JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
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Controlling Reversible Elastic Deformation of Carbon Nanotube Rings

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S *Supporting Information*

ABSTRACT: We show that bundles of carbon nanotubes can be coiled into ring structures by controlling the contraction of their polymer shells. With the robust carbon nanotubes, we demonstrate their reversible transformation between circular and compressed rings in a colloid.

The interconversion of kinetic and elastic potential energy is of critical significance for device fabrication. In particular, springs provide a means to store and release mechanical energy, enabling energy storage (e.g., clock mainsprings), structural restoration (e.g., springs in pens and clamps), shock absorption (e.g., car suspensions), and timekeeping (e.g., clock hairsprings). These basic functions should be common in future nanodevices, particularly for fictional nanorobots, which represent an extreme case of device miniaturization. It is thus conceivable that nanoscale alternatives to springs would be required. Obviously, the reversibility of such nanocomponents is of utmost importance.

We are interested in fabricating functional mimics of springs in colloidal solutions, which is a more facile and scalable approach in comparison with solid-state methods.[1] Recently, we reported the coiling of ultrathin Au nanowires (AuNWs) through control of the contraction of their polymer shells.[2] The stored elastic potential energy was released by spontaneous uncoiling when the polymer shell was swelled or removed. However, it remains a challenge to develop the coiling and uncoiling of the AuNWs into a reversible process. The fusion and inelastic buckling of the ultrathin AuNWs adds to the difficulties. Hence, we are in need of a robust nanofilament for developing reversible processes.

Carbon nanotubes (CNTs) are known for their extreme chemical and mechanical stability, which results from the strong network of C−C covalent bonds. It has been reported that direct synthesis or sonication can coil CNT bundles into ring structures.[3] A driving force was believed to be the strong $\pi-\pi$ stacking interactions among the multiple loops. Hence, low concentrations of CNTs minimized the interbundle aggregation and thus favored the circular stacking among the loops of each individual CNT bundle (i.e., intrabundle aggregation). While the yields of the previous methods were generally low, a larger problem for our purpose was that those CNT rings could not undergo environment-responsive structural changes. The internal energy of a single-component system always decreases, and changes in solvent typically cannot provide enough driving force for creating a structural change. Nanocomposites of CNTs and polymers have been studied extensively in recent years.[4] The main objective has been to improve the solubility of CNTs and the mechanical and electrical properties of the polymer. The creation of CNT−polymer two-component systems does provide a new type of opportunity: one may exploit their mutual interactions to induce structural changes in the CNTs.

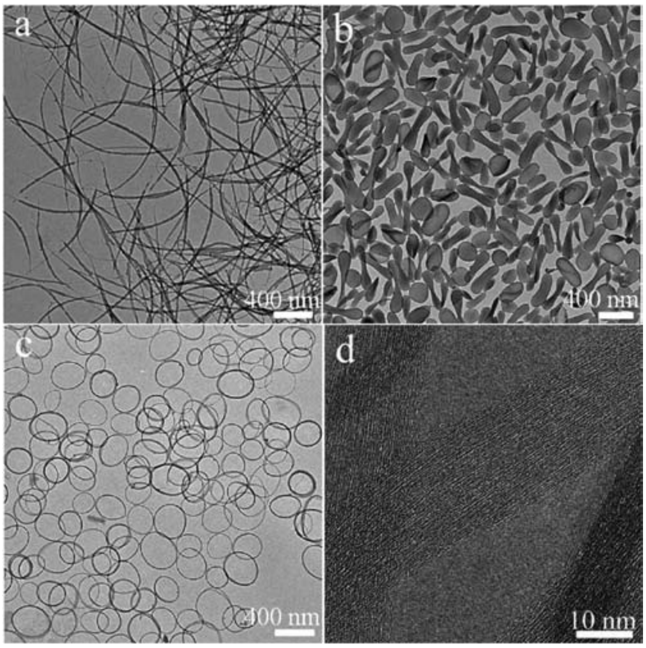

Figure 1. (a−c) TEM images of (a) PSPAA-encapsulated CNT bundles, (b) compressed CNT rings with PSPAA shells, (c) circular CNT rings after removal of the PSPAA shell. (d) HRTEM image of CNT bundles in a ring section of (c).

In this report, we modified our previous method[5] to encapsulate bundles of single-walled CNTs in shells of polystyrene-*b*-poly(acrylic acid) (PSPAA) and made the bundles coil into ring structures by contracting their polymer shells (Figure 1). In contrast to the AuNW rings, the CNT rings could not spontaneously uncoil when the polymer shells were removed, probably because of the strong interactions among their loops. However, we were able to utilize the robust CNT rings to develop a reversible structural transformation in a colloidal solution. In the CNT−polymer two-component system, the polymer shell could respond to changes in solvent and drive the compression of CNT rings. Conversely, the deformed CNT rings could spontaneously bounce back to circular rings when the force exerted by the polymer shells was relieved.

Received: March 14, 2011
Published: May 31, 2011

dx.doi.org/10.1021/ja2022976 | *J. Am. Chem. Soc.* 2011, 133, 9654–9657

Single-walled CNTs (carbonaceous purity 99%) with lengths of 0.3−5 μm were purchased from NanoIntegris. They were dispersed in *N*,*N*-dimethylformide (DMF) by sonication with PS$_{154}$-*b*-PAA$_{49}$ in an ice−water bath. The amphiphilic PSPAA behaved like a surfactant in DMF to prevent severe aggregation of the CNTs.[4c] With dropwise addition of water, the solvent was adjusted to 4.5:1 (v/v) DMF/water. The mixture was incubated at 50 °C with sonication for 2 h to promote PSPAA self-assembly[5] while minimizing CNT aggregation. After this step, the solution was concentrated by centrifugation, diluted with water, and then centrifuged again to collect the encapsulated CNT bundles (CNTs@PSPAA). The transmission electron microscopy (TEM) image in Figure 1a shows that 0.3−5 μm long CNT bundles with tapered ends were encapsulated in polymer shells with thicknesses of ~20 nm. In addition to the cylindrical shells, the excess PSPAA existed in the form of empty spherical micelles[6] that were removed during the centrifugation steps.[7] The excess polymer did not form cylindrical micelles under the conditions we used, and hence, the CNTs served as a structural template upon which the polymer self-assembled.[8]

However, the CNTs did not form rings after the above process. Previously, when water was added to straight AuNW@PSPAA in a 4:4:1 (v/v/v) tetrahydrofuran/DMF/water mixture,[2] the deswelling of the polystyrene (PS) cores increased the PS−water interfacial tension. At a critical point, the force exerted by the polymer shell exceeded the flexural strength of the AuNW and made it coil as the polymer shell contracted into a spheroid. While the applied conditions were similar, the CNT bundles were longer and flexurally stronger. Initially, we also believed that the oleylamine-stabilized AuNW surface was intrinsically different from the bare CNT surface, where PS could establish $\pi-\pi$ stacking interactions. Thus, we used 1,2-dichlorobenzene (DCB) to "lubricate" the CNT−polymer interface, as the molecule is known to adsorb on CNT surfaces through $\pi-\pi$ stacking.[9] Neat DCB (30 μL) was added to the CNTs@PSPAA in the 4.5:1 DMF/water mixture (990 μL total). The product was concentrated to 20 μL by centrifugation, removed of the excess supernatant, and then diluted with 1 mL of water to extract DMF from the PS cores and induce polymer contraction. As shown by the TEM image (Figure 1b), most of the CNTs@PSPAA were now coiled, although they gave a variety of different structures. Only a few small circular rings ("O-shaped"; Figure 2k) were observed. In addition, some of the encapsulated CNT bundles formed compressed rings with large ends and narrow waists ("peanut-shaped"; Figure 2e), and some were compressed and twisted nearly 180° to form the "8-shaped" rings (Figure 2f). Because of the similar contrast of the CNTs and the polymer under TEM, the individual CNTs in the bundle could not be clearly identified.

These compressed CNT rings were quite different in structure from the circular rings of AuNWs.[2] A key difference was that the circumference of the CNT rings was significantly longer than that of AuNW rings, probably because the CNT bundles were longer and stronger. Thus, the larger CNT rings can be compressed further to noncircular structures by the continued contraction of the PSPAA micelles. The inward-curved waists and the outward-curved ends of the "peanut-shaped" rings are indications of the strong compressive force exerted by the polymer shells. Obviously, a variety of factors could contribute to the final ring structure, such as the length of the initial CNT bundle, the number of CNTs in the bundle, and the complex and dynamic interactions between the wobbling CNT ring and the contracting polymer shell during the coiling process.

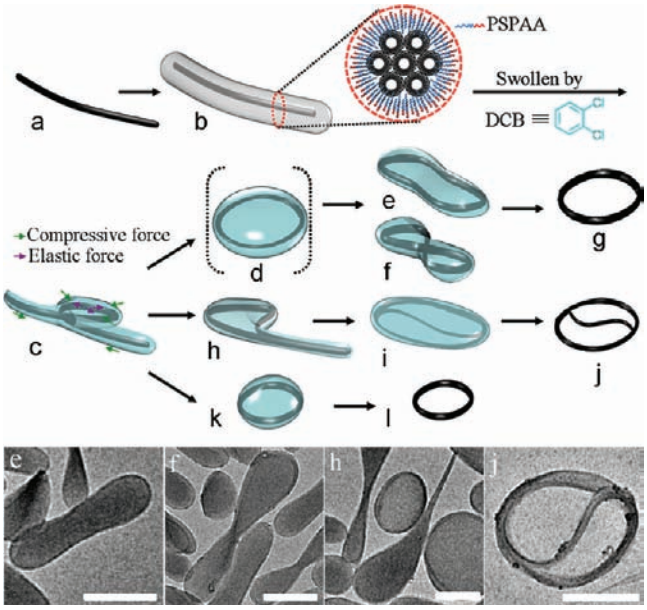

Figure 2. (top) Schematics illustrating the fabrication and structural transformation of CNT rings. Bundles of CNTs (a) were encapsulated in PSPAA shells (b). With the addition of DCB and water, the polymer shell contracted and coiled the embedded CNTs via intermediates (c) to racket-shaped (h) and ring structures. While the small CNT rings (k) remained, the large circular rings (d) were further compressed to "peanut-shaped" (e) and "8-shaped" (f) structures. After removal of the polymer shells, the CNT rings did not uncoil (g, j, and l). (bottom) TEM images of the typical structures. All scale bars represent 200 nm.

It is clear that DCB played an important role in the coiling of CNTs, but in addition to being a "lubricant", this molecule could also swell the PS cores. PSPAA micelles swollen by organic solvent are known to have higher mobility, and this could affect the coiling process.[10] To distinguish the two roles, control experiments in which toluene and cyclohexane replaced DCB were carried out. Both of the additives are insoluble in water, but cyclohexane is not aromatic. To our surprise, the CNTs were coiled into rings in both cases.[7] Thus, we concluded that the $\pi-\pi$ stacking between DCB and the CNTs was not the critical factor. Additional control experiments showed that water-soluble additives such as 1-hexanol did not work, lending support to the swelling effect. Presumably, when 1 mL of water was added to 20 μL of concentrated CNTs@PSPAA, the DCB originally dissolved was excluded from the aqueous solution and moved into the PS cores.[11] This assumption was confirmed by experiments: A sample of CNTs@PSPAA was added to the same amount of DCB and concentrated to ~1 μL (instead of 20 μL), after which 1 mL of water was added; the CNTs did not coil.[7] In this experiment, all of the conditions were the same except that the amount of DCB *outside* the PSPAA micelles was different. Though DCB could be enriched on the CNTs by $\pi-\pi$ stacking or in the micelles by solvophobic effects, the amount of enriched DCB prior to the water addition was clearly insufficient to coil the CNTs.

To understand the effects of DCB-induced swelling, we must envision the deswelling process when a large amount of water is added to the DMF-swollen CNTs@PSPAA. Since DMF is highly miscible with water, it is quickly extracted from the PS cores. The process increases the PS−water interfacial tension[12] while reducing the mobility of the PS cores. The point at which the force exerted by the polymer shell exceeds the flexural strength of the CNT bundle is most critical. If the PS cores solidify[5c,13] before this critical point, the polymer shell cannot contract and thus leaves straight CNT bundles. In view of the fact that the CNT bundles are flexurally strong, it makes sense that the critical point may have occurred later in the deswelling process than it did in the AuNW system. The presence of DCB may have increased the mobility of the PS cores at the critical point. Unlike DMF, DCB (or cyclohexane) is insoluble in water and could swell the PS cores after the DMF is extracted.

The coiling of the CNT bundles was probably similar in mechanism (Figure 2) to that of AuNWs[2] on the basis of the intermediate structures discussed below. The contraction of the PSPAA micelles caused the CNT bundle to bend and then twist to form an initial loop, which could serve as a template for the subsequent coiling of the bundle into a ring structure.[2] Racket-shaped intermediate structures (Figure 2h) were trapped; they were probably derived from the initial loops that did not successfully coil but joined their two ends in parallel. If the rackets resulting from this process were still too long, the continued contraction of PSPAA micelles could force them to coil again to give structures resembling the Yin−Yang symbol of Daoism (Figure 2i,j). Bundled CNTs were observed in the central strand of such structures, in contrast to the single AuNW observed in the central strand of similarly coiled AuNW rings.[2]

As discussed above, it is likely that large circular rings (Figure 2d) were the predecessors of peanut- and 8-shaped compressed rings. While we could not identify the presumed helical stacking[2] of the bundles in the CNT rings, the 8- and Yin−Yang-shaped rings were clearly chiral nanostructures. This was noteworthy because the original polymer-coated CNT bundles were not chiral. The origin of this chirality probably had to do with the random vibration of CNT nanostructures in solution during the coiling process.

When the PSPAA shells on CNT rings were dissolved away by neat DMF, the CNT rings did not spring back to form straight bundles. Instead, circular rings with diameters of 160−450 nm[7] without polymer shells were obtained (Figures 1c and 2g). The compressed peanut- and 8-shaped rings disappeared in this sample, indicating that they were transformed to O-shaped rings after the removal of polymer shell. The width of the CNT bundle in the rings ranged from 15 to 25 nm, indicating the large number of single-walled CNTs in the multilooped bundle. In the absence of the polymer shells, the CNT rings could be characterized by high-resolution TEM (HRTEM) (Figure 1d), which revealed the component CNTs. Importantly, these uncoated rings were very stable in colloidal solution: no structural change was observed after they were sonicated or heated (100 °C) for several hours. They did not aggregate like straight CNTs, probably because of inefficient stacking among the various rings of different diameter.

Two possible scenarios can explain the inability of CNT rings to uncoil. If the packing energy (the sum of van der Waals attraction, $\pi-\pi$ stacking, and solvophobic effects) of the multiple loops of the CNT bundle exceeds the elastic potential energy therein, the CNT rings would be thermodynamically stable and would not spontaneously uncoil. Alternatively, it is also possible that the CNT rings were thermodynamically unstable but could not uncoil because the initial uncoiling had a sizable activation barrier. We cannot rule out the second scenario, since the CNT rings were forced to coil by polymer contraction, unlike those in the literature that coiled spontaneously.[3b,c,14] Nevertheless, on the basis of the structural similarity between our uncoated CNT rings and those in the literature, we believe that the first scenario is more likely. Since very few CNT rings in Figure 1c showed partially uncoiled ends,[2] we ruled out the entanglement of the CNTs within the rings as a major factor in their behavior.

While we do not have direct evidence for the elastic force in the coiled CNT bundles, it is conceivable that when a straight filament is bent, the inner side is compressed and the outer side stretched. This geometric requirement would be true for macroscopic as well as microscopic filaments unless they are inelastically bent. Interestingly, few CNT rings in Figure 1c showed sharply bent kinks that would be indicative of inelastic deformation. This observation was in contrast to the AuNW rings, which produced multiple sharp kinks after uncoiling.[2] While the CNTs are chemically and mechanically more robust than the AuNWs, the compression/expansion of CNT rings is also less dramatic than the coiling/uncoiling of the AuNW rings. Hence, the CNT rings provided a nice platform for the development of a reversible structural transformation, as shown in the following.

A key issue was to retain the polymer shell and minimize the changes in solvent ratio during the shape transformation of the CNT rings. After repeated experiments, we found that incubation of the encapsulated CNT rings in 2:1 (v/v) DMF/water in the presence of DCB was sufficient to swell the polymer shells. The compressed rings were relieved without losing their shells. Briefly, the encapsulated CNT rings were concentrated by centrifugation and then dispersed in 240 μL of 2:1 (v/v) DMF/water containing excess PSPAA and 10 μL of DCB. The mixture was heated at 70 °C for 1 h to convert the compressed rings to circular rings (Figure 3c). These rings were compressed again (Figure 3d) by concentrating the solution to 20 μL and then adding 1 mL of water. This expansion/compression cycle was repeated (Figure 3e,f). The polymer shells of the rings were finally removed by incubation in neat DMF, giving bare CNT rings (Figure 3g). After these processes, few CNT rings were found to buckle inelastically. They had diameters similar to those in Figure 1c, indicating that the contracting polymer shells did not coil the CNT rings into smaller rings over the multiple steps. In theory, the expansion/compression cycle should be able to repeat multiple times. However, after two cycles, a number of cases were observed where the polymer membranes covering the CNT rings were found to have ruptured, giving toroidal shells.[7] The resulting polymer structure was unable to compress the entire CNT ring and induce pronounced structural changes.

The fact that most of the CNT rings could be reversibly converted between compressed and circular forms suggested that the structural changes were in the range of elastic deformation. Clearly, these rings were under two major competing forces: the compressive force exerted by the polymer shells and the counteractive elastic force arising from the bent CNTs. As the polymer shells were swollen by DMF and DCB, the decreased PS−solvent interfacial tension relieved the compressive force, causing the compressed rings to spontaneously expand. Upon addition of water, the deswelling of the polymer spheroid caused strong PS−water interfacial tension and thus overcame the elastic force and compressed the CNT rings again.

Thus, by using the encapsulated CNT rings, we were able to mimic the reversible elastic motions of typical macroscopic rings. While elastic motion of nano-objects has been studied using rings[15] and helical nanostructures,[1f,h,16] most of the prior reports have been based on the manipulation of individual nanostructures. Our method provides a new strategy for manipulation of an

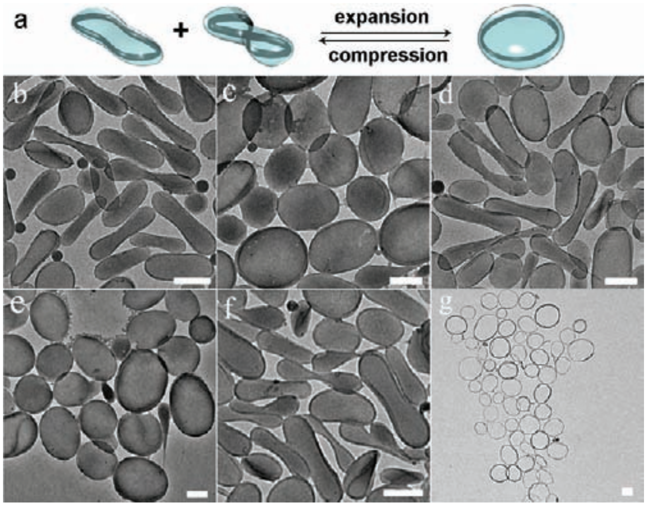

Figure 3. (a) Schematic illustration and (b−g) TEM images of CNT rings undergoing five consecutive steps of structural transformation. Compressed rings (b) were expanded to circular rings (c) by moderate swelling of their shells. They were compressed again (d), expanded again (e), compressed again (f), and then finally expanded by dissolving away their polymer shells (g). All scale bars represent 200 nm.

entire population of CNT rings in a colloid. The indirect shape control means that one does not have to act on a single nanostructure, which requires perfect dexterity and spatial resolution.

Environment-responsive structural changes of polymers have been well-documented in the literature.[6b,17] In particular, the micelles of block copolymers are known for their predictable behavior as well as their uniform structures. Thus, they provide an elegant platform for creating multicomponent structures wherein the incorporated nano-objects can interact with the polymer. Obviously, such interactions have yet to be fully explored. We are particularly fascinated by the energy transfer between the components. The compressed CNT rings (both peanut- and 8-shaped ones) can spontaneously expand to form circular rings, indicating that they are at high-energy states. They acquired the additional energy from their contracting shells: as the free energy of the overall system decreased, one component obviously did work on the other. This sequential transmission of energy is of great importance even though the current system is rudimentary. To date there are only very limited means to exert force and thus do work on nanostructures, but we are certain that the in-depth study and exploitation of similar behaviors will open up new opportunities in nanoscience and nanotechnology.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Details of experimental procedures, large-area TEM images, and complete ref 3d. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

The authors thank the Ministry of Education (ARC 13/09) and the Agency for Science, Technology, and Research (102-152-0018) of Singapore for financial support.

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