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Laser-induced production of large carbon-based toroids

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Abstract

We report on the production of large carbon-based toroids (CBTs) from fullerenes. The process involves two-step laser irradiation of a mixed fullerene target (76% C_{60}, 22% C_{70}). Transmission electron microscopy (TEM) clearly identifies toroidal-shaped structures as well as Q-shaped constructs. The typical diameters of the CBTs are ~0.2–0.3 μm with tubular diameters of ~50–100 nm, but toroids as wide as 0.5 μm are observed making them nanostructures on the verge of being microstructures.
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Since the first observation of C_{60} and related fullerene molecules [1], there has been widespread interest in these carbon species. From carbon onions to nanotubes, many novel and interesting carbon constructs have emerged. Toroidal carbon constructs, proposed as early as a decade ago [2–5], are intriguing partly because such shapes may possess anomalous magnetic properties [6–8]. For example, Liu et al. have recently proposed that a toroidal structure made of 1332 or 1296 carbon atoms may well possess novel magnetic properties owing to its ring current capabilities [9]. In the area of ring-like structures composed of carbon, a number of interesting observations have been made including 'crop circles' [10], tubes with 0.5 μm-sized diameters (but thicknesses of only a few nm) [11], rings analogous to carbon rope [12] and toroid-like structures [13]. Moreover, helical tubule structures have been observed and discussed [14,15] and the possible observation of a closed tubule, i.e., a toroid, has been put forth by Zhang and Zhang [16].

In the current paper, we present clear evidence for the production of large carbon-based toroids (CBTs). These doughnut-shaped carbon constructs often have diameters of ~0.2–0.3 μm with sealed tubular diameters of ~50–100 nm. They are generated via a two-step laser process involving a mixed fullerene target (76% C_{60}, 22% C_{70}; MER Corp.). Experimentally, the 248 nm output of a KrF excimer laser (Lambda Physik Lextra 200) operating at 10 Hz is focused onto the fullerene target inside a high vacuum chamber as shown in Fig. 1a.

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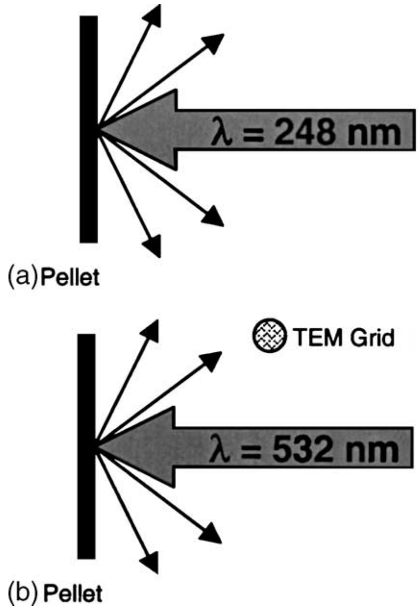

Fig. 1. Schematic diagram of the experimental approach.

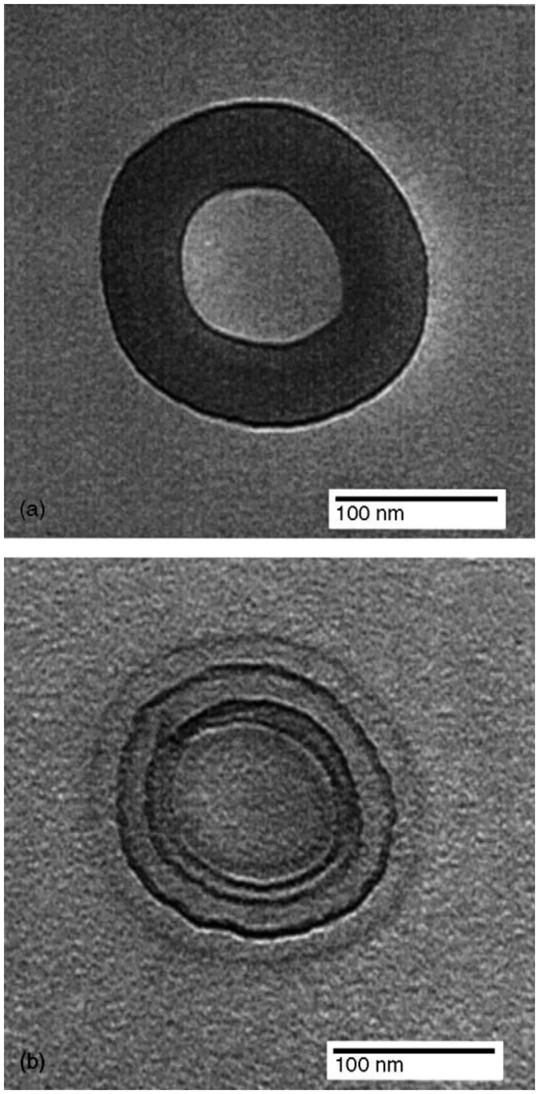

Fig. 2. TFM images of a doughnut-shaped CBT after (a) 30 s and (b) 330 s of irradiation with an 80 kV electron beam.

The ablated plume is monitored by a quadrupole mass spectrometer (QMS). The QMS is used a diagnostic tool to help determine the onset of laser ablation, since C_{60} cluster peaks are readily identified in the QMS once the ablation threshold has been reached.

Subsequent to the first ablation step, the same ablated target is irradiated for ~15 min with lower intensity 532 nm laser light produced by the second harmonic of a Nd: YAG laser (Coherent Infinity) operating at 10 Hz as shown in Fig. 1b. The ejected material is deposited ~1.5 cm away from the fullerene target onto a Formvar/carbon copper grid used for transmission electron microscopy (TEM). A JEOL JEM 2010 TEM instrument that interrogates with an 80 kV electron beam is then used to examine the deposited material. Representative features of what is observed on the grid are shown in Figs. 2a and 3a. Fig. 2a displays the image of a *bonafide* CBT in the shape of a doughnut with an inner diameter of 0.1 μm and an outer diameter of 0.2 μm. What distinguishes this CBT from rings and tubes observed in previous studies is that it appears to be a genuine toroid with a relatively large tubular diameter of ~50 nm. For shape contrast, Fig. 3a shows an incomplete CBT that is found to be in a "Q" configuration.

Note that it appears as though a two-step ablation procedure is important to (1) achieve CBT formation and (2) subsequently transfer the CBTs to the TEM grid. While a relatively intense laser pulse is needed to achieve CBT formation, if used solely, such a powerful pulse will also transfer large amounts of material (CBTs included) to the TEM grid. Analysis via TEM is then complicated by having too much material present. A second, softer laser pulse seems to

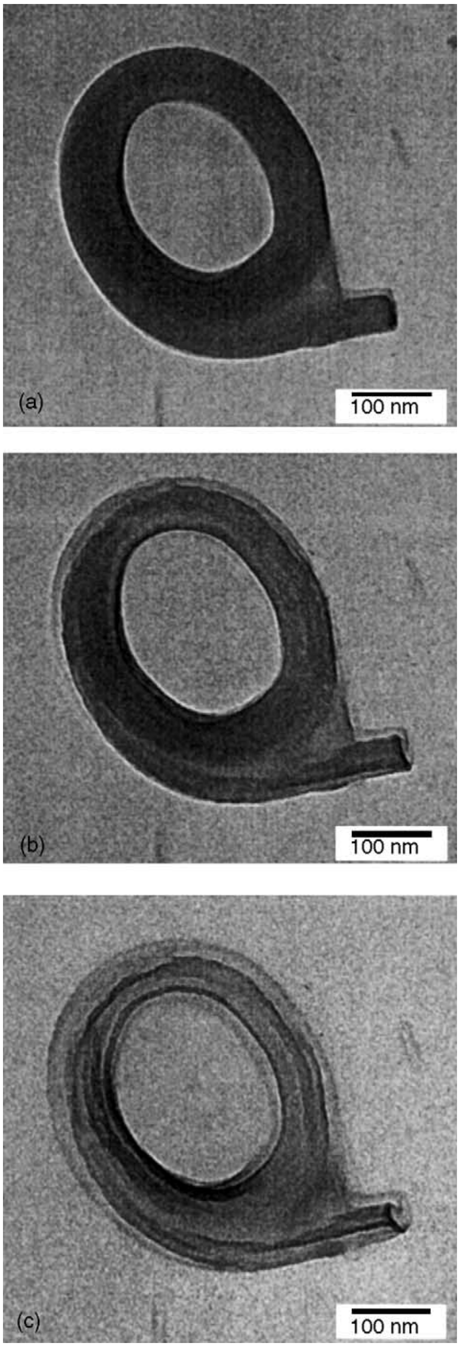

Fig. 3. TEM images of a Q-shaped CBT after (a) 30 s, (b) 330 s, and (c) 630 s of irradiation with 80 kV electron beam.

be more conducive to transfer without overwhelming the grid. Note, however, that work is currently underway exploring this aspect of the research.

We are only in the early stages of characterizing the properties of these CBTs; however, one observation is presented in Figs. 2b and 3b and c. These figures show what happens to the toroids over time as they are irradiated with the 80 kV electron beam having a current density of ~30 pA/cm^2. Essentially, the CBTs are degraded by the electron beam. In general, it was found that the degradation process could be expedited using higher current densities. Note that more systematic studies involving electron irradiation effects on carbon structures have been performed elsewhere [17]. As shown in Fig. 2b, the doughnut-shaped CBT does not appear to be single-walled. Rather, it appears to have several layers or is ‘‘filled’’ to some degree. We must point out that in this same experiment CBTs were observed by TEM that were probably very thin-walled toroids of dimensions comparable to the one shown in Fig. 2a. However, those toroids were already undergoing structural changes by the time they were observed under the 80 kV electron beam having current densities as low as 20 pA/cm^2, which is consistent with findings of Smith and Luzzi for the degradation of single-walled nanotubes [17]. Fig. 3b and c show a transformation with time due to the electron beam and suggest that the Q shape is composed of more than one wall. Further investigation of the electron beam interaction with the newly observed carbon constructs is underway [18].

In these experiments, a distribution of toroids is observed among tube-like carbon features. As an indicator of both relatiove yield and size distribution, Fig. 4 is included. This lower magnification TEM

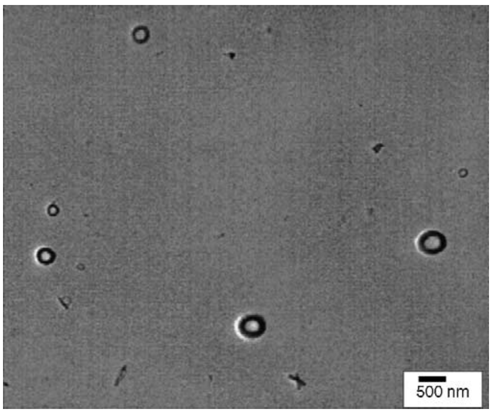

Fig. 4. TEM image of an expanded region of the grid.

image shows eight toroids of varying sizes distributed over an area of ~80 μm^2. The largest construct observed has an outer diameter of ~0.5 μm with a tube thickness of ~130–140 nm. In contrast, a much smaller toroid is observed having an outer diameter of ~170 nm and a tube thickness of 35–40 nm.

In conclusion, we note that these CBTs are exciting structures and differ from previously reported carbon nanotube toroids [10–16]. The degree to which these large CBTs are filled, hollow, or nested is under investigation. We are currently using atomic force microscopy (AFM) and scanning tunneling microscopy (STM) to further explore issues of morphology and conductivity. Plans to investigate the magnetic properties of these CBTs are also on the horizon. Whether or not interesting magnetic behavior will be found remains to be seen, but the preliminary morphological findings are clearly intriguing.

Acknowledgments

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