Omnidirectional Deformable Energy Textile for Human Joint Movement Compatible Energy Storage

Joonwon Lim, Dong Sung Choi, Gil Yong Lee, Ho Jin Lee, Suchithra Padmajan Sasikala, Kyung Eun Lee, Seok Hun Kang, and Sang Ouk Kim

National Creative Research Initiative Center for Multi-Dimensional Directed Nanoscale Assembly, Department of Materials Science and Engineering, KAIST, Daejeon 34141, Republic of Korea

Supporting Information

ABSTRACT: Omnidirectional deformability is an unavoidable basic requirement for wearable devices to accommodate human daily motion particularly at human joints. We demonstrate omnidirectionally bendable and stretchable textile-based electrochemical capacitor that retains high power performance under complex mechanical deformation. Judicious synergistic hybrid structure of woven elastic polymer yarns with carbon nanotubes and conductive polymers offers reliable electrical and electrochemical activity even under repeated cycles of severe complex deformation modes. The textile-based electrochemical capacitors exhibit omnidirectional stretchability with 93% of capacitance retention under repeated 50% omnidirectional stretching condition while demonstrating excellent specific capacitance (412 mF cm$^{-2}$) and cycle stability (>2000 stretch). The wearable power source stably powers red LED under omnidirectional stretching that accompanies human elbow joint motion.

KEYWORDS: energy storage, supercapacitors, textile, wearable, carbon nanotubes

INTRODUCTION

Research attention on wearable electronics is ever-increasing along with the rapid advent of portable or patchable devices. The ideal prototype of wearable electronics should be bendable, twistable, and stretchable to accommodate our daily mechanical motions, while sustaining the device performance in the undeformed states. In the past decade, a significant amount of research effort has been devoted to the realization of wearable devices, mainly focusing on the engineering of device structures. For instance, buckling of ultrathin inorganic active materials stabilized on prestrained elastomeric substrates successfully realizes uniaxially or biaxially stretchable devices. Fiber-shaped devices can offer high tolerance for complex mechanical deformation modes owing to the intrinsic one-dimensional geometry. Nonetheless, a significant issue still remains unsolved for the realization of genuine wearable power devices, that is, reliable high power performance even under complex omnidirectional deformation.

In the realm of truly wearable devices, omnidirectional deformability needs to be distinguished from simple bendability or uniaxial stretchability. While conventional stretchability toward one or a few fixed directions can accommodate only a limited range of physical motions, omnidirectional deformable devices ensure a distinctive degree of freedom for physical movement and comfort. Indeed, practical wearable powering devices are expected to accommodate 50% of omnidirectional strains to tolerate the large deformation occurring particularly at joints, such as knee, elbow, and knuckle. A sophisticated strategy is expected in the design of materials and/or the layout of devices for the simultaneous attainment of omnidirectional deformability along with high conductivity and energy storage/supply capability. Moreover, development of systematic and standardized analytical methodology for the evaluation of omnidirectional deformability is urgently demanded to resolve the ambiguity among previous relevant approaches.

Textile integration of powering devices is considered a promising platform for upcoming wearable electronics. Textile platform offers certain inherent flexibility and stretchability arising from the distinct woven structures, even when composed of inelastic rigid materials. Nonetheless, it is still challenging to synchronize the contradictory goals of high stretchability and reliable electrical conductivity, which are indispensable requirements for wearable powering textiles as active materials as well as current collectors. To date, most of...
the research on textile-based power sources has relied on inelastic textile platform. In a few rare attempts to employ elastic yarns, the resultant devices have suffered from insufficient cycle stability, commonly caused by the fracture or delamination of rigid active components from the elastic yarns, which deteriorate the electrical connectivity over device architecture during multiple repeated deformation cycles.

In this work, we present omnidirectionally deformable textile-based electrochemical capacitors, capable of stable power storage/supply under complex mechanical deformation. A straightforward reliable interfacial treatment method is developed for the commercially available woven elastic polymer yarns based on the solution deposition of carbon nanotubes (CNTs) and the interfacial synthesis of conductive polymer (polyaniline, PANI) layers. Simple capacitor structures consisting of symmetric stacking of the hybrid textiles attain highly stable reliable energy storage and supply under severe complex deformation conditions along with ready adaptability to our typical clothes. We also propose a standardized quantitative evaluation method for the omnidirectional stretchability in the functional device structures as well as in the materials level.

EXPERIMENTAL METHODS

Preparation of CNT/Textile. Aqueous CNT ink was prepared by dispersing MWCNTs with sodium dodecylbenzenesulfonate (SDBS) as surfactant. The mass ratio of CNTs to SDBS was 1 to 5 for aqueous CNT ink of various concentration. Tip sonication of 20 W was applied to the CNT ink for 1 h, and the resultant CNT ink was centrifuged at 8000 rpm for 1 h to remove nondispersed CNT clusters. Stretchable textile made of polyurethane and polyester copolymer was immersed in the as-prepared CNTs ink for 10 min and then dried out on a hot-plate at 50 °C for 2 h. The CNT-coated stretchable textile (CNT/ textile) was washed out with deionized water with vigorous shaking to remove unattached and agglomerated CNT particles on the textile. Subsequent washing with 2 M nitric acid was conducted to completely remove SDS surfactants adsorbed on the surface of CNTs. The same process was repeated to increase the loading amount of CNT on the stretchable textile.

Preparation of PANI/CNT/Textile. 0.2 M aniline in 1 M hydrochloric acid (HCl) aqueous solution (20 mL) was prepared for in situ polymerization of PANI. High purity ethanol (4 mL) was added to the prepared aniline solution. CNT/textile was immersed in ethanol for tens of seconds to improve wettability and then placed into the reaction solution containing aniline monomer for 3 h in ice bath. 0.1 M ammonium persulfate (APS) in 1 M HCl (20 mL) solution was slowly added drop by drop into the reaction bath. The degree of in situ polymerization of PANI was controlled by adjusting the reaction time. After polymerization reaction, the synthesized PANI/CNT/textile was thoroughly washed with ethanol with vigorous shaking to remove undesired PANI particles on the surface of PANI/CNT/textile and dried out on the hot-plate at 50 °C for 2 h.

Measurement of Electrical Stability under Uniaxial Stretching. Specimens were stretched by homemade stretching test equipment. Both ends of specimens were clipped by holders with platinum foils for electrical contact for measuring electrical property. The magnitude of applied tensile strain was defined as following formula: magnitude of applied tensile strain (%) = 100 × (L − L₀)/L₀, where L₀ and L denote the length of specimen before and after applied tensile strain, respectively. Electrical stability under uniaxial stretching was evaluated with the variation of electrical resistance, defined as R/ R₀ where R₀ and R denote electrical resistance before and after applied tensile strain, respectively.
Measurement of Electrical Stability under Omnidirectional Stretching. Omnidirectional stretchability was evaluated by investigating the variation of $R/R_0$ under omnidirectional stretching. Specimens were held by homemade stretching test equipment. All edges of specimen were clipped by holders, and platinum foils are placed at two sides facing each other for electrical contact for measuring electrical property. Omnidirectional stretching was generated by sphere shape strain loader pressing specimen. The degree of applied omnidirectional strains was controlled by adjusting vertical location of sphere loader. The magnitude of omnidirectional strains was defined with the identical formula with that of uniaxial stretching condition. $L_0$ and $L$ denote the sectional line length passing through a tangential point between specimen and sphere loader before and after omnidirectional stretching, respectively. Electrical stability under omnidirectional stretching was evaluated with the variation of electrical resistance ($R_{\text{omni}}/R_0$).

Material information and evaluation method for electrochemical performance of supercapacitors are provided in the Supporting Information.

RESULTS AND DISCUSSION

Omnidirectionally Deformable Energy Textile Preparation. Figure 1a illustrates our synthetic route. Highly stretchable textiles woven from elastic polyester–polyurethane copolymer yarns were immersed in aqueous dispersion of CNTs with amphiphilic surfactants (Figure S1). The immersion condition was precisely optimized for a desired uniform and conformal coating quality (Figure 1b–d, Figure S2). Several repeated CNT coating cycles (typically five times) dramatically decrease the sheet resistance of textile down to 20 Ω/□ (Figure S3). Subsequently, PANI conductive polymer layer was grown from the entire surface of CNT/textile (Figure 1e–g, Figures S4 and S5). Aniline monomers are sufficiently absorbed on the CNT coated textile surface before polymerization so that the following solution polymerization leads to a conformal coating of PANI layer (Figure S4).42,43 PANI forms dense surface layer and plugs the cavities among CNTs and the base textile (Figure S5). The polyester–polyurethane textile used here possesses aromatic moieties that can share π–π interaction with CNTs and PANI chains.44 Besides, –NH–functional groups of PANI may cause hydrogen bondings with the C=O groups of polyester–polyurethane textile to accommodate reliable interfacial adhesion even under severe complex deformation (Figure S6).45 The interfacial interactions enhanced the mechanical property of the textile (Figure S7).

Energy Textile under Bending, Twisting, and Uniaxial Stretching. Any kind of complex mechanical deformation, including those at human skin or clothing, can be considered as a combination of bending, twisting, and stretching modes. Electrical conductivity of our conductive textiles was charac-
terized under those three different modes. Figures 2a and 2b show the electrical stabilities of PANI/CNT/textile and CNT/textile (without PANI layer) under bending and twisting, illustrated by the variation of relative resistance, i.e., $R/R_0$, where $R_0$ and $R$ correspond to the electrical resistance before and after deformation, respectively. Interestingly, severe bending to a small radius of 0.1 cm and strong twisting to 180° cause a minor enhancement of electrical conductivity. While the preexisting electrical junctions among CNTs reinforced by PANI layer are well maintained, additional physical electrical contacts can be supplemented under the geometric buckling or wrinkling of textile. The electrical property of our energy textile is also endurable for repeated deformation cycles. After 10000 cycles of bending or twisting, only a 2% increase in the electrical resistance was measured (Figure S8).

Figure 2c compares the uniaxial stretchability of PANI/CNT/textile and CNT/textile, evaluated by the variation of $R_{uni}/R_0$ under tensile stretching toward $X$, $Y$, or $XY$-direction, as defined in Figure 2d. For the 50% of $X$, $Y$, and $XY$-directional stretching of CNT/textiles, $R/R_0$ values were measured to be 2.06, 1.64, and 1.11, respectively. This direction dependency is obviously ascribed to the anisotropic woven structure of textile. Figure 2d compares the configurational modification of yarns and bundles under stretching toward different directions, observed by scanning electron microscopy (SEM). Given the intrinsic electrical properties of each component, the overall electrical conductivity of textile is determined by the areal density of conductive components (CNTs and PANI) as well as effective electrical junctions between them. The characteristic angle between neighboring woven bundles, denoted by the inner angle of V-shape (insets in Figure 2d), strongly depends on the stretching direction. A smaller angle may offer a tighter contact among CNT junctions with larger contact area and lead to an enhanced electrical connectivity. The angles for $XY$- and $Y$-directional stretching were 31° and 61°, which is smaller than unstretched state (66°). By contrast, $X$-directional stretching leads to a large increase in angle (77°) as well as sparse configuration of bundles.

As shown in Figure 2c, the electrical stability under stretching is remarkably improved by in situ polymerized PANI layer (Figure S9). PANI/CNT/textile exhibited 1.15, 1.06, and 0.94 of $R_{uni}/R_0$ values at the 50% of $X$, $Y$, and $XY$-directional...
Conformal coating of PANI improves the electrical connectivity among CNT strands as well as PANI/CNT/polymer yarns by filling the voids among them. It also enhances the mechanical stability of electrical contact junctions and tightens the overlap among woven yarns. The synergistic effect from CNT and PANI coating strengthens the electrical connectivity and prevents the delamination and fracture of composite structure even under severe complex deformation (Figures S10−S12).

Omnidirectional Stretchability of Energy Textile. Omnidirectional stretchability of our energy textile was quantitatively evaluated, as illustrated in Figure 3a. For an equivalent tensile stretching toward every direction, we used a solid sphere tensile loader. The sphere-loaded textile surface generates isotropic tensile strains from the tangent points with sphere surface to every direction. The applied tensile strain can be quantified by the ratio of initial length ($L_0$) to a length increment ($L - L_0$) of specimen. The magnitude of stretching was simply controlled by the vertical location of spherical loader. Investigation on the variation of electrical stability ($R_{\text{omni}}/R_0$) along with the degree of omnidirectional stretching rationally quantifies the omnidirectional stretchability of a specimen. Notably, this evaluation method also facilitates the diverse stretching situations with different surface curvatures by employing different radius of sphere loader (Figure S13). For instance, stretching and bending motions on the knee, the elbow, and the knuckle have different surface curvatures. The radius of curvature of sphere loader used in this work was 11 mm, which can cover human’s motions on knee, shoulder, and elbow, on which the radii of curvatures are known to be 20 mm and over.46,47

According to the suggested methodology, we evaluated the omnidirectional stretchability of PANI/CNT/textile. Polymer-free textile (CNT/textile) was investigated again as a reference to verify the reinforcing effect from PANI layer. Figure 3b shows SEM image of omnidirectionally stretched PANI/CNT/textile. Figure 3c presents that PANI/CNT/textile exhibits a very small increase of $R_{\text{omni}}/R_0$ up to 20%, followed by gradual
research article

ACS Applied Materials & Interfaces

Research Article

Discharge activity of energy textile is dominated by the CV curves for scan rates from 5 to 40 mV s\(^{-1}\). Cyclic voltammetry (CV) and galvanostatic charge/discharge of PANI/CNT/textile capacitor reaches 412 mF cm\(^{-2}\) without PANI layer. Figure 3d shows the cycle stability for stretching. CNT/textile showed a similar tendency in the capacitance (Figure 4f) and, moreover, maintained 93% of well-maintained with stable CV curves (Movie S1). Ragone plot dynamic strain operation, the electrochemical performance was characterized in a symmetric device configuration. The devices were composed of textile separators infiltrated with poly(vinyl alcohol) (PVA)/H\(_3\)PO\(_4\) aqueous gel electrolyte, sandwiched between two textile electrodes (Figure 4a and Figure S16). Cyclic voltammetry (CV) and galvanostatic charge/discharge cycles were measured between 0 and 0.8 V. Figure 4b shows the CV curves for scan rates from 5 to 40 mV s\(^{-1}\). Compared to CNT/textile capacitor, PANI/CNT/textile-capacitor shows substantially large inner area of CV curve, owing to the redox activity of PANI layer.46,49 Figure S17 presents the typical charge/discharge profiles for current densities from 0.2 to 0.8 mA cm\(^{-2}\) (current: 0.5 to 2 mA). The specific areal capacitance of PANI/CNT/textile capacitor reaches 412 mF cm\(^{-2}\), which is about 80-fold enhancement from CNT/textile capacitor (Figure 4c). The specific gravimetric capacitance of PANI/CNT/textile capacitor was also calculated to be 211 F g\(^{-1}\) at 0.2 mA cm\(^{-2}\), comparable to those of high performance PANI-based electrochemical capacitors (without mechanical deformability) reported thus far.30,53 Additionally, textile capacitors showed an outstanding stability up to 10000 cycles of charge/discharge (Figure S18). The capacitance of PANI/CNT/textile capacitor gradually increased up to 5000 cycles primarily due to the electrochemical activation of PANI and the improvement in the wetting of gel electrolyte at textile surfaces.

Figure 4d is a schematic illustration of the omnidirectional stretchability of our PANI/CNT/textile capacitor. Discharge profiles in the galvanostatic measurements show no distinct modification under the omnidirectional stretching up to 50% (Figure 4e). Energy capacity retained 95% of original capacitance (Figure 4f) and, moreover, maintained 93% of capacitance after 2000 cycles of stretching (Figure 4g). While the electrochemical activity of energy textile is dominated by CNT and PANI layers, their effective surface area and electrical conductivity are well-preserved under the severe deformation of textile. We also evaluated our textile capacitors under bending and twisting deformations. The capacitors retained their original CV curves under harsh bending up to 0.1 cm bending radius and 90° twisting condition (Figure S19). Even under a dynamic strain operation, the electrochemical performance was well-maintained with stable CV curves (Movie S1). Ragone plot in Figure 4h compares the areal (red circles) and gravimetric (blue circle) power and energy densities of PANI/CNT/textile capacitor with other uniaxial or biaxial stretchable electrochemical capacitors reported thus far.13,17,18,52–57 The maximal areal and gravimetric energy densities of the as-prepared device are 36.7 μWh cm\(^{-2}\) and 18.7 Wh kg\(^{-1}\) with high power densities of 0.11 mW cm\(^{-2}\) and 58.3 W kg\(^{-1}\), respectively. The outstanding energy storage/supply capability retained 95% of original energy and power densities under 50% omnidirectional stretching (star). As a demonstration of device application, three 25 cm\(^{2}\) PANI/CNT/textile capacitors with PVA/LiCl gel electrolyte were serially connected to light up a red light-emitting diode (LED) (Figure S20). By virtue of high energy capacity of our devices, the LED lighting prolonged over 1 h with a single full charge. The sustainability of LED lighting was also tested under repeated omnidirectional stretching/releaseing. Interestingly, LED maintained its original brightness without any noticeable flickering or diminishing of intensity under the dynamic deformation cycles, as shown in Figure 4i (Movie S2). The energy textile capacitors could also be integrated into our daily clothes as wearable power sources compatible to human elbow joint motion for lighting LED (Movie S3 and Movie S4).

CONCLUSION

Electrochemically active hybrid textile structure is introduced for the high performance wearable energy storage adaptable to the complex omnidirectional deformation at human joints. The platform presented here relies on three key design features for truly wearable power devices: (1) providing omnidirectional deformability with elastic and woven substrate structure, (2) retaining electrical activity for energy delivery under repeated mechanical deformation with robust interfacial treatment with CNT/conductive polymer layer, and (3) facilitating active redox behavior for high energy storage with in situ polymerized conductive polymers. Significantly, intimate conformational interfacial growth of conductive polymers effectively strengthen the physical junctions among one-dimensional CNT strands such that electrical conductive pathway through CNT network structure is well-sustained even under complex large deformation modes and provides highly stable electrical and electrochemical performances. This rational material design and integration concept represents a typical instance generally applicable to many different wearable devices other than energy storage. We also propose a methodology for the quantitative evaluation of omnidirectional stretchability for functional materials and devices, while imposing well-defined deformation analogous to human joint motion. Overall, this study defines the importance of deformability toward arbitrary direction for the practical utilization of wearable materials and devices and suggests a viable way to cloth-integrated electronics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b14981.

Experimental procedures and materials characterization, Scheme S1, Figures S1–S20 (PDF)

Movie S1 (AVI)

Movie S2 (AVI)

Movie S3 (AVI)

Movie S4 (AVI)

ACS Appl. Mater. Interfaces 2017, 9, 41363–41370

41368
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the KOLON Corporation, Korea, through the KOLON-KAIST Lifestyle Innovation Center Project (LS14-MAKSW0001), the Multi-Dimensional Directed Nanoscale Assembly Creative Research Initiative (CRI) Center (2015R1A1A0203306), and the Nano-Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (2016M3A7B4905613).

REFERENCES


