Bending single-walled carbon nanotubes into nanorings using a Pickering emulsion-based process

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ABSTRACT

Single-walled carbon nanotube (SWCNT) nanorings have been fabricated on a large scale using a Pickering emulsion-based process. The formation mechanism was attributed to liquid/liquid interface-induced SWCNT bending. Mechanical analysis shows that curved water/1,2-dichlorobenzene interface created during the miniemulsion process is sufficient to bend the SWCNT into closed rings. Raman spectroscopy was used to study SWCNT structural change after the nanoring formation. It was shown that compressive and tensile strains were introduced in these rings. We anticipate that a variety of functionalized SWCNT nanorings can be fabricated using our method for various applications.

1. Introduction

Due to their unique chemical and physical properties, single-walled carbon nanotubes (SWCNT) have attracted considerable attention since their discovery [1–5]. Carbon nanotubes (CNTs) often grow as long fibers with a high aspect ratio; this shape anisotropy largely determines their properties [5]. While extensive research work has been devoted to studying structure and properties of individual CNTs, patterning them into ordered structures remains one of the main challenges in nanoscience. Of particular interest is controlled assembly of individual CNTs, or a bundle of them, into defined structures such as nano-sized rings [6]. Bending of rigid, polymer-like CNTs into highly curled geometry affects transport properties [7,8]. Peculiar curvature-dependent electronic and magnetic properties of these SWCNT rings have also attracted great deal of interest over the past several years [9]. Numerous applications are anticipated for CNT rings: from a polymer CNT composite standpoint, bending long CNTs into rings dramatically decreases entanglement of CNTs, leading to lowered viscosity of the corresponding composites, which has a profound impact on composite processing.

After Liu et al. reported SWCNT rings as a low-yield byproduct in CNT synthesis [10], a number of experimental approaches have been reported to fabricate them. SWCNT rings can be produced on solid surfaces by various templating methods. For example, Tsukruk et al. reported the formation of bent SWCNT on a silicon surface by trapping the tubes at liquid–solid–vapor contact lines [11]. Based on molecular-template-directed assembly, Schatz et al. reported a method to fabricate SWCNT rings with specified diameters on a surface; SWCNT assembled into rings with radii as small as 100 nm at the edge of the circular patterns on COOH-functionalized monolayers [12]. Relatively larger scale SWCNT ring synthesis has also been accomplished by introducing a floating chemical vapor deposition technique [13]. On the other hand, formation of SWCNT rings in solution is of particular interest because the process is compatible with SWCNT surface chemistry that has been developed to functionalize SWCNT for application purposes [3,4,14,15]. To this end, Avouris et al. reported the formation of SWCNT rings by ultrasonication of a SWCNT solution in concentrated sulphuric acid and hydrogen peroxide [6]. The formation mechanism was believed to involve the hydrophobic nanotubes acting
as nuclei for bubble formation and being bent mechanically at the bubble–liquid interface as a result of bubble collapsing during cavitation [6]. Bundles of double-walled carbon nanotubes can also form rings after sonication an oxidized and acid treated sample [16]. Sano et al. synthesized SWCNT rings by noncovalent hybridization of porphyrins and SWCNT [18]. The SWCNT rings formed using these processes typically have diameters about 500 nm and the yields are low. None of the above mentioned approaches provide a large scale, solution-based method to synthesize nano-sized CNT rings, which has become a technical hurdle that prevents them from practical applications.

In this paper, we report a Pickering emulsion-based method to fabricate SWCNT rings at a large scale. In a water/oil/colloidal particle system, particles tend to segregate into liquid/liquid interface to lower the overall free energy of the system, a phenomenon known as Pickering emulsion [19]. The stability of the emulsion depends on particle diameter and the interfacial energy between particle/oil, particle/water, and water/oil (W/O). Numerous micro- and nanoparticles have been studied in Pickering emulsion systems; examples are silica nanoparticles, quantum dots and nanorods [20]. SWCNT has been employed as a solid emulsifier in W/O systems for different purposes. For example, Wang and Hobbie reported that amphiphobic SWCNT can be used to stabilize macroemulsion of water/toluene; water droplets with the size from a few tens to hundreds micrometers were stabilized by SWCNT in toluene [21]. This approach was then adopted to fabricate 1–20 µm diameter polymer colloids with a SWCNT coating in order to achieve a lower electrical percolation threshold of the polymer/SWCNT composites [22]. Other work studying CNT and liquid/liquid interfaces focused on flat interfaces. For example, Niu and co-workers reported an approach to self-assemble flexible SWCNT films at the W/O interface after modifying SWCNT with imidazolium [23]. Similarly, Matsui and co-workers fabricated monolayer SWCNT and closely packed ultrathin CNT films at a liquid–liquid interface [24–26]. Interfacial trapping methods have also been used to remove SWCNT bundles from individual tubes [27]. However, none of these works were intended to fabricate CNT rings at nanometer scale. Herein we report that by carefully choosing a W/O/SWCNT system, miniemulsions can be formed, within which SWCNT act as the solid emulsifier. Because of the small oil droplet size in the miniemulsion, curved W/O interfaces bend SWCNT into nano-sized rings with well-defined radius and width. This method offers an easy, solution-based approach to synthesize SWCNT nanorings at a large scale. It may also be adopted in other 1D nanomaterial systems.

2. Experimental

2.1. Materials

CoMoCAT SWCNT was purchased from SouthWest NanoTechnologies, Inc. Arc discharge Multiwall carbon nanotubes (MWCNT) were purchased from Sigma Aldrich. MWCNT were washed with concentrated H2SO4/HNO3 Mixture (3:1) overnight [3,28,29]. Products were washed until neutral pH using deionized water before use. 1,2-Dichlorobenzene (DCB) and ethanol were purchased from Aldrich and were used as received.

2.2. Experiments and sample preparation

SWCNT (0.65 mg), DCB (6.5 g), and a few drops of ethanol were added to a test tube. A multiple step sonication process (40 min bath sonication, 40 min probe sonication, and 40 min bath sonication again) was used to produce SWCNT/DCB dispersion. 0.2 mL of such dispersion was mixed with 8.0 mL deionized water using micropipette. The mixture was homogenized via probe sonication for about 40 min. The mixture became oyster white after sonication. Miniemulsions were drop-cast on selected substrates, blotted, and allowed to dry before the microscopy and spectroscopy experiments.

2.3. Instrumentation

A Bransonic 8510 bath sonicator and a vibra cell VC130 probe sonicator were used to disperse SWCNT in DCB. Scanning electron microscopy (SEM) experiments were conducted using a Zeiss Supra 50VP microscope. Transmission electron microscopy (TEM) experiments were performed using a JEOL JEM-2100 LaB6 TEM at an accelerating voltage of 200 kV. Raman spectra were measured using a Renishaw RM1000 Raman microspectrometer equipped with a 514.5 nm argon ion laser as the excitation source and a 100 X objective. SEM and Raman spectroscopy were used to collect the signals from individual SWCNT rings. The SWCNT rings were deposited on gold-patterned silicon wafer (Fig. S3a). The rings were identified by SEM and the relative location of the rings to the gold patterns was recorded (Fig. S3b and c). Then signals from individual rings were identified under Raman spectrometer according to the corresponding SEM images. To ensure the signals are from a single ring, the inter-ring distance was controlled to be well above 1 micron, which is the beam size of the laser.

3. Results and discussion

1,2-Dichlorobenzene (DCB) and deionized water were used as the two immiscible phases to prepare the miniemulsion. SWCNT was dispersed in DCB by sonication. The dispersion was then mixed with water, and probe sonication was used to homogenize the mixture. The miniemulsion was then drop cast onto glass slides/silicon wafers for microscopy and Raman spectroscopy experiments. The detailed procedure can be found in Section 2. Fig. 1(a) shows a scanning electron microscopy (SEM) image of a typical sample. Numerous SWCNT rings can be clearly seen from the micrograph. Most of the rings are closed; SWCNT ends are not visible from the image (Fig. 1(c)). There are, however, a number of straight as well as slightly bent SWCNT bundles in Fig. 1(a) with an average bundle length of 1–3 µm. Fig. S1 shows a lower magnification, larger area SEM image. Counting the rings and straight tubes from Fig. S1 indicates a yield of rings of ~80%, suggest-
ing that most of the tubes were bent into rings during emul-
sification. Fig. 1(b) shows the size distribution of SWCNT rings. The average diameter of the rings is 202 ± 76 nm. There are various morphological features of these SWCNT rings. In addition to perfect rings and straight (or, slightly bent) SWCNT bundles, relatively irregular ring structures can also be seen as shown in Fig. 1(d) and indicated with arrows. These include large enclosed rings with a figure “8” shape (denoted as 1 in Fig. 1(d)), SWCNT rings with separated tube bundles (2 in Fig. 1(d)), SWCNT rings with largely uneven ring thickness (3 in Fig. 1(d)), and a ring with a “crossed lattice” (4 in Fig. 1(d)). All these peculiar morphologies “record” the formation process of these rings, a point we will return to in the following section. Transmission electron microscopy (TEM) was used to illustrate the detailed structure of SWCNT rings. One drop of SWCNT miniemulsion prepared as previously dis-
cussed was deposited on a lacey carbon grid, blotted and al-
lowed to dry. Fig. 2 shows a typical sample. SWCNT rings can be seen from the image. Again Fig. 2(a) shows a figure of “8” shape, which is due to ring collapsing on the edge of the carbon film on the lacey grid. Fig. 2(b) and (c) shows a high resolution TEM image of the “wall” of the ring. The wall thickness is approximately 30 nm, indicating that there are ~500–800 tubes aggregating together. SWCNT rings with walls as thin as 5 nm have also been observed, corresponding to ~15–20 tubes bundling in the ring.

In a classical surfactant/W/O system, probe sonication typically induces miniemulsion, with the oil droplet size in the range of a few tens to hundreds of nm [30]. In the present case, as previously discussed, SWCNT can be viewed as a so-
lid state emulsifier and the overall free energy of the SWCNT/ W/O system can be dramatically decreased by confining the nanoparticles at the interface – the Pickering emulsion state [19,31]. Because of the physical length of typical SWCNT (or,
SWCNT bundles) exceeds the diameter of the oil droplets in the miniemulsion, the curved W/O interface then “bends” the long tube bundles into a curled shape. Furthermore, strong van der Waals interaction among the SWCNT also drives them to aggregate into bundles at the W/O interface. As the length of the SWCNT bundles exceeds the circumference of the DCB droplets, two ends of the bundles meet and SWCNT rings are closed by forming van der Waals bonds. Fig. 3 shows the proposed formation mechanism of the SWCNT rings. Tubes are first dispersed in DCB, then SWCNT dispersion is mixed with water at a predetermined volume ratio. After probe sonication, miniemulsion occurs and the final dispersion is mixed with water at a predetermined volume ratio. These bundles collapse and form the relatively complex morphologies shown in Fig. 1(c)–(f) and Fig. 3(b). Small SWCNT bundles tend to form uniform rings as shown in Fig. 1(b). Large bundles lead to non-uniform rings (2 in Fig. 1(d)). In the case that multiple SWCNT bundles are forced to bend, these bundles are relatively parallel with each other, collapsing would lead to multibundle rings (3 in Fig. 1(d)). If the bundles are oblique to each other, cage-like structures (4 in Fig. 1(d)) can be formed. The straight and bent SWCNT bundles might be formed by loosely bent SWCNT, which are mechanically less stable. During the drying process, the straight SWCNTs unbind, forming straight or bent bundles (Fig. 1(a), (e) and (f)). Since formation of the rings is due to bending of SWCNT bundles by the W/O interface, the formation process is a competition between the elastic energy trying to maintain the straight CNT shape and the interfacial energy to keep a curved W/O interface [11]. In general, two scenarios could take place during the miniemulsion process: (1) SWCNT bends into rings (curved bundles) as previously discussed, and (2) SWCNT is too rigid to bend and the W/O interface is forced to follow the straight/slightly bent shape of SWCNT bundles. In the present case, we observed SWCNT rings; Fig. 4(a) shows the detailed formation process. During sonication, the DCB phase became progressively smaller and SWCNT was trapped at the water/DCB interface. Further decreasing DCB droplet size led to bent SWCNT with continuously increased curvature until stabilized SWCNT rings were formed. Fig. 4(b) shows a simplified schematic of bending 1D CNT at the water/DCB interface. Assuming the CNT has a length of L and a radius of r, and is bent at the interface with a central angle of 2θ (Fig. 4(b)). For small θ, we can treat the system as a simply supported beam with uniformly distributed loading case. When the uniformly distributed loading is w (force per unit length), then the center deflection is:

\[ d = \frac{5wl^4}{384El} \]  

where \( l \) is the second moment of area of the beam, \( E \) is the elastic modulus. Here

\[ d = \frac{L}{2θ}(1 - \cosθ) \]  

Hence the required loading \( w \) applied along the CNT should be:

\[ w = \frac{48Er^4}{5L^3} \left( \frac{1 - \cos θ}{θ} \right) \]  

Eq. (3) shows the loading needed in order for a CNT with length L to bend to a conformation with a 2θ central angle. On the other hand, bending is due to the interfacial energy at water/DCB interface. For simplicity, we assume that CNT stays at the center of water/DCB interface [20,29]. For a system as shown in Fig. 4(b), the force from the interfacial energy is:

\[ F_1 = γ_{water/DCB} \cdot 2r \cdot 2sinθ = 4γ_{water/DCB}sinθ \cdot r \]  

Here \( F_1 \) is the vertical component of the interfacial force; \( γ_{water/DCB} \) is the interfacial energy of water/DCB. Comparing Eqs. (3) and (4), as long as \( F_1 \) is greater than \( wL \), the interfacial force will be sufficient to bend the CNT. We can use the SWCNT’s elastic modulus of ~1TPa [32] to roughly compare the two forces. Assuming \( L = 1 \mu m, r = 0.5 \) nm, and
\[ \gamma_{\text{water}/\text{DCB}} = 0.04 \text{ N/m}, \quad \frac{F}{wL} = 42.5 \text{ mN/m} \]

Note that when \( \theta \) is small, \( F/wL \sim 85 \), indicating that the initial bending of the SWCNT at the interface of a large droplet occurs easily. When droplet size became smaller and smaller during the process of sonication, the SWCNT was bent to a larger extent (Fig. 4(a)). The final ring size is determined by the emulsion droplet size and the stiffness of SWCNT. During the bending process, the work done by interfacial force \( \gamma_{\text{water}/\text{DCB}} \) along the SWCNT will be stored in the tube as potential energy, which is at maximum when the SWCNT ring reaches its minimum radius. Eq. (3) also shows that the loading is proportional to flexural modulus. To achieve the same deflection, CNTs with higher flexural modulus would require a greater force. However, the interfacial force is from the interfacial energy between water and DCB, which is constant for a given deflection. If the flexural modulus is very high, the CNTs cannot be bent.

To confirm this hypothesis, MWCNT, which has higher flexural modulus, was used for a control experiment. Following the same experimental procedure, no MWCNT rings were formed (Fig. S2). We can also tune the bending moment of the SWCNT bundles by varying the concentration of the SWCNT, hence the bundle size. SWCNT/DCB concentration was controlled to be 0.01, 0.02, 0.04 and 0.08 wt.% before the mini-emulsion process. Fig. 5 shows the overall structure of the SWCNT assembles (For 0.01 wt.%, see Fig. 1). SWCNT rings can be seen for all concentrations. However, for the 0.08 wt.% sample, most of the SWCNT remained straight or formed only slightly bent bundles. This can be attributed to an increased SWCNT concentration leading to larger tube bundles in the miniemulsion, which are much more difficult to bend according to Eq. (3).

Eq. (4) also shows the possibility to control the ring size by changing the interfacial tension between oil and water. Lower interfacial tension would have smaller interfacial force, which would lead to a larger ring size. To test this hypothesis, toluene and p-xylene were used. The interfacial tension of \( \gamma_{\text{toluene}/\text{water}} \), \( \gamma_{\text{p-xylene}/\text{water}} \) and \( \gamma_{\text{p-xylene}/\text{water}} \) are 36.10 mN/m, 37.77 mN/m, and 40 mN/m respectively [33]. Using toluene and p-xylene as the oil phase to prepare SWCNT stabilized emulsion, the resulting average ring sizes are 241 nm and 243 nm (Fig. S3), larger than that observed in the DCB/Water system, which is consistent with Eq. (4).

Micro-Raman spectroscopy is widely used to study the structure and diameter of SWCNT [34]. Micro-Raman spectroscopy experiments were conducted on individual rings to determine the effect of nanoscale curvature on the SWCNT spectra and strain in the rings. Detailed procedures can be found in Section 2. In brief, SWCNT rings were deposited on a gold patterned silicon wafer. Each individual ring was identified using SEM and the position was recorded (Fig. S4). Raman signals from single rings were collected. To ensure the signals are from a single ring, inter-ring distance was controlled to be much larger than the laser beam size, which was \(~1 \mu \text{m}\) in our experiment. Fig. 6(a) shows the D band and G band of typical Raman spectra for a single SWCNT ring and a straight SWCNT, measured at a laser excitation wavelength of 514.5 nm. G band of CNTs can be differentiated into two main components: \( G^+ \) and \( G^- \). The \( G^+ \) peak, which dominates
We have demonstrated a new approach to synthesize SWCNT which is weaker than G+, is around 1567 cm⁻¹, matures from metallic nanotubes in the sample. The average compressive stress[35–39]. In general, G+ band downshifts/strain induced Raman shift for SWCNT under tensile and range. Significant research has been devoted to studying having no clear dependence on ring diameter in the examined our case, the strain caused by ring formation is increases from 45 cm⁻¹/C0 to 3091–3. This work was funded by the NSF Grant Nos. DMR-0804838 and DEG-0654313.

4. Summary
We have demonstrated a new approach to synthesize SWCNT rings on a large scale using a Pickering emulsion-based process. TEM showed that these rings had a diameter of ~200 nm. Each ring was made of SWCNT bundles, comprising of a few tens to hundreds of nanotubes. The formation of rings introduces both compressive and tensile strain on SWCNT, as revealed by Raman spectroscopy. The formation mechanism was attributed to liquid/liquid interface-induced SWCNT bending. The Pickering emulsion process reported here is scalable and compatible with the well-developed CNT surface chemistry. We anticipate that a variety of functionalized CNT rings can be fabricated using our method, which will therefore enable applications of CNT rings in various fields ranging from polymer composites to sensing.

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Appendix A. Supplementary data

REFERENCES


