Highly Stretchable and Conductive Hybrid Fibers for High-performance Fibrous Electrodes and All-solid-state Supercapacitors

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Abstract The development of lightweight, flexible, and stretchable energy storage systems is essential for state-of-the-art electronic devices. We propose a new and broad strategy to fabricate a stretchable and conductive GO/CNTs-TPU fiber electrode by direct wet spinning, from which a flexible fibrous supercapacitor is fabricated. The fibrous electrode exhibits a high strength of 11.68 MPa, high conductivity of 342 S/cm, and high specific capacitances (21.8 mF/cm³, 36.45 F/cm³, and 95 F/g). The specific capacitance of the assembled all-solid-state hybrid fiber-shaped supercapacitor reaches 14.3 F/cm³. After 5000 charge-discharge cycles, 97% of the capacitance of the hybrid supercapacitor is maintained. These high-strength electrochemical electrode materials could be potential candidates for applications in practical and large-scale energy storage systems and textile clothes.

Keywords Graphene; Carbon nanotubes; Thermoplastic polyurethane; Supercapacitor; Flexibility

INTRODUCTION

The development of flexible and wearable electronic devices with high mobility and energy functional ability has stimulated the development of flexible power sources to usher in a subversive evolution of our daily lives. To satisfy the requirements of flexible textile-like electronic devices, the energy storage devices should have similar textile/fiber shapes, excellent flexibility, mechanical stability, and lightweight, and be capable of bearing deformation in all dimensions. As important energy storage devices, supercapacitors (SCs) offer high power capability, fast charge/discharge rates, long cycle life, and simple structures and bridge the power-energy gap between traditional dielectric capacitors and batteries. These features make SCs a potential energy solution for wearable and textile electronics.

Paper-like, figure-printed, and fibrous SCs have been widely investigated because they are lightweight, long-lasting, flexible, and conformable. Before that, fiber-shaped devices used in other fields (such as semiconductor transistor, sensors, and solar cells) have been widely studied and proved to have great practical value. Among these devices, fiber-shaped supercapacitors (FSCs) are in high demand because of their softness, high strength, multi-functionalities, and ease of integration with the existing textile industry. To date, materials such as metal wires, carbon fibers, and carbon nanotubes (CNTs) have been successfully adopted as substrates for the fabrication of fibrous SCs.

Among these materials, CNTs play an important role and have wide applications in SCs because of their combined excellent mechanical, electronic, and thermal properties. Since the appearance of CNTs fibers in 2000, researchers have increasingly focused on these one-dimensional macroscopic fibers for its light weight, excellent flexibility, and large surface area. Peng et al. fabricated twisting FSCs, coaxial FSCs, and multifunctional FSCs such as shape-memory FSCs, ring-type SCs, and chromatic FSCs which were all based on CNTs fibers. However, despite the outstanding electrochemistry performance of these devices and their various functions, disadvantages such as the complicated preparation processes and the high price of pure CNTs still limit their large-scale application in flexible and wearable electronics.

Moreover, wearable SCs must exhibit sufficient stretchability. Wang et al. prepared a fiber-shaped strain sensor based on multi-walled CNTs and thermoplastic polyurethane (TPU) via a wet-spinning method. Although the strain sensors exhibited good elasticity, the CNTs were highly entangled with...
each other. Yang et al. developed a stretchable FSC, in which aligned CNTs sheets wrapped on an elastic fiber served as two electrodes, however, the complex process was both time-consuming and expensive.

Herein, we produced a graphene oxide/CNTs thermoplastic polyurethane composite (GO/CNTs-TPU, GCT) fiber with honeycomb porous structure using a simple one-step wet-spinning method, in which the GO nanosheets, CNTs, and TPU were homogeneously dispersed. In the internal structure network of the hybrid fiber, GO can efficiently prevent the entanglement of CNTs as well as reduce the speed of condensation of TPU in the coagulation bath, which may lead to the macroporous structure. This hybrid fiber displayed excellent stretchability, as it could be easily stretched by 200% without an obvious decrease in the structural integrity. Furthermore, the specific capacitance of the GO/CNTs-TPU hybrid fiber electrode reached up to 36.45 F/cm$^3$ at a scan rate of 100 mV/s. An all-solid-state SC was also assembled using this hybrid fiber with a specific capacitance of 14.3 F/cm$^3$, and 100% of its initial capacitance was maintained after 5000 charge-discharge cycles.

**EXPERIMENTAL**

**Chemicals**

GO powder (XF205) was purchased from Nanjing XF NANO Materials Technology Corporation (Nanjing, China). Graphitized −COOH functionalized multi-walled CNTs (99.9 wt%) were obtained from Chengdu Organic Chemicals Co., Ltd. Deionized water (H$_2$O) was obtained from a Millipore deionized water system with a resistivity of 18.0 MΩ·cm. Polyester-based TPU (4000 mg) was slowly added to the above GO/CNTs suspension. Deionized water (H$_2$O) was obtained from a Millipore deionized water system with a resistivity of 18.0 MΩ·cm. Polyester-based TPU (4000 mg) was slowly added to the above GO/CNTs suspension.

**Fabrication of GO/CNTs-dispersed TPU Suspension**

All the reagents were of analytical grade and used as obtained without further purification. GO (40 mg) was dispersed in 20 mL of dimethylformamide (DMF) with ultrasonication for 2 h. The obtained suspension was mixed with pristine CNTs (160 mg) and then sonicated for another 1 h in an ice bath. A black colloidal dispersion with no visible precipitation was obtained. TPU (4000 mg) was slowly added to the above GO/CNTs colloidal dispersion and heated to 60 °C while stirring vigorously. After refluxing for 2 h and subsequent cooling to room temperature, a spinable mixture was obtained (GO/CNTs-TPU). The resulting gel-like mixture was used for fiber fabrication.

**Fabrication of GO/CNTs-TPU Fiber-shaped Electrode**

The as-prepared spinning composite gel was loaded into a plastic syringe and further injected into deionized water (H$_2$O) at a rate of 1 mL/min. Due to the different solubility of the TPU in DMF and H$_2$O, the DMF solvent was extracted and removed rapidly from the spinning fiber surface directly into the water to form the initiate fibers. After the initiate fibers immersing in H$_2$O for 2 h, the hybrid and strong GO/CNTs-TPU fibers were collected on a drum and dried naturally. Pure PU, GO-PU, and CNTs-PU were also fabricated for comparison. The injection needle size was 18, 20, 21, 22, and 27 G. The corresponding internal and external diameters were 840/1250, 600/900, 500/800, 400/700, and 200/400 μm, respectively.

**Assembly of All-solid-state Fibrous Supercapacitor**

The PVASO$_4$ gel electrolyte was prepared using the previously reported method. Before device assembly and electrochemical testing, the as-prepared GO/CNTs-TPU fibers were immersed in a PVA/H$_2$SO$_4$ electrolyte overnight. This process ensured that the electrolyte fully infiltrated the pores. One side of the fibers was kept outside of the electrolyte for test connection. Then, the immersed fibers were retrieved to dry at room temperature for tens of minutes to vaporize the excess water. Two pairs of PVA/H$_2$SO$_4$ penetrated fibers were pressed and winded together as electrodes in all-solid-state fibrous supercapacitors (ASF SCs).

**Characterization**

The morphologies of the as-prepared fibers were characterized by the high-resolution field-emission scanning electron microscopy (FESEM, JSM-6700F) at 10.0 kV. Raman spectra were obtained using a Renishaw in plus laser Raman spectrometer with $\lambda_{rc}$ = 532 nm. The mechanical ability was tested by a universal testing machine (Model 5969, Instron). Electrochemical characterization, cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) tests, and electrochemical impedance spectroscopy (EIS) were performed using a Bio-Logic VSP-300 potentiostat system. EIS test was performed using a potential amplitude of 5 mV. Photographs and videos were taken using a charge-coupled device (CCD) video camera (PowerShot G10, Canon).

**Electrochemical Calculations**

The CV curves were used to calculate the specific mass, area, and volumetric capacitances of single electrode fiber/device/textile and active materials using the following equation:

$$C_M = \frac{\int U \, dU}{2vM\Delta U}$$

where $\int U \, dU$ is equal to the integrated area under the CV curves; $M$ is the electrode/device mass (m), area (A), or volume (V); $v$ is the scan rate; and $\Delta U$ is the test potential window.

For an all-solid-state fiber-based supercapacitor, the area and volume are from both electrodes, as follows:

$$A = 2\pi DL$$

$$V = 0.5 \times \pi D^2 L$$

where $D$ and $L$ are the diameter and length of the fibers, respectively.

**RESULTS AND DISCUSSION**

Stretchable and Conductive GO/CNTs-TPU Fibrous Electrode and Devices

Fig. 1 shows the overall process of the GO/CNTs-PU fiber fabrication. A simple and typical wet-spinning process was used for injection molding of the high-strength and stretchable fiber-shaped electrode. As illustrated in Fig. 1(a), the GO and CNTs were well mixed with a line-liner networks and then alloyed with TPU as a precursor for fiber fabrication. Deionized water was used as a coagulation bath, and the temperature was maintained at 25 °C. The liner fiber was obtained immediately when the gel was injected into the water; meanwhile, the DMF
solvent was extracted and dissolved in water. Then, the fiber was directly collected via mass production. The as-prepared fibers (TPU and hybrid GO/CNTs-TPU) were immersed into the H₂O for 30 min to obtain a stale fiber shape, and then dried naturally in air. The as-spun fiber displays a high stretch-ability and excellent flexibility (Fig. 1). The length of the resulted GO/CNTs-TPU hybrid fibers can reach almost 5 m, which could be collected and wound on a cylinder (Fig. S1a in the electronic supplementary information, ESI). Therefore, this process could be used as a large-scale mass production process. In addition, a Chinese knot was woven using this hybrid fiber, indicating its good weave-ability and lightweight (Figs. S1b and S1c in ESI); the weight density was only 0.83 mg/cm.

Preparation and Characterization of GO/CNTs-TPU Dispersion
Achieving a uniform and stable precursor for fiber fabrication is critical. Fig. 2(a) presents a digital image of the resulting GO/CNTs-TPU gel with a total additive concentration of 10 mg/mL (2 mg/mL GO and 8 mg/mL CNTs). The fully agitated gel is highly stable for several weeks under a sealed or water-insulated environment. This stability is essential for and beneficial to fiber fabrication and can prevent decreases of the stress and electronic conductivity resulting from CNTs or GO nanoparticles reuniting. This liner-layer structure is important for charge storage ability, as discussed in the following sections. On the one side, the CNTs are well dispersed on GO particles, which can prevent their reunion and the formation of large holes during solidification in the forming process. Yet, the GO particles can also be activated for charge storage thanks to the attached high conductivity of the CNTs. As shown in the digital image in Fig. 2(b), an unbroken fiber can be produced continuously and quantitatively using this gel. It can be seen from SEM image that the surface of the fiber is smooth enough and the thickness is uniform. (Fig. S2a in ESI). The morphologies,
structures, and phases of the resulting liner-layer hybrid gel were first characterized by (S)-TEM and elemental distribution. The samples for TEM (Fig. 2c), STEM (Fig. 2d), and STEM mapping (Figs. 2e and 2f) were directly prepared from a diluted GO/CNTs-TPU dispersion. The 1D CNTs were well dispersed and distributed on the 2D GO nanosheets without obvious accumulation. The TPU particles were evenly spread in amorphous form. Pure TPU was also confirmed by HR-TEM, as shown in Fig. S2(b) (in ESI), and the distribution of the carbon and oxygen elements was also characterized, as shown in Figs. 2(e) and 2(f), which further confirmed that the contents were well mixed.

Characterization of TPU and GO/CNTs-TPU Hybrid Fibers
The morphologies of the as-prepared TPU and hybrid GO/CNTs-TPU fibers were compared using SEM, as shown in Figs. 3(a) and 3(b), respectively. As observed in Fig. 3(a), the TPU fiber had a hollow structure with many small internal pores. This hollow structure may have arisen from the different inward and outward mass transfer rates of the fiber or the fast exchange between the solvent (DMF) and coagulating bath (water). A curtained place was occupied by the H₂O inside the fiber during the solidification process and then evaporated during the post-processing, such as drying, yielding abundant pores and the porous structure. Enlarged cross-sectional SEM images of the TPU fiber are also displayed in Fig. S3 (in ESI), revealing stretched irregular holes and confirming the above explanation. Cross-sectional SEM images of the hybrid GO/CNTs-TPU fiber are presented in Figs. 3(c) and 3(d). An abundant porous structure was formed rather than the hollow structure of the TPU fiber. This fascinating internal structure is attributed to the GO/CNTs networks addition. The GO/CNTs network served as a conductive filler to connect the TPU molecules without large distortion during the formation. In addition, as illustrated in Fig. 3(d), these holes were still connected and even contained high amounts of GO and CNTs. The TPU was well dispersed with the GO/CNTs in the gel, and this homogeneous state was beneficial to mechanical and electrical property enhancement. In addition, the connected holes had an average diameter of 2 μm, which was also good for electrolyte infiltration and improving the charge-transfer rate.

To further confirm this result, the distribution of carbon

Fig. 3  Cross-sectional SEM photographs of (a) pure TPU and (b–d) hybrid GO/CNTs-TPU fibers at different magnifications. (e) Carbon and (f) oxygen element SEM mapping of cross-section of hybrid fiber. (g) Raman spectra of TPU and GO/CNTs-TPU fibers. XPS fitting of C elements for (h) pure TPU and (i) GO/CNTs-TPU hybrid fiber.

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and oxygen elements in the hybrid GO/CNTs–TPU fiber was analyzed using energy-dispersive X-ray spectrometry (EDS) mapping. Figs. 3(e) and 3(f) present EDS mapping images of the signals from C (red) and O (green) elements measured on the cross-section of the GO/CNTs-TPU fiber. All the elemental analyses were repeated three times and presented after normalization. As observed in Figs. 3(e) and 3(f), the CNTs and GO were homogeneously distributed in the hybrid film. Semaphore feedback from carbon and oxygen indicated that the CNTs in the hybrid supramolecular hydrogel were significantly uniformly suspended with layered connection with GO NSs and TPU particles in the hybrid fiber. The Raman spectra of pure TPU reveal a typical amorphous state with no obviously disordered band (D band, approximately 1300 cm$^{-1}$) or graphitic G-band (usually approximately 1580 cm$^{-1}$), as indicated by the grey line compared with GO/CNT-TPU fiber in Fig. 3(g). Otherwise, as the enlarged image on the top-right corner shows, a typical diisocynate (N=C=O) functional group was assigned around 1443 cm$^{-1}$ for pure TPU matrix. For the hybrid GO/CNTs-TPU fiber, a distinct G-band was observed, corresponding to the graphene lattice. The Raman observations were also consistent with the HR-TEM images, revealing well-ordered carbon for the GO/CNTs-TPU fiber different from TPU. It was also confirmed that the strong intensity G-band in the hybrid fiber resulted from the CNTs, which were also stabilized by the connection with the fiber.

The presence of CNTs, GO, and TPU components in the wet-spun fiber was also verified by XPS, as shown in Figs. 3(h) and 3(i) and Fig. S4 (in ESI). In Figs. 3(h) and 3(i), the C1s peaks of pure TPU and hybrid GO/CNTs-TPU fiber are observed, including three main peaks: C−C, C−O−C, and O−C=O. The quantitative results for the fitted individual peaks are provided in Table S1 (in ESI). The C−C bond position of TPU was shifted to a slightly lower energy level by the additive. The percentage of each bond was determined, and the results indicated that the proportion of C−C bonds was higher for the GO/CNTs-TPU fiber than for pure TPU because both GO and CNTs consist of C−C bonds. In addition, the percentage of O−C=O bonds in the hybrid fiber was also higher than in the pure TPU because of the presence of carboxyl groups in GO.

**Mechanical Performance of TPU and GO/CNTs-TPU Hybrid Fibers**

To quantify the mechanical properties of the fibers, tensile tests were conducted. Fig. 4(a) presents digital photographs of the GO/CNTs-TPU fibers under stretching from 100% to 200% strains. The fiber was easily stretched by 200% without an obvious decrease in the structural integrity. The stress-strain curves of the fibers were obtained for various mass fractions of CNTs (Fig. 4b). These fibers were gradually stretched to greater
than 350% strain; in particular, stretching of up to 520% strain was achieved for CNTs mass fractions of 30 wt%, and the tensile strength of the GO/CNTs-TPU fiber was 11.68 MPa. The strength and stretchability of the TPU fibers were better than those of the GO/CNTs-TPU fibers, which was related to the closer linkages among all the TPU particles without any interruption from GO or CNTs. To investigate the tensile fatigue of the GO/CNTs-TPU fibers, we applied repeated tensile deformation up to 50% strain for 20 cycles. Stress-strain curves were obtained during the tensile fatigue test for the GO/CNTs-TPU (30 wt%) fibers. As shown in Fig. 4(c), we plotted the stress-curves at the 1st, 4th, 8th, 12th, 16th and 20th cycle as representative cycles. As the number of fatigue cycles increased, stretching up to 50% strain, the stress decreased from 1.7 MPa to 1.62 MPa.

Electrochemical Performance of GO/CNTs-TPU Hybrid Fiber Electrode

To investigate the electrochemical properties of the fiber, we used a three-electrode configuration to explore the electrochemical storage properties in different electrolytes and observed...
that the fitting area of the CV curve measured in H$_2$SO$_4$ was larger than that in other electrolytes (H$_3$PO$_4$, NaOH, Na$_2$SO$_4$) (Fig. 5a). EIS measurements were performed to determine the resistance during charge transfer. As shown in Fig. 5S (in ESI), the charge-transfer resistance was less than 10 $\Omega$, which is much lower than that of pure GO and even of the reduced GO fiber or some composite fibers.[30] The GO/CNTs-TPU fiber had different CVs for different potential windows (Fig. 5b). For a scan rate of 50 mV/s, an evident signal of polarization was observed when the potential window expanded from 0.8 V to 0.9 V, indicating that the optimal potential window range was 0–0.8 V. Fig. 5(c) presents CV curves of the fiber electrode with increasing scan rate from 10 mV/s to 200 mV/s. When the scan rate reached 200 mV/s, the voltage still rapidly responded to the current because

![Graph](https://doi.org/10.1007/s10118-020-2381-2)
of the porous structure of the GO/CNTs-TPU fiber. The unique structure is beneficial to electrolyte infiltration during charge and discharge and to ion intercalation/deintercalation embedding and ejection. From Fig. 5(d), GCDs were recorded at various current densities ranging from 0.05 mA/cm to 2 mA/cm. The rapid charge and discharge and tiny IR drop on the discharge curve at 0.1 mA/cm suggest the ideal capacitive characteristics and favorable electrical conductivity. Fig. 5(e) presents curves of the specific capacitance versus scan rate. The volume specific capacitance reached up to 36.45 F/cm², and the length specific capacitance was 21.87 mF/cm (95 F/g in mass). In addition, the electrochemical stability was evaluated by performing a long-term cycle test (Fig. 5). With increasing number of charge and discharge cycles, the stability of the circulation decreased and then showed an upward trend, with 89.17% retention after 3000 times and 97.7% retention after 8000 times. This finding is mainly due to the presence of TPU, which makes it difficult for the electrolyte to enter the fiber initially and only makes contact with the active substances on the surface. Because of the porous structure of the fiber and the electroactivating beginning gradually inside the fibers with increasing charging and discharging times, the specific capacitance of the fiber increased.

Electrochemical Performance of GO/CNTs-TPU Fiber Based All-solid-state Fibrous Supercapacitor

An all-solid-state fiber-shaped supercapacitor was prepared from the two twisted GO/CNTs-TPU fibers and can be woven into fabrics, as shown in Fig. 6(a) (in ESI). The microscopic structure is displayed by SEM image in Fig. 6(b) (in ESI), and the electrochemical performance was evaluated using CV and GCD analysis with the electrolyte of 1 mol/L PVA/H_2SO_4 gel. To determine the operating potential range of the all-solid-state fiber-shaped supercapacitors, the CVs were tested under different potential windows at a fixed scan rate of 50 mV/s (Fig. 6a). When the potential window reached 1.2 or 1.4 V, the CV curves exhibited a relatively obvious polarization phenomenon; thus, 0–1 V was selected as the operating potential range. For the extended potential window of 1.0 V, the CV curves of the all-solid-state fiber-shaped supercapacitor at different scan rates are given in Fig. 6(b). The distortion of the CV curve at high scan rate can be attributed to the generally unfavorable reaction kinetics under fast charge/discharge rates. Fig. 6(c) presents the GCD curves obtained at different current densities, with a typical symmetric triangular shape for all-solid-state fiber-shaped supercapacitors based on GO/CNTs-TPU fiber electrodes, indicating the nearly ideal capacitive behavior with a high volumetric efficiency. As observed in Fig. 6(d), similar to the results for the single electrode, the specific capacitances for the all-solid-state fiber-shaped supercapacitor decreased gradually with increasing scan rate because of the heavier polarization of the electrode at higher current density. To further test the cycle life of the all-solid-state fiber-shaped supercapacitor, 5000 cycle stability tests were performed on the all-solid-state fiber-shaped supercapacitor at a scan rate of 100 mV/s. Almost 97% of the specific capacitances were maintained after 5000 charge/discharge cycles. The CV curves of the fiber-shaped supercapacitors by stretch with different strains are further compared in Fig. 6(e). The shape of CV curve still kept a regular rectangle relatively even at a strain of 50% of the all-solid-state fiber-shaped supercapacitor. At 50% strain, the fiber-shaped supercapacitor can be used in fabric to meet the wearability requirements; at the same time, it also has good capacitance characteristics in the case of stretchability. Furthermore, the stability of the fiber-shaped supercapacitors was tested during cyclic stretching (50% strain) (Fig. 6f). We found that the specific capacitance was maintained by more than 83% after stretching for 200 cycles at a strain of 50% without obvious structural damages.

CONCLUSIONS

In this study, a stretchable conductive composite fiber was prepared by wet spinning of elastic TPU and was modified by active materials of GO and CNTs. The fiber exhibited a desired initial electrical conductivity of 342 S/cm. In this hybrid fiber, GO and CNTs were well mixed as liner-layer networks to build this porous structure for charge transportation. This method has the advantages of being a wild, simple, high-throughput process with low cost for the direct preparation of high-strength conductive fibers without requiring a current collector or substrates. The GO/CNTs-TPU hybrid fiber displayed good electrochemical performance with a volume capacitance of 36.45 F/cm³ (21.87 mF/cm and 95 F/g in length and mass, respectively). The all-solid-state fibrous-based supercapacitor was assembled, which exhibited exceptional energy storage properties and high electrochemical ability (96.95% capacitance retention after 5000 charge/discharge cycles).

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2381-2.

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REFERENCES

1. Ma, W.; Chen, S.; Yang, S.; Chen, W.; Weng, W.; Cheng, Y.; Zhu, M. Flexible all-solid-state asymmetric supercapacitor based on transition metal oxide nanorods/reduced graphene oxide hybrid fibers with high energy density. *Carbon* 2017, 113, 151–158.
2. Shi, Q.; Sun, J.; Hou, C.; Li, Y.; Zhang, Q.; Wang, H. Advanced functional fiber and smart textile. *Adv. Fiber Mater.* 2019, 1, 3–31.
3. Shao, Y.; El-Kady, M. F.; Wang, L. J.; Zhang, Q.; Li, Y.; Wang, H.; Mousavi, M. F.; Kaner, R. B. Graphene-based materials for flexible supercapacitors. *Chem. Soc. Rev.* 2015, 44, 3639–3665.
4. Kou, L.; Huang, T.; Zheng, B.; Han, Y.; Zhao, X.; Gopalsamy, K.; Sun, H.; Gao, C. Coaxial wet-spin yarn supercapacitors for high-energy density and safe wearable electronics. *Nat. Commun.* 2014, 5, 3754.
Huang, G.; Hou, C.; Shao, Y.; Zhu, B.; Jia, B.; Wang, H.; Zhang, Q.; Li, Y. High-performance all-solid-state yarn supercapacitors based on porous graphene ribbons. *Nano Energy* 2015, 12, 26–32.

Hu, Y.; Cheng, H.; Zhao, F.; Chen, N.; Jiang, L.; Feng, Z.; Qu, L. All-in-one graphene fiber supercapacitor. *Nanoscale* 2014, 6, 6448–6451.

Guttfeisch, O.; Willard, M. A.; Brück, E.; Chen, C. H.; Sankar, S.; Liu, J. P. Magnetic materials and devices for the 21st century: stronger, lighter, and more energy efficient. *Adv. Mater.* 2011, 23, 821–842.

Zou, J.; Zhang, M.; Huang, J.; Bian, J.; Jie, Y.; Willander, M.; Cao, X.; Wang, N.; Wang, Z. L. Coupled supercapacitor and triboelectric nanogenerator boost biomimetic pressure sensor. *Adv. Energy Mater.* 2018, 8, 1702671.

Fan, L.; Lin, K.; Wang, J.; Ma, R.; Lu, B. A nonaqueous potassium-based battery-supercapacitor hybrid device. *Adv. Mater.* 2018, 30, 1800804.

Coully, C.; Alhabeb, M.; Van Aken, K. L.; Kurra, N.; Gomes, L.; Navarro-Suárez, A. M.; Anasori, B.; Alshareef, H. N.; Gogotsi, Y. Asymmetric flexible mxene-reduced graphene oxide micro-supercapacitor. *Adv. Electron. Mater.* 2018, 4, 1700339.

Li, J.; Shao, Y.; Shi, Q.; Hou, C.; Zhang, Q.; Li, Y.; Kaner, R. B.; Wang, H. Calligraphy-inspired brush written foldable supercapacitors. *Nano Energy* 2017, 38, 428–437.

He, G.; Ling, M.; Han, X.; El Amaiem, D. I. A.; Shao, Y.; Li, Y.; Li, W.; Ji, S.; Li, B.; Lu, Y. Self-standing electrodes with core-shell structures for high-performance supercapacitors. *Energy Stor. Mater.* 2017, 9, 119–125.

Shao, Y.; El-Kady, M. F.; Lin, C. W.; Zhu, G.; Marsh, K. L.; Hwang, J. Y.; Zhang, Q.; Li, Y.; Wang, H.; Kaner, R. B. 3D freeze-casting of cellular graphene films for ultrahigh-power-density supercapacitors. *Adv. Mater.* 2016, 28, 6719–6726.

El-Kady, M. F.; Shao, Y.; Kaner, R. B. Graphene for batteries, supercapacitors and beyond. *Nat. Rev. Mater.* 2016, 1, 16033.

Shao, Y.; Li, J.; Li, Y.; Wang, H.; Zhang, Q.; Kaner, R. B. Flexible quasi-solid-state planar micro-supercapacitor based on cellular graphene films. *Mater. Horiz.* 2017, 4, 1145–1150.

Ma, W.; Chen, S.; Yang, S.; Chen, W.; Cheng, Y.; Guo, Y.; Peng, S.; Ramakrishna, S.; Zhu, M. Hierarchical MoO3 nanowire/graphene hybrid fibers with excellent electrochemical performance for flexible solid-state supercapacitors. *J. Power Sources* 2016, 306, 481–488.

Shao, Y.; Wang, H.; Zhang, Q.; Li, Y. Fabrication of large-area and high-crystallinity photoreduced graphene oxide films via reconstructed two-dimensional multilayer structures. *NPG Asia Mater.* 2014, 6, e119.

Wang, G.; Huang, W.; Eastham, N. D.; Fabiano, S.; Manley, E. F.; Zeng, L.; Wang, B.; Zhang, X.; Chen, Z.; Li, R. Aggregation control in natural brush-printed conjugated polymer films and implications for enhancing charge transport. *Proc. Natl. Acad. Sci.* 2017, 114, E10066–E10073.

Wang, G.; Persson, N.; Chu, P. H.; Kleinhenz, N.; Fu, B.; Chang, M.; Deb, N.; Mao, Y.; Wang, H.; Grover, M. A. Microfluidic crystal engineering of π-conjugated polymers. *ACS Nano* 2015, 9, 8220–8230.

Wang, G.; Melkonyan, F. S.; Facchetti, A.; Marks, T. J. All-polymer solar cells: recent progress, challenges, and prospects. *Angew. Chem. Int. Ed.* 2019, 58, 4129–4142.

Wang, G.; Swick, S. M.; Matta, M.; Mukherjee, S.; Strzalka, J. W.; Logisdon, J. L.; Fabiano, S.; Huang, W.; Aldrich, T. J.; Yang, T. Photovoltaic blend microstructure for high efficiency post-fullerene solar cells. To tilt or not to tilt? *J. Am. Chem. Soc.* 2019, 141, 13410–13420.

Yang, Z.; Ren, J.; Zhang, Z.; Chen, X.; Guan, G.; Qiu, L.; Zhang, Y.; Peng, H. Recent advancement of nanostructured carbon for energy applications. *Chem. Rev.* 2015, 115, 5139–5223.

Vigolo, B.; Penicaud, A.; Coulon, C.; Sauder, C.; Pailler, R.; Journet, C.; Bernier, P.; Poulin, P. Macroscopic fibers and ribbons of oriented carbon nanotubes. *Science* 2000, 290, 1331–1334.

Zhang, X.; Lu, W.; Zhou, Q.; Li, Q. Understanding the mechanical and conductive properties of carbon nanotube fibers for smart electronics. *Adv. Mater.* 2019, 1902028.

Deng, J.; Zhang, Y.; Zhao, Y.; Chen, P.; Cheng, X.; Peng, H. A Shape-memory supercapacitor fiber. *Angew. Chem. Int. Ed.* 2015, 54, 15419–15423.

Wang, L.; Wu, Q.; Zhang, Z.; Zhang, Y.; Pan, J.; Li, Y.; Zhao, Y.; Zhang, L.; Cheng, X.; Peng, H. Elastic and wearable ring-type supercapacitors. *J. Mater. Chem. A* 2016, 4, 3217–3222.

Chen, X.; Lin, H.; Chen, P.; Guan, G.; Deng, J.; Peng, H. Smart, stretchable supercapacitors. *Adv. Mater.* 2014, 26, 4444–4449.

Wang, X.; Sun, H.; Yue, X.; Yu, Y.; Zheng, G.; Dai, K.; Liu, C.; Shen, C. A highly stretchable carbon nanotubes/thermoplastic polyurethane fiber-shaped strain sensor with porous structure for human motion monitoring. *Compos. Sci. Technol.* 2018, 168, 126–132.

Yang, Z.; Deng, J.; Chen, X.; Ren, J.; Peng, H. A highly stretchable, fiber-shaped supercapacitor. *Angew. Chem. Int. Ed.* 2013, 52, 13453–13457.

Li, J.; Shao, Y.; Jiang, P.; Zhang, Q.; Hou, C.; Li, Y.; Wang, H. 1T-Molybdenum disulfide/reduced graphene oxide hybrid fibers as high strength fibrous electrodes for wearable energy storage. *J. Mater. Chem. A* 2019, 7, 3143–3149.

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