Downsized diameter superelastic conducting fibers are needed for electronic interconnects having a strain-independent conductance, sensitive strain sensors enabling giant stroke ranges, artificial muscles, and energy storage and chemical sensing fibers whose performance is largely independent of the applied strain.\[1\] Such fibers, when used alone or inserted into elastomeric textiles, could potentially be used for such diverse applications as monitoring health during daily activities and characterizing the performance of morphing structures.\[2,3\]

We here describe the fabrication of superelastic conducting sheath–core fibers that are as thin as 40 µm, characterize the properties of these downsized sheath–core fibers, and show that they could be deployed as capacitors and sensors whose realized performance is either usefully highly sensitive or usefully insensitive to applied strains that can exceed 300%. Even when smaller in diameter than a human hair, these sheath–core fibers, which comprise a carbon nanotube sheath on a rubber core, can be reversibly stretched by 800%, while undergoing a 72-fold increase in fiber conductivity and a desirably low resistance change of 12%. The present downsizing has reduced the cross-sectional area of such strain sensors by a factor of 400, and correspondingly decreased the applied forces needed for their practical deployment by about the same amount. We show that Pt-containing carbon-nanotube-sheath, rubber-core fibers provide amperometric biosensors for glucose, whose response is insensitive to a 45% stretch, as well as supercapacitor electrodes that can be stretched 300% without significantly changing capacitance. Variants of these sheath–core fibers were woven as wires to transport current in highly uniaxially or biaxially stretched textiles, and deployed as high sensitivity, capacitance-based sensors for measuring the contraction of giant stroke artificial muscles.

While many exciting previous advances have provided highly stretchable structures for energy harvesting, energy storage, sensing, and external transmission of sensor responses,\[4–17\] most of these strategies work by embedding relatively rigid microdevices having these functionalities into an elastomeric structure.\[4,5\] Important targeted applications are for such needs as wearable devices that monitor human body fluids, like sweat, and sensor systems for morphing mechanical structures, like aircraft wings and robots.\[18–22\] For stretchable electronics applications, micrometer-scale elastic conducting fibers with high electrical conductivity, large reversible elastic strain, and high quality factor (\(Q_\text{f} = \text{percent strain/percent resistance change}\)) are desired,\[23–26\] where the percent resistance change for a given strain range is defined using the difference between maximum and minimum resistances divided by the resistance at lowest strain. Conducting elastomers have been fabricated by methods such as incorporating conducting particles in rubbers\[27–29\] or attaching sheets of conducting nanofibers\[6–9\] or graphene\[30,31\] or other conductors to the surface of a rubber sheet.\[32\] Although strains exceeding 700% have been achieved in reversible elastic fibers, their diameters are in the range of...
400–1300 µm with quality factors below 3 when strains over 500% are applied.\cite{9,10,33–36} Other approaches include filling a hollow rubber tube with liquid metal alloys, which can be stretched up to 1000% strains with large resistance change (\(Q_R \approx 0.14\)).\cite{37}

We recently demonstrated fabrication of superelastic conducting fibers by wrapping multivall carbon nanotube sheet (NTS) layers around a stretched rubber fiber, so that the nanotube direction is parallel to the rubber fiber direction, and then providing a stretch release, restretch, and stretch release process.\cite{38} The thereby formed hierarchically buckled NTS sheath–core structure can be reversibly stretched to over 10 times their initial length while maintaining resistance change as small as 5%. These sheath–core fibers have resistance quality factors as high as 421, which is 97 times higher than the previously reported values for superelastic fiber conductors.\cite{38} However, since the conducting phase of the sheath–core fibers is a few-hundred-nanometer thick NTS sheath wrapped on a large diameter (2 mm) rubber core, the overall electrical conductivity of the conducting fiber was low due to the high core-to-sheath volume ratio. Downsizing the rubber core diameter of sheath–core fibers will thus significantly increase fiber conductivity with the same NTS sheath thickness, and consequently benefit applications for stretchable electronics and smart textiles.

Small-diameter rubber fibers having uniform diameters were fabricated using a home-made apparatus for melt draw. As illustrated in Figure 1a, a cylindrical wood rod was vertically dipped into a reservoir of molten rubber and subsequently withdrawn at fast draw rate, so the attached molten polymer solidified in air during the draw to form the polymer fiber. The used rubber was a 1:5 weight ratio of a mixture of a styrene-(ethylene-butylene)-styrene (SEBS) block copolymer (Kraton, G-1651H) and a plasticizer (ExxonMobil, Marcol 82). Under the used draw rate (about 10 cm s\(^{-1}\)) and temperature of the molten polymer bath (200 °C), the diameter of the rubber fiber was linearly proportional to the depth that the wood rod was inserted into the molten rubber, as shown in Figure 1b. For example, using a rod diameter of 2.2 mm, polymer fiber diameters of 450 and 40 µm were obtained for immersion depths of 18 and 1 mm, respectively. The typical length of the rubber fibers was 15 cm. Representative metallurgical microscopic images of these thin rubber fibers are shown in the insets of Figure 1b and in Figure S1 (Supporting Information).

Like for previous work on typically 2-mm-diameter electrically conducting sheath–core fibers,\cite{38} a rubber fiber was stretched to a large strain, called the fabrication strain, wrapped with \(m\) NTS layers so that the nanotubes were oriented along the rubber core, and then the applied strain was released (Figure 1c). While restretch of the sheath–core fiber formally...
completes the needed sheath deformation processes in axial and circumference directions, a few cycles of stretch and release are useful to insure reversibility of structure and properties. Highly oriented multilwall carbon nanotube (CNT) aerogel sheets drawn from CNT forests were the NTSs used for the conductive sheaths.\textsuperscript{[39]}

The nanotubes and nanotube bundles within the CNT sheets are aligned in the nanotube draw direction. The height of the precursor CNT forest was typically ≈350 µm and the nanotubes had an outer diameter of ≈9 nm and contained ≈6 walls. The sheet resistance for a single nanotube sheet ranges from ≈700–1000 ohms per square in the draw direction, depending upon the areal density of the NTSs (which is a function of the forest height). In addition to the remarkable mechanical strength and electrical properties, the NTSs are remarkably flexible, and can be bent to below 100 µm radius. These combined novel mechanical and electrical properties of the NTSs are critical for realizing our downsized superelastic conductors.

The nomenclature NTS\textsubscript{m}@fiber\textsubscript{d} is used to denote the sheath–core structure of the elastic conducting (EC) fiber, where m is the number of NTS layers wrapped around a rubber fiber and d is the core diameter in micrometers at zero strain before attaching the sheath. The available strain range of the present small diameter electrically conducting fiber was maximized by using a fabrication strain of typically 900%, and the alignment direction of the CNTs in the NTS sheath was along the rubber fiber length.\textsuperscript{[38]} Unless otherwise indicated the fabrication strain was held constant, the average buckle period also increased, which is likely due to the increase of the NTS sheath bending force constant, relative to the stretch force constant of the rubber core, when the sheath thickness was increased. This increase of relative NTS sheath force constant relative to the stretch force constant of the rubber core, in turn, decreased the diameter of the EC fiber in the relaxed state (Figure S3, Supporting Information), reflecting the constraint on fiber circumference expansion provided by the NTS sheath during fiber contraction. For the NTS\textsubscript{m}@fiber\textsubscript{d} the ratio of the diameter of the sheath/core fiber in the relaxed state to the diameter of the precursor core fiber was 0.74, 0.66, and 0.60 for d = 200, 150, 100 µm, respectively (Figure S2, Supporting Information). Since the rubber core is volume invariant, the available strain range decreased with increasing m. The constraint on fiber belt expansion is enhanced for sheath–core fibers with small initial core diameters because of the increased NTS sheath to rubber core mass ratio. As a result, the available elastic strain range of EC fibers decreased with decreasing core diameter when the number of sheet layers was kept constant (Figure 2a).

The stretchability, structure, and electronic properties of the sheath–core fibers depend on the ratio of the fiber radius r to the sheath thickness t. This dependency results since the cross-sectional area of the core is πr\textsuperscript{2} and cross-sectional area of the sheath is π(\textit{r} + \textit{t})\textsuperscript{2} − π\textit{t}\textsuperscript{2}. In the limit where \textit{r} > t is large, which is the case for the present downsized fibers, the ratio of the core cross-section to the sheath cross-section (which is the weight ratio of the core to sheath, as well as the ratio of the core modulus to the sheath modulus) becomes \textit{r}/\textit{t}. The present downsized sheath–core fibers are not hierarchically buckled like those previously reported,\textsuperscript{[38]} because of the low ratio of sheath thickness to core diameter (which means that the sheath modulus is too low relative to the core modulus to provide the core deformation needed for the formation of long-period buckles in the axial direction).

NTS\textsubscript{m}@fiber\textsubscript{d} (for d = 200, 150, 100 µm) formed buckles along the fiber length direction. As the precursor fiber core diameter decreased in this range (Figure S2, Supporting Information), the buckles became less regular and separated by longer average interbuckle distances (3.3, 3.6, and 5 µm for d = 200, 150, 100 µm, respectively). When the number of NTS layers (m) increased, while d was held constant, the average buckle period also increased, which is likely due to the increase of the NTS sheath bending force constant, relative to the stretch force constant of the rubber core, when the sheath thickness was increased. This increase of relative NTS sheath force constant relative to the stretch force constant of the rubber core, in turn, decreased the diameter of the EC fiber in the relaxed state (Figure S3, Supporting Information), reflecting the constraint on fiber circumference expansion provided by the NTS sheath during fiber contraction. For the NTS\textsubscript{m}@fiber\textsubscript{d} the ratio of the diameter of the sheath/core fiber in the relaxed state to the diameter of the precursor core fiber was 0.74, 0.66, and 0.60 for d = 200, 150, 100 µm, respectively (Figure S2, Supporting Information). Since the rubber core is volume invariant, the available strain range decreased with increasing m. The constraint on fiber belt expansion is enhanced for sheath–core fibers with small initial core diameters because of the increased NTS sheath to rubber core mass ratio. As a result, the available elastic strain range of EC fibers decreased with decreasing core diameter when the number of sheet layers was kept constant (Figure 2a).

Figure 2a shows the dependence of R(\textit{t})/\textit{L}_{\text{max}} on tensile strain (\textit{ε}) for sheath–core NTS\textsubscript{m}@fiber\textsubscript{d} where R(\textit{t}) is the resistance at strain \textit{ε} for a fiber having a maximum stretched length of \textit{L}_{\text{max}} = \textit{L}_{\text{fab}} where \textit{L}_{\text{fab}} is the stretched length (corresponding to the fabrication strain) used for sheath wrapping. Here and elsewhere when we refer to applied strains on sheath–core fibers, the strain is the engineering strain measured with respect to the relaxed length of the sheath–core fiber, which is longer than the corresponding nondeformed rubber core. We found that the corresponding R(\textit{t})/\textit{L}_{\text{max}} monotonically increases from 16.0 to 47.2 Ω cm\textsuperscript{−1} when the rubber core diameter decreases from 250 to 100 µm for fibers having the same number of NTS layers (m = 3). This is because NTS sheath mass per length for the same NTS sheath thickness decreases with decreasing fiber diameter, resulting in an increased resistance per fiber length. Figure 2b shows the strain dependence of electrical resistance change (R(\textit{t}) − R_{\text{0}})/R_{\text{0}}, where R_{\text{0}} = R(0) for NTS\textsubscript{m}@fiber\textsubscript{d}. The maximum percent resistance change over the strain range, \textDelta R_{\text{max}}/R_{\text{0}} = (R(\text{\textit{L}_{\text{max}}}) − R_{\text{0}})/R_{\text{0}} increased with increasing fiber diameters (from 12.3% for d = 100 µm to 63.8% for d = 250 µm). This result is a consequence of structural evolution of the NTS buckling as fiber
For large fiber core diameters, the NTS sheath formed regular short-period buckling, which increases lateral contacts of the adjacent NTS buckles when strain is released, resulting in a large percentage resistance change. For small fiber core diameters, however, the observed NTS buckles were mostly irregular in shape with relatively large buckle interspacing as shown in Figure S2a in the Supporting Information, which decreased or eliminated lateral contact of adjacent NTS buckles during contraction of the sheath–core fiber.

From the electrical conductivity equation \( \sigma = L/RS \), \( \sigma = L^2/RV \), where \( S \) and \( V \) are the cross-sectional area and volume of the sheath–core fiber, respectively. During stretch, the volume of the sheath–core fiber is largely conserved, since most of the fiber volume is occupied by the rubber core and the Poisson’s ratio of the rubber core is close to 0.5. Therefore, electrical conductivity increases quadratically with fiber length increase if the fiber conductance is nearly strain independent. This remarkable increase of electrical conductivity with increasing strain is shown in Figure 2c. For example, the
conductivity of a NTS₁₀₀ fibre increased 72 times, from 2.7 to 194.7 S m⁻¹, when this fibre is stretched from 0% to 800% strain, which is three times higher than for a NTS₁₅₀ fibre (which has an electrical conductivity of 64.1 S m⁻¹ at 800% strain). Figure 2d shows the ratio of conductivities at maximum strain (εₘₐₓ) to that at 0% strain as a function of the fibre length ratio (L/L₀). The dashed line is the theoretically predicted dependence (σ/σ₀ = (L/L₀)³) for a conducting fibre with a Poisson’s ratio of 0.5, whose resistance is strain independent. Our micrometer-size NTS₁₀₀ fibres conductors show a very high conductivity increase when stretched, as compared with previous results for other types of stretchable conductors (Figure 2d). Also, all data points for our EC fibres are located in the vicinity of the theoretical dashed line, indicating small resistance change when stretched.

The quality factors (Qₚ) for our small diameter EC fibres are comparable to those for our previously reported millimeter-size EC fibres,[38] which are significantly higher than those previously reported for other elastomeric fibre conductors (Qₚ < 3 for strains over 500%).[9,10,30,33–36] As shown in Figure S4 (Supporting Information), the Qₚ for our small diameter NTS₁₀₀ fibre increased from 14.1 to 65.1 as the rubber core diameter decreased from 250 to 100 μm, and Qₚ increased from 31.8 to 44.5 as the number of NTS layers decreased from 15 to 5.

Upon decreasing fibre diameter from 250 to 100 μm, the available strain range for reversible performance decreased from 900% to 800%, the conductivity in the fully stretched state increased from 74.9 to 194.7 S m⁻¹, and the percentage resistance increase during stretch decreased from 63.8% to 12.3%. This indicates that both largely strain insensitive conductance and high conductivity could be obtained with downsizing the fibre diameter.

The conductance of the EC fibres can be increased by increasing the number of NTS layers (NTS sheath thickness). Figure S5a (Supporting Information) shows the dependence of R(ε)/Rₘₐₓ on strain (ε) for NTS₁₅₀ fibre with different m. In the relaxed state (0% strain), R(0)/Rₘₐₓ decreased from 39.0 to 6.2 kΩ cm⁻¹ when m increased from 3 to 15. The observed percent resistance change (ΔRₘₐₓ/Rₙ₀) of EC fibres over the available strain range dramatically decreased with increasing m, from 27.0% to 7.1% (Figure S5b, Supporting Information). However, the available strain range (εₘₐₓ) decreased from 900% to 320% with increasing m from 3 to 15 (Figure S5c, Supporting Information). This decrease of available strain range with increasing m is due to the constraint on fibre belt expansion provided by the NTS sheath during fibre contraction (Figure S3, Supporting Information). This effect is more profound for smaller diameter EC fibres because the mass ratio of NTS sheath to rubber core (which is proportional to d⁻¹) increases with decreasing fibre diameter when the number of sheath layers is kept constant. Increasing m decreases the resistance decrease during fibre contraction by providing an increased modulus for sheath bending, which increases the separation between sheath buckles and thereby decreases or eliminates interbuckle contact for the unstrained sheath–core fibres.

Since our micrometer-size EC fibres can be conveniently woven into insulating elastomeric textiles, they can be used as electrical conductors that function during giant textile deformations. The Figure 2e inset shows two cm-long NTS₁₀₀ fibres that were orthogonally inserted into an elastomeric textile, and the data in this figure shows that little resistance change occurred for the horizontal NTS₁₀₀ fibre during textile stretch and stretch release when a tensile strain of up to 100% was applied in either the vertical or horizontal textile direction. Movie S1 (Supporting Information) shows six parallel NTS₁₀₀ fibres that are inserted into a fishnet stocking. The fishnet fabric was attached to the surface of a rubber balloon and used to provide electrical power from a 2.7 V battery to a 50 mW light-emitting diode as the balloon was inflated with air and then deflated. The resistance of the six in-parallel-connected NTS₁₀₀ fibres (210 μm in diameter and 3 cm long at 0% strain) was 930 Ω at 0% strain and increased by only 2% when stretched by an expansion of the balloon by roughly 76% in all directions. Since the resistance change of the sheath–core fibres was too small, the LED glowed at visually constant brightness when the EC fibres were reversibly stretched and unstretched during inflation and deflation of the balloon.

The availability of these small diameter NTSₙ₀₀ fibre conductors enabled our fabrication of micrometer-size, giant-stroke capacitive strain sensors of the type NTSₙ₀₀@rubber@NTSₙ₀₀ fibres, wherein a sheath containing n NTS layers is wrapped on a rubber-coated NTSₙ₀₀ fibre. The rubber dielectric layer was deposited on the NTSₙ₀₀ fibre while this fibre was nonstretched. Like for the inner sheath, the outer sheath was applied (with nanotubes oriented parallel to the fibre core) while the fibre was highly stretched. Unless otherwise indicated, n was 10 and m was 6 for the reported devices.

As a result of downsizing fibre diameter, the force required to drive the strain sensor over a large strain range was dramatically decreased, thereby minimizing the effect of mechanical interference on measured displacements. For example, only a 1.26 mN force was needed to stretch a NTS₁₀₀@rubber@NTS₁₀₀ fibres sensor to 100% strain. As shown in Figure 3a, stretching a 4 cm-long NTS₁₀₀@rubber@NTS₁₀₀ fibre to 200% strain provided 80 mm of elongation, a 119% linear increase in capacitance, and negligible hysteresis. In contrast, large stroke resistive strain sensors show large hysteresis.[40] The linear capacitance-strain dependence, micrometer-size-diameter, and large displacement of our sheath–core–fiber sensor are important for strain sensing applications. To our knowledge, this is the smallest diameter (160 μm at 0% strain) capacitive strain sensor so far reported. Strain sensors capable of measuring large displacements are sought for applications ranging from monitoring the motions of morphing microair vehicles and robots to characterize the displacements of large stroke artificial muscles.[41]

Approximating the rubber to be incompressible and the dielectric permittivity (εₖ) to be strain independent, the equation for the capacitance of a coaxial capacitor (C = 2πεₖL/ln(a/b), where L is the length of the fibre and a and b are the diameters of the inner and outer electrodes) predicts that ΔC/𝐶₀ = ΔL/L₀, where the subscripts indicate zero strain values.[38] Although the observed slope (ΔC/𝐶₀)/(ΔL/L₀) is constant, this slope of 0.6 deviates from theoretical predicted value of 1 (Figure 3a).[38] which might be a consequence of either nonuniform thickness of the dielectric layer or a strain
dependence of dielectric permittivity. This approximation that the rubber is incompressible is consistent with the observation that the SEBS polymer has a Poisson’s ratio of close to 0.5. Hence, the strain sensitivity of capacitance results from a decrease in the thickness of the capacitive SEBS layer with increasing stretch, so to maintain the volume of this layer. Although a dependence of fiber resistance on stretch would affect the RC time of the capacitor, it would not affect the strain dependence of capacitance.

This large percent change of fiber capacitance during elongation and its linear dependence on strain for this 160-µm-diameter strain sensor is complemented by cycle-independent values of ΔC/C₀ for the investigated thousands of identical stretch-release cycles. Figure 3b shows the percent capacitance changes during stretch-release cycles from 0% to 40%, 0% to 70%, and 0% to 100% strain vary over the 1000 to 5000 cycles by a standard deviation of only 0.38%, 0.27%, and 0.07%, respectively, indicating the exceptional reversibility of our downsized sheath–core strain sensors. A “step-and-hold” experiment of stretching a fiber sensor to a desired strain value, and keeping it at this strain for ten seconds before strain release, showed that the obtained capacitance change accurately reflected the applied strain, independent of the path used to reach this strain or the cycle number (Figure 3b and Figure S6a, Supporting Information). The used 160 µm-diameter, 4 cm-long strain sensor was then subjected to progressively increased strains from 1% to 105%, as shown in Figure S6b (Supporting Information). The sharp changes in capacitance during fast fiber stretch and release indicate that the strain sensor is sensitive to strain changes of below 1% (0.4 mm stretch). Another benefit of these downsized strain sensors is their low RC times, corresponding to the product of fiber resistance (R) and fiber capacitance (C), which enables fast strain measurements. Even in the highly stretched state, where the capacitance per length is highest, the above 160-µm-diameter, 4-cm-long strain sensor has a RC time of only about 0.3 µs.

Real-time actuation measurements for giant-stroke artificial muscles have been challenging, since the displacement range of commercial material-based strain sensors is short and the force needed to deform the strain sensor can easily be much larger than needed to deform a small diameter muscle. Conventional approaches that we have used include video cameras and contactless magnetic and laser-based displacement sensors. While a high-speed video camera can accurately record muscle displacement versus time, subsequent frame-by-frame analysis is needed to translate the video recording to strain versus time data. Although magnetic and laser displacement sensors can provide real-time data on actuation, they are more expensive
than material-based sensors and can be limited in measurable displacement range.

Our large-stroke sheath–core-fiber strain sensors with a micrometer-sized diameter offer a convenient means to provide real-time strain measurements over large displacement ranges without significantly perturbing muscle stroke. We demonstrated this application by attaching our fiber strain sensor to a twisted and coiled, thermally powered artificial muscle made from 230-µm-diameter nylon-6,6 fishing line, which can generate large tensile contractions (and a displacement of 12 mm). A sheath–core-fiber strain sensor was tethered to one end of the polymer artificial muscle and kept under tension between a load and a fixed end, so that both contraction and expansion of the muscle could be measured (Figure 3d inset). A capacitance meter was used to collect the data, while tensile actuation was also monitored using a video camera. When the polymer muscle was electrothermally heated by a copper wire wrapped around the muscle, tensile actuation providing 16.9% stroke and 12 mm displacement were observed. As shown in Figure 3d, the real time data from the capacitive sensor agrees with the data obtained by analysis of the movie frames recorded by a video camera.

The above described insensitivity of the resistance of micrometer-size diameter sheath–core fibers to giant applied strain motivated the following investigation of their suitability as electrochemical supercapacitors and chemical sensors whose targeted performance is similarly independent of applied strain. The argument that led to this new category of possible applications is as follows. The invariance of fiber resistance to applied strain results from the buckled fiber sheath acting like a cylindrical Chinese lantern made from conducting paper. Until the buckles contact at the final stage of strain release, the end-to-end resistance does not significantly depend upon strain, since the path length that the electronic carriers must transverse in largely strain independent and bend radii associated with buckling are so large (compared with MWNT bundle diameters) that they little affect electronic transport within bundles.

So that performance comparisons could be provided, we used the same electrochemical electrodes for investigation of the effect of strain on electrochemical capacitance and on the current output of an amperometric sensor for glucose. These platinum-containing NTS₅@fiber₁₅₀ electrodes were made the same way as described for the Pt-free electrodes, except that the utilized MWNT sheet layers were coated by ion sputtering with 50 nm of Pt before sheet stacking and wrapping to make the sheath (Figure S7, Supporting Information). A Pt counter electrode was used for all experiments and the aqueous electrolytes used for capacitance and glucose sensor measurements were 1.0 M Na₂SO₄ and 0.10 M phosphate buffer saline (PBS, pH 7.5, containing various concentrations of glucose), respectively. The nonstretched Pt-containing NTS₅@fiber₁₅₀ electrode has a diameter of 220 µm and an electrochemical capacitance of 20 F g⁻¹, based on the weight of the fiber sheath and included Pt, and we will show that stretching little changes this capacitance. As shown in Figure 59 in the Supporting Information, the Pt-containing NTS₅@fiber₁₅₀ electrode also provides high rate performance and at least thousands of highly reversible cycles. However, addition of the platinum does decrease the maximum strain to failure (from 700% for a neat NTS₅@fiber₁₅₀ to 300% for a platinum-containing NTS₅@fiber₁₅₀).

The cyclic voltammetry (CV) curves for this sheath–core electrode were remarkably insensitive to strain over an applied tensile strain range between 0% and 300%, with the CV curves for 100% to 300% strain nearly coincident (Figure 4a). The capacitance change over the 0% to 300 % range is only 5% (Figure 4b inset), and most of this capacitance increase (3%) occurs on going from 0% strain to 100% strain. This increased sensitivity to strain in the low strain region (whose effect is likely much closer to 0% strain than 100% strain) is a predicted consequence of interbuckle contact that increases the effective diffusion distance in the sheet to electrochemically access internal surface area and to sheath densification caused by interbuckle contact, which also reduces access to sheath surface area.

Remarkable elastomeric supercapacitors have also resulted from the pioneering work of the Dai and co-workers and Peng and co-workers.[⁸,¹⁰] Dai and co-workers fabricated an elastomeric electrochemical supercapacitor by wrapping CNT sheets around two elastic polymer fibers, overcoating the CNT covered fibers with poly(vinyl alcohol)/H₃PO₄ hydrogel, and then plying together the resulting fiber electrodes.⁶ The produced supercapacitors could be stretched up to 350% strain and had a capacitance (based on the weight of the bare CNT wrapped

![Figure 4](https://www.advmat.de)
Most importantly, since the present goal is to make a glucose sensor that is strain insensitive (rather than one in which other sensor characteristics are optimized), the results of Figure 4c show that the current response at a given glucose concentration is essentially unchanged when the Pt-containing NTS@fiber150 is stretched by 45%. However, further stretch from 45% to 100% strain does effect sensor current response (by significantly increasing the percent range in current response from about 0.6% for the 0% to 45% strain range to 8.4% for the 0% to 100% strain range). Fortunately, the need for strain-independent biosensors (such as wearable sensors in clothing textiles that detect the components of sweat) are unlikely to be ever subjected to tensile strains of above 45%. Additionally, Figure 4c shows that the detection limit for glucose is below 0.66 × 10⁻³ M and the sensor response at such low glucose concentrations is little changed even when 100% strain is applied.

Focusing on the likely applications-relevant strain range of 45% or below, the quality factor (Qgs) for amperometric glucose sensing (where Qgs is the percent tensile strain normalized to the percent current change resulting from tensile elongation) is above 47 for a strains increase from 0% to 45%. No literature results are provided for comparison with these figures of merit, since we could not find a previously reported glucose sensor (or any other amperometric biosensor or chemical sensor) that can deform to provide large strains without failing. The obtained strain insensitivity of this sheath–core electrode for glucose sensing up to 45% strain encourages the development of more generally applicable amperometric chemical sensors based on similarly structured sheath–core fibers.

The present work has demonstrated that sheath–core fibers can provide a sensitive amperometric biosensor for glucose, whose response is insensitive to a 45% stretch, as well as supercapacitor electrodes that can be stretched 300% without significantly changing capacitance. We have shown that these sensing and energy storage fibers, as well as sheath–core fibers for electronic interconnects, can be downsized to micrometer-scale diameters. Hence, long fiber lengths can be woven into even extremely fine denier elastomeric textiles to provide sensor outputs and energy storage capabilities that are strain independent. Using appropriate biocatalysts and redox mediators, as already demonstrated for high-power-output glucose fuel cells based on wearable (but largely nonelastic) carbon nanotube yarns that are operated in human serum, a textile woven sheath–core fiber could become the power source for charging a woven sheath–core-fiber-based supercapacitor, for subsequent antennae-based transmission of the sensor output. On a much more easily realized application level, the presently demonstrated downsized capacitance-based sensors provide a convenient means to measure large deformations of a morphing structure, while negligibly effecting structural morphing.

**Experimental Section**

Fabrication of Sheath–Core Fibers with Micrometer Range Diameters: The rubber used for the fiber core, as well as the dielectric layer separating the two NTS layers for NTS@rubber@NTS@@fiberN was SEBS block copolymer (Kraton, G-1651H), which was mixed with a plasticizer...
Fabrication of Downized Sheath–Core Fibers and Capacitive Strain Sensors: The process\(^{[36]}\) for making an NTS\(_{5}\)@fiber\(_{4}\) is illustrated in Figure 1c. First, a rubber core fiber was stretched to 900% strain (the fabrication strain) and tethered on the spindles of two motors. Freestanding NTS layers were then applied on the stretched rubber core using a U-shaped frame mounted on a translation stage. To attach the NTS onto the rubber fiber, the motors synchronously rotated the stretched rubber fiber. The NTS was contacted with the rotating rubber fiber, so it was wrapped like a jelly roll onto the fiber. Importantly, the CNT alignment direction was in the length direction of the rubber fiber. The number of NTS layers \(m\) was controlled by counting the number of turns of the rubber fiber. After NTS wrapping, ethanol (98%) was used to densify the NTS layers onto the rubber fiber core. After drying in air, the strain on the stretched rubber fiber was slowly released to form the nonstretched NTS\(_{5}\)@fiber\(_{4}\). Unless otherwise indicated, all stresses and strains mentioned are engineering values. To fabricate a capacitive strain sensor, a layer of SEBS elastomer solution in cyclohexane (5 wt%) was coated onto a nonstretched NTS\(_{5}\)@fiber\(_{4}\) using an air spray gun. After the SEBS layer was dried (to provide \(10 \mu m\) layer thickness), the sheath–core fiber was stretched to the same strain as the fabrication strain of the NTS\(_{5}\)@fiber\(_{4}\) and then \(n\) NTS layers were wrapped onto the sheath–core–fiber surface (with CNT alignment direction parallel to the fiber direction) to form a NTS\(_{5}\)@rubber@NTS\(_{n}\)@fiber\(_{4}\) coaxial structure. The NTS layers were then densified using ethanol. After air drying of the ethanol, the prestrain of the fiber was released.

Microscopy and Resistance and Capacitance Measurements: SEM images were obtained on a Nova NanoSEM450 field emission scanning electron microscope. A metallurgical microscope (NMM-800TRF) was used to measure the diameter and to characterize the surface morphology of the thin rubber core fibers. The electrical resistance of the EC fibers was obtained by two-probe resistance measurements using a Keithley SourceMeter (2400). Capacitance was measured using a capacitance meter (BK precision 810 C).

Electrochemical Measurements: The Pt-coated NTS was prepared by ion sputtering 50 nm of Pt on freestanding NTS. The Pt-containing NTS\(_{5}\)@fiber\(_{350}\) electrodes used for electrochemical measurements were pretreated by cycling between 0 and 1 V (vs \(3 \mu m\) Ag/AgCl) at 100 mV s\(^{-1}\) for two hours in 1.0 M Na\(_2\)SO\(_4\) solution. The amperometric experiments for the glucose sensor, which used a Pt wire reference electrode, were conducted in 0.1 M PBS buffer (\(pH = 7.5\)) electrolyte by applying 0.35 V (vs the SCE reference electrode). A magnetic stirrer was used to provide convective transport during glucose introduction and amperometric measurements of glucose concentration, which were obtained. The sensor response was the current measured 30 s after glucose addition.

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

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[1] H. J. Chung, M. S. Sulkin, J. S. Kim, C. Goudeseune, H. Y. Chao, J. W. Song, S. Y. Yang, Y. Y. Hsu, R. Ghaffari, I. R. Efimov, Adv. Healthcare Mater. 2014, 3, 59.
[2] F. J. Bandodkar, J. Wang, Trends Biotechnol. 2014, 32, 363.
[3] E. Gibney, Nature 2015, 528, 26.
[4] J. A. Rogers, T. Someya, Y. Huang, Science 2010, 327, 1603.
[5] S. Park, M. Vosguerichian, Z. Bao, Nanoscale 2013, 5, 1727.
[6] L. Liang, L. Li, X. Niu, Z. Yu, Q. Pei, Nat. Photonics 2013, 7, 817.
[7] F. Xu, Y. Zhu, Adv. Mater. 2012, 24, 5117.
[8] T. Chen, R. Hao, H. Peng, L. Dai, Angew. Chem., Int. Ed. 2015, 54, 618.
[9] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-Najafabadi, D. N. Futaba, K. Hata, Nat. Nanotechnol. 2011, 6, 296.
[10] Z. Zhang, J. Deng, X. Li, Z. Yang, S. He, X. Chen, G. Guan, J. Ren, H. Peng, Adv. Mater. 2015, 27, 356.
[11] X. Xiao, T. Li, P. Yang, Y. Gao, H. Jin, W. Ni, W. Zhan, X. Zhang, Y. Cao, J. Zhong, ACS Nano 2012, 6, 9200.
[12] Z. Niu, H. Dong, B. Zhu, J. Li, H. H. Hng, W. Zhou, X. Chen, S. Xie, Adv. Mater. 2013, 25, 1058.
[13] B. Xie, C. Yang, Z. Zhang, P. Zou, Z. Lin, G. Shi, Q. Yang, F. Kang, C. P. Wong, ACS Nano 2015.
[14] M. Mecklenburg, W. A. Hubbard, E. White, R. Dhall, S. B. Cronin, S. Aloni, B. Regan, Science 2015, 347, 629.
[15] M. Park, J. Im, M. Shin, Y. Min, J. Park, H. Cho, S. Park, M. B. Shim, S. Jeon, D. Y. Chung, Nat. Nanotechnol. 2012, 7, 803.
[16] S. J. Kim, Y. S. Kim, C. K. Yoon, V. Sundaram, R. Tummala, presented at Electronic Components and Technology Conference (ECTC), San Diego, CA, USA, May 2015.
[17] W. Zeng, L. Shu, Q. Li, S. Chen, F. Wang, X. M. Tao, Adv. Mater. 2014, 26, 5310.
[18] V. F. Curto, C. Fay, S. Coyle, R. Byrne, C. O’Toole, C. Barry, S. Hughes, N. Moyna, D. Diamond, F. Benito-Lopez, Sens. Actuators, B 2012, 171, 1327.
[19] L. Q. Rong, C. Yang, Q. Y. Qian, H. Xia, Talanta 2007, 72, 319.
[20] H. Kudo, T. Sawada, E. Kazawa, H. Yoshida, Y. Iwasaki, K. Mitsubayashi, Biosens. Bioelectron. 2006, 22, 558.
[21] J. R. Windmiller, J. Wang, Electroanalysis 2013, 25, 29.
[22] T. Someya, Y. Kato, T. Sekitani, S. Iba, Y. Noguchi, Y. Murase, H. Kawaguchi, T. Sakurai, Proc. Natl. Acad. Sci. USA 2005, 102, 12321.
[23] D. Zou, Z. Lv, X. Cai, S. Hou, Nano Energy 2012, 1, 273.
[24] M. Chappell, R. Robinet, E. M. Costello, J. Frei, US 8726534, 2014.
[25] M. Stals, S. Verhoeven, M. Bruggeman, V. Pellens, W. Schroeyers, S. Schreurs, J. Environ. Radioact. 2014, 127, 56.
[26] H. H. Kim, R. Ghaffari, N. Lu, J. A. Rogers, Annu. Rev. Biomed. Eng. 2012, 14, 113.
[27] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, T. Someya, Nat. Mater. 2009, 8, 494.
[28] K. Y. Chun, Y. Oh, J. Rho, J. H. Ahn, Y. J. Kim, H. R. Choi, S. Baik, Nat. Nanotechnol. 2010, 5, 853.
[29] Y. Kim, J. Zhu, B. Yeom, M. Di-Prima, X. Su, J. G. Kim, S. J. Yoo, C. Uher, N. A. Kotov, Nature 2013, 500, 59.
[30] J. Zang, S. Ryu, N. Pugno, Q. Wang, Q. Tu, M. J. Buehler, X. Zhao, Nat. Mater. 2013, 12, 321.
[31] T. Chen, Y. Xue, A. K. Roy, L. Dai, ACS Nano 2013, 8, 1039.
[32] Y. Sun, W. M. Choi, H. Jiang, Y. Y. Huang, J. A. Rogers, Nat. Nanotechnol. 2006, 1, 201.
[33] C. S. Boland, U. Khan, C. Backes, A. O’Neill, J. McCauley, S. Duane, R. Shanker, Y. Liu, I. Jurewicz, A. B. Dalton, ACS Nano 2014, 8, 8819.
[34] P. Lee, J. Ham, J. Lee, S. Hong, S. Han, Y. D. Suh, S. E. Lee, J. Yeo, S. S. Lee, D. Lee, Adv. Funct. Mater. 2014, 24, 5671.
[35] M. K. Shin, J. Oh, M. Lima, M. E. Kozlov, S. J. Kim, R. H. Baughman, Adv. Mater. 2010, 22, 2663.
[36] U. H. Shin, D. W. Jeong, S. M. Park, S. H. Kim, H. W. Lee, J. M. Kim, Carbon 2014, 80, 396.
[37] S. Zhu, J. H. So, R. Mays, S. Desai, W. R. Barnes, B. Pourdeyhimi, M. D. Dickey, Adv. Funct. Mater. 2013, 23, 2308.
[38] Z. Liu, S. Fang, F. Moura, J. Ding, N. Jiang, J. Di, M. Zhang, X. Lepró, D. Galvão, C. Haines, N. Yuan, S. Yin, D. Lee, R. Wang, H. Wang, W. Lu, C. Dong, R. Zhang, M. Chen, Q. Yin, Y. Chong, R. Zhang, X. Wang, M. Lima, R. Ovalle-Robles, D. Qian, H. Lu, R. Baughman, Science 2015, 349, 400.
[39] M. Zhang, S. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson, R. H. Baughman, Science 2005, 309, 1215.
[40] C. Mattmann, F. Clemens, G. Tröster, Sensors 2008, 8, 3719.
[41] C. S. Haines, M. D. Lima, N. Li, G. M. Spinks, J. Foroughi, J. D. Madden, S. H. Kim, S. Fang, M. J. de Andrade, F. Göktepe, Science 2014, 343, 868.
[42] S. P. Lacour, J. Jones, S. Wagner, T. Li, Z. Suo, Proc. IEEE 2005, 93, 1459.
[43] M. M. Engelgau, K. Narayan, W. H. Herman, Diabetes Care 2000, 23, 1563.