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Nanorings of Self-Assembled Fullerene C_{70} as Templating Nanoreactors

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The extraordinary electronic, mechanical, chemical, and structural properties of fullerenes and nanotubes have stimulated research in the fabrication of all-carbon superstructures.[1−3] The structural diversity within these graphene-based families, from C_{28} fullerene to giant fullerenes containing over 10^6 carbon atoms, from nanotubes to nanowhiskers, and from 'crop circles' to 'onion rings',[4−10] suggests that a wide variety of carbon superstructures could be prepared incorporating different properties. Self-assembly provides an avenue to facilitate a bottom-up approach to design and fabricate fullerene based materials of higher complexity. The use of nanoscale templates such as micelles and polyelectrolytes are commonplace in nanotechnology,[11] whereas the use of fullerene-based superstructures as 'nanoreactors' has yet to be recognized. In this article, we present a simple, green route for the bottom-up assembly of C_{70} fullerene into nanorings using the ubiquitous starch−iodine complex and establish the use of the self-assembled structures as nanoreactors in which silver nanoparticles are prepared.

The diversity of structures within the fullerene and nanotube families has been illustrated in many reports. Toroidal structures based on graphene offer yet another range of possibilities in terms of electronic, mechanical, chemical, and structural properties. Theoretical predictions suggest that such structures should allow ring currents and therefore display novel magnetic properties;[12] for instance, an enormous paramagnetic response has been predicted for undoped carbon nanotori.[13] Topologically toroidal forms have been constructed from carbon nanotubes by bending the tube section over and joining the ends. These circular types of single wall carbon nanotubes have now been famously referred to as fullerene 'crop circles'. Despite intrinsic difficulties in synthesizing carbon nanotube toroids from their linear precursors, toroidal structures are commonly reported for synthetic polymers like dextran sulfate, polylysine, and poly(glutamic acid).[14] The ability of these semiflexible homopolymer chains to collapse from an extended random chain to a compact ringlike structure has been investigated extensively in both theory and experiment. A variety of solution conditions can initiate this collapse, most notably in the presence of counterions. In the case of a DNA molecule, although strong chain repulsions compel the formation of an extended coil conformation, changes in solution conditions favor strong interchain interaction leading to collapse of the structure.[15] Furthermore, most of the theoretical investigations predict that a ringlike structure may indeed result for any colloidal macromolecule with sufficient stiffness.[16] These changes in structure, and the simplicity by which they may be induced, provides the inspiration for a bottom-up approach to prepare all-carbon ringlike constructs.

Recently we developed a simple approach to self-assemble C_{60} molecules into nanowhiskers in an aqueous medium under continuous flow using a spinning disk processor.[17] This involved formation of the blue starch−iodine complex with the hydrophobic and electron-deficient C_{60} molecules then being drawn into the electron-rich confines of the starch−iodine complex to form the nanowhiskers. This approach was also reported to solubilize single wall carbon nanotubes in water.[18] Given the versatility of the starch−iodine complex in solubilizing hydrophobic material in water and creating new nanostructures of fullerene C_{60}, we have investigated the uptake and self-assembly of C_{70} molecules in an aqueous medium templated by the same complex. Following the uptake of C_{70} molecules, the solution was treated with ascorbic acid (vitamin C), which is an effective reducing reagent for iodine in general and indeed features in its quantitative analysis.[17] After removal of the iodine from the amylose helix, which is indicated by loss of the blue-black color of the iodine complex with starch, the solution turns magenta in color (see characteristic UV−vis spectra, Supporting Information), which is remarkably the same color as that for C_{60} dissolved in toluene. The UV−vis absorbance of the final product has multiple absorption peaks characteristic of clusters of

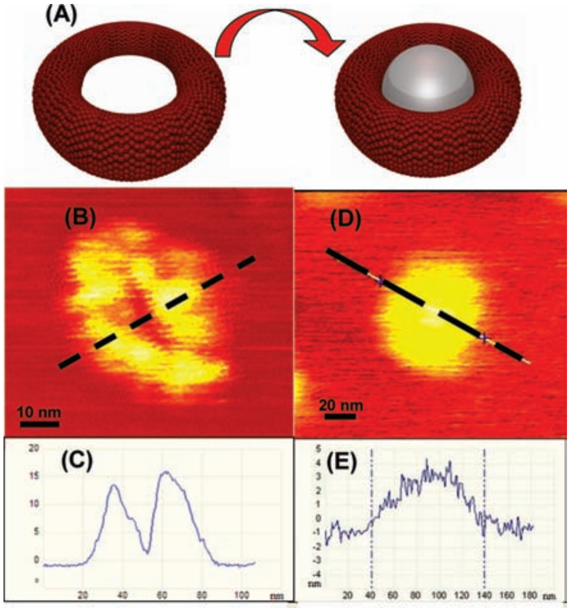

Figure 1. (A) A schematic representation of a C_{70} nanoring and its potential utility as a nanoreactor to nucleate particle growth within the central cavity in a spinning disk processing setup. (B) SPM topography image illustrating the ringlike structure and (C) a representative line scan across the AFM image as indicated by the dotted lines. (D) SPM phase image of the silver/C_{70}/starch nanocomposite showing the absence of the internal cavity as indicated by (E) the AFM line scan.

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fullerenes in water.[19] Analysis of the self-assembled system using scanning probe microscopy (SPM) revealed an unusual ringlike topography, with a central cavity (Figure 1B,C). Interestingly, jet cooked corn starch has been reported to form small torus shaped particles which arise from the collapse of a helical inclusion complex with native lipids.[20] DNA molecules usually fold into tightly packed toroidal condensates upon the addition of a small amount of condensing agent, such as cationic polyamines, and multivalent metal cations. The role of the condensing agents is to induce an attraction between the DNA monomers (chain neutralization or crowding effect), with the toroidal morphology adopted because of the native rigidity of the DNA double-stranded chain. Herein we hypothesize that the C_{70} molecules play a similar role as a condensing agent upon inclusion into the amylose helix resulting in transformation of the helical starch inclusion complex in water to a ringlike self-assembled composite.

Micelles, polyelectrolytes, peptides, and plasmid DNA with well-defined growth cavities have been reported to function as nanoreactors for the synthesis of nanocrystals.[21,22] In these reports it was inferred that the higher concentration of metal ions inside the structure resulted in the growth of the nanoparticles within the cavity. We believed that the ringlike nanostructures of C_{70} could similarly be effective in controlling the nucleation and growth of nanoparticles inside their cavities (Figure 1A). To test the utility of the above-mentioned nanoring assemblies as nanoreactors, silver nitrate was reduced with ascorbic acid using spinning disk processing. In this method, ascorbic acid was used not only to remove iodine from the starch inclusion complex by reduction but also to simultaneously reduce silver ions *in situ*. SPM imaging showed that the nanorings were transformed into globular structures, as indicated by the filling of the central cavity (Figure 1D, E).

The three-dimensional nature of the nanorings and the silver nanoparticles so produced was further confirmed by imaging at various tilt angles (±40°) using transmission electron microscopy (TEM) (Figure 2A, B). The silver nanoparticles produced were 8−12 nm in size, which corresponded to the minor radius of the C_{70} nanorings (Supporting Information Figure S3). High resolution TEM confirmed the crystalline nature of the silver core (Figure 2C) which was surrounded by a polycrystalline sheath. Analysis of the FFT pattern of the core and the surrounding sheath (Figure 2C, inset) revealed that the silver nanocrystals had a typical *fcc* close-packing, with the presence of a 0.49 nm spacing confirming the presence of ordered C_{70}. High resolution TEM of the shell further revealed the crystalline nature of the shell (Figure 2D).

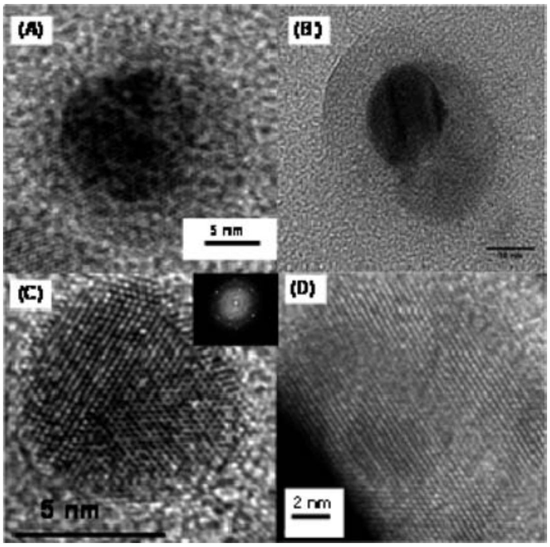

Figure 2. TEM of self-assembled C_{70} torus nanostructure with an encapsulated silver nanoparticle at (A) 0° tilt angle and (B) 40° tilt angle. (C) High resolution TEM of the encapsulated silver nanoparticle (Inset: corresponding FFT pattern) and (D) high resolution TEM of the surrounding C_{70} shell; the dark region corresponds to the silver core.

In summary, we report an unusual self-assembly of C_{70} nanorings in water using the amylose helix as a template. Furthermore, the potential of these self-assembled structures as nanoreactors was confirmed by the growth of silver nanoparticles within the central cavity. The finding suggests that the formation of nanorings templated by the amylose helix (compared to linear nanowhiskers for C_{60}) is caused by the anisotropic shape of C_{70}. Nonetheless, modeling the self-assembly process of these nanostructures is necessary to understand the fullerene packing. Indeed, in consideration of the many forms and properties of graphene-based carbon structures, we consider this research important in being able to fully realize the ability to tailor the self-assembly of carbon superstructures and controlling their properties.

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Supporting Information Available: Materials and Methods. Analysis data: UV−vis spectrum, low magnification TEM. This material is available free of charge via the Internet at http://pubs.acs.org.

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