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Controlling the length of self-assembled nanotubes by sonication followed by polymer wrapping†

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This work demonstrates that sonication, followed by polymer-wrapping, is an effective strategy to modulate the length of self-assembled nanotubes. The length distributions of the nanotubes were controlled by varying the amplitude of sonication. Wrapping the nanotubes with ionic polymers suspended the propensity of the nanotube fragments to re-assemble over time into their elongated precursors.

Molecular self-assembly offers tremendous potential as a method to create nanomaterials with a wide range of properties.[1] Self-assembled nanotubes have exhibited utility for applications in material science,[2] medicine,[3–9] catalysis[10,11] and optoelectronics.[12,13] These applications generally require a capability to finely tune the structural dimensions of the nanotubes to optimize performance. For example, the biodistribution, circulation time, and cellular uptake of nanoparticles used for drug delivery critically depend on size, particularly length.[3,14,15] Similarly, the dimensions of carbon nanotubes are an important factor in determining their optoelectronic[16] and physical properties.[17] Whereas solid nanoparticles and carbon nanotubes are static structures with dimensions that can be modulated by physical processing or separation,[18,19] self-assembled materials are dynamic structures with dimensions that are usually determined thermodynamically.[20] Thus, the propensity for these systems to undergo self-healing precludes physical control of their structural features. Nanotube self-assembly generally affords highly uniform structures with diameters that are controllable *via* choice of assembly conditions and/or the structure of the building blocks. However, the process often results in nanotubes with a wide distribution of micrometer-scale lengths, which is difficult to control.[2] Therefore, methods to control the lengths of dynamically assembled nanotubes have to overcome or circumvent the thermodynamic preference of the assembling molecules. For example, multiple building blocks have been co-assembled in solution using either the interactive nature of the components[21,22] and/or their ratio to one another[23] to control the final length distributions. Another approach used controlled vapor deposition to modulate nanotube length, avoiding the use of a solution phase altogether.[24] However, these clever strategies to regulate the length distributions of dynamically assembled systems are difficult to apply broadly to other systems.

Acoustic waves created by sonication in liquids induce the nucleation, growth and collapse of gas bubbles,[25] which create a hydrodynamic flow field in the surrounding liquid.[26] This cavitation process has been shown to efficiently disperse aggregates and to cut polymers[27] and carbon nanotubes (CNTs)[28,29] into smaller fragments. Recently, the sonication-induced fragmentation of polymeric nanotubes based on crosslinked poly(glycidyl methacrylate) into shorter segments was used to optimize intracellular drug delivery.[3] However, sonication-induced scission is not broadly applicable to noncovalent systems because the shortened fragments are in equilibrium and are, therefore, capable of regaining the prior elongated states. In this work, we show that sonication-induced scission of long, self-assembled nanotubes creates shorter fragments that can be stabilized by wrapping with a polyelectrolyte polymer, which suspends the self-healing process (Fig. 1).

The naphthalenediimide-lysine bolaamphiphile (**NDI-Bola**),[30] shown in Fig. 1, has been previously shown to assemble into an array of nanotubes with diameters of 12 ± 1 nm and lengths ranging from ~250–1000 nm.[31,32] The capability of acoustic cavitation to cleave CNTs into short fragments prompted us to explore the effect of ultrasound on a "soft" nanotube, such as nanotubes formed by **NDI-Bola**, as a strategy to modulate length. Ultrasound has a more profound impact on soft materials, often inducing a reorganization of the noncovalent interactions that stabilize the assembly, resulting in changes in morphology,[33] alternate assembly pathways,[34,35] induced patterning[36] and gelation.[34,37,38] To explore the impact of ultrasound, the **NDI-Bola** nanotubes were sonicated with a 100 watt (22.5 kHz),

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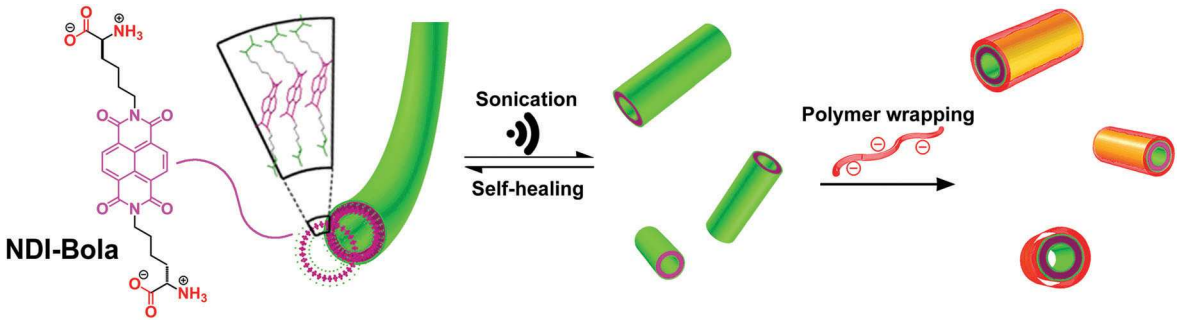

Fig. 1 Schematic illustration of sonication induced scission and polymer wrapping induced stabilization of self-assembled nanotubes.

ultrasonic processor with a probe diameter of 3 mm over a range of 10–60% maximum amplitude. Dissolving **NDI-Bola** in water (20 mM, 12 h) produced nanotubes with lengths ranging from ~250–1000 nm, as measured by TEM imaging (Fig. 2a). The preformed nanotubes were sonicated in water (20 mM) over a range of 10–60% maximum amplitude for 3 min to induce scission into smaller fragments. TEM imaging revealed that whereas the structure and diameter of the nanotubes were maintained, the range of lengths were progressively decreased as the amplitude was increased from 10 to 20% (Fig. 2). Histograms of the length distributions, extracted from AFM images, indicated that the initial nanotubes exhibited a maximum population of lengths of 575 nm, with 54% of the nanotubes in the range of 500–700 nm (Fig. 3). After sonication at 10% amplitude, the length distribution significantly decreased with a peak in the distribution curve at 145 nm, with 48% of the nanotubes

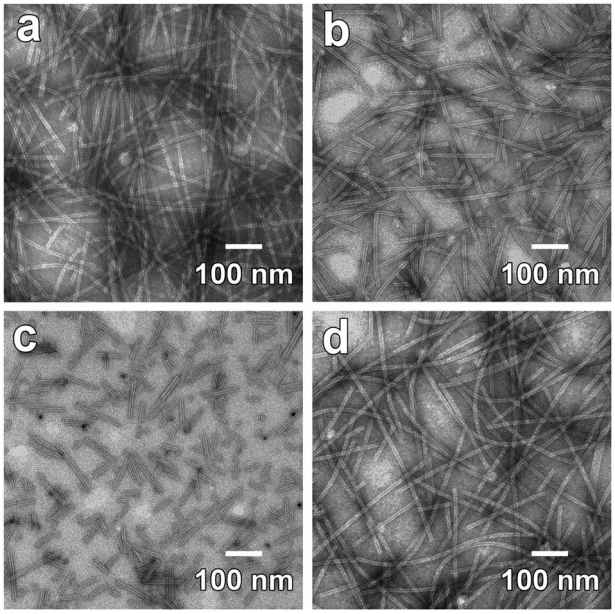

Fig. 2 Transmission electron microscopy (TEM) images of **NDI-Bola** (2 mM) in water (carbon-coated copper grid, 2% (w/w) uranyl acetate as a negative stain). (a) Original nanotubes prepared by incubating in water (20 mM) for 12 h, then diluting to 2 mM for imaging. (b and c) After sonication at (b) 10% and (c) 20% amplitudes for 3 min, respectively. (d) Nanotubes sonicated for 3 min at 20% followed by 3 days of aging, indicating re-healing into elongated nanotubes.

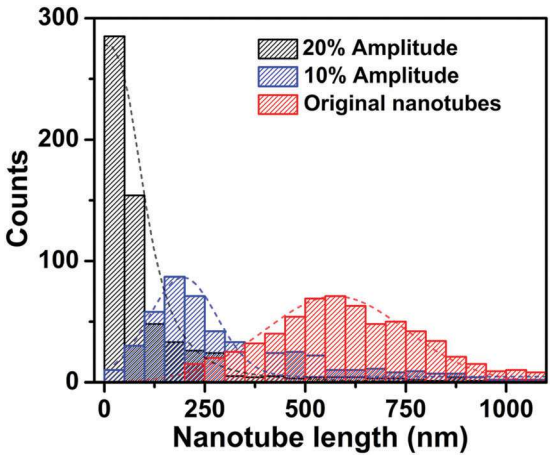

Fig. 3 Histograms of length distributions, extracted from atomic force microscopy (AFM) images, of original **NDI-Bola** nanotubes (red) and nanotubes sonicated at 10% (blue) and 20% (black) amplitudes.

exhibiting lengths of 100–200 nm. At higher amplitude (20%), 72% of the nanotubes were shorter than 100 nm. At 30%, the shortened fragments began to bundle and, at 60%, precipitation was observed (Fig. S5 and S6, ESI†).[34,37,38] At 60%, TEM imaging revealed a conversion from nanotubes to twisted ribbons that were extensively bundled together. As expected for noncovalent assemblies, the shortened nanotubes in samples sonicated at 10% and 20% amplitude re-assembled into their longer initial states over 3 days (Fig. 2d and Fig. S1, S2, ESI†). In contrast, after 3 days, the sample sonicated at 30% amplitude remained in bundles (Fig. S5, ESI†). The cloudy sample produced at 60% amplitude also did not return to the original nanotube structures after 3 days (Fig. S6, ESI†).

Recently, we demonstrated that ionic polymers could be used to coat the surface of self-assembled nanotubes.[39] The polymer electrolytes were shown in this work to associate with the surface of the nanotube *via* a combination of electrostatic interactions, hydrophobic effects and entropic changes due to counterion release.[40] The strong association between the polymer and the nanotubes suggested that wrapping the shortened nanotubes with a polymer might prevent recovery of the elongated nanotubes after sonication. **NDI-Bola** (pI 7.6) was dissolved in pure water (20 mM, 12 h) to assemble the nanotubes, producing a transparent solution with a pH of 6.7. At this pH, the nanotubes

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maintain a positively charged surface. Accordingly, the **NDI-Bola** nanotubes, shortened by sonication at 10 and 20% amplitude for 3 min, were treated with the negatively charged polymer, poly[2,6-(4,4-bis-sodium butanylsulfonate-4*H*-cyclopenta-[2,1-*b*;3,4-*b*′]-dithiophene)*alt*-1,4-phenylene] (PCT-SO_3Na).[41] Adding the polymer to the sonicated nanotube fragments in a molar ratio of 10 : 2 (**NDI-Bola**/PCT-SO_3Na) produced transparent hydrogels. Ultraviolet and CD spectra of the shortened nanotubes of **NDI-bola** and **NDI-Bola**/PCT-SO_3Na were identical to the original elongated nanotubes (Fig. S12–S14, ESI†). The lack of any CD transitions in the range of the PCT-SO_3Na absorption (420–600 nm) indicated that chirality transfer from the nanotube to the polymer had not occurred in the composite nanostructures. Similarly, the fluorescence spectra of the shortened **NDI-Bola**/PCT-SO_3Na composites exhibited quenching of the NDI emission band at 450–525 nm, as observed for the elongated composites (Fig. S15, ESI†).[39] These observations indicate that the sonication/polymer-wrapping process maintains the original monomer packing arrangement of the **NDI-Bola** nanotubes.

After 24 h, the hydrogels were centrifuged and the pellet was analyzed by TEM and AFM (Fig. 4). The nanotube–polymer composites exhibited length distributions that were nearly identical to lengths observed for the sonicated nanotubes prior to polymer wrapping. The polymer wrapping process was quantitated through mass-per-length (MPL) measurements. MPL values were extracted from tilted-beam transmission electron microscopy (TB-TEM) images using co-deposited tobacco mosaic virus filaments as the internal mass calibration standard (Fig. S10, ESI†). After treatment with PCT-SO_3Na, MPL values increased from 187.5 ± 12.2 kDa nm^{-1} for **NDI-Bola** to 286.5 ± 17.0 kDa nm^{-1} for **NDI-Bola**/PCT-SO_3Na (10 : 2, 10%) nanotubes. TEM imaging similarly revealed an increase in diameter from 12 ± 1 nm for the starting nanotube fragments to 17.4 ± 0.4 and 17.4 ± 0.8 nm for the polymer-coated nanotube fragments produced by sonication at 10 and 20% amplitude, respectively. After 3 and 7 d, images of the samples indicated that the nanotube-polymer composites were stable with respect to length and structure (Fig. 4 and Fig. S7, ESI†).

The tendency of physical defects within self-assembled materials to undergo self-healing emerges from the ability of monomeric building blocks to dynamically associate and dissociate with the assembly in a manner to reorganize local defects in morphology. Thus, polymer wrapping of the nanotubes likely impedes this dynamic exchange of monomers, which precludes self-healing. Alternatively, the restricted mobility of the shortened nanotubes within the hydrogels may also have contributed to stability of the sonicated nanotube structures. The movement of nanoparticles through hydrogels is known to depend on size, charge and noncovalent interactions with the hydrogel matrix.[42] To probe this possibility, **NDI-Bola** (20 mM, sonicated at 10% amplitude) was diluted to 5 mM prior to mixing with PCT-SO_3Na, which circumvented the formation a hydrogel. After 5 d, TEM images (Fig. S9, ESI†) indicated that the **NDI-Bola**/PCT-SO_3Na (10 : 2, 10%) composites retained the shortened nanotube length distribution. This suggests that the stability afforded to the shortened nanotubes emerged from the polymer wrapping process rather than the presence of a hydrogel structure.

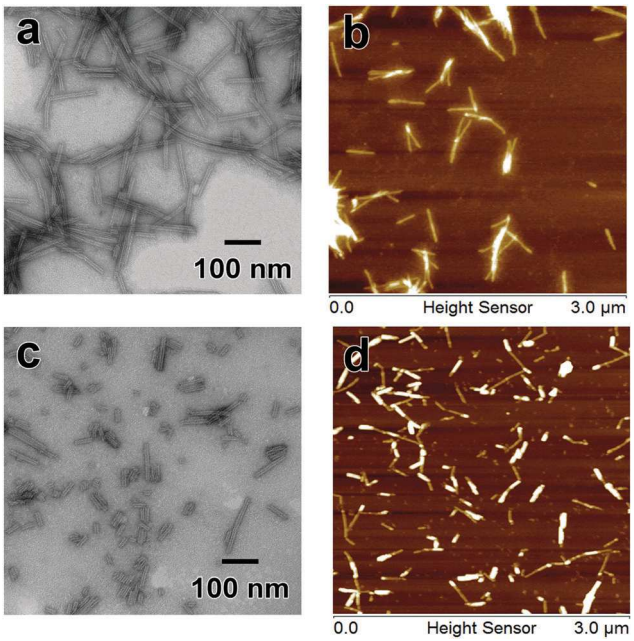

Fig. 4 TEM and AFM images of the co-assembly of **NDI-Bola** (2 mM) nanotubes, fragmented by sonication, and PCT- SO_3Na (0.4 mM) in water. **NDI-Bola** was sonicated at (a and b) 10% and (c and d) 20% amplitudes for 3 min, prior to mixing with PCT-SO_3Na to afford **NDI-Bola**/PCT-SO_3Na composites. TEM and AFM images were taken from composites after aging for 3 d.

To explore the potential of an optically transparent, biocompatible polymer to stabilize the shortened nanotubes, curdlan sulfate was used to coat the sonicated nanotubes. Curdlan, a linear polysaccharide of (1–3) linked β-D-glucose units, has been previously used as a supramolecular wrapping agent for CNTs.[43] To enhance water solubility, the hydroxyl groups of curdlan were sulfonated with chlorosulfonic acid in pyridine, which produced curdlan sulfate (Cur-SO_3Na) with ∼2.3 sulfate groups per glucose unit.[44] Cur-SO_3Na exists in water as a loosely bound triple or single strand, which should be capable of binding to the surface of the positively charged **NDI-Bola** nanotubes. After sonicating at 20% amplitude for 3 min, shortened **NDI-Bola** nanotubes were treated with Cur-SO_3Na (10 : 1 **NDI-Bola**/Cur-SO_3Na), resulting in the formation of a hydrogel similar to **NDI-Bola**/PCT-SO_3Na composites. TEM images of the **NDI-Bola**/Cur-SO_3Na composite exhibited a distribution of shortened nanotubes with increased diameters (Fig. S11, ESI†). Specifically, the diameters of **NDI-Bola**/Cur-SO_3Na nanotubes ranged from 14–17 nm (Fig. S11a, ESI†), reflecting a less uniform polymer coating than produced with PCT-SO_3Na, probably due to the more rigid structure of Cur-SO_3Na.[45] After 3 d, the nanotube length distribution remained stable, indicating that coating with Cur-SO_3Na also prevents elongation of the shorted nanotube structures. This result demonstrates that the shortened **NDI-Bola** nanotubes could also be coated by Cur-SO_3Na, which similarly prohibited elongation of the **NDI-Bola** segments.

The lack of reliable methods to control the lengths of self-assembled nanotubes hampers the application of these materials

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to important problems in biology and materials. In contrast to static nanomaterials, such as CNTs, the ability of soft assembled materials to self-heal precludes physical processing as a method to modulate length. In this work, we have shown that sonication can be used to modulate the length of the nanotubes formed by the self-assembly of **NDI-Bola**. Although the nanotube fragments re-assemble over time into their elongated precursors, wrapping with ionic polymers stabilizes the nanotubes to this healing process. The efficacy of the polysaccharide, Cur-SO_3Na, in addition to PCT-SO_3Na, in stabilizing the nanotube fragments suggests that this process will be useful for a variety of diverse applications.

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Conflicts of interest

There are no conflicts to declare.

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