Giant-Stroke, Superelastic Carbon Nanotube Aerogel Muscles

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Improved electrically powered artificial muscles are needed for generating force, moving objects, and accomplishing work. Carbon nanotube aerogel sheets are the sole component of new artificial muscles that provide giant elongations and elongation rates of 220% and (3.7 × 10⁴)% per second, respectively, at operating temperatures from 80 to 1900 kelvin. These solid-state–fabricated sheets are enthalpic rubbers having gaslike density and specific strength in one direction higher than those of steel plate. Actuation decreases nanotube aerogel density and can be permanently frozen for such device applications as transparent electrodes. Poisson’s ratios reach 15, a factor of 30 higher than for conventional rubbers. These giant Poisson’s ratios explain the observed opposite sign of width and length actuation and result in rare properties: negative linear compressibility and stretch densification.

Actuator materials and mechanisms that convert electrical, chemical, thermal, or photon energy to mechanical energy have been sought for over a century. Electrostatic attraction and repulsion between two nanotubes was used for cantilever-based nanotweezers (1) and mechanically based switches and logic elements (2, 3). On the macroscale, electrically powered (4–6) and fuel-powered (7) nanotube actuators provided up to a few percent actuator stroke and a hundred times higher stress generation than natural muscle. Demonstrated large-stroke pneumatic nanotube actuators used electrochemical gas generation within nanotube sheets (8). Carbon nanotube composites with organic polymers provided photosensitive (9), shape memory (10, 11), and electromechanical (12) actuators.

Carbon nanotube aerogel sheets. We have developed carbon nanotube actuators from aerogel sheets that are drawn from forests of carbon multiwalled nanotubes (MWNts). They typically have a density of ~1.5 mg/cm³, an areal density in the sheet plane of ~1 to ~3 μg/cm², and a thickness of ~20 μm (13, 14). The sample dimension in the sheet draw direction is the sheet length (L), and the orthogonal sheet dimensions are the sheet width (W) and the sheet thickness (H), which have initial values L₀, W₀, and H₀ before actuation. Liquid-based densification of the aerogel sheets can decrease sheet thickness ~400-fold to typically 50 nm, which is useful for decreasing actuator volume. These nanotube aerogel sheets can be drawn from forests at above 2 m/s and a gram of sheet could cover over 30 m² (fig. S1). The aerogel sheets act as a low-modulus rubber when stretched in the sheet-width direction by up to 300%, which is important for accommodating large-stroke actuation.

Actuation in sheet width and thickness directions. Actuation results from applying a positive voltage to a nanotube sheet electrode with respect to a counter electrode, which is usually a distant ground plane. Figure 1, A to C, demonstrate width-direction actuator strokes of about 220%, as well as actuation from ambient to 1500 K. Figure 1D shows that externally produced actuation of ~3× can be permanently frozen by laying the electrically expanded sheet on a substrate and using van der Waals bonding between nanotubes and substrate to prevent return to the initial nonexpanded state. This freeing of electrically driven actuation enables tuning of areal density and related properties for transparent electrode applications. The consequence of “ballooning” in the width direction, from 0% at the sample grips to about 220% at the center of the nanotube strip, is periodic corrugation in the width direction during nanotube sheet cycling (Fig. 1, E and F). Corrugation formation can be avoided by either increasing the length-to-width ratio of the sheets, so that strains in the width direction become more uniform, or decreasing the applied potential.

The observed voltage dependence of actuator stroke in the width direction at length center, normalized to the initial width to provide generated strain ε_w = ΔW/W₀, is shown in Fig. 2A for single and stacked aerogel ribbons having the same L₀/W₀ ratio. Although ε_w increases approximately quadratically with applied voltage V, a crossover occurs at higher voltages to a weaker dependence, ~V²/³. A similar transition in the voltage dependence of lateral deflection has been observed and explained for a charged single nanotube that is clamped at both ends (15). At relatively low applied voltage (260 V), the observed width-direction actuation (fig. S5) was 14% for a sheet strip having L₀/W₀ = 13.9 (14). Movie S1 shows width-direction actuation during cycling at high applied voltage, as well as simultaneously recorded changes in optical diffraction from the sheet.

This crossover in voltage dependence from ~V² to ~V²/³ results from ballooning caused by end clamping. In this geometry, width-direction expansion requires stretch in the high-modulus nanotube orientation direction, and this elonga-

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tion provides the dominant elastic energy term at the large strokes produced at high applied voltages. The charge-injection–generated force needed to provide strain \( \varepsilon_w \) is approximately \( F = A\varepsilon_w + B\varepsilon_w^3 \), where \( A \) and \( B \) are coefficients proportional to elastic stiffness in the width and nanotube orientation directions, respectively. The \( \varepsilon_w \) term is just the ordinary linear dependence of force on elastic strain in the width direction. The \( \varepsilon_w \) term arises from combination of the \( \varepsilon_w^2 \) dependence of fractional elongation of the bowed nanotubes and the \( \varepsilon_w \) dependence of the projection of the resulting restoring force onto the width direction.

Because the electrostatic repulsive force \( F \) producing \( \varepsilon_w \) depends quadratically on injected charge and the injected charge is \( CV \), where \( C \) is the sheet capacitance, the combination of linear and cubic terms in \( \varepsilon_w \) for \( F \) leads to the correct prediction that \( \varepsilon_w \) increases as \( -V^2 \) when \( \varepsilon_w \) is small and as \( -V^{2/3} \) when \( \varepsilon_w \) is large. The crossover voltage and the \( \varepsilon_w \) obtained at high voltage should increase with increasing \( L_o/W_w \), which is experimentally confirmed (fig. S4).

The Fig. 2A data on the voltage dependence of \( \varepsilon_w \) can be reduced to a universal curve (fig. 2A, inset) that is independent of the number \( N \) of stacked sheets (between \( N = 1 \) and 8), by plotting \( \varepsilon_w \) versus \( V^2S_N \), where \( S_N = (N^{-1} - R)/(1 - R) \) and \( R \) is a fitting parameter \((0.095)\). We theoretically derived this normalization factor \( S_N \) using a simple mechanical model. The average charge-induced stress in the width direction scales as \( 1/N \), while the average stress in the thickness direction is largely independent of \( N \) (14). If charge-injection–generated stress in the thickness direction had no effect on width-direction strain, \( R \) would be zero and \( \varepsilon_w \) would therefore be a function of only \( V^2/N \). The \( N \)-independent stress in the thickness direction upon charge injection will decrease width-direction strain as a result of sufficiently strong elastic cross-coupling between these parameters, thereby giving rise to a finite \( R \). Although use of \( S_N \) as a normalization factor accurately predicts the dependence of actuation strain on voltage over an eightfold change in sheet thickness, it becomes unreliable for thicker sheet stacks having low actuation strains at all voltages. The decrease in width-direction stroke by a factor of about 3.7 upon densification of an eight-sheet stack (Fig. 2A) is consistent with the increase in nanotube-nanotube interconnects and the corresponding increase in specific stiffness (16) as a result of densification.

The average actuation rate in the width direction was determined in air (14) for a high–aspect ratio single sheet \( (L_o/W_w = 36) \) by measuring the time delay (5 ms) between applying 5 kV to the nanotube sheet and subsequent 180% width expansion (fig. S6). This average actuation rate was a notable \((3.7 \times 10^4)\%/s\), as compared with the maximum 20%/s achieved rate for other electrically driven carbon nanotube yarn or sheet actuators and the 50%/s maximum rate of natural muscle (17). A comparable average actuation rate \((3.4 \times 10^4)\%/s\) was obtained for artificial muscles based on silicon elastomers, but this rate was obtained for electrical drive at resonant frequency where the actuator stroke was about 12% (17, 18).

Resonant actuation in vacuum caused large strokes in the width direction at low applied voltages because of a surprisingly high observed quality factor \( Q \) (fig. S7). Applying \( V_{RMS} \) (root mean square voltage) ac drive voltage to a 25-by-1.8-mm single sheet resulted in a resonant frequency of 1089 Hz and a \( Q \) of 455, which markedly decreased (fig. S8) when air was in-
introduced (14). The high mechanical quality factor in vacuum, as well as the high quality factor for electronic resonance (due to the largely capacitive nature of electronic load of nanotube sheet and cables), enabled an observed ±30% oscillatory actuation to be driven at high frequency by a 10 $V_{\text{rms}}$ ac power supply (fig. S9). The trick here is to place a small inductor coil between the power supply and the nanotube sheet, where the inductance of the coil and the capacitance of the sheet and associated leads provide an electronic resonant frequency that is close to the mechanical resonance frequency of the nanotube sheet (14). The electronic resonance increased the 10 $V_{\text{rms}}$ voltage applied to the inductor to a measured 150 $V_{\text{rms}}$, which combined with mechanical resonance enhancement to provide this ±30% oscillation at 1100 Hz.

Because charge-injection-based forces act only at the sides of a conductor sheet, sheet deformation during actuation is expected to be uniform on the macroscale across sample width, as long as large sheet aspect ratio ensures that width constraints at end supports are unimportant. Optical measurements demonstrate strain uniformity in the sheet-width direction on dimensional scales where sheet mechanical properties achieve bulk values (14). The expected increase in charge density close to sheet boundaries (figs. S10 and S11) was evident from potential measurements using a Kelvin probe attached to an atomic force microscope (14).

Charge-induced actuation in the sheet thickness is much like that for sheet width: Actuator strokes in the thickness direction are also giant (~200%), and the voltage dependence of this actuation again switches from approximately a $V^2$ dependence to close to a $V^{0.5}$ dependence as applied voltage increases (Fig. 2B). A likely reason for this similarity in actuator stroke for sheet thickness and width directions is the approximate structural equivalence of these directions.

**Actuation in the sheet-length direction.**

Large-stroke actuation by expansion in sheet width during charge injection is accompanied by contraction of a few percent in sheet length, where modulus and strength are much higher than for other directions. Length-direction actuation generates an isometric specific stress of up to 4.0 MPa cm$^3$/g (corresponding to the data point for $\Delta L/L_w = 0$ and 1.6 kV in Fig. 2C). Because electrostatically generated stress is proportional to $1/H$, densification of the sheet by decrease in sheet thickness $H$ leaves the isometric specific stress unchanged. Hence, a densified sheet strip with a density of 0.8 g/cm$^3$ has an isometric stress–generation capability of 3.2 MPa, which is about 32 times as high as the maximum sustainable stress–generation capability of natural skeletal muscle (17). The actuator stroke for a specified change in applied potential decreases with increasing initially applied stress, because the Young’s modulus increases with strain, so the specific work per cycle reaches a plateau, where there is little sensitivity to the initially applied stress. The maximum achieved work per cycle (Fig. 2C, inset) is ~30 J/kg, compared with the maximum capability of ~40 J/kg for natural muscle (17).

**Actuation at extreme temperatures.**

The data in Fig. 2D show that width direction actuator stroke does not significantly change upon increasing temperature from 300 to 1365 K by resistively heating the sample. Considering the high-temperature changes and the possibility that permanent modulus changes will occur because of irreversible annealing, it is also surprising that the nanotube sheets can be repeatedly cycled between 300 K and at least 1500 K without causing substantial change in actuation at either temperature (14). Also, no change in actuator stroke was observed in going from 300 K to the lowest observation temperature (80 K).

Because essentially constant electrostatically generated stresses are acting against the elastic modulus to provide the actuator stroke, the observed near-temperature-invariant actuator stroke indicates that the nanotube sheet modulus is largely temperature independent. This is a signature of enthalphic elasticity and contrasts with the highly temperature-dependent modulus of ordinary entropic rubbers. Single MWNT and MWNT bundle rigidity explains the absence of a noticeable entropic contribution to rubber elasticity. The ~12-nm-diameter, approximately nine-wall MWNTs used have very high bending modulus, and further modulus increase results from MWNT bundling (providing an average of ~25 nanotubes in a bundle) (14). The ability of these bundles to act as rigid rods is described by the persistence length, which equals the ratio of the bending modulus to $k_B T$, where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. Assuming that walls in the MWNTs can easily slip with respect to each other, and making the same approximation for MWNTs in a bundle, a lower-limit estimate of the bending stiffness of the MWNT bundles is obtained as the product of the number of MWNTs in a bundle and the sum of the known bending stiffnesses of single nanotube walls in a MWNT (19). The thereby obtained persistence length of the MWNT bundles is so long (about a meter at 1900 K) that stress-induced change in entropy cannot appreciably contribute to rubberlike elasticity (14).

**Giant Poisson’s ratios and their effects on actuation.**

Giant Poisson’s ratios are observed, which are important both for actuation and for possible use of nanotube sheets and sheet strips for strain amplifiers. This ratio of percent lateral contraction to the percent applied tensile elongation was measured optically (14) for stretch in the length direction to provide a width-direction Poisson’s ratio of 9.5 ± 2.0 for sheet stacks with between 1 and 15 layers and strains up to 2%. The corresponding measured Poisson’s ratio in the thickness direction was even larger (15 for a 30-layer sheet stack). A similarly giant Poisson’s ratio (~12), but of opposite sign, has been observed for nanoporous polytetrafluoroethylene (20). These large Poisson’s ratios indicate that the nanotube sheets can function as previously sought strain amplifiers (21), which amplify strain over an order of magnitude without providing the added bulk and frequency limitations associated with conventional lever systems (14). Because both the width- and thickness-direction Poisson’s ratios are so large, a percent extension in the nanotube sheet direction would produce a ~23.5% decrease in sheet volume. This property of decreasing volume when stretched, called “stretch densification,” is extremely rare (22) and implies that the aerogel will have a negative linear compressibility in the length direction, meaning that it will expand in this direction when hydrostatically compressed without infiltration.

Because of the giant Poisson’s ratios for length-direction stretch, confinement of sheet length by rigid end supports substantially reduces actuation in width and thickness directions. The overall width (or thickness) change during actuation for a length-confined nanotube sheet is approximately equal to the sum of those for a two-step process: actuation in the absence of length constraint followed by applied stretch to return the length to its initial value. Correspondingly, for a 2% contraction in length for an unconfined sheet during actuation and the above Poisson’s ratios, length confinement using rigid end supports decreases actuation strain in the width and thickness direction by about 19 and 30%, respectively.

Why does the nanotube sheet contract in the length direction during charging, when repulsive interactions between injected charges are normally expected to produce expansion in all directions? The explanation has the same structural origin as the giant Poisson’s ratios for length-direction stretch. Because injected charge can freely move in the electrically conducting aerogel to eliminate internal electric fields, except very near the sheet surfaces, the actuator strokes arise from electrostatically generated tensile stresses $\sigma_L$, $\sigma_W$, and $\sigma_H$ applied in the length, width, and thickness directions, respectively (14).

The elastic compliance coefficients $S_{LH}$, $S_{LW}$, and $S_{WH}$ then provide a length direction strain of $\varepsilon_L = S_{LH}\sigma_L + S_{LW}\sigma_W + S_{WH}\sigma_H$. Because diagonal terms like $S_{LH}$ must be positive as a requirement for structural stability and $\sigma_L$ must be positive when $\sigma_L$ is electrostatically generated, the first term would produce an expansion in the length direction. Even though $\sigma_L > \sigma_W >> \sigma_H > 0$ (14), the contributions from the other terms (with $S_{LW}$ and $S_{WH}$ negative, corresponding to the observed positive Poisson’s ratios) must be sufficient to reverse the sign of $\varepsilon_L$. Support for this is provided by the giant positive observed Poisson’s ratio in width ($\nu_{WL}$) and thickness directions ($\nu_{WH}$) for length-direction stretch: $\nu_{WL} = -S_{LW}/S_{WH}$ and $\nu_{WH} = -S_{WH}/S_{WH}$. The existence of a contraction for electrostatically generated stresses implies the existence of a negative linear compressibility, because increase of the tensile stresses in the width and thickness direction to equality with $\sigma_L$ would further increase the shrinkage in the length direction for the resulting negative hydrostatic pressure.
Dopamine replacement therapy is useful for treating motor symptoms in the early phase of Parkinson’s disease (PD), but it is less effective in the long term. Electrical deep-brain stimulation is a valuable complement to pharmacological treatment but involves a highly invasive surgical procedure. We found that epidural electrical stimulation of the dorsal columns in the spinal cord restores locomotion in both acute pharmacologically induced dopamine-depleted mice and in chronic 6-hydroxydopamine–lesioned rats. The functional recovery was paralleled by a disruption of aberrant low-frequency, synchronous corticostriatal oscillations, leading to the emergence of neuronal activity patterns that resemble the state normally preceding spontaneous initiation of locomotion. We propose that dorsal column stimulation might become an efficient and less invasive alternative for treatment of Parkinson’s disease in the future.

Spinal Cord Stimulation Restores Locomotion in Animal Models of Parkinson’s Disease

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Dopamine replacement therapy is useful for treating motor symptoms in the early phase of Parkinson’s disease, but it is less effective in the long term. Electrical deep-brain stimulation is a valuable complement to pharmacological treatment but involves a highly invasive surgical procedure. We found that epidural electrical stimulation of the dorsal columns in the spinal cord restores locomotion in both acute pharmacologically induced dopamine-depleted mice and in chronic 6-hydroxydopamine–lesioned rats. The functional recovery was paralleled by a disruption of aberrant low-frequency, synchronous corticostriatal oscillations, leading to the emergence of neuronal activity patterns that resemble the state normally preceding spontaneous initiation of locomotion. We propose that dorsal column stimulation might become an efficient and less invasive alternative for treatment of Parkinson’s disease in the future.

Patients suffering from Parkinson’s disease (PD) experience chronic and progressive motor impairment (1). The main cause of PD is basal ganglia dysfunction, resulting from degeneration of neurons in the dopaminergic nigrostriatal pathway (2). Dopamine replacement therapy, through administration of the dopamine precursor 3,4-dihydroxy-L-phenylalanine (L-dopa), effectively ameliorates symptoms associated with PD and remains the treatment of choice to date (3). Unfortunately, L-dopa pharmacotherapy has proven less efficient in the long term and is associated with several complications (4). Additional therapeutic strategies, employed in conjunction with pharmacological treatment, have thus attracted considerable attention. In particular, improved techniques for electrical stimulation of the basal ganglia—referred to as deep-brain stimulation (DBS)—are effective for treatment of motor symptoms in PD (5). Furthermore, DBS permits a reduction of L-dopa dosage in PD patients (6). However, a disadvantage of DBS is the requirement of a highly invasive surgical procedure, as well as the crucial dependence on accurate targeting of very small brain structures (7). Hence, it is desirable to identify a less invasive method to electrically stimulate neuronal circuits to obtain beneficial effects similar to those of DBS.

Some clues for new PD therapies may come from epilepsy studies. In both animal models and in epileptic patients, stimulation of peripheral nerve afferents is effective in desynchronizing aberrant low-frequency neural oscillatory activity, thereby reducing the frequency and duration of seizure episodes (8–10). Aberrant low-frequency neural oscillations are well documented in patients (11, 12) and in animal models of PD (13). These findings led us to hypothesize that stimulation of different somatic pathways could alleviate motor symptoms of PD by disrupting aberrant low-frequency oscillations.

Dopamine, akinesia, and synchrony. The first set of experiments was carried out using an inducible mouse model of PD, first in wild-type animals and then in dopamine-transporter knockout (DAT-KO) mice (14). Through pharmacological inhibition of dopamine synthesis, we induced acute dopamine depletion in both types of animals (2, 13, 14). In patients, the cardinal symptoms of idiopathic PD have been reported to be clinically apparent after degeneration of 60 to 70% of the dopaminergic neurons of the substantia nigra pars compacta, which results in a 30 to 50% reduction of striatal dopamine levels (15, 16). By means of two intraperitoneal injections (250 mg/kg) of the tyrosine hydroxylase inhibitor alpha-methylpara-tyrosine (AMPT) during a 6-hour period (15, 16), we achieved acute pharmacological dopamine depletion slightly below the levels observed in PD patients in wild-type C57/BL6J mice (69% reduction of striatal dopamine levels; mean ± SD = 4.5 ± 2.0 mg dopamine per mg brain weight).

References and Notes

3. V. V. Deshpande et al., Nano Lett. 6, 1092 (2006).
14. See supporting material on Science Online.
16. Specific strength (strength normalized to density) and corresponding specific Young’s modulus and work capacity are used because of their fundamental and practical importance, as well as ease of reliable determination from force and weight-per-length measurements.
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Supporting Online Materials

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