Superstrong Ultralong Carbon Nanotubes for Mechanical Energy Storage

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Energy storage in a proper form is essential for a good grid strategy. The systems developed so far mostly use batteries or capacitors in which energy is stored electrochemically or electrostatically. Mechanical energy storage is also one of the most important ways for energy conversion. In fact, water reservoirs on high mountains store mechanical energy using the gravitational potential on the earth, and the surplus energy can be mechanically stored in water pumped to a higher elevation using pumped storage methods. Other systems for mechanical energy storage were realized, such as flywheels storing mechanical energies by the use of a rapidly rotating mass and steel springs storing mechanical energies by their elasticity. However, such mechanical energy storage usually is operated on a macroscopic scale, and the energy density is not very high. With the fast development of nano- and micro-electromechanical systems (N/MEMS) and actuators, nanoscale mechanical energy storage is highly required.

Developing a robust nonmaterial with good mechanical performance and stable supply is the first step. Ultralong carbon nanotubes (CNTs) with the properties of 1–2 TPa modulus and 100–200 GPa strength,[1–4] the strongest material ever known, have shown promising potential for the storage of mechanical energy, either by their deformation in the composite materials,[5–7] or by their elastic deformation produced by stretching or compressing the pristine tubes or tube arrays.[8] Theoretical calculation suggested that the energy storage capacity, in the latter case, can be at least three orders higher than that of steel spring and several times that of the flywheels and lithium ion batteries.[9,10] The mechanical energy storage capacity of CNTs depends on their mechanical properties, which directly depend on their molecular structures. Besides, CNTs that simultaneously have theoretically high strength (100–200 GPa), high tensile modulus (1–2 TPa) and high breaking strain (>15%) are not yet experimentally available on the macroscale.[2,11–20] This is mainly due to the existence of defects in the fabricated CNTs. Even for CNTs with little defects, the highest reported breaking strain is 13.7% ± 0.3%,[21] which is still lower than the theoretical value.[22,23]

Here we experimentally demonstrate that the as-grown defect-free CNTs with length over 10 cm, have breaking strain up to 17.5%, tensile strength up to 200 GPa and Young’s modulus up to 1.34 TPa. They could endure a continuously repeated mechanical strain-release test for over 1.8 × 10^8 times. The extraordinary mechanical performance qualifies them with high capacity for the storage of mechanical energy. The CNTs can store mechanical energy with a density as high as 1125 Wh kg\(^{-1}\) and a power density as high as 144 MW kg\(^{-1}\), indicating the CNTs can be a promising medium for the storage of mechanical energy.

Recent breakthroughs in preparation techniques have made it possible to get centimeter-long CNTs with perfect graphitic structure.[24–26] To date, the length of individual ultralong CNTs has reached 20 cm,[26] which is far beyond the characterization scale of the normally used instruments, such as SEM, AFM, TEM, etc. Manipulation of individual ultralong CNTs is not an easy task due to their nanoscale diameters while macroscale lengths, which hampered measurement of their mechanical performance. To avoid the constraint of normally used instruments, we constructed a special device with individual ultralong CNT as a demonstration platform for mechanical energy storage. The device and auxiliary set-up were carried out as follows. First, millimeter-wide slots were inscribed on a silicon substrate (Figure 1a). Then, ultralong CNTs were grown on the substrate from the left edge to the right edge by CH\(_4\) decomposition on Fe catalyst particles. Their lengths were as long as 10 cm after 20 min growth at 1000 °C. Based on the “kite mechanism”,[27] ultralong CNTs floating in the gas flow during growth gradually sank down onto the silicon substrate to lie across the slots on it. Figure 1b shows four of these CNTs lying across a 0.75 mm wide slot on the substrate. Several suspended CNTs were thus naturally produced due to the strong interaction of the CNTs with the silicon substrate.[28] In this contribution, several triple walled CNTs (TW-CNTs, as shown in Figure 1c) with outer diameters of 2.9–3.2 nm were selected for the mechanical performance test.

Deposition of gold nanoparticles has been used to make individual ultralong CNTs visible under optical microscopes,[29] but the strong surface tension of the liquid lets the suspended CNTs break easily during the nanoparticle deposition process. Thus, a solution-based decoration method is not suitable for the suspended CNTs. To make the suspended CNTs optically visible for the study of their mechanical performance and energy storage capacity on the macroscale, a simple but effective optical visualization method was developed. TiO\(_2\) particles
tips during the elongating or vibrating process. A special device was designed to test the mechanical strength of the bead-like chain structure. The suspended CNT /TiO$_2$ chain can be exited to vibrate by the acoustic wave from the loudspeaker linked to a signal generator (Figure S3, Supporting Information). They can even vibrate for $>1.8 \times 10^8$ times continuously. Neither slip-page of TiO$_2$ particles on CNT, or decrease in their number, nor breaking of the chain was observed. This allowed us to use it as a good mechanical testing device.

The mechanical performance measurement of the CNTs was performed by introducing a steady nitrogen flow used to blow the suspended CNTs embedded with TiO$_2$ particles (Figure 2a). The tips of the CNTs, which were firmly affixed by the formation of a TiO$_2$ layer on the silicon substrate by the same method (Figure S2, Supporting Information), which prevented the slippage of their in large amounts were deposited on the suspended CNTs by the hydrolysis of TiCl$_4$ which was sprayed onto the tubes. This is shown in Figure 1d and 1f, which describes that a bead-like chain was formed across the slot on the silicon substrate. There were several hundred particles with a number density of approximately 1000 mm$^{-1}$ along the suspended CNT. Uncoated CNT segments with pristine shells can be observed between the particles (Figure 1g). The strong brightness and reflectivity of TiO$_2$ particles upon illumination allowed us to precisely locate the position of the CNTs with an optical microscope (Figure 1f, 2c, and S1, Supporting Information). The two ends of the suspended CNTs were firmly affixed by the formation of a TiO$_2$ layer on the silicon substrate by the same method (Figure S2, Supporting Information), which prevented the slippage of their tips during the elongating or vibrating process. A special device was designed to test the mechanical strength of the bead-like chain structure. The suspended CNT/TiO$_2$ chain can be exited to vibrate by the acoustic wave from the loudspeaker linked to a signal generator (Figure S3, Supporting Information). They can even vibrate for $>1.8 \times 10^8$ times continuously. Neither slippage of TiO$_2$ particles on CNT, or decrease in their number, nor breaking of the chain was observed. This allowed us to use it as a good mechanical testing device.

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is the cross-sectional area of the outer shell of a multi-walled CNT contributes to its strength under axial tensile deformation). is the thickness of one single CNT shell (0.34 nm), and is the pull exerted along the axis of the CNT (Figure 2d), which is originated from the drag force sum exerted on all the TiO₂ particles. At the end of the suspended CNT, can be expressed as

\[ T = \sqrt{T_0^2 + F_0^2} \]  

(2)

where is the pull exerted at the middle point of the suspended CNT, and is the drag force sum exerted on all the TiO₂ particles (see Text S1). The Young’s modulus of the tested CNTs was obtained by fitting the linear portion of their stress-strain curves (Figure 3b). The modulus values range from 10⁷ to 10⁸ N/m, which was close to the upper theoretical limit for ideal CNTs. is conventionally used to detect the defect degree of CNTs. is the density of the CNTs. The high stiffness and ability of the CNTs to keep high strain render their extraordinary performance on mechanical energy storage. The gravimetric energy density is

\[ u_m = \frac{1}{\rho} \frac{A}{A_T} \int_0^\varepsilon \sigma \, d\varepsilon \]  

(3)

where is the cross-sectional area of the outer shell, is the total enclosed area, is the applied stress, is the strain, and is the density of the CNTs. The highest energy densities were 1125, 1085, and 970 Wh kg⁻¹ for the three CNTs in Figure 3b, respectively. The theoretical value was 1163 Wh kg⁻¹ at 17% strain (see Text S2). It is shown in Figure 4 that the CNT string system is advantageous over all existing energy storage systems, including all kinds of batteries, super-capacitors, and flywheels, both in energy density and power density. Its energy density was nearly 3 times that of Carbon T1000 flywheels (350 Wh Kg⁻¹) and 5–8 times that of Li ion batteries (120–180 Wh Kg⁻¹) and 25 000 times that of steel springs (0.039 Wh Kg⁻¹).
frequency, could vibrate continuously for $1.8 \times 10^8$ times with a strain of 0.08%, and maintained unbroken. In comparison, Li ion batteries and super-capacitors often suffer from unavoidable energy loss in charge-discharge cycles. The energy density in the vibration test case was 10 Wh Kg$^{-1}$ and the power density was as high as 144 MW kg$^{-1}$, obtained from the energy density divided by the discharging time of 0.00025 s (the vibration frequency was 1000 Hz). This capacity is sufficient for the energy supply of small electronic devices including cell phones, micro-scaled sensors, watches, etc. In addition, the working mode of the individual CNTs, which were sensitive to ambient tiny vibrations, is promising for the fabrication of self-powered N/MEMS, flexible devices, sensors, actuators, and antennas.\[39\]

In addition, the CNTs offer a cleaner and safer energy storage manner compared to batteries and super-capacitors. The further scale-up of the CNT system can have astonishing applications due to their ultrahigh strength.

In summary, we have fabricated superstrong ultralong CNTs with perfect structures and measured the mechanical properties of them. The CNTs simultaneously exhibited high strength, high Young's modulus, and large breaking strain. The high energy density and power density of CNTs made them promising materials for the storage of mechanical energy. This work also provides a structural model towards the mechanical energy storage that might be used in areas such as N/MEMS, flexible device, sensors, actuator, and antenna.

**Experimental Section**

*Substrate preparation:* Single crystal silicon slices (10 cm long, 0.5–1 cm wide, and 0.5 mm thick) were used as substrates. First, several slots (0.5-1 mm wide, 0.3-0.5 mm deep) were inscribed on the substrates using a laser etching technique. The substrates were then cleaned by acetone, ethanol, and deionized water in sequence, each for 3.0 min, in an ultrasonic bath. After that, the silicon substrates were oxidized by dry O$\text{2}$, and then wet O$\text{2}$, then dry O$\text{2}$ at 1000 °C for 5, 50, and 5 min in sequence at a flow of 500 sccm. The SiO$\text{2}$ layer was about 500 nm thick.
CNT fabrication: A solution containing catalyst precursor FeCl₃ in ethanol (0.03 mol L⁻¹) was dabbed onto the upstream end of the silicon substrate. After reduction in H₂ and argon (H₂/Ar = 2:1 in volume with a total flow of 200 sccm) at 900 °C for 25 min, the iron precursor became iron nanoparticles that were the catalysts for the subsequent chemical vapor deposition for CNT growth at 1000 °C. CH₄ and H₂ (CH₄:H₂ = 1:2 in volume with a total flow of 75 sccm) were used as carbon source, together with 0.43% H₂O for accelerating CNTs growth. The growth time for the CNTs was usually 10–20 min, which depended on the length of CNTs desired.

TiO₂ particles deposition: A TiCl₄ mist was sprayed onto the suspended CNTs first. Due to the rapid hydrolysis of TiCl₄ in air, it soon became TiO₂ particles with an average diameter of 0.6 μm. There was a strong interaction between the TiO₂ particles and the shells of the CNTs, which made the TiO₂ particles very stable on the CNTs.

Characterization: The CNTs were characterized by scanning electron microscopy (SEM, JSM 7401F, 1.0 kV), high-resolution transmission electron microscopy (TEM, JEM-2010, 120.0 kV), and Raman instrument (Horiba JY, 632.8 nm). The suspended CNTs embedded with TiO₂ particles and their mechanical behaviour were recorded by an optical microscopy (Shanghai Optical Instrument Co. Ltd).

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

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