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Densifying carbon nanotubes on assembly surface by the self-contraction of silk fibroin

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ABSTRACT

High densification of carbon nanotubes (CNTs) is important for high utilization efficiency of their superior properties in macroscopic assemblies. However, the conventional "top-down" compressing strategies have met problems to modify CNT assemblies at and below the micrometer scale. Here we report a molecular way to strap CNTs together via the self-contraction of silk fibroin (SF) during its drying process, resulting in a localized densification below the micrometer scale. Importantly, after the thermal removal of SF molecules, the densified assembly was well maintained. The SF-induced densification increased the average strength from 355 MPa to 960 MPa for CNT fibers, and from 1.45 GPa to 1.82 GPa for CNT ribbons, which contain much more CNTs on the surface.

1. Introduction

Strapping, also known as bundling and banding, is an everyday process widely used in human activities. For long straws, strapping is also one important process in thatching, an ancient worldwide roofing technique, where the dry vegetation is bundled, strapped, and layered so as to shed water away from the inner roof. Wheat and rice straw, sorghum stalks, millet stalks, and reeds traditionally were used throughout north and northeastern China. The bundling and strapping of such straw materials, by hand-tying with twine or rope, can cause them tightly packed and result in a certain strength to benefit the application. Such process is also a standard strategy to produce straw brooms. Today, this ancient technique is now reminiscent of an assembly material, carbon nanotube (CNT) fiber, where millions of CNTs are aligned and bundled together [1–3]. Generally, one might ask whether we can use a "nano" rope to strap CNT fibers to make them more densified and stronger.

After being assembled together, usually with a twisting treatment, CNTs are spun into a continuous fiber, as long as several to hundreds of meters [4]. These CNTs transfer loads mainly by intertube friction [5–7]. Assembly densification [8,9], chemical modification of CNT surface [10,11], and intertube covalent functionalization [12,13] have been used to remarkably enhance the friction. Recently, a pressing treatment with mechanical rolling was used to densify and strengthen CNT fibers, increasing the mass density up to 1.8–1.85 g/cm^3 [14,15]. However, there is an interesting conflict for the pressing-induced densification: the CNTs are assembled in a "bottom-up" way and the assembling is not easy to be affected by hand manipulation, while the various post-treatments are "top-down" strategies and are also difficult to modify the assembly at and below the micrometer scale.

Here, by mimicking the straw bundling and strapping, CNT fibers can get densified and enhanced from the self-contraction of silk fibroin (SF), owing to the β-sheet self-assembling during the drying of SF molecules. By applying such localized densification on CNT fibers, especially on the outer skins, the highest fiber strength was enhanced from 373 MPa to 1051 MPa. When aligned CNT ribbons with a thickness of several micrometers were treated with SF, the enhanced strength could be much higher, up to 1.82 GPa. It is also important that the removal of SF molecules by thermal heating did not recover the original CNT assemblies and thus had no influence on the mechanical properties (the mechanical tests were conducted both before and after the SF removal).

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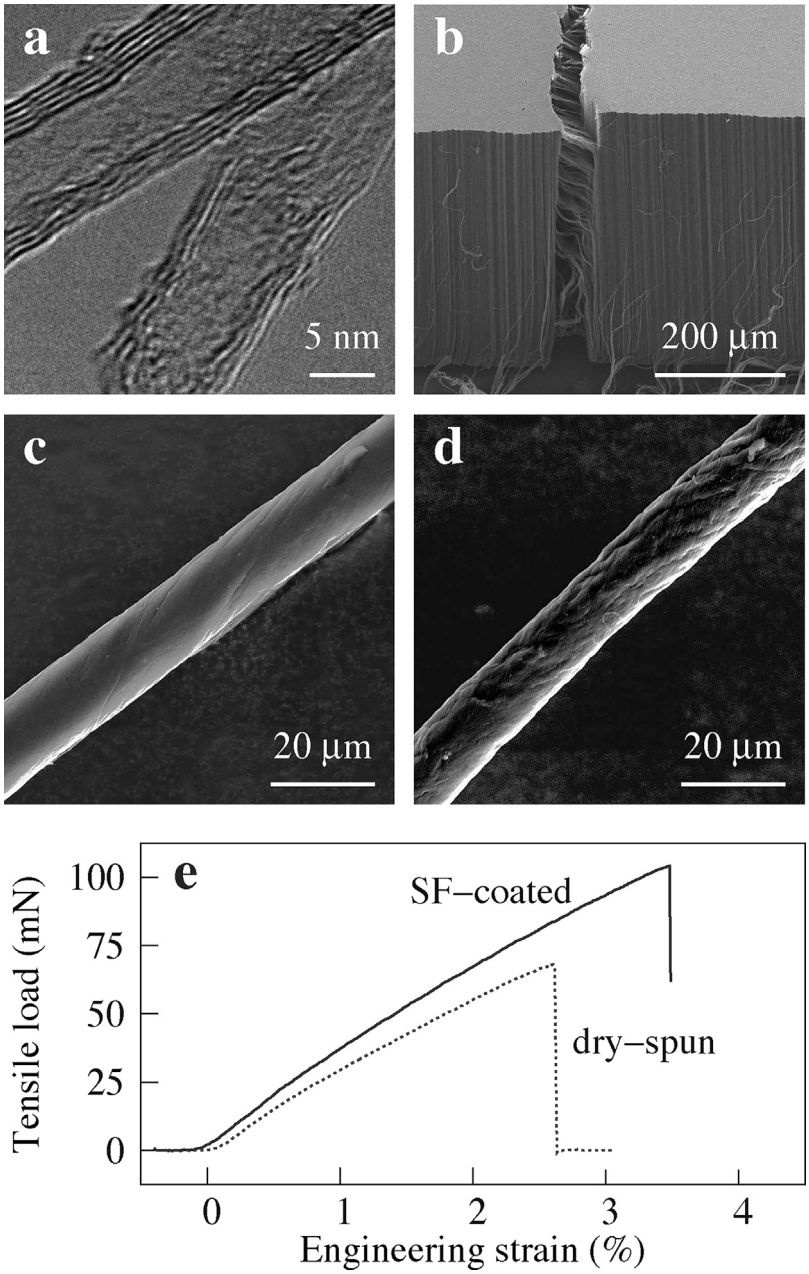

Fig. 1. (a–d) TEM and SEM images of individual CNTs, CNT forest, dry-spun CNT fiber, and SF-densified CNT fiber. (e) A comparison of load–strain curve for a dry-spun and SF-coated fiber.

2. Experimental

2.1. Materials

The spinnable CNT forests were grown on SiO_2/Si wafers by a sustained chemical vapor deposition, where C_2H_4 was used as carbon source and a 1.8-nm-thick Fe film was coated on the wafer as the catalytic layer [16]. The growth was performed at 740 °C at 750 Torr with a gas flow containing 1600 sccm Ar, 100 sccm H_2, and 300 sccm C_2H_4. The grown CNTs were multi-walled (wall number ≈3–6), 6–8 nm in diameter, and ≈380 μm in length (forest height), see the TEM, SEM images shown in Fig. 1a and b. The fiber spinning was performed by drawing and twisting [16,17,9,18,11], while without imparting the twist, untwisted and more-densified CNT ribbons were obtained by passing the drawn-out CNT sheet through a V-shape guide [19]. The untwisted ribbons were also compressed by pressurized rolling [14], which could make the ribbon surface as smooth as possible.

2.2. Post-treatment with SF

The SF solution was prepared from cocoons of *Bombyx mori* silkworm [20]. The cocoons were cut into 10 mm × 10 mm pieces and boiled in an aqueous solution of 0.5% (w/v) Na_2CO_3 for 40 min, then rinsed thoroughly with distilled water to remove the glue-like sericin proteins. The extracted fibroin bundles were dried in an oven overnight and then dissolved in 9.3 mol/L LiBr solution at 60 °C for 1 h. The obtained solution was dialyzed in deionized water using a cellulose dialysis membrane at room temperature for 3 days to remove LiBr. The dialyzed silk solution was then centrifuged at 10,000 rpm for 20 min. Finally, the supernatant with a concentration of 8.94 wt% was collected. For the SF coating, the solution