Stretchable, Porous, and Conductive Energy Textiles

Liangbing Hu,† Mauro Pasta,† Fabio La Mantia,† LiFeng Cui,† Sangmoo Jeong,† Heather Dawn Deshazer,† Jang Wook Choi,† Seung Min Han,† and Yi Cui†,*

†Department of Materials Science and Engineering and ‡Department of Electrical Engineering, Stanford University, Stanford, California 94305

ABSTRACT Recently there is strong interest in lightweight, flexible, and wearable electronics to meet the technological demands of modern society. Integrated energy storage devices of this type are a key area that is still significantly underdeveloped. Here, we describe wearable power devices using everyday textiles as the platform. With an extremely simple “dipping and drying” process using single-walled carbon nanotube (SWNT) ink, we produced highly conductive textiles with conductivity of 125 S cm\(^{-1}\) and sheet resistance less than 1 \(\Omega/\text{sq.}\) Such conductive textiles show outstanding flexibility and stretchability and demonstrate strong adhesion between the SWNTs and the textiles of interest. Supercapacitors made from these conductive textiles show high areal capacitance, up to 0.48 F/cm\(^2\), and high specific energy. We demonstrate the loading of pseudocapacitor materials into these conductive textiles that leads to a 24-fold increase of the areal capacitance of the device. These highly conductive textiles can provide new design opportunities for wearable electronics and energy storage applications.

KEYWORDS Energy storage, textile, carbon nanotube, supercapacitor

We arable electronics represent a developing new class of materials with an array of novel functionalities, such as flexibility, stretchability, and lightweight, which allow for many applications and designs previously impossible with traditional electronics technology. High-performance sportswear, wearable displays, new classes of portable power, and embedded health monitoring devices are some examples of these novel applications. Recently there is strong interest in lightweight, flexible, and wearable electronics to meet the technological demands of modern society. Integrated energy storage devices of this type are a key area that is still significantly underdeveloped. Here, we describe wearable power devices using everyday textiles as the platform. With an extremely simple “dipping and drying” process using single-walled carbon nanotube (SWNT) ink, we produced highly conductive textiles with conductivity of 125 S cm\(^{-1}\) and sheet resistance less than 1 \(\Omega/\text{sq.}\) Such conductive textiles show outstanding flexibility and stretchability and demonstrate strong adhesion between the SWNTs and the textiles of interest. Supercapacitors made from these conductive textiles show high areal capacitance, up to 0.48 F/cm\(^2\), and high specific energy. We demonstrate the loading of pseudocapacitor materials into these conductive textiles that leads to a 24-fold increase of the areal capacitance of the device. These highly conductive textiles can provide new design opportunities for wearable electronics and energy storage applications.

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* To whom correspondence should be addressed. E-mail: yicui@stanford.edu.

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SWNTs wrapping around cellulose fibers to create a 3D porous structure. To realize such structure, a ink with well-dispersed SWNTs is prepared by dispersing 1.6 mg/mL laser ablation tubes in water with 10 mg/mL sodium dodecylbenzenesulfonate (SDBS) as surfactant. Then a textile is dipped into the black SWNT ink. Because of the strong absorption, the textile is quickly coated by the SWNT ink. The textile with SWNT ink is subsequently dried in oven at 120 °C for 10 min to remove water. A highly conductive textile is achieved through this simple dipping and drying process. Textiles investigated in this study include cotton sheet (Figure 1a) and woven polyester fabric (see Supporting Information). Figure 1c shows a conductive fabric with sheet resistance ($R_s$) of $\sim 4 \Omega$/sq. These highly conductive textiles retain their texture and structure after SWNT coating and feel the same as the original material. This fabrication process can be easily applied to other ink made of nanostructured materials and scaled up with roll-to-roll techniques using slot-die or curtain coating processes. SEM images of Figure 1d,e reveal the macroporous structures of a cotton sheet and a fabric, respectively. Conformal coating of SWNTs onto the fibers was observed for both the cotton and the fabric (Figure 1f). This conformal coating is a result of the mechanical flexibility of individual SWNTs and the strong binding energy between SWNTs and the cotton fibers and accounts for the high conductivity of the textile. Previous studies have shown that SWNT films have microscale porosity, which is required to maximize the electrical double layer capacitance. The microporous structure on top of the macroporous textile leads to what we call a double porous structure. Such double porous structures facilitate the easy access of electrolyte ions to the SWNTs, which is essential for high power SC applications. TEM images taken on SWNT-cotton fiber hybrids (Figure 1g) show the SWNTs are well bonded to the fiber and forming cross-linked networks, which provide conducting pathways.

Such porous textile conductors demonstrate excellent electrical, mechanical, and chemical resistance performance. Figure 2a shows that the conductance increases as the dipping number in SWNT ink increases. The $R_s$ difference for cotton and fabric with different dipping number is due to the SWNT ink absorption difference for cotton and fabric per area (Supporting Information, Figure S1). Soaking the conductive cotton sheets in 4 M nitric acid for 30 min followed by blowing dry can wash away the surfactant molecules and induce hole doping, which resulted in decrease of their $R_s$ by approximately three times. The thickness of cotton sheets decreases from $\sim 2$ mm to $\sim 80 \mu$m with mechanical pressing, which changes the electrical conductivity from 5 to $\sim 125$ S/cm. Conductive textiles with a large range of conductance could be achieved by tuning the SWNT ink concentration and dipping number.

The conductive textiles show outstanding mechanical properties, that is, strong binding between SWNTs to the
textile, foldability, and stretchability. The mechanical adhesion tests for SWNTs to cotton by the standard tape test and by washing in water show no visible nanotubes in the solution, or on the tape, and no conductivity degradation of the sample. In the water-washing test, the conductive cotton is soaked in water, then squeezed and wrung out. SWNTs stick well to the cotton without peeling or dissociating and precipitating in water. (Supporting Information, Figure S3b). These tests suggest that SWNTs adhere very strongly to the cotton fibers, which is critical for wearable electronic and power devices. Such strong binding may be due to the following reasons: (1) Large van der Waals forces and hydrogen bonding exist between SWNTs and the textile fibers.14 (2) The flexibility of SWNTs allow them to be conformally adhered to the surface of cotton fibers which maximize the surface contact area between SWNTs and textile fibers.19 The superior mechanical adhesion of SWNTs on cotton is essential for high-speed roll-to-roll fabrication and energy storage device stability. To test the stretchability, the resistance of a fabric sample with a dimension of 2.5 cm × 7 cm e-Fabric is monitored as it is being loaded in tension using a tensile tester. More detailed information can be found in the Supporting Information. In contrast to stretchable conductors reported by others7,20,21 in which the conductivity decreases with stretching, as our SWNT-fabric is stretched, the conductance increases. It is remarkable that the conductance keeps increasing until the strain reaches a value of 140%, that is, the fabric is stretched to 2.4 times of its original length. This increase in conductance is due to the improvement of the mechanical contacts between fabric fibers, which leads to the better electrical contacts for SWNTs. As the strain increases further, the conductance starts to decrease, which is likely due to severe inhomogeneous deformation at large strains, as well as the reduced cross sectional area. Such stretchability of conductive textile could enable various stretchable electronic devices.30 Fibers in cotton and fabric, as well as SWNTs, are known to be resistant to acid, base, and organic solvents.22 Therefore, conductive textiles should also show the same chemical resistance. Figure 2d shows the Rs for e-Cotton after being exposed to water washing, thermal treatment at 200 °C for 6 h, 4 M HNO3 acid for 30 min, and 2 M KOH for 50 min, respectively. Only 2 M KOH slightly increases the Rs of conductive cotton, while the others actually decrease the Rs possibly due to removing the surfactant or doping the nanotubes.16–18 The chemical stability of the e-Textile allows a wide range of operations of energy storage devices when the porous textile conductor is used.

**Porous Textile Conductor for Energy Storage.** Porous textile conductor with SWNT coating was tested as both active charge storage electrodes and current collectors in SCs. Figure 3a shows the schematic drawing of the SC tested, where 1 M LiPF6 electrolyte is used. The porous structure of conductive cotton facilitates the access of electrolyte to SC

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**FIGURE 2. Properties of textile conductors.** (a) Sheet resistance of fabric and cotton sheet after SWNT coating, which shows the same values on both faces for either fabric or cotton. The sheet resistances decrease by a factor of approximately 3 after HNO3 treatment. (b) Excellent mechanical properties of conductive textile, that is, strong adhesion between SWNTs and textile (passing the scotch tape test), foldable, and stretchable. (c) The SWNT-coated textiles show unusual stretching properties. The film sheet resistance decreases as the SWNT/fabric is stretched up to 240% of its initial length, after which the resistance starts to increase. (d) SWNT/cotton is resistant to water washing, thermal treatment at 200 °C for 6 h, 4 M HNO3 acid, and 2 M KOH.
electrode materials, that is, SWNTs. We tested the SC performance under galvanostatic cycling with a variety of currents (Figure 3b). The linear voltage–time profile confirms the charging and discharging of the SCs. To evaluate the advantage of using porous textiles over flat plastic substrates, SCs were assembled and tested with a SWNT loading of 0.24 mg/cm² on a cotton sheet and on a polyethylene terephthalate (PET) substrate. The specific capacitance of SC with porous textiles is around 2–3 times better than that with PET substrates in the range of current density 20 µA/cm² to 20 mA/cm² (Figure 3c). Values of 140 F/g at 20 µA/cm² and 80 F/g at 20 mA/cm² are achieved in our conducting textiles, which are comparable to the highest specific capacitance achieved with SWNTs as electrode material. The higher SC capacitance with SWNTs on textile is likely due to its better ion access in the porous structure. We also use the porous structure to load SWNTs with high mass in our SCs, up to 8 mg/cm². The areal capacitance increases with the areal mass (Figure 3d). Compared with the reported values using SWNT electrodes in literature, our SCs reached much higher areal mass loading and areal capacitance with respect to the geometric area of the device. Our devices achieve an areal capacitance equal to 0.48 F/cm², the highest value reported for SWNTs and close to commercial values.

Gravimetric energy density and power are important parameters for SCs in large-scale energy storage. Heavy metal strips are widely used as current collectors in commercial SCs. We tested the SC performance under galvanostatic cycling with a variety of currents (Figure 3b). The linear voltage–time profile confirms the charging and discharging of the SCs. To evaluate the advantage of using porous textiles over flat plastic substrates, SCs were assembled and tested with a SWNT loading of 0.24 mg/cm² on a cotton sheet and on a polyethylene terephthalate (PET) substrate. The specific capacitance of SC with porous textiles is around 2–3 times better than that with PET substrates in the range of current density 20 µA/cm² to 20 mA/cm² (Figure 3c). Values of 140 F/g at 20 µA/cm² and 80 F/g at 20 mA/cm² are achieved in our conducting textiles, which are comparable to the highest specific capacitance achieved with SWNTs as electrode material. The higher SC capacitance with SWNTs on textile is likely due to its better ion access in the porous structure. We also use the porous structure to load SWNTs with high mass in our SCs, up to 8 mg/cm². The areal capacitance increases with the areal mass (Figure 3d). Compared with the reported values using SWNT electrodes in literature, our SCs reached much higher areal mass loading and areal capacitance with respect to the geometric area of the device. Our devices achieve an areal capacitance equal to 0.48 F/cm², the highest value reported for SWNTs and close to commercial values.

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mercial SCs, with lightweight plastic and paper substrates emerging as their replacements.\textsuperscript{15,23,24,26} The reported energy density and power density for SWNT electrodes in literature normally only includes the mass of SWNT, which is only $\sim 4 \text{--} 10\%$ of the total weight of the device.\textsuperscript{23} Because of the lightweight of cotton at $\sim 12 \text{ mg/cm}^2$, and the high mass loading of SWNTs allowed by the porous structure of cotton, the weight percentage of SWNTs in our full device is up to $\sim 30\%$. In the Ragone plot (Figure 3e), the mass of electrode materials ($\sim 16 \text{ mg/cm}^2$), the cotton ($\sim 24 \text{ mg/cm}^2$), electrolyte ($\sim 6 \text{ mg/cm}^2$), and separator ($\sim 2 \text{ mg/cm}^2$) are all included in our complete SC device. The reference data indicated by the blue dot is by Niu et al.,\textsuperscript{27} which is also based on the total mass of the full SC. Our SCs have $> 10$ times higher specific energy than both SCs on metals and commercial SCs at the same specific power. For example, the specific energy reaches a high value of 20 Wh/kg at a specific power of 10 kW/kg. The specific power can be further improved by reducing the overall resistance down to $\sim 0.1 \Omega$\textsuperscript{28} through means of coating the textiles with even more conductive inks, such as inks that incorporate small amount of metal nanowires. Our textile SC devices show also extremely good cycling stability with only 2\% variation and change in capacitance over a remarkably large cycle number of 130 000 cycles (Figure 3f). The initial increase of the specific capacitance upon cycling is likely due to the improvement in wetting of the SWNTs by the electrolyte. This cycling performance meets the requirements for commercial applications.\textsuperscript{29} By using stretchable fabric sheets, instead of cotton sheets, as both the electrode substrates and the separator (Figure 3g), we were able to fabricate a fully stretchable SC. Figure 3h displays the specific capacitance of for a SC before and after being stretched up to 120\% strain 100 times. The mass loading of SWNT is 0.24 mg/cm\textsuperscript{2} and the specific capacitance for the stretchable SC is 62 F/g at 1 mA/cm\textsuperscript{2}. We observed no change in the specific capacitance after stretching. The stretchable SCs show high Coulomb efficiency ($> 99\%$) and good cycling stability, <6\% decrease after 8000 cycles, which could be improved with better device sealing. Our stretchable SCs are attractive for powering the emerging stretchable or wearable electronics.\textsuperscript{20}

One approach to further increase the specific energy of SWNT SCs is to incorporate pseudocapacitor materials such as MnO\textsubscript{2}, RuO\textsubscript{2} or conducting polymers.\textsuperscript{30,31} These pseudocapacitor materials have high reversible specific capacitance.

FIGURE 4. Loading pseudocapacitor or battery materials in porous conductor. (a) Schematic drawing of electrodeposition of MnO\textsubscript{2} onto the SWNT coated textile fibers. Due to the porous structure, the MnO\textsubscript{2} particles are coated on all the textile fibers including those in the interior of the textile. (b) A photo of MnO\textsubscript{2}-coated SWNT/Cotton. (c) SEM of a top view of conductive textile after MnO\textsubscript{2} coating. (d) SEM of cotton fibers inside the textile after peeling the fiber layers apart, which shows that the MnO\textsubscript{2} nanoparticles coated the fibers in the interior of the textile, not just the surface layers. (e) High-magnification SEM image showing the flower structure of MnO\textsubscript{2} particles on SWNTs. (f) Charge-discharge of aqueous SC with SWNT/cotton electrodes and 2 M Li\textsubscript{2}SO\textsubscript{4} as the electrolyte with current of 20 $\mu$A/cm\textsuperscript{2}. The areal capacitance increases by 24-fold after MnO\textsubscript{2} deposition. (g) Specific capacitance of SWNT/cotton with and without MnO\textsubscript{2} for different discharge current densities. (h) Cycling stability of a SC with SWNT-MnO\textsubscript{2} nanoparticles and porous textile conductor.
Previously, pseudocapacitor materials were either mixed with SWNTs, which significantly decreases the film conductivity, or coated on the surface of SWNTs but with only very small mass loading, ~0.03–0.2 mg/cm² to maintain good electrical contact with SWNTs. In our case, as shown in the schematic in Figure 4a, MnO₂ was uniformly electrodeposited on the SWNTs. This was effective in significantly increasing the mass loading of the pseudocapacitor, while maintaining contact between SWNTs and providing a good electrical conduction path. MnO₂ was deposited along the conducting path which allowed intrinsically good contact with the SWNTs. Here the conductive cotton was utilized without mechanical pressing to take advantage of its open structure (Figure 4b). The open structure of cotton allows excellent deposition of the MnO₂ conformally along the fibers (Figure 4a, d, and e). The deposition is observed not only on the surfaces of the SWNT/cotton but also inside the layers of cotton fibers. The conductive cotton was peeled apart and SEM was taken of the interior cotton (Figure 4c). Conformal coating of MnO₂ on cotton fiber surface is observed, and the peeling leads to the partial delamination of MnO₂ from the cotton fibers (Figure 4c). Figure 4e reveals the flower structure of MnO₂ particles deposited on the SWNT surfaces. The MnO₂ nanoparticles are entangled with the SWNTs, which ensures good electrical contacts between them. To demonstrate the feasibility of this pseudocapacitor approach for wearable power devices, SCs of SWNT/cotton with MnO₂ were tested with a 2 M aqueous Li₂SO₄ electrolyte. In this particular SC, the mass density is 0.24 mg/cm² for SWNTs and is 1.60 mg/cm² for the MnO₂ which is 50 times higher than the reported value in literature. The time required to charge the SCs for SWNT/cotton after MnO₂ deposition is significantly increased, suggesting a large charge capacity increase (Figure 4f). The areal capacitance with respect to the device increases by a factor of 24 after MnO₂ deposition. In literature, the electrodeposition of oxides typically increase the capacitance by a factor of less than 6. The areal capacitance of the device reaches 0.41 F/cm², which is much higher than reported values with SWNT electrodes. The specific capacitance data, considering the mass of both SWNTs and MnO₂ is plotted in Figure 4g.

In this study, we report the use of porous conductive textiles as a platform for energy storage device applications. This porous conductor allows high mass loading of electrode materials and excellent access of electrolyte to those materials, which leads to outstanding device performance. Such textile-based power will boost the development and application of wearable electronics. With lightweight and cheap cotton or fabrics and the existing textile fabrication infrastructure, large-scale energy storage with low material and processing costs is also feasible. When combined with inks of other functional materials, other types of electronics could be created, such as wearable solar cells and batteries. These porous conductors with excellent properties will find a wide range of applications.

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Supporting Information Available. This material is available free of charge via the Internet at http://pubs.acs.org.

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