

Self-Assembled Supramolecular Nanotube Yarn

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In biological systems, small organic molecules and macromolecules self-assemble up into macroscopic objects with hierarchically regulated structures over different scales through both covalent and non-covalent bonds.^[1] It is easy for the covalent-linked polymers to be fabricated into macroscale materials. For supramolecular systems, however, it remains a great challenge to use non-covalent interaction to assemble the small blocks into robust materials with structural ordering over macro-scale.^[2] Although robust carbon nanotubes have been spun into yarns,^[3,4] no supramolecular nanotube,^[5] which is one of the sophisticated and fundamental supramolecular assemblies^[5–16,18–23] has been spun into macroscopic yarns so far. Here we report the first macroscopic supramolecular nanotube yarns directly spun from the diluted aqueous solution. We have found that an L-histidine terminated bolaamphiphile could self-assemble into ultra-long supramolecular nanotubes in slightly alkaline aqueous solution (pH 8–9). By an automatic spinning process, such solution can be spun into bundled nanotube yarns with lengths in meter-scale and diameters of 1.5–5 μm at a large yield. Although the yarns are built totally via non-covalent interaction, they showed nominal tensile strength of 45–60 MPa with Young's modulus coming to 6.8–9.9 GPa, which could be comparable to many covalent-linked polymers. Furthermore, porphyrin solution can move more than 1 centimeter along the vacuum dried supramolecular nanotube yarns, indicating the mass transportation through the macroscopic bundled tubular structures. These results provided the new horizon of hierarchical self-assembly and the continuous spinning of microscopic yarns from the solution of self-assembled small amphiphilic molecules opens a new strategy for building the nanoscale assemblies into ordered macroscopic supramolecular materials.

The natural microtubules show nice mechanical properties for maintaining cell structures, and special structural properties

for the transport of proteins or organelles in the cell. In the axons of sciatic nerves in the human body, the paralleled microtubules assemble into 1 meter fibers to perform their functions.^[17] Scientists have built well-defined tubular nanostructures via the self-assembly of peptides,^[6,9–11] amphiphiles^[5,13–15] and π -conjugated molecules.^[7,8,16] These supramolecular nanotubes showed excellent potential for constructing transmembrane channels,^[18] encapsulation and release,^[19] template synthesis,^[6] making microelectronics,^[9] medicine,^[20] and catalysis.^[21] However, it has been proven to be very difficult to assemble these supramolecular nanotubes hierarchically into a macroscopic scale with regular structures,^[22,23] let alone their mechanical properties. In this paper, we report the first metric length macroscopic supramolecular nanotube yarns, which have been fabricated at ambient temperature and pressure by spinning a diluted aqueous solution containing self-assembled nanotubes. These experiments were inspired by the spinning of silkworms, producing natural silk at ambient temperature and pressure with water as a solvent.^[24] In our case, the yarns are completely composed of supramolecular nanotubes interacting via non-covalent bonds. With an electrical motor, the yarn can be spun into metric length at ambient conditions.

The molecular building block (Figure 1a) is the bolaamphiphile containing two L-histidine hydrophilic headgroups and a long hydrophobic spacer (*N,N*-eicosanedioyl-di-L-histidine, EDH). In slightly alkaline aqueous solution (pH 8–9), EDH can assemble into randomly distributed extremely long supramolecular nanotubes with length-to-diameter ratio coming to above 5000, which can be fabricated into supramolecular nanotube yarns. Actually, the self-assembly of EDH is pH dependent, which could form a hydrogel at pH 1, and assemble into vesicles at pH 13 (Figure S1, Supporting Information). In neutral Milli-Q water, EDH could be dissolved upon heating to 90 °C, and quickly precipitated when the mixture was cooled down to room temperature. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements identify the precipitations as supramolecular nanotubes (Figure S2).

The pH titration curve shows EDH has a pKa value of 8.50 (Figure S3). In this condition, the coexistence of the neutral and the anionic form of EDH molecules may lead to extraordinary aggregation behaviors. EDH can easily form transparent solution in pH 8.5 water upon heating; this solution would become nattier blue within several days and can be stored for several months at ambient temperature without phase separation (Figure 1b). The Cryo-transmission electron microscopy (Cryo-TEM) measurements show very nice nanotubes from EDH pH 8.5 solutions aged after several weeks (Figure 1b). These nanotubes are randomly distributed and nicely separated from each other. The internal diameters and wall thicknesses of pH 8.5 EDH nanotubes are about 22 nm and 10–14 nm, respectively, which is similar to EDH nanotubes obtained under neutral conditions. Presumably, the slightly alkaline environment would

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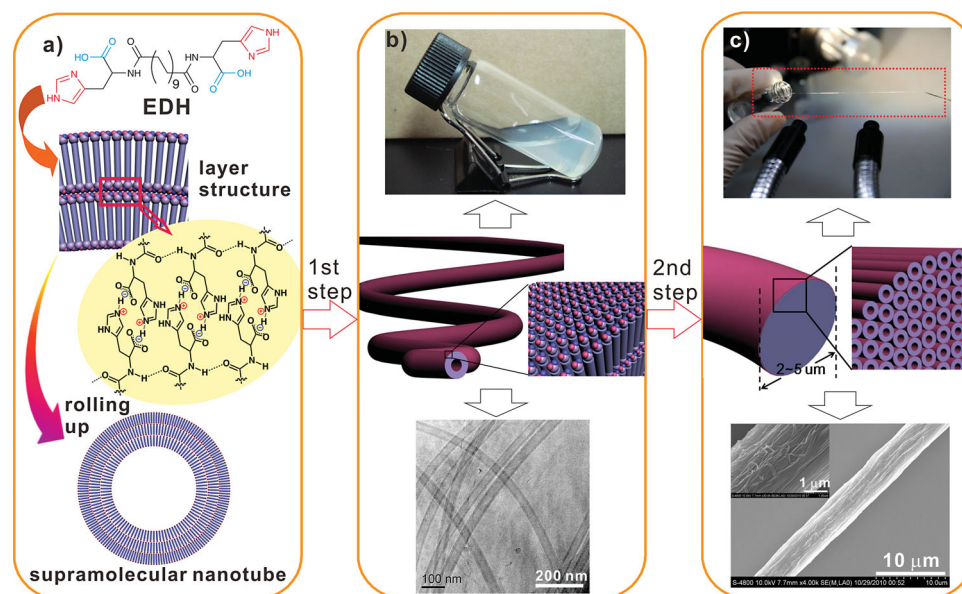


Figure 1. Schematic illustrations of two step assembly from small molecules to macroscopic nanotube yarns. The first step is from molecules to supramolecular assemblies, in which EDH (0.1 wt%) self-assembles into ultra-long supramolecular nanotubes upon aging in pH 8.5 solution. The second step is from supramolecular assemblies to macroscopic fibers, which contain aligned nanotubes, by spinning. From top to down: a) molecular structure of EDH; multilayer structures formed by self-assembly of EDH and hydrogen bonds and electrostatic interaction between the head-groups of EDH; the rolling up of multilayer EDH membranes in supramolecular nanotubes; b) photograph of supramolecular nanotube solution; model of ultra-long nanotubes; cryo-TEM picture of supramolecular nanotubes; c) photograph of drawing nanotube yarn from solution; model of nanotube yarns; SEM images of nanotube yarn.

produce negative charges on the surface of the nanostructures, which could straighten the nanotubes without coiling^[25] and help the solubility of nanotubes instead of precipitation.

The driving forces for forming EDH nanotubes in solution could be the hydrogen bonds between the amide groups, the electrostatic interactions and hydrogen bonds between the histidine head-groups and the hydrophobic interaction between alkyl chains, as proved by FT-IR measurement. The broad band appeared at around 1932 cm^{-1} indicates imidazolium carboxylate salts.^[26] The amide I and amide II bands, which appear at 1635 and 1543 cm^{-1} respectively, suggest the hydrogen bonding between the amide groups. While the stretching vibrations of CH_2 (2920 and 2850 cm^{-1}) demonstrated the orderly packing of EDH alkyl chains (Figure S4b). The H-bonds between amide groups support the bolaamphiphiles to self-assemble into stable monolayer lipid membranes (MLM) (Figure 1a), and the interaction between the head-groups can further reinforce the interaction and stabilize the multilayer MLM nanostructures. Such packing was confirmed by XRD pattern (Figure S4a), which shows that the 2.87 nm layer distance is attributed to the whole length of EDH molecules. Moreover, the multilayer structure of the nanotube walls could be verified from high-resolution TEM (HR-TEM) picture (Figure S5). Thus, parallel aligned EDH molecules assembled into MLM, and then the rolling up of 4–6 layers MLM would produce the supramolecular nanotubes due to the chiral nature of the head-group.^[5,13] The nanotubes would become extremely long after aging in pH 8.5 water through the balance of H-bonds and electrostatic interactions (Figure S6). The lengths of many nanotubes are even larger

than the maximum visual field area of SEM, and can be estimated as more than several hundred micrometers (Figure S6e).

The amazing result is the formation of macroscopic yarns, which could be spun by direct drawing from pH 8.5 solutions containing EDH nanotubes. When a needle was put into the solution with gentle stirring and then carefully lifted out of the water surface, a thin fiber with a length about ten centimeters can be dragged out of the solution (Figure 1c, movie S1). The SEM measurements show that each yarn has essentially a uniform diameter of $1.5\text{--}5\text{ }\mu\text{m}$ (Figure 1c), and the magnified view indicated the yarns are actually constructed by many well aligned nanotubes (Figure 1c). Because the outer diameter of each single pH 8.5 supramolecular nanotube is about 40 nm , each cross section of the corresponding macroscopic yarn should contain at least 1500 nanotubes. This bundled nanotube structure can be confirmed by the SEM image of the divergent end on macroscopic yarn (Figure S7), which shows separated nanotubes. The most direct evidence comes from the SEM images of the cross section of nanotube yarns (Figure 2a). The yarns on very thin glass slides ($150\text{ }\mu\text{m}$) were dipped into liquid nitrogen for 20 seconds, and then the fibers together with slide glasses were quickly cut into several fragments. The opening ends of the bundled nanotubes can be identified from the SEM measurements.

The surface of newly prepared yarns could be quickly dried in air and form free-standing fibers. Different fibers are able to intersect each other without fusion, and the pattern like networks could be prepared with relatively large suspended area (Figure 2c). Cross-polarized microscope was used to investigate

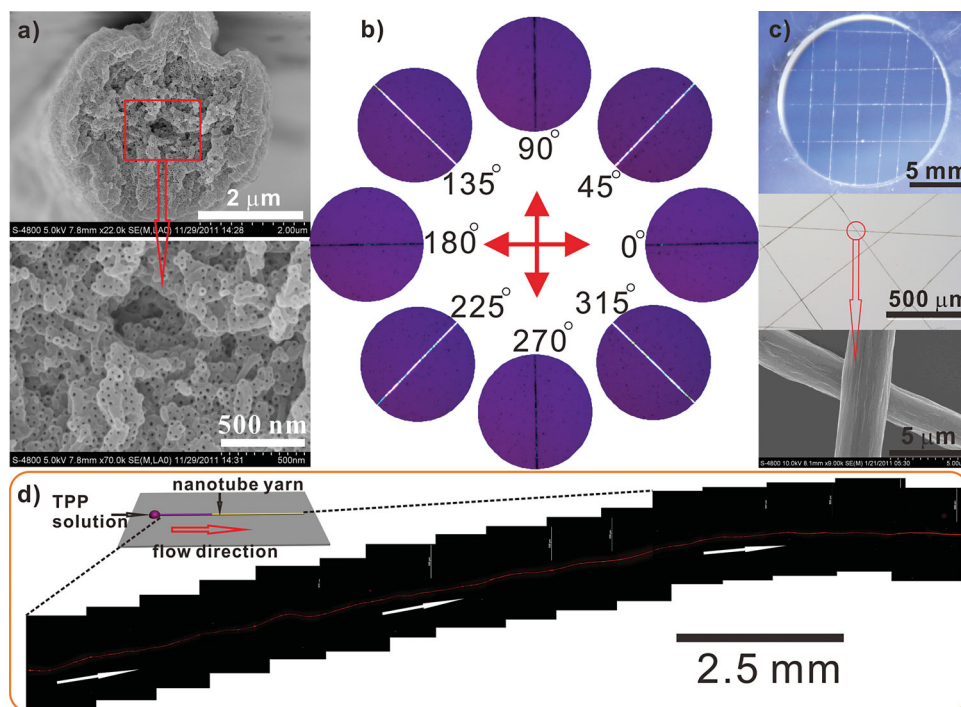


Figure 2. a) Well-ordered pores on the cross section of nanotube yarns clearly show the bundled nanotubes; b) Nanotube yarn under cross-polarized microscope; c) Pattern constructed by nanotube yarns; d) Fluorescence microscopy images of one nanotube yarn over centimeter scale show the movement of TPP toluene solution in nanotube yarn.

the molecular packing and hierarchical arrangement of the nanotubes within the assemblies. When those macroscopic fibers were aligned 45° to the polarizer, the anisotropy birefringence would come to the maximum; while the birefringence of these fibers became very weak once placed parallel to the polarizer (Figure 2b). These results suggest that the anisotropic entities exist throughout the nanotube yarns, with length in the scale of tens of centimeters. The anisotropic properties at such large scales is astonishing and the yarns represent hierarchical ordering from the self-assembly of molecules up to the well-arranged alignment of nanotubes, which form ordered architectures at macroscopic level.

The vacuum-dried supramolecular nanotube yarns can maintain the bundled tubular nanostructures after immersing them in toluene for 1 hour (Figure S8). For understanding the mass transportation along the nanotube yarns, a toluene solution (5 μL) of tetraphenylporphyrin (TPP, 1×10^{-4} M) was added to the open end of a vacuum-dried nanotube yarn. Since the porphyrin is fluorescent when excited by green light of a Hg lamp (500–550 nm), while the nanotube yarns themselves cannot show fluorescence (Figure S9c), the movement of the porphyrin solution can be monitored by fluorescence microscopy. The results show that TPP could move more than 1 centimeter along the yarns before the solvent was evaporated (Figure 2d), presumably due to the capillarity forces and the wetting process of the surface. In order to confirm the porphyrin solution moving along the supramolecular nanotube yarns, the controlled experiment was executed by carefully adding porphyrin solution to only one end of two crossing yarns. The fluorescence

microscopy measurements clearly show the movement of porphyrin along exclusively one nanotube yarn (Figure S9d).

The mechanical properties of the EDH nanotube yarns were studied by using a home-developed instrument based on a precision electronic balance at room temperature and with a relative humidity about 30% (Figure S10). The detailed experimental processes are shown in the Experimental Section and the Supporting Information.

The surface of as-spun yarns can be quickly air-dried, while the water inside the nanotubes would be removed under high vacuum for 48 hours. Although the tensile strengths of as-spun macroscopic yarns can be measured, the water inside the supramolecular nanotube yarns could make the non-covalent interaction variable during the stretching process and further weaken the self-assembly (Table S1). Therefore, we focused on the mechanical properties of vacuum-dried macroscopic yarns to reveal the relationship between the macroscopic mechanical strength of supramolecular nanotube yarns and different non-covalent interactions, on which the whole self-assembled architectures relied. The typical stress-strain curve of the vacuum-dried nanotube yarn with a fracture cross section diameter of ca. 2.10 μm (Figure S11) is shown in Figure 3a. The yarn linearly proceeds up to the fracture point upon stretching. The nominal tensile strength was determined as 54.32 MPa with an elongation of 0.81%, and the corresponding Young's modulus is 6.81 GPa. The mechanical data of different vacuum-dried supramolecular nanotube yarns were collected and analyzed. The stress-strain curves show that all yarns have a large linear mechanical response. Moreover, the tensile strength of these

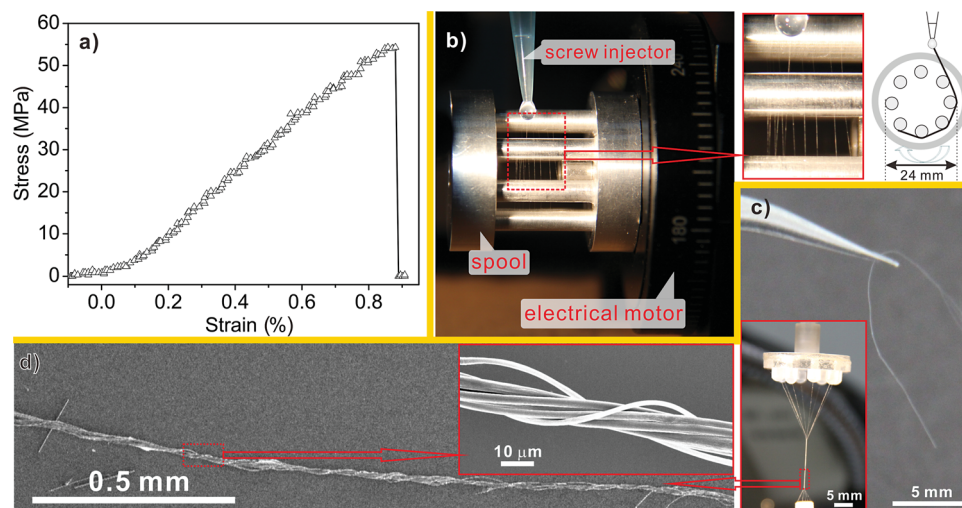


Figure 3. a) A typical stress-strain curve of a vacuum-dried EDH nanotube yarn; b) Photograph of spinning nanotube yarns by motor and spool, with sectional drawing and a magnified view of the spinning on the right; c) Eight in-situ spinning nanotube yarns were twisted into a thread, which can be handled by tweezers; d) SEM image of the thread constructed by eight supramolecular nanotube yarns.

vacuum-dried supramolecular nanotube yarns was determined to be about 45–60 MPa with a Young's modulus coming to 6.8–9.9 GPa (Table S1). Interestingly, although the nanotube yarns are constructed by self-assembly of small bolaamphiphilic molecules with non-covalent interactions, their tensile strength is comparable with some biological materials as well as with widely used covalently linked polymers (Table 1). The hydrogen bonds and electrostatic interactions not only render single EDH molecules capable to form supramolecular nanotubes, but also drive different ultra-long nanotubes to assemble into macroscopic yarns, and most importantly, equip them with outstanding mechanical properties.

In order to obtain longer continuous fibers, we introduced an electrical motor and spool to perform the spinning (Figure 3b, movie S1). The bulk solution was provided continuously from a screw injector on the top of the spool, and the spinning was carried out at 40 °C to let the extra water evaporate rapidly. When the end of the nanotube yarn drawing from the droplet on the injector tip was put on the duralumin spool, the motor started to rotate with a constant

speed ($\omega = 0.07 \text{ rad} \cdot \text{s}^{-1}$). Normally, macroscopic fibers with lengths exceeding 80 centimeters can be wrapped around the spool (Figure 3b). Considering that the diameters of nanotube yarns are only 1.5–5 μm , the length-to-diameter ratio of 80 centimeter fibers with nanotubes in an ordered alignment is amazing. In order to enhance the operability of the yarns, further hierarchical assemblies of these macroscopic nanotube yarns into much bigger one-dimensional materials with ordered structures was also investigated. Inspired by cotton spinning, we developed a process for twisting eight in-situ spinning nanotube yarns into a helical thread (Figure 3c). The SEM image shows the thread containing orderly twisted nanotube yarns, with diameters reaching tens of micrometers (Figure 3d). One single helical thread can be handled by common tools. This process demonstrates that the supramolecular nanotube yarns have good capability for being operated at macroscopic scale.

In summary, using small organic molecules and by means of a simple spinning procedure, we obtained yarns of supramolecular nanotubes with metric lengths, whose mechanical

Table 1. Comparison of the typical mechanical properties of the supramolecular nanotube yarns with some biological materials^[27] and conventional covalent-linked polymers.^[28,29]

Materials	Tensile Strength [MPa]	Young's modulus [GPa]	Materials	Tensile Strength [MPa]	Young's modulus [GPa]
Vacuum-dried nanotube yarn	45–60	6.8–9.9	Ligament	10–50	0.06–0.3
ABS polymer	40	2.3	Skin	5–17	0.01–0.05
HDPE	15	0.8	Collagen	25–250	1–7
Polystyrene	40	3	Wool	40–200	1–6
Polypropylene	40	1.9	Silk(cocoon)	200–2000	0.1–20
Nylon 6	70	1.8	Tendon	45–190	1–2.2
			Leather	4–35	0.005–0.08

properties are comparable to some covalent-linked synthetic or biological polymers. The results about self-assembled supramolecular nanotube yarns demonstrate that delicate supramolecular assemblies from synthetic building blocks can be further constructed into macroscopic objects via non-covalent interactions with hierarchical regular structures through different scales. This process paves the way to supramolecular assemblies for a wide range of applications.

Experimental Section

Micro-tensile tests: The as-spun supramolecular nanotube yarns were first dried under high vacuum for 48 hours. The tensile properties of the macroscopic fibers were measured at a stretching speed of $30\ \mu\text{m min}^{-1}$, and the real-time changes of force and displacement were recorded by a computer. After the nanotube yarns were broken upon stretching, the disconnected fibers were carefully collected and placed on the surface of clean silicon wafers for SEM measurement. The diameters of supramolecular nanotube yarns could hardly be measured by SEM without destructing on the integrality of the yarns. Moreover, considering the elongations of supramolecular nanotube yarns upon stretching are less than 1%, the contraction of the diameters of the fractures from different broken yarns would be relatively small, so we measured diameters after the micro-tensile tests. And the average diameters which were measured close to the fractures were used for calculating stress-strain. Then the nominal tensile strength and the Young's modulus of these supramolecular nanotube yarns can be obtained.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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