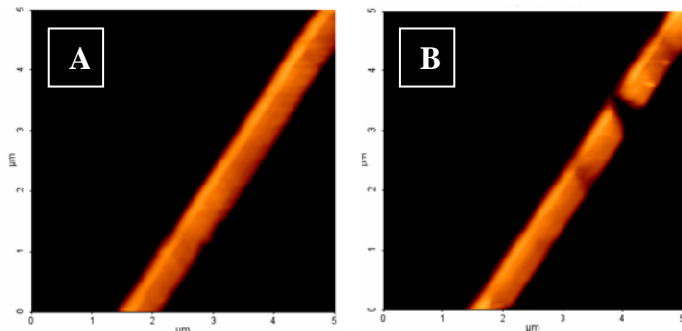


Figure 11. Atomic force microscope image of a [60]fullerene nanotube subjected to a nanoindentation stress test as described in the text. Topographical imaging before (A) and after (B) Z-pushing. The dent created by the 210 nN Z-push is ~13 nm deep (bottom circle). A 420 nN Z-push (top circle) broke the structure into three pieces, two of which are shown.

In summary, [60]fullerene nanotubes possess an interesting structure including a hollow interior that can potentially be filled with a variety of organic or inorganic materials, but they do not possess exceptional thermal or mechanical properties. Their electronic properties are largely unexplored and this represents an area for future investigation. Indeed, it is important to note that the dimensions of the [60]fullerene nanotubes prepared here appear to be ideal for organic photovoltaic devices incorporating fullerenes. Almost all state-of-the-art organic photovoltaic devices utilize a simple fullerene derivative named PCBM as the electron acceptor in a bulk heterojunction active layer that includes an electron donor like poly-3-alkylthiophene. During processing, the fullerene phase segregates from the polythiophene to produce fullerene rich channels that carry current in the device. The morphology and dimensions of this fullerene rich phase are critical to the overall performance of the device. In order to avoid electron recombination events (which can dramatically reduce efficiency) after photo-excitation and electron transfer, the fullerene channels should be several hundred nanometers in diameter. The [60]fullerene nanotubes reported here are precisely this dimension. In future studies, we will blend [60]fullerene nanotubes together with poly-3-alkylthiophene to produce and test novel photovoltaic active layers.

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and also see:

Rauwerdink, K., Liu, J.-F., Kintigh, J. and Miller, G. P., "**Thermal, Sonochemical and Mechanical Behaviors of Single Crystal [60]Fullerene Nanotubes,**" *Microsc. Res. Techn.*, **2007**, *70*, 513-521.

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